# EFFECTS OF SCRAP ADDITION ON THE PHYSICO-CHEMICAL PROPERTIES OF RIGID POLYVINYL CHLORIDE PRODUCTS

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**Md. Jalal Uddin**

Student No. 0409114001P

DEPARTMENT OF MATERIALS AND METALLURGICAL ENGINEERING

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY

DHAKA, BANGLADESH

## CANDIDATE`S DECLARATION

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Signature of the Candidate

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Md. Jalal Uddin

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## List of Abbreviations of Symbols and Terms

| | |
|---|---|
| ABS | Acrylonitrile–Butadiene–Styrene |
| BFB | Bubbling Fluidized Bed |
| CPE | Chlorinated Polyethylene |
| CPVC | Chlorinated Polyvinylchloride |
| $CaCO_3$ | Calcium Carbonate |
| $CaSO_4$, $2H_2O$ | Hydrated Calcium Sulfates |
| $CASO_4$ | Unhydrated Calcium Sulfates |
| CFBC- | Circulating Fluidized Bed Combustor |
| DMTA | Dynamic Mechanical Thermal Analysis |
| DSC | Differential Scanning Calorimetry |
| DTG | Derivative Thermo-Gravimetry |
| DOP | Dioctyl Phthalate |
| DIDP | Di-Isodecyl Phthalate |
| DMA | Dynamic Mechanical Analysis |
| ESBO | Epoxidized Soya Bean Oil |
| EVA | Ethylene Vinyl Acetate |
| FTIR | Fourier Transform Infrared Spectroscopy |
| HIPS | High Impact Polystyrene |

| | |
|---|---|
| HIPS | High-Impact Polystyrene-G-Butadiene |
| HDPE | High Density Polyethylene |
| HCL | Hydrochloric Acid |
| LDPE | Low Density Polyethylene |
| LT | Light Transformers |
| MSW | Municipal Solid Waste |
| MW | Molecular Weight |
| NBR | Acrylonitrile-Butadiene Rubber |
| OM | Optical Microscopy |
| PA | Polyamides, Trade Name Nylons |
| PC | Polycarbonate |
| PE | Polyethylene |
| PIB | Polyisobutylene |
| PTFE | Polytetrafluorethylene, Trade Name Teflon |
| PVC | Polyvinyl Chloride |
| PE | Polyethylene |
| PP | Polypropylene |
| PS | Polystyrene |
| PET | Polyethylene Terephthalate |
| POM | Polyoxymethylene |

| | |
|---|---|
| PSW | Plastic Solid Waste |
| PCDDS- | Polychlorinated Dibenzo-*P*-Dioxins |
| PCDF S | Polychlorinated Dibenzofurans |
| PMMA | Polymethyl Methacrylate |
| PB | Polybutadiene |
| SAN | Styrene-Acrylonitrile |
| SBR | Styrene-Butadiene Rubber |
| SENB | Single-Edge-Notch Bending |
| SEM | Scanning Electron Microscopy |
| TEM | Transmission Electron Microscopy |
| TGA | Thermo-Gravimetric Analyzer |
| TMA | Thermo-Mechanical Analysis |
| $T_g$ | Glass Transition Temperature |
| $TiO_2$ | Titanium Dioxide |
| TPU | Thermoplastic Polyurethane |
| uPVC | Unplasticized Polyvinyl Chloride |
| UV | Ultraviolet |
| VCM | Vinyl Chloride Monomer |
| vPVC | Virgin Polyvinylchloride |
| VST | Vicat Softening Temperature |

| | |
|---|---|
| VC | Vinyl Chloride |
| XRD- | X-ray Diffraction |
| XRF | X-ray Fluorescence |

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# ABSTRACT

Raw material powder mixtures have been prepared with polyvinylchloride (PVC) resin, unplasticized polyvinylchloride (uPVC) scraps and additives by melt mixing method. A twin screw extruder has been used to make pipe for sample preparation from the mixture. Domestic and external uPVC scraps were formulated and blended with PVC resin to form melt compound. Domestic samples designated as DS-10, DS-20, DS-30, DS-40, DS-50 and DS-100 have been prepared by blending 10, 20, 30, 40, and 50phr and 100% uPVC domestic scrap with PVC resin and various additives followed by extrusion, flattening and machining. Following the similar procedure, external samples such as ES-10, ES-20, ES-30, ES-40, ES-50 and ES-100 have been prepared using external uPVC scraps. Effects of the proportions of uPVC scraps in the raw material mix on the properties of the recycled uPVC products have been investigated. The specific properties under studies include the (i) physical (ii) mechanical properties, (iii) chemical (iv) thermal properties, (v) surface morphology and (vi) structural properties of the recycled uPVC products.

All the samples prepared have successfully satisfied the requirements of acetone test. Density of samples containing domestic scraps shows the minimum value of 0.64% for DS-50 and the maximum value of 1.91% for DS-20. On the other hand, in samples containing 10 and 40 phr external scraps the density increases by 0.64% while in sample containing 30 phr external scraps the density decreases by 4.46%. Mechanical properties, such as break stress and % elongation-at-break, impact strength, flexural strength and harness values vary with proportions of scraps in the samples.

The maximum decrease in break stress is 11.40% for 20 phr domestic scraps, while in samples containing external scraps this decrease is 15.71% for 40 phr scraps. The decrease in break stress for sample containing 100% external scraps is 38.95%.

The minimum decrease (9.48%) in viscosity number is found in sample containing 30 phr domestic scraps, while in sample containing external scraps the maximum

decrease is 42.24% in sample containing 30 phr scraps. Fourier transform infrared (FTIR) spectroscopic investigation has been followed to detect new functional groups with the addition of different proportions of domestic and external scraps. Only a variation in IR light intensity has been observed. X-ray fluorescence investigation shows a decrease in the percentage of carbon revealing the maximum decrease of 15.53% in sample containing 50 phr domestic scraps. The amount of lead added to samples as a stabilizer from lead sulphate, increases with the amount of scraps in the sample. The maximum increase is 18.52% in sample containing 40 phr domestic scraps and 37.04% in sample containing 40 phr external scraps.

Scanning electron microscopy together with energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD) analysis show the same phases in all samples. However, variation in shape and distribution of the phases and interfaces has been observed in different samples. EDS spot analysis shows a variation in elemental composition. XRD analysis shows an amorphous polymer and crystalline calcium carbonate ($CaCO_3$) phases. The relative intensities of the different peaks were different and these results can be attributed to the presence of different amount of $CaCO_3$ in the different samples. Results of thermogravimetric analysis(TGA) and EDS are in good agreement with the observation suggesting that no new phases are formed due to the addition of different proportions of scraps.

Differential scanning caloriemetry indicates two glass transition temperatures indicating a immiscibility of two components. In different samples, differences in thermal expansion or contraction have been detected by thermo-mechanical analysis (TMA). The observed values by TMA have been attributed to the difference in coefficient of thermal expansion of the different phases. TGA thermograms show that degradation temperature (around 300$^{o}$C) is much higher than the processing temperatures used (around 200$^{o}$C).

Thermal analysis results have shown that the residue content left at 1000$^{o}$C is in general higher in the samples containing external scraps. Vicat softening temperature values show that the resistance to heat increases with an increase in the amount of scraps in the samples, wherein the effect of external scraps is more pronounced. This has been attributed to the increased amount of $CaCO_3$ in the sample containing external scraps.

# CHAP TER ONE

## 1. Introduction

Polyvinylchloride is a synthetic polymeric material or resin, which is built up by the repetitive addition of the vinyl chloride monomer (VCM) with the formula [$-CH_2-CHCl-$]. PVC has thus the same chain structure as polyethylene (PE) except for the presence of chlorine. Pure PVC is a rigid material that is mechanically tough, having a fair degree of weather resistance. It is water and chemical resistant, electrically insulating, and relatively unstable to heat and ultraviolet light [1, 2].

PVC is ranked second behind polyethylene in terms of worldwide polymer consumption because it can be used in different applications such as building and construction, packaging, wires and cables, transport, furniture, etc [3]. World production of PVC today is more than 20million tonnes per year (up from 3 million tonnes in 1965), which corresponds to about one fifth of the total plastics production. Production is mainly located in the US, Western Europe and Asia [1]. The main applications of PVC in Europe are in the building sector, which accounts for 57% of all uses; PVC is also used in many other applications such as household appliances (18%), packaging (9%), electric and electronic equipment (7%), automotive equipment (7%), furniture (1%) and other applications (1%) [4].

Its ability to compound with many additives to form a wide range of flexible and rigid products constitutes the major factor responsible for the versatile application of PVC. Because of the low cost and the processability by a wide variety of techniques (injection molding, extrusion, calendaring and plastisol techniques) combined with good physical, chemical and weathering properties, PVC has become a universal polymer [5]

Most of the spent PVC products used to be disposed of via either landfill or incineration. In a sanitary landfill, PVC wastes may contaminate ground water due to leaching of pigments/dye stuff in the waste plastics products. Plastics in a landfill also cause hindrance to water filtration. Soil compactness is also hindered by throw-away plastics. In incineration, PVC burns much like other organic materials. Harmful greenhouse gases (carbondioxide, $CO_2$; carbonmonoxide CO; nitric oxide NO;

nitrous oxide, $N_2O$), hydrochloric acid (HCl), etc are emitted to the atmosphere from burning PVC [6]

Recycling saves more energy than is generated by incinerating mixed solid waste in an energy-from-waste facility. Recycling conserves energy that would otherwise be expended in extracting virgin raw materials from nature. Furthermore, energy conserved by recycling exceeds electricity generated by energy-from-waste incineration by much more than the additional energy necessary to collect recycled materials separately from mixed solid waste, process recycled materials into manufacturing feeds tocks, and ship them to manufacturers, some of whom are located thousands of miles away [5].

The disposal of spent plastics is viewed as a matter of environmental concern. In recent years recycling is being promoted as a means to address the disposal problem. At the same time recycling of plastics helps preserve natural resources and reduces consumption of energy and emissions of $CO_2$, NO and $SO_2$ gases. Recycling of plastics is a challenging task [7-10], particularly in view of the diversity of sources of waste plastics, higher potential for contamination of plastics wastes and a wide range of requirements for the intended products.

There are two ways of recycling. These are mechanical recycling and chemical or feedstock recycling. Mechanical recycling refers to processes which involve sorting, melting, shredding or granulation of waste plastics. Most of the work on mechanical recycling concentrated on separation of the different types of plastics as a pretreatment for recycling [11,12], raw materials burdening [12], thermal degradation of plastics [13,14]. Chemical or feedstock recycling involves a range of plastic recovery techniques which break down polymers into their constituent monomers. Chemical recycling technologies include pyrolysis [15, 16], gasification [17], dissolution [18] and thermal cracking [19, 20]. Chemical recycling has a greater flexibility over composition and is more tolerant to impurities than mechanical recycling. However, it is capital intensive and requires very large quantities of used plastics for reprocessing to be economically viable. Properties and morphology of recycled plastics have also been investigated [21].

In Bangladesh, a large quantity of used PVC products is mechanically recycled. The recycled products are usually of low quality and have a limited useful life. A detailed study [22] on the quantity of recycled plastics, on the persons involved in recycling, effects on the environment, etc has been undertaken by Non-Government Organisations (NGOs). However, results of systematic study on the properties of recycled PVC products, particularly how the proportions of recycled PVC in the raw materials mix affect the properties of the products have not, so far, been reported.

## 1.1 Objectives of the Research Work

In this study, different proportions of scrap uPVC, called the unplasticized PVC(uPVC) have been blended with PVC resin and additives with recycled PVC products. The main aim of this work is to determine the effects of the proportions of scrap PVC on the properties of the recycled uPVC products. The specific properties under consideration include the (i) physical (ii) mechanical properties, (iii) chemical (iv) thermal properties, (v) surface morphological and (vi) structural properties of the recycled uPVC products. The academic interest of the work includes the identification of the mechanism that causes the variation in properties, if any, due to addition of scraps to PVC resin and additives.

It is expected that the results obtained will help to determine the optimum quantity of scrap that could be used in the raw material mix without any significant harmful effect and thus help improve the properties of the recycled PVC products produced in Bangladesh for various uses.

## 1.2 Structure of the thesis

This dissertation is divided into six chapters. The relevant literature is reviewed in chapter Two. The materials and experimental procedure used in this study have been described in chapter Three. The results of investigation have been presented and discussed in chapter Four. The conclusion drawn from the research work and suggestions for future work have been provided in chapter Five. Experimental data and graph drawn have been shown in annexure I and II.

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# CHAPTER TWO

## 2. Literature Review

### 2.1. History of polyvinylchloride

The history of polyvinylchloride started in 1835, when the monomer was discovered by Liebig and his student Regnault, but about 80 years later the polymer received industrial interest [1] In about 1910 Zacharias and Klatte at Griesheim Elektron near Frankfurt, Germany, investigated the addition of several chemicals to acetylene, a product which was technically available at this time from calcium carbide, but whose application for illumination was falling off because of the use of electricity for this purpose. F. Klatte (1880-1934) described not only the light-induced polymerization of vinyl chloride, which was first observed by Baumann in 1878, but also the initiation of the vinyl chloride polymerization by oxygen-containing compounds such as peroxides or ozone. Klatte can, therefore, be named as the inventor of the free-radical polymerization with peroxides. He also found it possible to process PVC under the influence of heat and pressure and proposed PVC as a substitute for films, fibers, and natural lacquers. From an economic point of view Klatter's invention was not successful, and in 1926 Griesheim-Elektron allowed the PVC patents to lapse, thus opening the door for other companies.

Because of the difficulties in processing and the insufficient thermal stability of PVC, the first technical products between 1928 and 1930 were copolymers of vinyl chloride with vinyl acetate, vinyl ethers, and acrylic esters. Later, homo-polymerization of vinyl chloride in emulsion, chlorination of PVC, plasticization and the suspension as well as (in the early 60s) the bulk polymerization were the next important steps in PVC history, which is summarized in Table 2.1.

Table 2.1: Milestones in PVC History [2].

| Year | Historical Development of PVC. |
|---|---|
| 1835 | Liebig and Regnault discovered vinylchloride. |
| 1878 | Baumann observed the light-induced polymerization of VC. |
| 1912 | Zacharias and Klatte obtained VC by addition of HCI to acetylene. |
| 1913 | Klatte polymerized VC with organic peroxides and described the processing of PVC into a substitute for horn and for films, fibers, and lacquers. |
| 1926 | Griesheim-Elektron allowed the PVC patents to lapse; this opened the door for other companies. |
| 1928 | Union Carbide and Du Pont copolymerized VC and vinyl acetate. |
| 1930 | IG-Ludwigshafen copolymerized VC with vinyl ethers and acrylic esters; emulsion polymerization of VC, stabilization with alkali salts, characterization by K-value (Fikentscher). |
| 1932 | Chlorination of PVC (IG-Bitterfeld). |
| 1933 | Semon found phthalates and phosphates to be plasticizers for PVC. |
| 1935 | Suspension polymerisation of VC (Wacker) (capacity, 1945: 35000 tons). PVC pilot plant in Bitterfeld (600 tons/year). |
| 1936 | Manufacturing of PVC by Union Carbide and B. F. Goodrich. |
| 1962 | Bulk polymerization of VC (two-stage reactor; 1975, one stage reactor) by St. Gobain and Pechiney, Rhone-Poulenc |

One of the most serious problems for PVC processing and handling is the rather low thermal stability. The dehydrochlorination of PVC starts at about 100°C and is the reason for discoloration, owing to the formation of polyene (poly-unsaturated organic compounds that contain one or more sequences of alternating double and single carbon–carbon bonds) sequences. In spite of all efforts and many research activities, the details of these reactions are not completely understood even today. It was found very early in the beginning of the PVC industry that a number of chemicals can be used as stabilizers against these very undesirable degradation processes. The basic principles of stabilization against heat and light were developed between 1930 and 1950, but the search for more effective, less toxic, and environmentally friendly systems has been one of the most important tasks of the PVC industry up to now. Table 2.2 shows some of the milestones in the development of PVC stabilizers.

Table 2.2: Milestones of PVC Heat Stabilization [2].

| Year | Development of different types of stabilizers |
|---|---|
| 1930 | Alkali and organic bases |
| 1934 | Frazier Groff (union carbide) discovered alkaline earth soaps |
| 1934 | Lead salts (carbide and carbon chemicals) |
| 1935 | Dialkyltin soaps (carbid and carbon Chemicals) |
| 1936-37 | Synergistig combination of barium. cadmium, calcium and zinc soaps |
| 1952-53 | Dibutyltin thioglycolates (elliot weinberg, metal and thermit corporation ) |

Table: 2.3 Physical Parameters of PVC [3].

| Salient feather of PVC | | Values | |
|---|---|---|---|
| Percent crystallinity | as polymerized | 19% | |
| | from the melt | 4.9% | |
| Density (uncompounded) | whole | 1.39 grams/cc. | |
| | Crystallites . | 1.53 grams/cc | |
| Glass transition temperature | | 83$^{o}$C | |
| Coefficient of linear thermal expansion (uPVC) | | 7 X 10-5/$^{o}$C. | |
| Specific heat for rigid PVC | | 23$^{o}$C | 0.22 cal./gram |
| | | 50°C | 0.25 |
| | | 80°C | 0.35 |
| | | 120°C | 0.39 |
| plasticized PVC (50 phr DOP) | | 23 °C | 0.37 |
| | | 50 °C | 0.40 |
| | | 80 °C | 0.42 |
| | | 120 °C | 0.45 |
| Thermal conductivity (unplasticized) | | 4.2 X 10$^{-4}$ cal/cm sec °C. | |
| Dielectric strength | | 20 kVolts/mm. | |
| Solubility parameter | | 9.75 (average)[cal./cm$^{3}$]$^{0.5}$ | |

## 2.2 Processing of uPVC

uPVC is processed through a number of stages to the finished product on a wide variety of machines. The various processing routes involve three interconnected stages of pre-mixing with additives, compounding and shaping. Each step is not mutually exclusive of the others but there is considerable merging of stages particularly in modern machines where the latter two stages are often completed in a single step.

In all uPVC processing techniques the first stage involves pre-mixing with additives by a simple low speed mixer through to high speed mixing at elevated temperatures. Twin-screw extruders are normally fed with dry blend which is produced in a high speed mixer. Depending on the dry blend properties required, the mix is taken to different temperatures before being discharged to the cooler.

uPVC is a predominantly amorphous polymer, although there is a low but significant degree of crystallinity. Highly crystalline polymers do not exhibit a sharp melting point, but gradually softens above Tg, ultimately forming a viscous melt, which becomes more fluid with increasing temperature. In the absence of heat stabilisers, degradation through dehydrochlorination would generally occur before temperatures for satisfactory processing could be reached. Even with the addition of stabilisers, the temperature at which degradation and subsequent coloration occurs quite rapidly is not far above that reached in some melt processing operations. Thus, there is a requirement for careful temperature control, streamlined flow paths and absence of stagnation in the processing of rigid PVC compositions.

It is not surprising that the visco-elastic properties of PVC melts are complex and variable. The nature of this complex behavior and its practical significance in processing and fabrication constitute a principal theme of the presentation that follows. The relatively broad transition between the solid and melt states, and the visco-elastic properties of the PVC melt, provide advantages as well as problems to the processor. Thus, the high melt stiffness of a rigid PVC extrudate facilitates handling and sizing. Whilst high melt viscosity and limited heat stability limit flow paths during injection molding, the molded article exhibits much less shrinkage or distortion than is encountered with many other plastics. PVC foil may be readily thermoformed because of the controlled and partial softening that can be achieved by reheating. With continuing improvements in machine design, in formulation technology, and in the range of polymer grades available, rigid PVC is processed today by all the major techniques available to the plastics industry. These include the extrusion of pipe, complex profiles, sheet and foil, calendaring, thermoforming, injection molding and blow molding. The application of these various techniques is fully described in standard texts [4-6]. The most frequent reference will be extrusion, because it is the most commercially important of the techniques used to convert unplasticised PVC into useful products, and because as a consequence it has been the subject to the most detailed and fundamental study.

In 1996, Wenguang *et al* [7] studied mechanical properties and processing of recycled PVC and of homopolymer blends with virgin PVC blends of recycled and pipe grade PVC. It was found that the particle size and the re-stabilization of the recycled PVC are the two main points to be considered for obtaining virgin/recycled PVC blends with uniform and good mechanical properties. In general, recycled PVC not only significantly reduce the Young's modulus and tensile strength, but also improves the impact strength and processing behavior of pipe grade virgin PVC. Only the thermo-mechanical resistance is slightly lowered. The latter points hold, of course, only when the recycled PVC contains both reinforcing and modifier agents.

In 1992, Covas *et al* [8] studied the behavior of unplasticized polyvinyl chloride (uPVC) during single screw extrusion. The melting and gelation mechanisms under a variety of operating conditions were identified using microscopy, density measurements, and thermal analysis. The compound followed the behavior of wall-slipping materials, the melt forming a pool near the passive flight of the screw. Gelation involved the progressive destruction of the original powder morphology and the development, upon cooling, of an entanglement network with primary and secondary crystallinity. Both the breakdown and internal fusion of the grains were observed, depending on the location of the material around the screw. Tensile yield parameters were found to be independent of the gelation level. The values of the post-yield parameters reached a maximum for gelation levels in the range of 70% to 85%.

In 1992, Endo [9] studied synthesis and structure of polyvinylchloride by radical and other polymerization mechanisms. The features of solution, bulk, suspension, and emulsion polymerization of vinylchloride were described. Terminal structure and defect structures introduced in the chain during the polymerization were discussed. Control of core–shell structure provided one method to improve the thermal stability of PVC. Tacticity (arrangement of elements within the macromolecules) and crystallinity (crystallinity: ratio of the hump area of amorphous phase to the crystalline area of inorganic phase calculated using relevant software*)* of PVC play an important role regarding the use of PVC. Radical copolymerization of VC with various vinyl monomers was described to improve the thermal stability of PVC. Graft copolymerization with other vinyl monomers including the use of labile chlorine atoms was useful method to improve the physical and thermal properties of PVC. Synthesis of block copolymers was described by mechano-chemical methods and using terminal functional polymers. Controlled polymerization was achieved with anionic polymerization catalysts. Promising metallocene catalyst promoting polymerization of VC was also described.

In 1992, Pena *et al* [10] studied plastification of polyvinyl chloride by polymer blending with different copolymers to obtain a plasticized PVC with improved properties and the absence of plasticizer migration. The copolymers used as plasticizers in the blends were acrylonitrile butadiene rubber, ethylene vinyl acetate (EVA), and ethylene-acrylic copolymer (E-Acry). Blends were studied with regard to their processing, miscibility, and mechanical properties, as a function of blend and copolymer composition. The results obtained were compared with those of equivalent compositions in the PVC/dioctyl phthalate (DOP) system. Better results than PVC/DOP were obtained for PVC/acrylonitrile butadiene rubber blends. The plasticizing effect on PVC of EVA and E-Acry copolymers was similar to that of DOP. It is shown that cross linking PVC/E-Acry blends or increasing the vinyl acetate content in PVC/EVA blends is an alternative that can increase the compatibility and mechanical properties of these blends.

### 2.3 Ingredients of uPVC Compound

Although PVC is a very versatile polymer, proper compounding and good lubricant balance are critical in obtaining good machine and end product properties.

#### 2.3.1 Resin

PVC resin is available in a wide range of molecular weights. In the United States, the molecular weight is expressed as inherent viscosity (I.V.); in Europe it is expressed as K value, in Japan it is the degree of polymerization. Commercial PVC resins available range from an I.V. of 0.50 to 1.15 (K value, 47 to 76). The higher the IV, the higher the molecular weight and the greater its stiffness. Below is a Table showing I.V. vs. processes and end use.

Table: 2.3. 1.1 Inherent Viscosity (IV) of PVC

| I.V. Range | Process | End Use |
|---|---|---|
| 0.05 - 0.65 | Injection molding | Very complicated molded end use |
| 0.65 - 0.85 | Injection molding and extrusion | Pipe fittings, monofilamenst, sheet, film, profiles, cellular |
| 0.85 - 0.98 | Extrusion | Pipe, siding, sheet, film, profiles, flexible window profiles |
| 0.98 - 1.16 | Extrusion | Complicated profiles, flexible, wire and cable |

#### 2.3.2 Fillers

There are many fillers which can be used with PVC including metal carbonates and silicates, gypsum, clay, alum, barytes and saw dust. The most common are metal carbonates, mainly calcium carbonate which is usually in the form of ground limestone and coated with stearic acid. The coating reduces the abrasiveness of the calcium carbonate. It also reduces extruder barrel and screw wear. Calcium carbonate is available in ground and precipitated grades with a range of particle sizes. As a general rule, the finer calcium carbonate yields better impact strength of the finished product. If the calcium carbonate is very fine, it can cause titanium dioxide to agglomerate. This will create a $TiO_2$ streak in the part. Normally, increasing calcium carbonate content reduces tensile strength and increases tensile modulus. For pressure pipe, the level should never exceed five parts per hundred resin (phr) because higher levels of calcium carbonate could lower the stress design below 15MPa which is normally required.

They are used to reduce the cost, increase stiffness, and reduce the cost of final plastic part [11]. As the level of calcium carbonate increases, overall material cost decreases, but the specific weight of the product increases. This is because the specific gravity of calcium carbonate is higher than the specific gravity of PVC. This relationship between compound cost reduction and increased weight per foot must be balanced to give an overall economic reduction. Today, this level is between 3 and 4 parts per hundred for pipe. Siding substrate is 8 to 12 phr.

Extruder barrel and screw wear are affected by the amount and the particle size of the calcium carbonate. As amount and coarseness increase, the wear will increase. At levels of 5 parts per hundred and below, wear is considered minimal, but higher levels increase wear drastically. Levels of above 40 phr have been reported. This can cause some barrels and screws to wear out in six weeks. Therefore, this cost must be considered. Calcium carbonate particles larger than ten microns often cause increased barrel wear and reduced impact strength because they act like holes or stress concentration points. Increased levels can also cause a reduction in tensile modulus (at high part levels). Calcium carbonate serves no useful purpose in PVC except to reduce compound cost and weatherability of compounds.

In 2006, Karayildirim *et al.* [12] investigated particulate fillers such as Red Mud (RM), $CaCO_3$ and dolomite on the thermal degradation of PVC. They concluded that in the presence of carbonates, the peak temperature ($T_{\max}$) of dehydrochlorination was shifted to a higher temperature and the rate of mass loss was decreased, while, in the presence of RM, $FeCl_3$ was formed and dehydrochlorination of PVC was accelerated, but the second decomposition step of PVC has been retarded.

### 2.3.3 Stabilizers

Polyvinyl chloride (PVC) is a heat and light sensitive material. It degrades by dehydrochlorination and oxidation. This can be seen by the development of color in PVC. In chemical terms, formation of conjugated double bonds causes the color change. PVC compounds experienced heat history in mixing cycles, extrusion/molding, embossing, thermoforming, laminating and scrap rework. Oxidation products occur by exposure to weathering. The job of the stabilizer is to delay heat degradation so that the compound can be formed into a product before it degrades. The stabilizer does this job by absorption of hydrogen chloride, displacement of active chloride atoms, free radical scavenging, disruption of double bond formation, and deactivation of degradation by products, peroxide decomposition and ultraviolet energy absorption.

Stabilizers in pipe extrusion are used mainly to process the PVC through the hot hostile environment of the extruder. They do not significantly affect shelf life or weatherability except in so-called “weatherable” compounds. In these weatherable compounds, the amount of stabilizer is five to seven times the level in pipe, and stabilizers do have a positive effect on weatherability. A given recipe, even with high levels of titanium dioxide, will have less weatherability at half the normal level of stabilizer. Any changes in level or supplier of stabilizers should be checked for weatherability before complete changeover has been made.

Lead stabilizers, particularly tribasic lead sulfate, are commonly used in plasticized wire and cable compounds because of its good non-conducting electrical properties [13]. Organotin stabilizers are commonly used for rigid PVC, including for pipe, fittings, windows, sliding profiles, packaging and injection molded parts. These repair unstable sites on PVC removing unstable: chlorine and replacing it with a ligand from the tin stabilizer molecule [14-16]. This produces stability at least an order of magnitude better than without stabilizer. Examples of effective tin compounds are di-alkyltin dilaurate, and mono-/di-alkyltin diisooctlythioglycolate. Certain grades of methyl tins and octyltins are used in food contact applications.

### 2.3.4 Ultraviolet light stabilizers

One form of stabilization is to absorb the ultraviolet light. Both titanium dioxide and carbon black are strong ultraviolet light absorbers and effective in protecting the PVC. The carbon black is a stronger absorber than titanium dioxide and can, therefore, be used at lower levels in PVC for protection. For ultraviolet light absorption in transparent PVC or to improve pigmented systems, various derivatives of benzotriazole are used such as 2-[2'-hydroxy-3', 5'-(di-t-butyl)phenyl] benzotriazole. Where tin carboxylate stabilizers are used instead of tin-mercaptide stabilizers, hindered amine light stabilizers, particularly with ultraviolet absorbers are effective [17].

### 2.3.5 Lubricants

Lubricants are materials that control the fluxing (melting) point in the extruder/molder to achieve the best processing characteristics and physical properties. There are three types of lubricants. They are external, internal, and external/internal. Many authors classify lubricants as internal or external [18– 20].

Internal lubricants are normally polar molecules. They are usually fatty acids, fatty acid esters or metal esters of fatty acids and are very compatible with PVC. They lower melt viscosity, reduce internal friction and promote fusion. Common problems of under-lubrication are rough extrudate, adhesion to metal surfaces, melt fracture, quick fusion and abnormally low barrel temperatures. In the end product, burning, plate-out, matte surfaces and poor impact strength are typical results of under lubrication.

External lubricants are normally non-polar molecules or alkanes. They are usually paraffin waxes, mineral oils or polyethylene. Some stabilizers have oils that carry active ingredients such as external lubricants. External lubricants are normally incompatible with PVC. They help the PVC slip over the hot melt surfaces of the dies, barrels and screws without sticking and contribute to the gloss on the end product surface. Extruder motor amperage is greatly affected by small changes of external lubricants.

Common problems resulting from over-lubrication include: surging of the extruder, lumpiness of the extrudate, incomplete fusing and the necessity of high barrel temperature. In the end product, low impact strength and acetone failure are the common manifestations found.

Others have shown classifications based on synergy between various lubricants [21-22] but did not explain the nature of that synergy. A model for the lubrication mechanism has been developed which explains synergy between certain lubricants [23]. This model treats lubricants as surface active agents. Some lubricants have polar ends which are attracted to other polar ends and to polar PVC flow units and to polar metal surfaces. These also have non-polar ends which are repelled by the polar groups. Synergy happens when non-polar lubricants, which are attracted to the non-polar ends and act as a slip layer, are added.

### 2.3.6 Pigments

There are three main reasons to use pigments in PVC compounding: to achieve opacity in non-weatherable compounds, for UV protection in weatherable compounds and to achieve a given color. Titanium dioxide is the major pigment used. Other pigments are used in small amounts to achieve the desired color in combination with the titanium dioxide.

In pipe and some profiles, opacity and color are the main purposes of the pigments. For these uses, titanium dioxide levels are normally between 0.5 to 5.0 phr. At these levels the effect on weathering is minor. Both color and properties will be drastically affected by long-term exposure to UV radiation. The titanium dioxide used in these compounds is normally controlled chalking rutiles.

### 2.3.7 Processing aids

As the name indicates, these additives assist the melt processing of PVC compositions, but in a way that is quite distinct from the role of lubricants. Processing aids do not reduce melt viscosity, and may even produce some increase in viscosity, but they improve the elastic behaviour of the melt. Rigid PVC melts are prone to rupture under high accelerating stresses, and many of the practical processing problems encountered are caused by melt rupture. For example, the ‘sharkskin’ surface sometimes met in extrusion is the result of a cyclic rupture/recovery mechanism in the surface layer of the melt when it cannot stretch sufficiently to accommodate the velocity changes at the die exit [24].

Processing aids glue these particles together before the PVC melts, thus acting as a fusion promoter. Processing aids also modify melt rheology (deformation and flow of molten materials) by increasing melt elasticity and die swell, or, some reduce melt viscosity and melt fracture. Some processing aids lubricate to reduce PVC sticking to metal. Processing aids also affect dispersion of fillers, impact modifiers, and pigments [25]. The most common processing aids are high molecular weight acrylics based primarily on polymethylmethacrylate copolymers.

### 2.3.8 Impact modifiers

In the early days of plastics, many uPVC products were brittle. This gave plastics a cheap reputation. It was therefore quite desirable to develop technology to produce tough plastics. In early 1950s, the Geon Company (then a part of BFGoodrich) began adding rubbery polymers to PVC to improve toughness [26]. Rubbery particles act as stress concentrators or multiple weak points, leading to crazing or shear-banding under impact load. This can result in cavitation and/or cold drawing, thus allowing the PVC to absorb large amounts of energy.

Certain applications require higher impact strength than PVC would demonstrate normally. Acrylic, CPE, MBS, and ABS polymers are normally used to modify impact strength of PVC. These polymers provide a shock absorber when the PVC is heated to a high enough melt temperature $196^{o}$C to fuse it. At lower melt temperatures, the impact is lower than it would be without impact modification. At this lower melt temperature, the impact modifier acts like a hole or stress concentrator making the impact lower. Using the proper melt temperature will ensure that the full properties of the impact modifier will be realized.

All impact modifiers reduce the weathering, chemical resistance, tensile strength and stress rupture of PVC compounds. If these properties are desired, the lowest possible level needed to achieve the desired impact should be used. Pipe generally has 0 to 2 phr of impact modifiers, while siding and profile have 0 to 10 phr. High impact PVC compounds with lower chemical resistance and stress rupture have 6 to 14 phr of impact modifiers.

Weatherability can be affected by both types and levels of impact modification. Normally, CPE, EVA and acrylic polymers are used in weatherable compounds. They allow good retention of properties, along with good color retention. Both MBS and ABS impact modifiers are poor in these characteristics, but are good for low temperature properties.

Impact modifiers generally promote flux, with the exception of CPE. As flux promoters, they tend to reduce the temperature of the extruder barrel needed for a given melt temperature. This point needs to be considered when compounding PVC.

### 2.3.9 Flame retardants

Since PVC contains nearly half its weight of chlorine, it is inherently flame retardant. It also acts chemically to inhibit the fast oxidation in the gas phase in a flame. When PVC is diluted with combustible materials, the compound combustibility is also increased. For example, plasticized PVC with >30% plasticizer, may require a flame retardant such as antimony oxide, a phosphate type plasticizer, or chlorinated or brominated hydrocarbons [27-28].

## 2.4 Effects of additives

Additives are becoming more technical, doing more work, offering greater value, and so commanding a higher price. PVC is still by far the largest user, in volume terms, but polyolefins have emerged as a growing second-runner and the development of engineering plastics has opened up a fast-growing market for speciality additives, ranging from flame retardants to stabilizers, pigments, and processing aids that will resist the higher processing and service temperatures involved. These naturally impose more critical performance requirements. Many additives have more than one effect on a plastics compound. Plasticizers will often aid in processing and lubrication. Light stabilizers also have an effect of weathering. Carbon black, which is widely used as a pigment, also functions as a light shield, as an electrically conductive component, and as reinforcement.

In 2006, Hakkarainen *et al.* [29] worked on environmentally friendly plasticizers for polyvinylchloride. In this study linear and branched polybutylene adipates (PBA) with molecular weights ranging from 2000 to 10,000 g/mol, and branching agent content between 0 and 1.8%, were solution cast with PVC to form 50- to 60-μm thick flexible films. Dry films were analyzed by tensile testing, FTIR, DSC, and OM to study the effects of molecular weight and branching on the plasticizing efficiency of the polyester. PBA formed a semimiscible two-phase system with PVC, where the amorphous part exhibited a single glass transition temperature. The degree of crystallinity for the polyester, surface composition, and mechanical properties of the films depended on the blend composition, molecular weight, and degree of branching of the polyester. They concluded that plasticizing efficiency was improved by higher degree of branching.

### 2.5 Effect of processing parameters

The effects of fundamental processing parameters such as heat, compression and shear are assessed herewith. If polymer powder is simply heated, relatively little change takes place until a temperature of 150°C is exceeded. Then a spontaneous loss of porosity occurs with slightly more obvious loss from the surface regions . When heat and pressure are applied together the relationship between powder density and applied pressure over a range of temperatures shown in Fig. 2.5.1 is recorded. Obviously the glass transition temperature of PVC (~80°C) must be exceeded before an appreciable increase is seen but the more quickly the material exceeds 100 °C the lower is the applied pressure needed to produce a dense compacted powder.

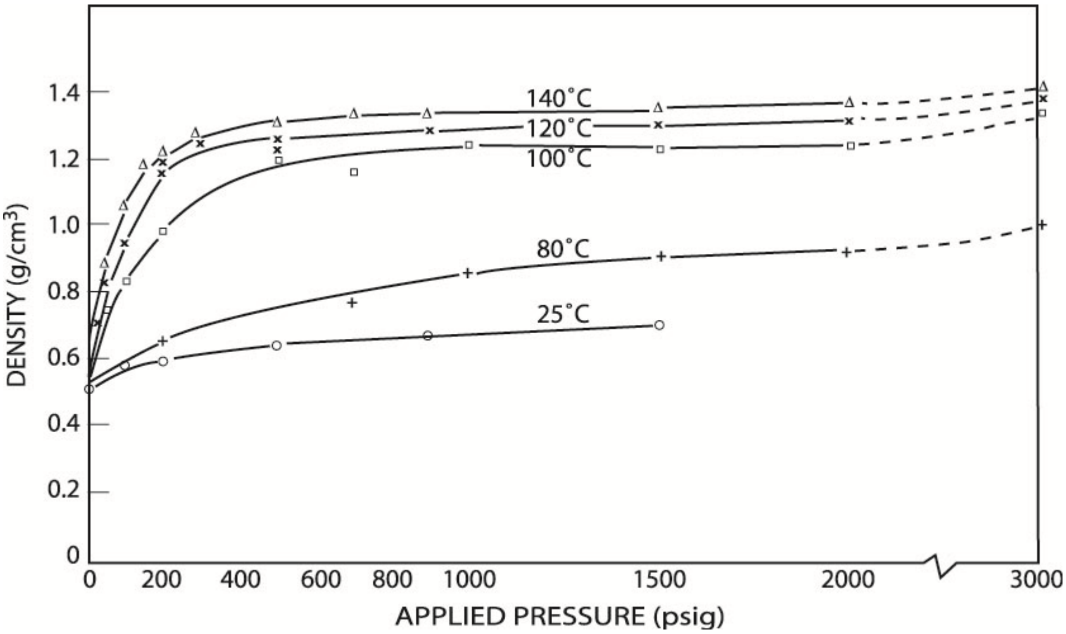
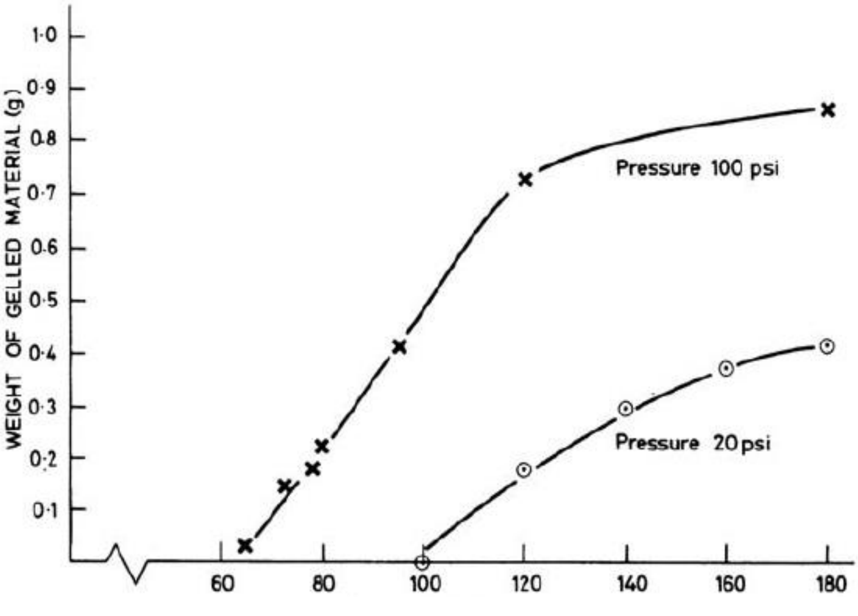


Fig. 2.5.1 The relation between density and applied pressure at different temperature [30]



Final temperature °C

Fig. 2.5.2 The relation between weight change with temperature [30]

If the shear component is now applied significant changes result. The influence of pressure and hence shear on the gelation process is clearly seen in Fig2.5.2. At low temperatures the low applied pressure cannot compact the material sufficiently and shear is not transmitted. Instead the grains simply move relative to one another dissipating the applied shear although some frictional heating is generated. At higher pressure more compaction results and hence the shear force is applied more effectively resulting in higher temperatures and a larger quantity of fused material.

Therefore, in extrusion the quicker the dry blend reaches a temperature in excess of 100–120 °C, the lower is the pressure required before the material is sufficiently compressed into a compacted powder which can transmit shear. Once the shear component is added the rate of fusion increases rapidly.

In 2006, Hassan *et al* [31] studied the impact properties of acrylate rubber-modified PVC to develop high impact strength polymers and exploited commercially on a large scale. Rubber-toughened uPVC or high impact uPVC is one such important class of rubber-toughened plastics material which has been developed and has a wide application in the building and furniture industries. The type of impact modifiers most commonly used for window frame applications are chlorinated polyethylene, ethylene-vinyl acetate and acrylate modifiers. The current trend shows the importance and popularity of high impact-acrylate-modified PVC. The understanding of toughness enhancement in rubber-toughened polymer materials to acrylate rubber-modified PVC has been extended. The effect of temperature on the impact strength of acrylate rubber-modified uPVC using the instrumented falling weight impact test (IFWI) method has also been reported in this paper. Toughening and fracture mechanism in acrylate-modified PVC were also investigated.

The results show that all the acrylate rubber-toughened PVC blends have successfully shifted the ductile–brittle transition points to a lower temperature. However, the impact modifiers were found to differ in their efficiency to shift the ductile to brittle transition. The findings from the SEM study show that the fibrous yielding phenomenon observed is an indication of the transition of the brittle stage to ductile stage and correlates well with the large increases of the impact strength.

In 2007, Fillot *et al* [32] studied thermo-mechanical history effects on rigid PVC microstructure and impact properties. Rigid PVC microstructure strongly depends on processing conditions: under both shear and heat influence, gelation process occurs, and the resulting morphology can be characterized by the so-called gelation level parameter. But thermo-mechanical history also affects several other features of the microstructure. In this work, two different aspects mainly related to orientation and molecular mobility are pointed out, and their respective effects on PVC impact properties are described. Charpy impact tests have been carried out on a typical extruded window profile formulation, showing a strong anisotropy effect in those extrudates. It turned out that modulated differential scanning calorimetry was able to prove macromolecular orientation. Then, the effects of heat treatments on impact properties were investigated. Below the glassy transition temperature ($T_g$) of PVC, physical ageing results in a decrease of the impact performance, without affecting PVC anisotropy. The reason of this performance loss is the reduction of the molecular mobility, as evidenced by dynamical mechanical analysis experiments. After performing a heat treatment above $T_g$, another important decrease of the impact performance was observed. This decrease was attributed to partial disorientation of the PVC macromolecular chains and reduction of the molecular mobility.

In 2003, Moghri *et al* [33] studied the effect of processing parameters on fusion and mechanical properties of a twin-screw extruded rigid PVC pipe. The effect of varying mass temperature and screw speed on the fusion level and mechanical properties of a rigid PVC pipe produced by a twin-screw extruder was investigated. DSC and capillary rheometry were used to determine pipe fusion levels. While yield stress was shown to be completely insensitive to fusion level, a very distinct maximum of falling weight and notched Charpy impact strengths and elongation at break was observed at moderate fusion level. Short-term burst strength values increased with degree of fusion while hydrostatic internal pressure tests revealed optimum resistance for pipes of varying fusion level.

In 1999, Yarahmadi *et al* [34] studied the effects of accelerated and natural ageing on PPVC. About 50 different cables and sheathings from 3, 24- to 34-year-old houses were investigated with respect to tensile properties, residual stability, composition and remaining lifetime. One type of PVC material used as a model and containing equal proportions of the plasticizer was subjected to accelerated ageing at 80-110$^{o}$C in air and in nitrogen atmosphere using low laminar gas flow. The effects of ageing were detected after fixed periods of time of up to 2 months of exposure, using measurements of mass loss, residual stability (the remaining effect of the stabilizer after consumption during processing and application) and elongation at break. The mass loss as well as the consumption of the stabilizer in the model material seems to be independent of the presence of oxygen. The activation energies were determined to about 98-99 kJ/mol for the mass loss in air and in nitrogen, and about 101-104 kJ/mol for the stabilizer consumption.

These results indicate that the mass loss is the dominant process in ageing of plasticized PVC at low temperatures. Ageing in air at 80 and 90$^{o}$C for up to 8 weeks caused no significant changes in elongation at break. At 100 and 110$^{o}$C, the maximum change in elongation at break was about one third of the original value, which corresponded to the maximum mass loss of about one third of the original amount of the plasticizer. Cables and sheathings collected from old buildings were tested and showed little change in elongation at break even after 34 years of use. In addition, the measurements of residual stability show high values, indicating good thermal stability of the old materials. Some materials were also subjected to accelerated ageing in air at 80$^{o}$C. Accelerated ageing did not significantly affect the tensile properties of the insulation materials. The maximum change in the content of extractable matter that was observed after ageing was 1%. The investigation has consequently shown that the technical quality and the remaining lifetime of the old cables and sheathings that had been collected are very good, making them suitable for reuse or mechanical recycling.

In 2002, Pita *et al* [35] studied the mechanical properties of PVC/plasticizers and PVC/thermoplastic polyurethane blends from extrusion processing. Mechanical properties of blends of PVC with DIDP and TPU were compared with DOP. The influence of processing conditions on the mechanical properties was studied by changing the content of the additives and using different twin screw speeds. The mechanical properties (tensile strength, modulus, and energy) of PVC/DIDP presented the same behaviour as PVC/DOP at all concentrations. The mechanical characteristics of PVC/DOP and PVC/DIDP show that these systems are probably affected by the speed of the twin screw. Polyurethane blends exhibit better structural properties compared to the other plasticizers. The twin screw speed exhibited no influence on the stress–strain property profile of the PVC/TPU blends. The results indicate a minor influence on the decrease of PVC properties when the plasticizer used is a TPU.

In 2003, Zhou *et al* [36] studied the influence of CPE and ABS on the mechanical properties of PVC)/CPE and PVC/ABS hybrids. The experimental results show that the toughness of the hybrids could be modified greatly by the introduction of CPE or ABS. The microstructure and impact surfaces of the blends were investigated by scanning electron microscopy and transmission electron microscopy. ABS dispersed in the form of particles or agglomerates in the PVC matrix, and CPE tended to disperse as a net structure. In the tensile test, ABS initiated crazes as stress concentrators to toughen the PVC matrix, whereas CPE, with the PVC matrix together, caused a yield deformation by shear stress to form a shear band. The formation of crazes and shear bands benefited the toughening of PVC, but to the different extent.

In 2003, Wan *et al* [37] studied three kinds of PVC/montmorillonite (MMT) nanocomposites prepared by melt blending of PVC with $Na^+$-MMT and two organically modified MMTs[7]. The nanostructure and relaxation behavior of the PVC/MMT nanocomposites were studied by wide angle X-ray diffraction (WAXD), TEM and DMTA. It was found that partially intercalated and disordered structure formed in PVC/$Na^+$-MMT nanocomposites, while partially intercalated and partially exfoliated structures coexisted in the two PVC/organic MMT nanocomposites. The stiffness and impact strength of the three kinds of nanocomposites were improved simultaneously within 0.5–3 wt% MMT content with respect to that of bulk PVC. Below 5 wt% MMT content, the three kinds of nanocomposites retain good optical clarity. In addition, the addition of organic MMT should be kept below 5 wt% in order to enhance the mechanical properties and improve the processing stability of the PVC/MMT nanocomposites.

## 2.6 Waste management and recycling

PSW presents challenges and opportunities to societies regardless of their sustainability awareness and technological advances. A special emphasis has been paid on waste generated. Four routes of PSW treatment covering primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (energy recovery) have been discussed below.

Primary recycling, which involves the re-introduction of clean scrap of single polymer to the extrusion cycle in order to produce products of the similar material, is commonly applied in the processing line. When plastic articles are discarded after a number of life cycles, mechanical recycling techniques present themselves as a candidate for utilizing a percentage of the waste as recyclate and/or fillers. The various waste products, consisting of either end-of-life or production (scrap) waste, are the feedstock of secondary techniques, thereby generally reduced in size to a more desirable shape and form, such as pellets, flakes or powders, depending on the source, shape and usability.

Collectively, all technologies that convert polymers into either monomers (monomer recycling) or petrochemicals (feedstock recycling) are referred to as chemical recycling. The technology behind its success is the depolymerization processes (e.g. thermolysis) that can result in a very profitable and sustainable industrial scheme, providing a high product yield and a minimal waste. Tertiary treatment schemes have contributed greatly to the recycling status of PSW in recent years. Advanced thermo-chemical treatment methods cover a wide range of technologies and produce either fuels or petrochemical feedstock. Nowadays, non-catalytic thermal cracking (thermolysis) is receiving renewed attention, due to the fact of added value on a crude oil barrel and its very valuable yielded products. But a fact remains that advanced thermo-chemical recycling of PSW still lacks the proper design and kinetic background to target certain desired products and/or chemicals.

Due to their high calorific value and embodied energy, plastics are being incinerated solely or in combination with MSW in many developed countries. Energy recovery was found to be an attainable solution to PSW in general and MSW in particular. The amount of energy produced in kilns and reactors applied in this route are sufficiently investigated up to the point of operation, but not in terms of integration with either petrochemical or converting plants. Cement kilns and fluidized beds are the two most common units used to recover energy from PSW or MSW with high PSW content. Primary and secondary recycling schemes are well established and widely applied but tertiary and quaternary treatment schemes appear to be robust and worthy of additional investigation.

In 2010, Al-Salem *et al* [38] worked on plastic solid waste (PSW) aiming to provide an in depth analysis regarding the recovery, treatment and recycling routes of PSW. There are many processing technologies and characterization techniques that deal with waste plastic solid including waste PVC. In this review, we have concentrated on those processes and techniques that deal with physic-mechanical properties of rigid polyvinylchloride. Some relevant literature review concerned with recycling and characterization techniques has been depicted below.

In 2004, Takeshita *et al* [39] developed a process to treat waste plastics in an environmentally friendly way. The increased awareness of possible problems caused by waste PVC plastics led to a need to develop a reliable technique for treating them in a safe and environmentally friendly way, that is, in a way that does not lead to the release of chlorinated organic compounds. They focused on using water vapor at sublimation pressure and subcritical and supercritical water as solvents for treatment. They found that chlorine in PVC dissolved in water as hydrochloric acid, and no harmful chlorinated organic compounds were observed in the liquid and gas fractions after treatment at 300 °C. Between 250 and 350 °C, this technique produced polyene as a residual solid, and low-molecular weight aromatic and aliphatic compounds in the liquid and gas fractions. Further decomposition at over 350 °C in supercritical water produced acetone, phenol, benzene, benzene derivatives, and aliphatic alkane and alkene in the liquid and gas fractions. The combustion enthalpy of the residual solid was 9270 kcal/kg, which was in the same range as the values for coal and coke.

In 2008, Tongamp *et al* [40] studied the mechano-chemical dechlorination of PVC. In this process PVC was milled with hydrated or unhydrated calcium sulfates ($CaSO_4 \cdot 2H_2O$ or $CaSO_4$) in air by using a planetary mill to investigate mechano-chemical dechlorination behavior. The milling process resulted in size reduction and in the breaking of bonds leading to mechanically induced solid state reaction, forming $CaCl_2$ and dechlorinated hydrocarbon with C=C double bonds in the product. Washing the milled mixtures with water at room temperature allowed removal of the chloride formed during milling, and more than 95% of the chlorine in PVC was removed from a mixture milled for 4 h. This process offered a potential route for the handling and disposal of both PVC and gypsum wastes. $H_2S$ gas was generated during milling; more $H_2S$ was released from the unhydrated sample than from the hydrated sample.

### 2.6.1 Mechanical Recycling

In 2008, Aznar *et al.* [41] described the mechanical recycling technique as follows:

**Crushing/Shredding**: Large plastics from already sorted plastic solid wastes are cut using saw or shear for further processing into chopped small flakes or in some cases powder. Contaminant separation: A cyclone is used for sorting and separating plastic materials from other municipal solid waste materials like paper, dusts and other forms of impurities.

**Floatation**: The separated plastics are floated in a liquid of higher density to allow for plastic materials to float according to their densities to make way for easy separation.

**Milling:** Separated plastic materials according to their resins obtained from the floatation method above are milled together, which is assumed as the initial step of recycling by most plastic recyclers around the world.

**Washing and Drying**: This step which refers to the washing stage of the mechanical recycling step is the beginning of the line with the actual plastic washing processes occurring if further treatment is required. This operation is usually carried out with water, while chemical washing processes may be employed in some rare cases (which might include glue removal from plastics) where caustic soda and surfactants are used.

**Agglutination**: This process involves addition of pigments and other substances aimed at improving the quality of the plastic materials after which the product is collected for storage to be sold or sent for further processing.

**Extrusion**: This is assumed to be the final stage of mechanical recycling where the plastic is extruded to strands and then pelletized to produce a single polymer plastic, which is subsequently followed by quenching which involves water-cooling the plastic by water to be granulated which is then sold as a final product.

The recycled materials often have limited applications as a result of exhibition of lower properties when compared to the virgin materials because of contaminations arising from lack of efficient separation and cleaning methods of the original plastic wastes. High quality recycled plastic wastes are achieved from recycling of municipal solid wastes of a single thermoplastic polymer which can be either of the following HDPE, LDPE, PP, PSetc.

In recent years, various alternatives have been proposed for massive use and promotion of recycled plastics through preparation of a three-layered plastic material for food packing which is among the largest sectors of plastic consumption with the middle thicker layer consisting of the recycled plastic material while the inner and outer thin layer is made of virgin plastic material. This is aimed at avoiding direct contact between the recycled plastic material and the food products.

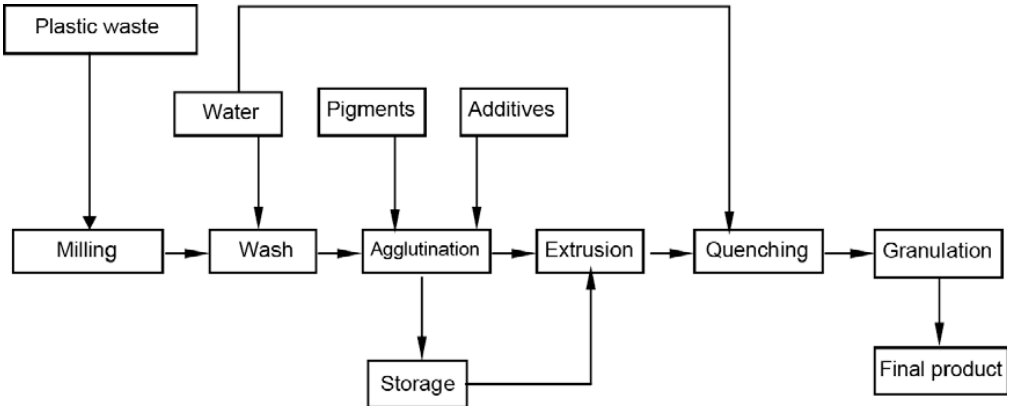


Fig. 2.6.1.1 Mechanical recycling steps as described by Aznar *et al.* (2006). [41]

In 2003, Sombatsompop *et al* [42] studied the processability, rheology, and thermal, mechanical, and morphological properties of three different commercial PVC compounds blended with postconsumer PVC bottles and PVC cables were examined with respect to the recycled PVC content. The addition of PVC bottle recyclates [recycled bottles (RBs)] to virgin PVC bottle (VB) and virgin PVC pipe (VP) compounds caused a progressive reduction in the average torque. No thermal degradation or color change in the RB-blended PVC compounds used was detected through carbonyl and polyene indices from IR analysis. The rheological properties for VP compounds were more sensitive to RB addition than those of VB compounds. The extrudate swell ratio did not change with the RB content. The decomposition temperature for the VB and VP compounds increased at 60–80% RB, whereas the glass-transition temperature was unaffected by the RB loading. The 20 and 80 wt % RB loadings were recommended for the VB and VP compounds respectively, for the optimum impact strength, the blends showing ductile fracture with a continuous phase. At the optimum impact and tensile properties, introducing RB recyclates into the VB compounds gave better results than the VP compounds. The hardness and density of the VB and VP compounds did not change with the RB content. The RB property change was comparatively faster than that of recycled PVC pipes. Adding the PVC cable recyclate [recycled cable (RC)] to virgin PVC cable (VC) had no obvious effect on the torque value of the RC/VC blends. The decomposition temperatures of the RC/VC blends stabilized at 20–60% RC and tended to decrease at 80% RC. The ultimate tensile stress was improved by the addition of the RC compounds, whereas the hardness and density of the VC compounds were unaffected by the RC content. It was concluded that the optimum concentrations of PVC recyclates to be added to virgin PVC compounds were different from one property to another and also depended on the type of virgin PVC grade used.

In 2001, Yarahmadi *et al.* [43] worked on rigid PVC recycling process aiming to evaluate the possibility of mechanical recycling of plastic waste. In this study, profiles made of rigid PVC have been investigated after various numbers of repeated extrusions to gain knowledge about the changes of properties and durability after conventional processing. New indoor profiles of PVC were re-extruded, from one to five times without adding new additives. The material was characterised after each extrusion using measurements of color, degree of gelation, stress–strain at break and UV-Vis-NIR spectroscopy. The durability of the material was evaluated by accelerated ageing in ventilated heat ovens with low laminar airflow, at various temperatures. Changes in elongation at break, color and chemical characteristics, depending on degradation, were measured and compared for the material after each extraction and various periods of ageing time.

They found an improvement of mechanical properties after the second extrusion. This was explained by an increase in the degree of gelation of the PVC material. Using a datacolor international SF600 spectrophotometer, changes in surface color of profiles were measured, according to ISO 7724/1 standard. The total difference in color, dE, was calculated using the formula, $dE= \sqrt{(\Delta L)^2+(\Delta a)^2+ (\Delta b)^2}$, where $\Delta L$ is the measure of greyness, $\Delta a$ is the measure of red-green shade and $\Delta b$ is the measure of yellow-blue shade.

The activation energies of the degradation were also determined for the material after each re-extrusion and were found to decrease with an increasing number of extrusions. The estimated lifetime for indoor use at room temperature for the material after five extrusions was one-third of the lifetime of the material extruded only once. Despite this finding, a long lifetime can be expected even for the material subjected to five consecutive extrusions, making the material suitable for mechanical recycling.

In 2001, Bensemra *et al*. [44] studied the properties of PVC/ABS blends. The aim of this work was to study the properties of PVC and ABS blends. For that, variable compositions of blends from 0 to 100 wt% were realized. Their physico-chemical properties were determined by DSC and FTIR. The variation of the mechanical properties such as tensile behaviour, impact resistance and hardness was studied according to the composition of blend. The influence of a plasticizer introduced at a level of 30 wt% on the same mechanical properties has been considered.

In 1992, Braun *et al* [45] studied the thermal degradation of PVC and heterogeneous 1:1 (w/w) blends of PVC with PC, SAN, high-impact PS, HIPS and SAN, ABS, particulate fillers such as Red Mud (RM), $CaCO_3$ and dolomite on the thermal degradation of PVC by DSC.

They concluded that $T_g$ of the PVC phase raises slower during degradation in the PVC/PS-blend, whereas in the other blends the cross linking is accelerated, due to a negative influence of the double bonds and/or the nitrile groups on the thermal stability of PVC.

In 2008, Phuong *et al.* [46] characterized the influence of the recycle processing of an homo-polypropylene on the mechanical, thermal, and rheological properties of the polymer by DSC at different time and temperature . In recycling process they used twin-screw extruder.

They concluded that at the high temperature profile (195-230°C), the rheological behavior of homopolypropylene is more influenced than at the low temperature profile (175-190°C), the viscoelastic properties are highly modified, the viscosity increases, and the mechanical properties decrease as much as the polypropylene matrix appears to be less accurate. They also found that the mechanical properties decrease according to the recycling times at two chosen different temperature profiles.

In 2006, Gonzalez *et al.*[47] characterized the tacticity of the samples of PVC obtained at different polymerization temperatures by FTIR and their thermogravimetric behaviour by high resolution TGA. Finally, they were able to detect two independent weight loss steps in the dehydrochlorination and these two steps respond to different syndiotacticity tendency of PVC samples, in accordance with FTIR results.

According to Braun [48] recycling of used PVC needs a careful characterization of PVC waste. The analysis of the scrap, especially with respect to the thermal stability and the molecular weight, is useful before reprocessing. He was able to find out that additional stabilization of used PVC can be done by up to 10 wt% fillers, e.g. chalk, which does not change the mechanical properties.

In 2002, Rao [49] experimented on thermal decomposition of calcium carbonate in a thermogravimetric analyser under non-isothermal conditions of different heating rates (10 to 100°C/ min). A new technique for determining the kinetic parameters from non- isothermal thermogravimetric data was described. The activation energy and frequency factors were determined from the proposed method and also by the widely used Coats and Redfern method. The kinetic compensation effect between the activation energy and frequency factors obtained from both the methods were found to be very consistent and are in very good agreement with the literature values. The activation energy and frequency factors were also determined from isothermal experiments in the temperature range from 680 to 875°C. The activation energy and frequency factors determined from isothermal data using initial rate method were also found to be in very good agreement with the above results. It is also found that the kinetic parameters determined by isothermal analysis were consistent with the values determined by non-isothermal analysis.

In 2007, Sun *et al.*[50] investigated the pyrolysis characteristics of PVC using a Netzschne TG thermo-balance coupled to a quadrupole mass spectrometer. The pyrolysis conditions were 0.1 MPa of argon, a heating rate of 10 °C/min and a final temperature of 1000 °C. Both the thermogravimetric properties and the simultaneous evolution of gaseous products during pyrolysis were studied. The TG/DTG results showed that as the pyrolysis temperature increases the weight loss rate of PVC increases. Near 412 °C the weight loss rate attained its peak value. At higher temperatures the rate of loss gradually decreases. The gases evolved during thermogravimetric analysis were analyzed by a mass spectrometer, monitoring the relative intensity of HCl, $C_6H_6$, light hydrocarbon and chlorine-containing gases. The evolution curves showed that HCl, $C_6H_6$, light hydrocarbon and chlorine-containing gases all peak at about 416 °C. This is consistent with the fact that the weight loss curves also peak at about 412 °C. The extensive HCl evolution is consistent with the high chlorine content of PVC. The formation of these gases can be explained by considering these reactions: dehydrochlorination, intramolecular cyclization and the addition of HCl to unsaturated hydrocarbons.

#### 2.6.1.1 Collection

In our PVC including other plastic wastes materials are collected from various sources by different groups of people. Different groups collect mixed plastic waste materials from most of the residential houses and commercial complexes and dumped these collected materials into selected container. The rest of the waste materials including plastic especially from street are collected by City Corporation and Municipal authority. Some people throw away their domestic garbage with plastic bags on the street or ditches. Few passersby throw away different types of plastic packaging materials on the street after usages. Tokais directly collect thrown away waste packaging plastic materials from streets, lanes, ditches, dustbin/containers and final disposal sites. After collecting different types of plastic materials, Tokais sell these plastic materials to vangaridokan followed by broker/wholesaler to the manufacturer/processor. Feriwalla/Van collector buys waste plastic materials from door to door and sells to vangaridokan followed by broker/wholesaler to the manufacturer/processor.

#### 2.6.1.2 Separation

Recycling is an important activity in the minimization of waste that results from human activities. The idea of re-using this waste has increased during the last decades due to environmental, economic and social factors. In the United States, 75 billion pounds of plastic are produced every year. Unfortunately, the majority of this plastic ends up in landfills where its decomposition process can take anywhere from 10 to 30 years. The United States currently recycles about 5% of its post-consumer plastic waste; however, as much as 55% could be recycled if economically viable methods can be developed to collect and process waste streams that contain at least 50% thermoplastic materials.

1. For better quality of the recycled plastic products, different types of polymers are separated from each other. The product which is made by different types of waste plastic ingredients shows low quality in comparison with the homogeneous and/or virgin ingredients. For this reason for mixed post-consumer plastics waste efficient separation systems are practiced [51-52].

Several techniques are used to separate mixed plastic wastes based on their physicochemical properties. Some of them have their own limitations [53-54]. Some of the separation methods are mentioned below with a brief explanation:

(i) Manual sorting is used in developing countries such as Bangladesh where labor cost is low. This type of separation method suffers some major disadvantages such as being very labour-intensive and hazardous for the labors [54, 58]

(ii) Gravity separation is based on plastic types and density. Therefore, separation of close density plastics (such as mixture of PVC, PET and POM) is very difficult [53]

(iii) Hydro-cyclones and centrifuges methods are based on the differences in plastic density [54, 56]

(iv) Froth flotation is the cheapest and most extensively used process for the separation of chemically similar minerals, and to concentrate ores for economical smelting. Flotation has a reduced cost compared to other separation operations. In this work, froth flotation was used to treat PVC and PET mixtures. The parameters studied are reagents, $p^H$, conditioning time and particle size. The results show a yield of 99.3% pure PVC separated from PET [53-57].

Many conventional plastics separation such as flotation, combination of air tabling and turboelectric system [59] and electrostatic system [60] are frequently used. But in the current recycling system, a plastic separation is accomplished mainly by a spectrometer that recognizes a near-infrared spectrum of each plastic and the laser diode [61].

#### 2.6.1.3 Feed Stock Preparation

Historically, the earliest exploitation of rigid PVC was on machines designed to accept and process pelletized compound rather than powder. The compound was therefore manufactured as a separate operation, either by the fabricator, or more usually by the polymer supplier or an outside company. This technique is still widely employed, particularly where the fabricator is required to use a range of compounds to produce a variety of exacting products, e.g. in profile extrusion. The compound operation is required to achieve adequate and uniform gelation of the polymer and thorough dispersion of additives.

The original process, following the experience of the rubber industry, entailed mastication of the mixed ingredients in a Banbury or similar internal mixer, followed by sheeting on a two-roll mill with subsequent cooling and cutting of the compound. In some respects this two stage process can be highly effective, in that it facilitates partial separation, and therefore sensitive control, of the heating and shearing process, but there are obvious disadvantages. It is essentially a batch process, relatively labour intensive, and needing a separate cutting step to produce the small chip or pellet form required for feeding fabricating equipment. Today, this procedure has been largely displaced, in rigid PVC compounding, by the use of continuous compounding machines. These are exclusively screw machines, but may be broadly divided into single-stage machines where compounding and extrusion of the melt through the die take place in one unit, and two-stage machines. These separate the high shear plasticizing homogenizing section from a lower shear extrusion section which simply transports melt to the die and die face cutter, to produce the required pellets. Twin-screw and planetary screw machines, reciprocating screws, and a combination of mixing rotors and separate single-screw extruder in sequence are all in commercial use. Whatever equipment is chosen, there is, of course, a common requirement for intensive shearing and homogenizing without localized overheating in the first stages, exact temperature control, and uniform treatment of all the material.

#### 2.6.1.4 Powder Blend Manufacture

In volume terms, the processing of rigid PVC is dominated today by the use of powder feed stocks, particularly in the area of twin-screw extrusion of pipe (see Section 9.3), which represents a major tonnage PVC application. The dry powder blend needs to be more than a superficial mix of the ingredients, and invariably requires the use of a ‘high speed’ mixer. The essential feature of such a mixer is that movement of the components is achieved by a rotor at the base of the chamber, rotating at speeds up to several thousand rotations per minute (rpm). The powder is thrown out by the centrifugal action of the rotor and rises up the walls of the mixing chamber, to return down the central zone, creating a fluid like movement with a vortex. Frictional heat is developed and can be augmented by heat from the jacket, to minimise cycle time in achieving hot mixing. It is customary to discharge the mixed material, at the end of the mixing cycle, into an associated low speed cooling chamber, where it cools to a temperature at which it will not suffer agglomeration and compaction on standing. This process not only provides intimate and thorough mixing, but also causes additives, particularly liquid or low melting point components, to adhere to, and in some cases to be absorbed by, the surface of the polymer grains. The performance of subsequent gelation/fabrication processes depends critically on the nature of the dry blend fed into them, which in turn is a function, not only of the efficiency of the dry blender, but of the properties of the polymer grade employed and the judicious choice of additives. The use of dry blend feedstock has the obvious advantage over pelletized compound of lower capital and energy costs for feedstock preparation. It has the minor disadvantage of not being readily applicable to solid additives that are not provided in a powdered or easily friable form, and can create dusty working conditions. In large scale operations, the latter disadvantage is increasingly being obviated by the use of automatic and largely enclosed systems of powder handling.

#### 2.6.1.5 Extrusion Machine

Single screw machines are in the most widespread use because of their adaptability to virtually all extrusion forms, and their inherent simplicity, which reflects itself in the ultimate cost [8]. Twin-screw units, which are more complex in nature, are widely used in processing rigid PVC pipes and profiles, and in compounding because of their lower operating temperatures [33]. This provides an end product with less heat history and which is less susceptible to degradation than an equivalent made on a single-screw extruder.

Extruder is used to convert crushed rigid PVC pellets into a granular form. Before making granules crushed PVC is mixed with different additives of various proportions depending on the requirements of the products using a mixture machine.

### 2.6.1.6 Extrusion process

Since studies of PVC processing relate so frequently to extrusion, it is pertinent to consider this process specifically. The use of screw extruders for rubber and plastics processing has been common since the earliest days of these industries, and the concept of extrusion will no doubt be familiar in some context to most readers. The earliest machines employed in the processing of rigid PVC were single-screw extruders, fed by compound. Because of the limitations of heat stability and high melt viscosity it was soon realized that particular care has to be exercised to ensure a continuous flow of material at all points of the flow path, with no stagnation through sharp corners or chips and scratches in metal surfaces. Obstructions in the flow path, such as the mandrel, torpedo or breaker plate, must be as streamlined as possible, whilst the screw tip should not be square but hemispherical or conical with a curved end. To avoid excessive frictional heating, compression ratios must be relatively low compared with plasticized PVC, whilst screws need to be long (e.g. employing flighted length of screw(L)/screw diameter(D) ratio of over 20:1). Single-screw machines continue to be used most successfully for compound feed stocks, but for rigid powder blends twin-screw extruders are much more widely employed today. With the increasing use of dry blend feed stocks for the very large tonnage manufacture of pipe and conduit, twin-screw machines have attained a dominant role in rigid PVC extrusion during the last ten years.

To appreciate the advantages of twin-screw machines in the extrusion of rigid PVC, particularly from powder blend, it is necessary to consider the very different mode of operation of single- and twin-screw extruders. A single-screw extruder has a screw rotating in a closely fitting barrel. If the molten polymer sticks to the screw and slips at the barrel surface the material will simply revolve with the screw and not be transported forward at all. To achieve maximum output, the polymer has to slip as freely as possible on the screw surface but have a high coefficient of friction at the wall. The rotational speed of the extrudate will then be less than that of the screw, so that the screw flights force the material along the barrel and through the die. The operation thus depends critically on friction between the polymer and barrel wall, and frictional heating supplies much of the heat input to the system. An increasing output requires increasing screw speed and therefore higher frictional heat generation, with increasing possibility of local overheating in a heat sensitive material.

In 2008, Phuong *et al.*[46] worked on polypropylene recycling process aiming to find the effect of recycling process on the mechanical, rheological and thermal characterizations for pure polypropylene. They also studied the behavior of polypropylene degradation with the help of a twin screw extruder to be able to make the polymer reinforced and ready for new applications.

They concluded that the structure and the characterizations of PP are so influenced by the extrusion condition and the temperature of recycling. The recycled polypropylene did not only have the same properties of the virgin polypropylene, it was even worse. They also offered some reinforcement to improve the properties or in some cases to make a better recycled materials than the virgin material.

### 2.6.2 Chemical Recycling

Chemical or feedstock recycling involves a range of plastic recovery techniques which break down polymers into their constituent monomers. Chemical recycling technologies include pyrolysis [62-63], gasification [41], dissolution [64] and thermal cracking [65]. However, it is capital intensive and requires very large quantities of used plastics for reprocessing to be economically viable. Properties and morphology of recycled plastics also have been investigated [66].

In 1996, Morris [67] studied recycling versus incineration and showed that for 24 out of 25 solid waste materials, recycling saves more energy than is generated by incinerating mixed solid waste in an energy-from-waste facility. Recycling conserves energy that would otherwise be expended extracting virgin raw materials from the natural environment and transforming them to produce goods that can also be manufactured from recycled waste materials. Furthermore, energy conserved by recycling exceeds electricity generated by energy-from-waste incineration by much more than the additional energy necessary to collect recycled materials separetly from mixed solid waste, process recycled materials into manufacturing feed stocks, and ship them to manufacturers, some of whom are located thousands of miles away.(re-write)

In 2006, Masuda *et al.* [68] investigated the thermal decomposition of mixtures of PVC and a variety of metal oxides including rare earth oxides under helium atmosphere at 400 and 800 °C. The emission of hydrogen chloride changes significantly with the oxides used. This feature is strongly concerned with the chlorine fixing ability of oxides. Together with the analysis of pyrolysis residues, the behavior of fixation of chlorine from PVC by oxides was compared. They found that the trivalent rare earth oxides ($Ln_2O_3$) show great ability to fix considerable amount (more than 95% in the case of lanthanum oxide) of initial chlorine in PVC in the form of oxychlorides (LnOCl).

In 2001, Kim *et. al.* [69] investigated the pyrolysis kinetics of waste PVC pipe with a thermal gravimetric analysis system at heating rates of 5, 10, and 30°C/min in a nitrogen atmosphere. Freeman-Carroll method was employed to evaluate kinetic parameters. Two dominant peaks were observed on derivative gravimetric curves. The first-stage reaction was likely to be represented by stoichiometric reaction to yield volatiles (mainly HCl) and intermediates. The second-stage reaction was described by thermal degradation of intermediates competitively into gas, liquid, and solid by-products. The effects of additives on the pyrolysis kinetics of waste PVC pipe were significant, especially on the first-stage reaction. The first-stage reaction was retarded. A merged peak at low temperatures was observed on the DTG curve instead of two peaks usually observed for that of pure PVC resin. The first peak on the DTG curve of pure PVC resin may shift more, resulting in the complete overlap of two peaks.

They found that the quantity of evolved HCl decreased because of interaction of metal components of stabilizers with either HCl or active chlorine atom or both. The final residual fraction increased as a result of pyrolysis of organic forms of additives to yield extra char. On the other hand, the second-stage reaction kinetics demonstrates a similar pattern to that of pure PVC resin, implying that the effects of additives were less significant in comparison with that at the first-stage reaction.

In 2002, Zevenhoven *et al.* [70] investigated the pyrolysis of PVC and mixtures of PVC with wood (Finnish pine) and LDPE in nitrogen at 250–400 °C. The aim was to optimise the temperature range for producing low-chlorine or chlorine-free fuel in a dehydrochlorination reactor without pyrolysing any of the other combustible fractions. Results were presented for various process temperatures for PVC, PVC/wood and PVC/LDPE mixtures. It was found that the PVC tested is dehydrochlorinated at approximately 350 °C, and that secondary pyrolysis is suppressed when LDPE is present.

In 2001, Miranda *et al.*[71] investigated the thermal decomposition of commingled (mixed) plastics comprising high and low density polyethylene, polystyrene, polypropylene and poly(vinyl chloride) under vacuum conditions by dynamic thermogravimetric analysis in the temperature range of 25–600°C. The mixtures were representative of the major polymeric materials found in a MPW stream. The study focused on the role of each polymer in the stabilization or destabilization of other interacting plastics, as well as the fate of chlorine produced from PVC.

The results obtained indicate that some interactions occurred during MPW pyrolysis, mainly at high temperatures (>375°C). PS and PVC appear to be the plastics responsible for the interactions through their intermediate pyrolysis products. The chlorine from PVC in the mixture is released almost completely before 375°C, when the conversion of the MPW to pyrolysis products was reached at 13%.

In 2005, Ali *et al.* [72]. studied the pyrolysis and hydropyrolysis of PVC mixed plastic waste alone and with petroleum residue at 150 and 350 °C under $N_2$ gas and at 430 °C under 6.5 MPa $H_2$ gas pressure. The behavior of plastic waste during thermal and catalytic decomposition was studied in single- and two-stage reaction processes. In the individual pyrolysis process, both the petroleum residue and PS undergo more than 90% conversion to liquid and gaseous products, whereas LDPE and HDPE yielded lower conversions products, and PP and PVC afforded somewhere a moderate to high conversion products.

In a single-stage pyrolysis reaction, PVC was processed with petroleum residue at 150 and 430 °C, under $N_2$ gas for 1 h at each temperature in a glass reactor. The model PVC and waste PVC showed slight variations in the products distribution obtained from the glass reactor. In two-stage process, model PVC, vacuum gas oil (VGO) and a number of different catalysts were used in a stainless steel autoclave micro tubular reactor at 350 °C under the stream of $N_2$ gas for 1 h and at 430 °C under 6.5 MPa $H_2$ pressure for the duration of 2 h. Significantly, different products distributions were obtained. Among the catalysts used, fluid catalytic cracking (FCC) and hydrocracking catalysts (HC-1) were most effective in producing liquid fuel (hexane soluble) materials. The study showed that the catalytic processing of PVC with VGO was a feasible process by which PVC and VGO materials were converted into transportation fuels.

In 2000, Jaksland *et al.* [73] studied a new environmentally sustainable technology for chemical recycling of PVC waste. The new technology transforms PVC waste into completely new chemical products/raw materials. The process is based on a combined thermal and chemical degradation of PVC in a reactor. In the reactor, the chlorine from the PVC reacts with fillers producing calcium chloride. The metal stabilisers (lead, cadmium, zinc and/or barium) are converted into metal chlorides. Exploiting the influence of pH, temperature, liquid to solid ratio and comminuting the metal solubility, metals and calcium chloride are sequentially extracted from the reaction product. This occurs in a downstream multi-stage extraction-filtration procedure. The products from the process are: (1) calcium chloride, which satisfies the specifications as thaw-salt, (2) lead (metal) product, which may be further purified and re-used, (3) coke and (4) organic condensate, which may be used as energy resources for the process. This paper presents the basis of the technology in terms of reaction and separation principles, selected process equipment and process design.

## 2.7 Weathering/Environmental effects

In 2007, Nesar [74] studied weathering effects on properties of CPVC pipe material. In this work, tensile and SENB specimens were prepared from locally manufactured CPVC commercial pipes which were naturally weathered for different periods (1–9 months) in harsh environment conditions, such as UV, moisture and high ambient temperature. The tensile test results show that exposure for periods up to 9 months, including summer season, had limited effects on the tensile strength and modulus of elasticity of the material. The damage due to weathering is mainly a surface phenomenon. The deterioration of the ultimate elongation is noticeable for exposure periods as low as 1 month. Analysis of fracture toughness results reveals a general trend that indicates a deterioration of this property at the beginning of the exposure time.

In 2002, Mersiowsky [75] studied the of PVC polymer, plasticizers, and stabilizers of PVC products in landfill waste. He found the PVC polymer was found to be stable. A loss of plasticizers may occur in case of insufficient compatibility with the PVC compound coupled with microbial consumption at the PVC product surface. Losses of stabilizers are generally restricted to transient leaching from the product surface.

In 2005, Selvadurai *et al.* [76] worked on mechanical behavior of plasticized PVC subjected to ethanol exposure. Series of experimental investigations were conducted to assess the influence of ethanol exposure at different concentrations on the mechanical properties of plasticized PVC membrane. Exposure to pure ethanol resulted in a reduction in flexibility, or embrittlement, and the transformation of the PVC membrane from a flexible material capable of undergoing large strain hyper elastic behavior to a stiffer material with pronounced yield behavior. Results of X-ray fluorescence measurements indicate the loss of the plasticizer from the PVC membrane as a contributing factor for the alteration in the mechanical properties of the PVC membrane. The experiments also indicate a slower rate of plasticizer leaching during exposure to lower concentrations of ethanol. Exposure of the PVC membranes to 80% and 50% concentrations of ethanol and pure water has a reduced influence on the loss of large strain deformability of the PVC membrane, even after more than one year of exposure. The PVC membranes exposed to a mixture of ethanol and pure water in equal volume proportions indicate that after longer period, the PVC membranes become softer and exhibit greater deformation under the same external load. This phenomenon can be attributed to the swelling of the PVC membrane.

### 2.8 Properties of recycled uPVC

In 1995, Okieimen *et al.*[77] studied thermal degradation of PVC in a nitrogen atmosphere with the presence of Jatropha seed oil, epoxidized Jatropha seed oil, and soaps (barium and cadmium) of Jatropha seed oil at various temperatures. The rate of dehydrochlorination measurement at 1% degradation, $R_{DH}$, and the time required for dehydrochlorination to attain 1% conversion were used to assess the effect of the additives on the susceptibility of the polymer to dehydrochlorination. It was found from the kinetic studies and the results from viscosity measurements on degraded polymer samples that the Jatropha seed oil derivatives suppressed the initial loss of HCl from the polymer and the extent of polymer chain scission accompanying the dehydrochlorination process. Thermal degradation studies of poly(vinyl chloride) in the presence of mixtures of barium and cadmium soaps of Jatropha seed oil were also carried out. It was found that soap mixtures containing less than 80 wt% cadmium soap exerted a deleterious (antagonistic) effect on the degradation of polyvinyl chloride while in the presence of soaps containing more than 80 wt% cadmium soap, considerably lower values of $R_{DH}$ and higher values of $t_{DH}$ were observed. The soap mixture containing 90 wt% cadmium soap was found to exhibit a remarkably improved stabilizing effect on the dehydrochlorination of polyvinyl chloride.

In 1999, Zhu *et al.* [78] investigated the mechanical properties of PVC/SBR blends compatibilized by NBR. A sulfur curing system was employed to crosslink the rubber of the blends. In the case of the blends without any curing agents, an increase in NBR content did not improve the tensile strength and elongation-at-break. However, a significant improvement in the mechanical properties was observed when NBR was added as a compatibilizer and the blend was vulcanized. In the PVC/NBR/SBR (50/10/40) blends, the tensile strength and elongation-at-break increased with an increase in sulfur concentration. This improvement was attributed to covulcanization between NBR and SBR. The fracture toughness of PVC/NBR/SBR (50/10/40) blends was characterized by the critical strain energy release rate, $G_c$. In the case of the PVC/NBR-29/SBR (50/10/40) blends, an increase in sulfur concentration resulted in a dramatic increase in $G_c$. However, the $G_c$ value of PVC/NBR-40/SBR (50/10/40) blends decreased with an increase in sulfur concentration owing to the brittle behavior of one of the blend components—the PVC/NBR-40 (50/10) phase.

In 2006, Garcia *et al.* [79] investigated mechanical properties of recycled PVC blends with styrenic polymers. The aim of this study was to improve the performance of blends made from recycled PVC, coming from credit card waste, so that these blends can be used for those applications that must fulfil some requirements with regard to mechanical properties and stability with temperature alterations. With this aim in mind, two polymers of styrenic origin were combined: SAN and ABS. These polymers were characterized by a satisfactory balance of mechanical properties and thermal stability. PVC blends with both virgin and recycled styrenic polymers were studied throughout the entire range of compositions. The prior degradation of the recycled materials was studied by means of FTIR. The behavior of the observed $T_g$ values was analyzed using DSC, and the existence of partial miscibility between the different components has been studied. The mechanical properties were determined using tensile and Charpy impact tests. The thermal stability of the PVC blends with temperature changes was determined using the VST. Finally, the fracture surface of the various blends was analyzed using SEM.

In 2001, Sombatsompop *et al.* [80] investigated rheology, morphology, and mechanical and thermal properties of recycled PVC pipes. This article demonstrated the possibility of recycling PVC pipes by investigating the effect of adding PVC pipes (varying from 0 to 80 % wt) into two commercial PVC virgin grades on the rheological, morphological, mechanical, and thermal properties of the PVC blends. The results obtained showed an increase in the melt viscosity and no change in the die swell ratio as the concentration of the recycled PVC was increased. The die swell ratio was observed to increase with temperature, this being associated with the presence of gelation that occurred at high temperature. The optimum tensile and impact strength DS were detected. The hardness result corresponded well to the density of the compounds. The glass transition, degradation, and heat-deflection temperatures were also found to shift with the recycled PVC loading.

In 1996, Arnold *et al.* [81] studied the mechanical properties of recycled PVC bottle compounds. A comparison was made between recycled post-consumer PVC waste in the form of flake and powdered material with virgin bottle compound.

The mechanical properties studied included tensile strength and fatigue lifetimes. The fracture surfaces were examined using scanning electron microscopy. Molecular weight distributions were determined via gel permeation chromatography and impurity levels were assessed. It was generally found that recycled flake material did show an appreciable reduction in strength, which was mainly attributable to large impurity particles. Pulverisation of the material to a powder improved the properties. Molecular weight changes were found to be of little importance.

In 2004, Yoo *et al.* [82] studied enhancement of the thermal stability, mechanical properties and morphologies of recycled PVC/clay nanocomposites. Recycled PVC/clay nanocomposites were prepared by melt mixing of recycled PVCs and modified clays. Characterization of the nanostructure of the nanocomposites was carried out using wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). In case of 10wt.%, the characteristic peak of modified clay perfectly disappeared because of aids of plasticizers as co-intercalator. Thermal stability was evaluated from the thermal decomposition behaviors and linear dimension changes by TGA and TMA system. Coefficients of thermal expansion of the nanocomposites were also observed from TMA analysis. Dynamic mechanical properties were evaluated using DMA system. The thermal and mechanical properties of the nanocomposites were improved simultaneously for varied clay loadings, 1, 3, 5, 10wt.%, compared to recycled PVC. The storage modulus of the nanocomposites with 10wt.% clay loading was increased 11 times compared to that of recycled PVC.

In 2005, Strapasson *et al.* [83] studied tensile and impact behaviour of polypropylene/low density polyethylene blends aiming to make PP/LDPE blends (0/100, 25/75, 50/50, 75/25 and 100/0 w/w) via injection molding carried out under various injection temperatures and to evaluate their tensile and impact properties. The blends yielded tensile stress–strain curves very dependent on their composition, especially regarding elongation at break and the presence of necking. An irregular behavior for the 50/50 w/w blend is reported. Nevertheless, a linear variation of the yield strength and elastic modulus with the blend composition was observed. The behavior of the blend was also very dependent on processing temperature. Addition of 25% of LDPE to the PP may result in similar degradation of its mechanical properties to that caused by a 10 °C processing temperature increase. Statistical analyses proved valuable when reporting results concerning blends.

## 2. 9 References

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# CHAPTER THREE

## 3. Experimental

The following tests (Fig.3.1) were performed to characterize recycled uPVC containing different proportions of domestic and external scrap.

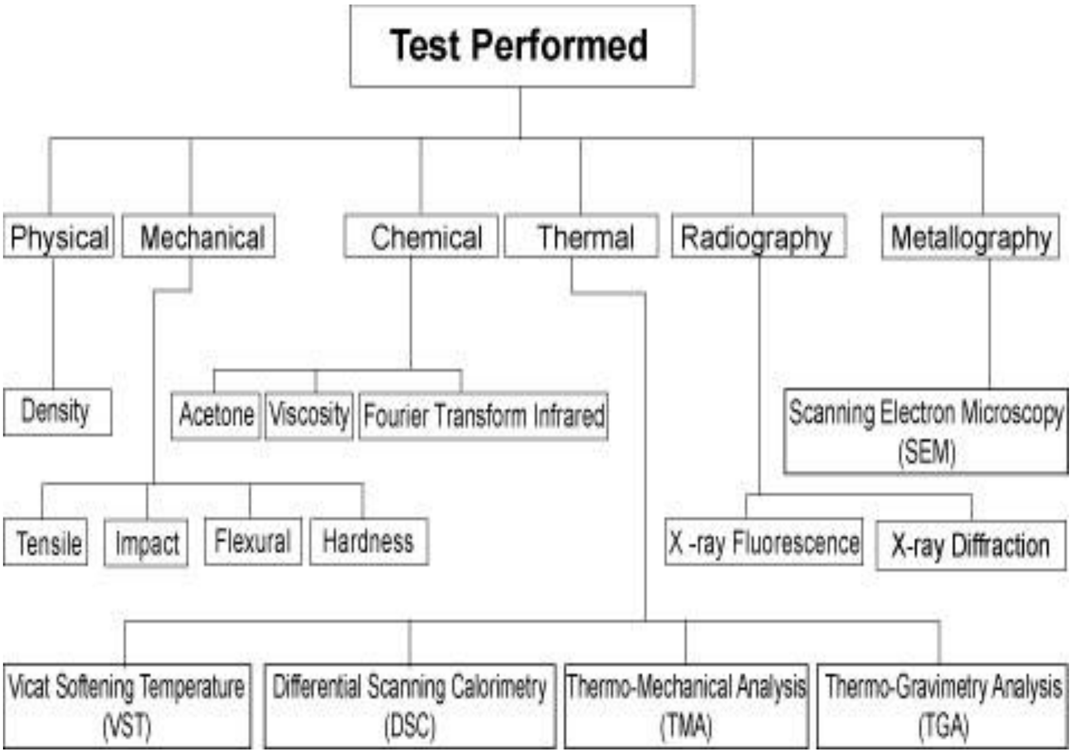


Fig. 3.1: Tests performed in this research work

### 3.1 Methodology

For the evaluation of physical, mechanical, chemical, thermal and morphological properties of rigid PVC products tensile, flexural, impact, shore hardness tests, inherent density, molecular weight/viscosity number, glass transition temperature determination; Vicat softening temperature, coefficient of thermal expansion (CTE) measurement, spectra analysis, and morphological investigation were done. Two different sets of samples were made; one set containing scrap from domestic waste and the other set containing external scrap purchased from local. Per hundred resin (phr) has been used as measuring unit of additives and scrap uPVC. For each set of specimens 10, 20, 30, 40, 50 phr and 100% scrap were blended with PVC resin and additives. uPVC pipe of 100 mm nominal diameter was extruded for each composition. Screw speed and temperature at different locations of the barrel was maintained as required. The methodology comprises of raw materials selection, preparation, formulation, mixing, extrusion, sample making, test set-up and test procedure.

### 3.1.1 Raw Materials Procurement

PVC resin, domestic and external uPVC scraps and additives were selected to manufacture 100 mm nominal diameter pipes. Domestic uPVC scrap was procured from a local factory named National Polymer Ltd., Tongi, Gazipur, Bangladesh. External uPVC scrap pipe materials were purchased from local market.

### 3.1.2 Scraps Materials Processing

Both domestic scrap (DS) and external scrap (ES) materials were cleaned and shredded by using a crusher machine (Model-PC800, Make-Qiwex, China) followed by pulverization using a pulverizing machine (Model-GSM560, Make-Qiwex, China).

#### 3.1.2.1 Cleaning

Cleaning is the process of removing contaminants such as clay/mud/dust, grease/mobile or any other non-plastic materials from waste products. It is done before or after crushing depending on size and shape of the waste products and nature of the contaminants. Generally, cleaning of highly contaminated products involves hand-wiping with rags/jute or scraper. After rough cleaning the waste products are broken into small pieces for next processing. Less contaminated waste products are also broken into small sizes. These small sized pellets are washed with water having necessary amount of detergent followed by fresh water rinsing. After thorough washing pellets are dried in sun or in a rotating drum supported by external electric or gas heater. These dried pellets are used to produce granules.

Some granule manufacturers do not wash the crushed pellets. They directly produce granules from unwashed pellets using compounding extruder. In this type of extruder, stainless steel mesh is used as a filtering unit to contaminants. The intermittent granules are typically~ 4.5mm diameter and ~7.5 mm long. After certain interval the technicians stop the extruder as well as the cutting knife. The extruder die and filtering unit are removed from the extruder. This clogged filtering unit is replaced by a new one. This technique is repeated after certain interval

### 3.1.2.2 Crushing/Shredding

The small parts or waste plastics are shredded into small chips, 5-6 mm in size, using crusher machine. This machine consists of a series of high speed rotating blades, motor, sizing net and a collecting bin.

### 3. 1.3 PVC formulation

PVC resin cannot be used directly to produce pipes. Many additives are added to make up the PVC formulation. Additives were weighed by a digital balance (Model: Aux-220 Shimadzu, Japan). PVC resin, various additives and uPVC scraps were mixed thoroughly in hot and cold mixers before being discharged for extrusion. Different formulations were attempted in extruding pipes of different composition. Table 3.1 shows the different PVC formulations.

Table 3.1: Different formulations attempted (phr).

| Sample | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| vPVC (kg) (-$CH_2CHCl$-) | 100 | 100 | 100 | 100 | 100 | 100 | -- |
| Filler ($CaCO_3$) kg | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | -- |
| Stabilizer ($3PbO.PbSO_4.H_2O$) (kg) | 2.60 | 2.60 | 2.60 | 2.60 | 2.60 | 2.60 | -- |
| Stearic acid (kg) ($C_{17}H_{35}COOH$) | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | -- |
| uPVC-scrap (kg) | 0.00 | 10.0 | 20.0 | 30.0 | 40.0 | 50.0 | 100% |
| Carbon(C)-black (kg) | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | 0.08 | -- |
| Pigment ($TiO_2$) | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | 0.60 | -- |

### 3.1.4 Designation of samples

The PVC resin in powder form and the requisite amount of different additives were blended in a mixture machine to make the target pipe without adding any scrap. The samples made from this pipe were designated as CS-0. Domestic samples designated as DS-10, DS-20, DS-30, DS-40, DS-50 and DS-100 have been prepared by blending 10, 20, 30, 40, and 50phr and 100% uPVC domestic scrap with PVC resin and various additives followed by extrusion, flattening and machining. Following the similar procedure, external samples such as ES-10, ES-20, ES-30, ES-40, ES-50 and ES-100 have been prepared using external uPVC scraps. Either domestic or external samples designated as DS-10, DS-20, DS-30, DS-40 DS-50, and DS-100 and ES-10, ES-20, ES-30, ES-40, ES-50, and ES-100 have been addressed as S-10, S-20, S-30, S-40, S-50 and S-100.

### 3.1.5 Mixing process

The mixing machine comprises the hot and cold mixing chambers. Each formation was put into the hot chamber, heated to 120°C by frictional force and during heating the mixture was continuously stirred to get a homogenous mixture. After attaining 120°C, the mixture was immediately discharged into the cold chamber which was surrounded by chilled water jacket. The rotating speed of cold chamber was 200 rpm and its rotation was continued up to 35°C. At this stage, the mixture was discharged into barrels for extrusion.

### 3.1.6 Machine parameter set-up

The speed of hot and cold chamber of mixing machine was set at 2800 rpm and 200 rpm respectively. A uniform temperature of 150°C was maintained throughout the entire length of the barrel for a period of three hours by 6 heaters set at regular intervals. A uniform temperature of 150°C was maintained all along the die by four heaters set at regular intervals. During extrusion the temperature of the six heaters along the barrel was maintained at 170-180-185-175-180-180°C and the temperature at the four different points of the die at 165-170-175-185°C. Holding time at the extrusion temperature was 30 minutes. The speed of screw was 35 rpm with a back pressure of 30 MPa. All the parameters were controlled by programmable logic controller.

After attaining 120°C the mixture was immediately discharged into the cold chamber which was surrounded by a chilled water jacket. The rotating speed of cold chamber was 200 rpm and its rotation was continued till the temperature reached 35°C. At this stage the mixture was discharged into barrels for extrusion.

### 3.1.7 Extrusion procedure

At the start and ending of production, purging materials were charged into the barrel to control the degradation of uPVC materials. After few minutes the blended mixture was discharged into the extruder (Fig.3.2). This extruder machine has the following parameters (Table 3.2).

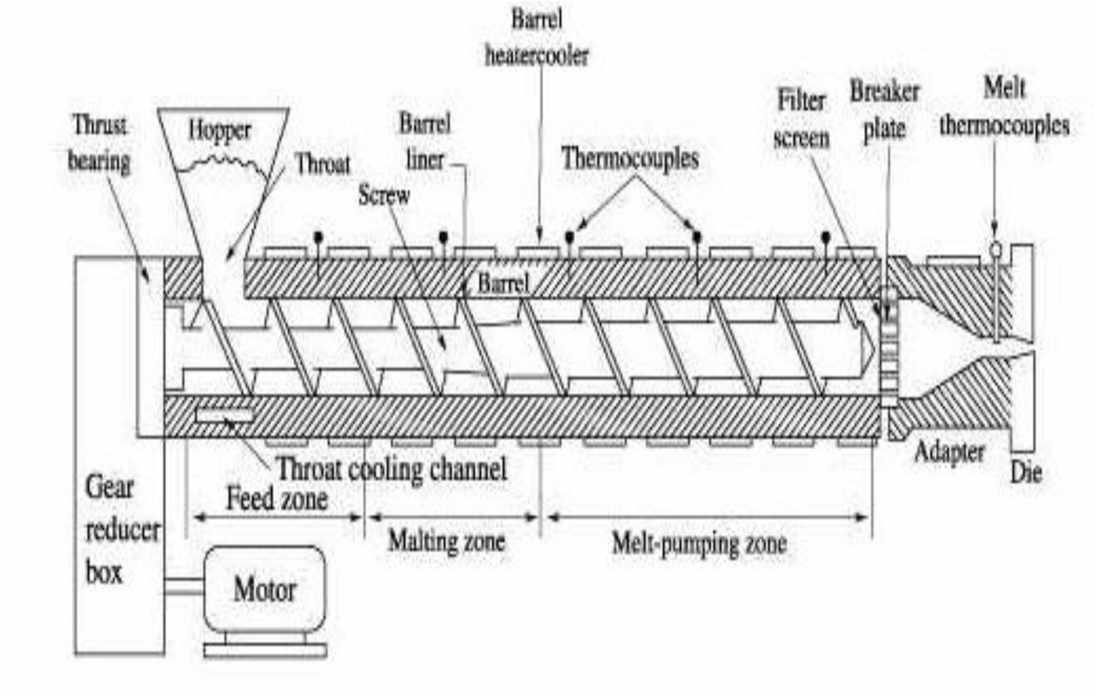


Fig. 3.2: Different components of extruder

Table: 3.2: Machine parameters

| Sl. No. | Salient feather of extruder | |
|---|---|---|
| 1. | Type | extruder |
| 2. | Model | 90/25 |
| 3. | Head pressure | 30 MPa |
| 4. | Screw diameter | 90mm |
| 6. | Output | maximum output: 450kg/hr |
| 7. | Speed | 10 rpm – 35 rpm |
| 8. | L/D | 25 |

Degassing was done during processing. The extruded pipe was immersed in chill water at 15°C. Chilled water was supplied from a chiller (Model: R4076, Make: Daikin, Japan). All the operating parameters of the extruder were kept constant during the production of pipes of different composition. From the extruded pipe 180mm long pieces were cut by planetary cutter (Model: S63-400, Make: Sica, Italy).

### 3.1.8 Flattening

180 mm long pieces were cut along longitudinal direction with a circular saw (Model: Cadore-350, Make: IMA, Pescara, Italy). The specimen was heated in an electric oven (Model: DV-160, Make: Gallenhamp, England) at a temperature of 80°C for 30 minutes. The piece of the pipe was then placed between two glass pieces. The two glass plates were placed between two metallic plates and pressed by approximately 20kg load for 2 hours to make the specimens flat. Thickness of the PVC plate was 4.75mm. The flattened plates were used to make the specimens.

### 3.1.9 Machining

A computerized numerical control machining centre (Model: PC Mill 155, Make: Emco, Austria) was used to prepare the test specimens. The cutting speed of the machine was 4000 rpm Care was taken to avoid any scratch or any mark in the edges of the samples. During cutting operation, coolant was used to control heat generation so that any degradation of the specimen material does not occur. At the end of machining the burrs remaining at the edges were removed by using hair brush. Then all the surfaces of the specimen were inspected to detect any flaws, scratches or imperfections by magnifying glass. All the surfaces were smoothed with fine abrasive paper. The specimens for measuring inherent density, viscosity number, shore hardness, tensile properties, flexural strength and impact strength were prepared by machining.

### 3.1.10 Measurement

After machining and smoothening, dimensions of the specimens were checked with a digital caliper (Model: 530-115, Make: Mitutoyo, Japan) and necessary action was taken to hold the sample dimensions within the allowable tolerances. Gauge length and the gripping lines on the specimens were marked with permanent marker to avoid scratch or impressions on the specimens.

## 3.2 Experimental Procedure

The quality of recycled uPVC samples containing domestic and external scrap was ascertained by performing most of the tests following the American Society for Testing and Materials (ASTM) standards. The details of the experimental procedure have been narrated in the following sections.

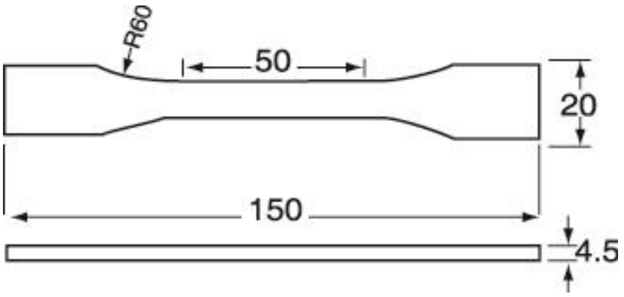
### 3.2.1 Acetone Test

In the polymer industry, acetone test is a preliminary but very useful test. The next relevant tests were performed only when the results of the acetone test were positive. Dimensions of the each sample were 75mm×75mm×4.5mm. Acetone test was carried out by immersing the samples in acetone for about two hours. If no disintegration or delamination is observed, the sample is said to have passed the test. BS-3505(1968) [1] was followed to carry out the test on 2 samples for each composition.

### 3.2.2 Density Test

Dimensions of the each sample were 30 mm x 28 mm x 4.5 mm. A Gravity Balance (Model: Cat Ref. X13, Make: Wallace, England) was used. Before testing, adjustment and calibration of the balance was done in accordance with the operating instructions. The immersion vessel was mounted on the support and the specimen suspended by a wire was completely immersed in water at a temperature of 23±2$^0$C in such a way that the vessel did not touch the wire or specimen. There were no bubbles adhering to the specimen and wire. After complete immersion of the test specimen and necessary adjustment the final result was taken from the dial of the machine. ASTM D 792-00 l8M [2] was followed to perform the density test of specimens of 7 different compositions.

### 3.2.3 Tensile Test



All dimensions are in mm

Fig. 3.3: The tensile testing specimen [3].

The test specimen (Fig. 3.3) was placed between the grips of Universal Testing Machine (Model: 3369, Instron, USA). The distance between the ends of the gripping surfaces and gauge length of the specimen were marked by permanent maker before gripping the specimen. The specimen was tightly gripped to prevent slippage of the specimen during the testing. Proper alignment was maintained during gripping the specimen. Tests were performed under the same experimental condition following ASTM D 638-03 [3].

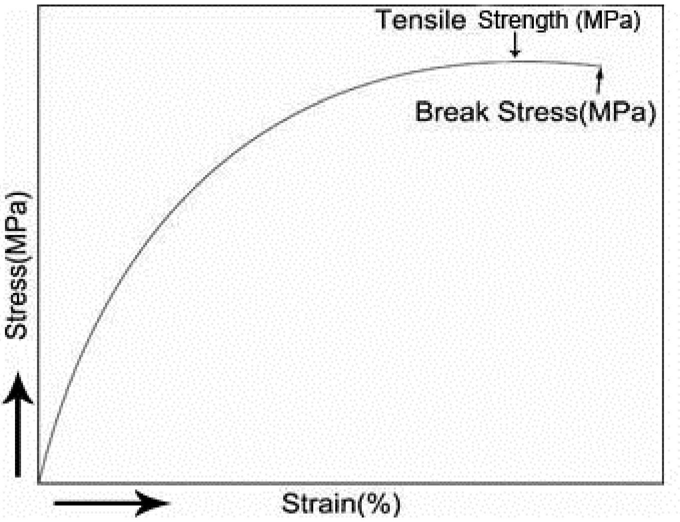


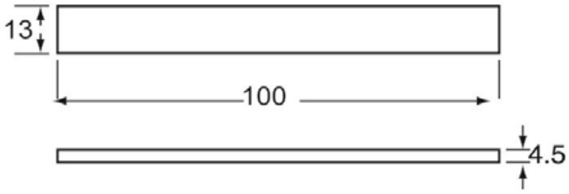
Fig. 3.4: Stress - strain curve showing the change in strain with stress

Out of 14, 7 tests were performed along longitudinal direction and other 7 tests were performed along transverse direction. The value of break stress as shown in Fig. 3.4 was determined. Average values of these 14 tests were taken as a test result of one composition.

Before testing, the prepared specimens were kept for 48 hours at $23\pm2^{o}$C and relative humidity of 50±5%. Testing was performed in the atmosphere of $23\pm2^{0}$C and relative humidity 50±5%. In this experiment 7 different compositions of uPVC were investigated.

The same procedure was followed to test a total of 98 tensile test specimens. Each test was carried out at a crosshead speed of 5 mm/min.

### 3.2.4 Flexural Test



All dimensions are in mm

Fig.3.5: Flexural strength test specimen (4)

Fig.3.5 shows a flexural strength test specimen. Width, thickness and span length of flexural strength test specimens were measured with digital caliper (Model: 530-115, Make: Mitutoyo, Japan) and marked by a permanent maker. The specimen was placed on the flexural tool of Universal Testing Machine (Model: 3369, Instron, USA). Proper alignment was maintained during placing the specimen. Load was applied on the test piece as a simple beam at mid-span without impact (Fig. 3.6). Load and deflection were recorded at the moment of reaching the conventional deflection. ASTM D790-03 [4] was followed and 10 tests were done under the same experimental conditions. Out of 10, 5 tests were performed along longitudinal direction and other 5 tests were performed along the transverse direction. Average values of these 10 tests were taken as a test result of one composition.

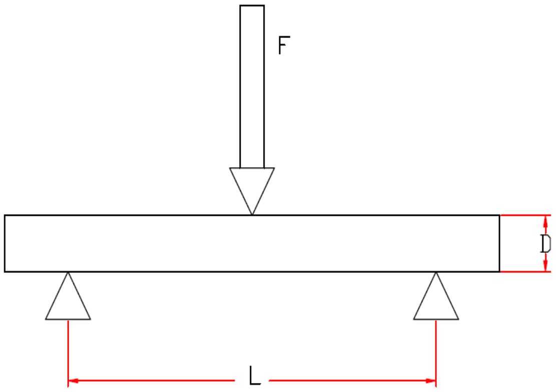


Fig. 3.6: The beam under 3 point bending

The flexural strength (FS), represents the highest stress experienced within the material at its moment of rupture. For a rectangular sample under a load in a three-point bending setup, as shown in Fig. 3.6, was calculated as[5]:

$$FS = \frac{3FL}{2bd^2} \text{ where} \qquad \text{(a)}$$

F is the load (force) at the fracture point (N),

L is the length of the support span (mm),

b is width (mm) and

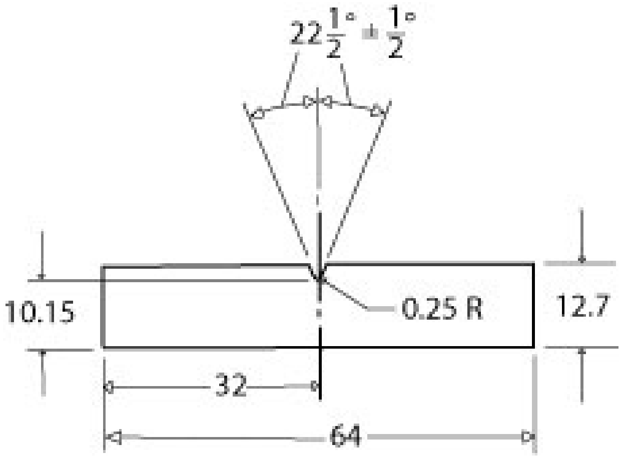
d is thickness (mm) of the sample

Storage of the test pieces and testing of the samples were under the same conditions as in tensile testing. The same procedure was followed to test a total of 70 flexural test specimens of 7 different compositions. Each test was carried out at a crosshead speed of 5 mm/min.

### 3.2.5 Impact Test

A method for determining behavior of material subjected to shock loading in bending, tension or torsion. The quantity usually measured is the energy absorbed in breaking the specimen in a single blow, as in the Charpy impact test, Izod impact test and tension impact test. Impact tests are also performed by subjecting specimens to multiple blows of increasing intensity, as in the drop ball impact test and repeated blow impact test.

In this experiment the Izod impact apparatus (Model: 5A02, Make: Zwick GmbH and Co., Germany) was used. It was calibrated and adjusted in accordance with the operating instructions. The test specimen was tightly clamped with the centre line of the notch in line with the clamping surfaces. The notch side of the specimen was struck by the blow. The pendulum was released by depressing the release lever and the reading of the pointer on the scale to the nearest sub-division was recorded. 20 tests were performed under identical conditions following ASTM D256-06 [6]. Out of 20, 10 tests were performed along longitudinal direction and other 10 tests were performed along transverse direction.



All dimensions are in mm

Fig. 3.7: Impact strength test specimen (6).

Average values of these 20 tests were taken as a test result of one composition. Before testing, the prepared specimens were kept in an atmosphere similar to that for tensile specimens. Testing was also performed in atmosphere similar to tensile tests. In this experiment the impact properties of samples of 7 different compositions of uPVC were investigated. The same procedure was followed to test a total number of 140 test specimens.

### 3.2. 6 Hardness Test

The hardness of a material characterizes its resistance to penetration. In these experiments, a Durometer device (Model: GS 702G, Make: TECLOCK, Japan) with D type indenter was used and ASTM D2240-81standar was followed. Dimension of the samples was 100 mm x 100mm x 4.5mm.

The adjustment and calibration of the Durometer instrument was done in accordance with the operating instructions. During testing, the indenter was pressed with sufficient hand force for 5 seconds into the plastic specimen perpendicularly so that the base took rest on the plastic surface. The load was applied to the sample in a shock and vibration free manner and depressed until the contact surface of the tester meets the surface of the sample under test. The amount of indentation was registered directly on the dial indicator.

Five indentations were performed in different positions on the samples for each composition following ASTM D2240-81 [7]. The distance between the test positions was more than 6 mm from one another and at a distance greater than 12 mm from the edge of the sample. Hardness indication was read directly from the drag pointer which remains in position until reset prior to another test. Average values of these 15 tests were taken as a test result of one composition.

In this experiment 7 different compositions of uPVC were investigated. The same procedure was used to make a total 35 of indentations.

### 3.2.7 Viscosity Number Determination

Most of the properties of polymeric materials depend on four attributes. These are viscosity number (polymer molecular weight), crystallinity, chemical composition, and macromolecular topology or architecture. These parameters interact with one another in a complex manner. By varying these parameters, polymers can be tailor-made to fit a list of desirable characteristics.

In this study the Viscosity Measuring Unit (Model: 074110/3, Make: Wallace, England) was used. ASTM D1243-79[8] was followed to perform the tests. Before testing, the measuring unit and accessories were thoroughly washed. 1.0 g of sample was weighed and transferred into a 100 ml glass-stoppered volumetric flask. The entire weighed sample was transferred into the flask carefully. Then 70 ml of cyclohexanone was added to the sample. The solution was thoroughly stirred and was then transferred into the heated chamber at 85$^{o}$C for 30 minutes.

After completion of heating the solution flask was removed from the heating chamber and cooled to 30$^{o}$C by immersing the flask into a water bath. The solution was filtered using filter paper (grade 40). After filtering the volume of the solution was adjusted to 100 ml by adding cyclohexanone.

The flow time of prepared solution and pure solvent in the viscometer was measured. For each sample 10 times of efflux time of solution and solvent were recorded. From this data the average time was calculated. Putting the obtained value in the following equation the viscosity number was determined [9].

$$\text{Viscosity Number, N} = \frac{T_s - T_o}{T_o \times C} \qquad \text{(b)}$$

where, $T_s$ = Efflux time of solution,

$T_o$ = Efflux time of solvent and

C = concentration (1/100) = 0.01 g.

### 3.2.8 Vicat Softening Temperature

The Vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. It is applied on materials that have no definite melting point such as plastics.

The Vicat Softening Temperature apparatus (Model: 074110/3, Make: Wallace, England) was used to determine the VST. Before testing, it was calibrated and adjusted in accordance with the operating instructions. The dimensions of each sample were 10mm × 10mm × 4.5 mm. The test specimen was so placed on the specimen support that it was approximately centered under the needle. The needle rod was gently lowered so that the needle rests on the surface of the specimen and holds it in position. The bulb of the thermometer was placed as close to the specimen as possible. The bath was thoroughly stirred. The assembly was carefully lowered into the high temperature oil so that any damage of the specimen does not occur. After placing the assembly 1 kg load was applied and immediately the penetration indicator was set at zero position. Then the electric circuit was switched on. The rate of temperature increase was set at 50$^{o}$C/hr. The temperature rise was recorded after penetration of indicator to 1 mm into the specimen from the surface.

ASTM D1525 [10] was followed and 2 tests were performed for each composition. In this experiment samples of 7 different compositions of uPVC were tested. The same procedure was followed to test a total number of 14 test specimens.

### 3.2.9 X-ray Diffraction Technique

Many materials, especially polymers, tend to form both crystalline and non-crystalline forms. Each structure produces a unique diffraction pattern that enables us to determine the relative amounts of each phase. Amorphous (glassy) phases produce one or more broad humps in the diffraction pattern, while crystalline materials produce a series of sharper peaks superimposed on the amorphous humps. X-ray diffraction studies were conducted to identify the crystalline and amorphous nature of the different blends.

The degree of crystallinity ($\gamma_c$) was calculated using the following equation [11]:

$$\gamma_c = \frac{I_{cr}}{I_{cr} + I_{am}} \times 100 \qquad \text{(c)}$$

where, $I_{cr}$ and $I_{am}$ are the integrated intensities of crystal and amorphous parts of the samples respectively.

In this study the X-ray diffractometer (Model: D8 Advanced, Make: Bruker, Germany) was used. CuKα and scintillation counter were used as source and detector respectively. The dimensions of each sample were20mm×20mm×4.5mm. The voltage and current were 40KV and 40 mA respectively. Scanning speed was $2^o$/minute. Normal atmosphere was maintained during the experiment.

### 3.2.10 Fourier Transform Infrared Test

Fourier Transform Infrared (FTIR) analysis provides spectral information that is essentially a molecular fingerprint for organic and in some cases inorganic materials having covalent bond character. This technique is extremely useful for identifying base polymer compositions and organic contaminants. FTIR spectrum of the unknown material can be compared for "best matches" with libraries of spectra that have been cataloged for known materials. The plot of a compound's IR transmission vs. frequency is compared to reference spectra to identify the unknown materials.

To find out the structural condition of the uPVC samples under investigations, KBr and powdered uPVC sample in the ratio of 100:0.1 were mixed by grinding in an agate mortar. About 100 mg mixture was put into a specific mold cavity of female part and pressed by the male part into thin films of size 30 mm diameter x 0.5mm thick with a pressure of 85kN to make the pallets for different formulation. FTIR spectra were recorded with FTIR 8400 Shimadszu. The samples were scanned 30 times in the range of 4000 to 400 $cm^{-1}$ and their spectra were recorded. Resolution was 2 $cm^{-1}$.

### 3.2.11 Scanning Electron Microscopy and Energy Dispersive X-ray

In this study a Field Emission Scanning Electron Microscope unit (Model: JSM-7600F, Make: JEOL, Japan) was used. Morphology study of uPVC was done by scanning electron microscopy and spot analysis for elements was done by EDS. The accelerating voltage was 5-15 KV and the working distance (WD) was 8 mm. Samples were taken from the fractured end of tensile specimens. The specimens were set on specimen holder using special carbon tape and foreign particles were removed by air blowing. Platinum flashing was done at vacuum pressure of around $5 \times 10^{-4}$ Pa. Prepared samples were inserted into the chamber of scanning electron microscope. A vacuum atmosphere and 25°C temperature were maintained throughout the experiment. PR-10 (90% argon) gas with a flow rate of 6 ml/min was used in the experiments.

### 3.2.12 X-ray Fluorescence Technique

Elemental analysis of PVC was done by XRF method. An X-ray fluorescence unit (Model: XRF-1800, Lab Centre, Make: Shimadzu, Japan) was used. The main components of the equipment are X-ray source, crystal and detector. Rhodium (Rh) target was used as source and proportional scintillation counter was used as detector. The voltage and current were 40 KV and 95 mA respectively. The size of the each sample was approximately 20 $mm \times$ 20 mm ×4.5 mm. Prepared samples were put into the holder. The holder was then placed in its proper position. A scanning speed of 8$^{o}$/minute was used. Vacuum atmosphere and 35$^{o}$C temperature were maintained throughout the experiment. PR-10 (90% argon) gas was used in the experiments with a flow rate of 6 ml/min.

### 3.2.13 Differential Scanning Calorimetry

Differential Scanning Calorimetry is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature.

In this study a Differential Scanning Calorimeter (Model: DSC 60, Make: Shimadzu, Japan) was used. On the commencement of the test, the sample holder was brought out from the analyzing instrument. It was cleaned and required amount of fine uPVC powder was put into the aluminium pan (diameter 6.5 mm, depth 1.5 mm). Then the pan was sealed and analyzed. During the experiment, a nitrogen atmosphere was maintained. The test sample was weighed and furnace was switched on. A heating rate 10$^{o}$C/min and a gas flow rate of 20ml/min were maintained. The test was performed in the temperature range of 30 – 250$^{o}$C. The specimen was burnt and the obtained data were analyzed using a software to get glass transition ($T_g$) temperature.

### 3.2.14 Thermo-Mechanical Analysis

Thermo-Mechanical Analyzer is used to determine the linear thermal expansion of a solid as a function of temperature. In thermomechanical analysis, a constant, usually small load acts on the specimen. The measured expansion of the specimen is used to determine the coefficient of linear thermal expansion $\alpha$. The 1st heating phase yields information about the actual state of the specimen, including its thermal and mechanical history. When thermoplastics soften, especially above the glass transition, orientations and stresses may relax, as a result of which post crystallization and recrystallization processes may occur. On the other hand, the specimen may deform under the applied test load. To determine the coefficient of expansion as a material characteristic, the material must not undergo irreversible changes, such as post crystallization, post poly-merization, relaxation of orientation or internal stress and so forth during a 2nd heating phase that has followed controlled cooling.

In this study a Thermo-Mechanical Analyzer (Model: TMA/DMA-SS6300, Make: Seiko Instruments Inc. (SII), EXSTAR-6000, Japan) was used. The equipment consists of a very sensitive LVDT (Linear Voltage Displacement Transducer), measuring probe, thermocouple and an oven. The size of each sample was 10mm × 6mm × 4.5 mm. 100 mN load was applied on the sample. Tests were performed in nitrogen atmosphere. TMA was used to measure glass transition ($T_g$) temperature and co-efficient of thermal expansion (CTE). The tests were performed in the range 30 to 200°C. A heating rate 5°C/min and a gas flow rates of 70ml/min were used.

### 3.2.15 Thermo-Gravimetric and Differential Thermal Analysis

Thermogravimetric and differential thermal analysis is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes the measurement is performed in a lean oxygen atmosphere (1 to 5% $O_2$in $N_2$or He) to slow down oxidation. In addition to weight changes, some instruments also record the temperature difference between the specimen and one or more reference pans (differential thermal analysis).

A thermogravimetric and differential thermal analyzer (Model: TG/DTA-6300, Make: Seiko Instruments Inc. (SII), EXSTAR-6000, Japan) was used for thermogravimetric and differential thermal analysis. It consists of a very sensitive balance (hundreds of a microgram) and an oven. The material under study was weighed automatically by the computer. Analysis was performed in nitrogen atmosphere. The analyzer was used to identify the weight loss of the blends. The temperature range of the instrument covered from 30°C to 1000°C.

Before the test, the sample holder was brought out from the analyzing instrument. It was cleaned and the required amount of fine uPVC powder was put into the holder.

The holder was then put back in its right position. During the experiment, a nitrogen atmosphere was maintained within the furnace. The heating rate was set at 20°C/min and gas flow rate was set at 20ml/min. Test was performed in the temperature range of 30 – 1000°C. The obtained data such as weight loss, residue (amount of filler) were processed and recorded by the computer connected to the machine.

### 3.3 Reference

1. Standard Test for Resistance to Acetone American Society for Testing and Materials, 2006 (Designation: BS 3505/1968).
2. Standard Test Method for Density and Specific Gravity (Relative Density) of Plastics by Displacement, American Society for Testing and Materials, 2006 (Designation: ASTM D792-008M).
3. Standard Test Method for Tensile Properties of Plastics, American Society for Testing and Materials, 2006 (Designation: ASTM D 638-03).
4. Standard Test Method for Flexural Properties of Plastics, American Society for Testing and Materials, 2006 (Designation: ASTM D 790-03).
5. William D. Callister, Jr., Materials Science and Engineering, Hoken: John Wiley & Sons, Inc., 2003(flexural).
6. Standard Test Method for determining the Izod Pendulum Impact Resistance of Plastics, American Society for Testing and Materials, 2006 (Designation: ASTM D 256-06).
7. Standard Test Method for Rubber Property-Durometer Hardness, Annual Book of American Society for Testing and Materials (ASTM) Standards, 1982 (Designation: ASTM D 2240).
8. Standard Test Method for Dilute Solution Viscosity of Vinyl Chloride Polymers, American Society for Testing and Materials (ASTM D 1243-79).
9. Standard Test Method for Dilute Solution Viscosity of Polymers, American Society for Testing and Materials (ASTM D 2857-70(Reapproved 1977).

10. Standard Test Method for Vicat Softening Temperature Plastics, American Society for Testing and Materials (ASTM D 1525-76).

11. http://www.rigaku.com/products/xrd/rapid/app003.

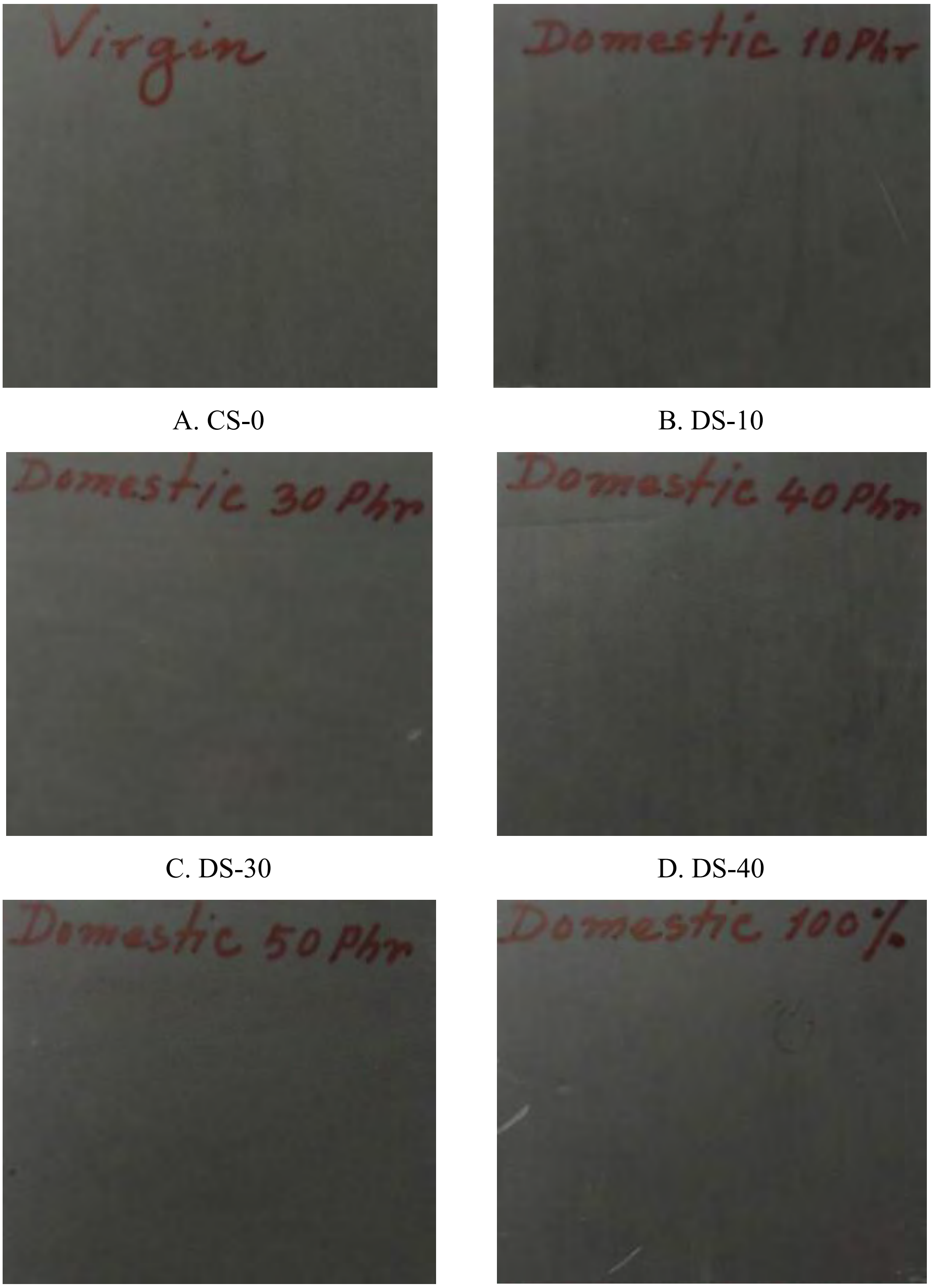
# CHAPTER FOUR

## 4. Results and Discussion

### 4.1 Acetone Test

Figs. 4.1.1 and 4.1.2 show the camera images of the surface of samples CS-0, DS-10, DS-20, DS-30, DS-40, DS-50 and DS-100 before and after immersion of the samples in acetone reagent. No surface flaws such as blistering, voids, scratch and burrs were seen on the surface of samples before immersion. After immersing 2 hours in the acetone solution, the immersed samples were removed from the solution. These samples are allowed to dry completely. No delamination or disintegration was observed during physical observation of the immersed samples. But color change from deep grey to light grey or white on all the immersed samples was observed. Besides, samples DS-40, DS-50 and DS-100 showed a little variation in swelling from sample to sample. Similar testing procedure has been followed for all the samples of ES-10, ES-20, ES-30, ES-40, ES-50 and ES-100. Similar results were also obtained during physical observation of the external samples except a little variation in swelling.

According to BS-3505, 1968[1] standard, these results are acceptable. It is important to note that this type of test detects only inadequacy of gelation (the term gelation embraces changes involved in conversion of separate particles of polymer to more or less into continuous matrix.). It does not determine the overall quality of the PVC pipe or fitting. This test cannot differentiate between thermally degraded and adequately fused PVC products. This technique cannot be used to give actual properties, such as burst and impact strength. In this investigation, it seems all the ingredients of each sample were sufficiently bonded. Because no separation of any ingredients or portion of the samples and loose particles were observed after immersion in acetone solution, which is the indication of sufficient fusion development of all ingredients of each sample in both domestic and external. It is also notable that no suspended particles were observed in the immersed acetone reagent.



A. CS-0

B. DS-10

C. DS-30

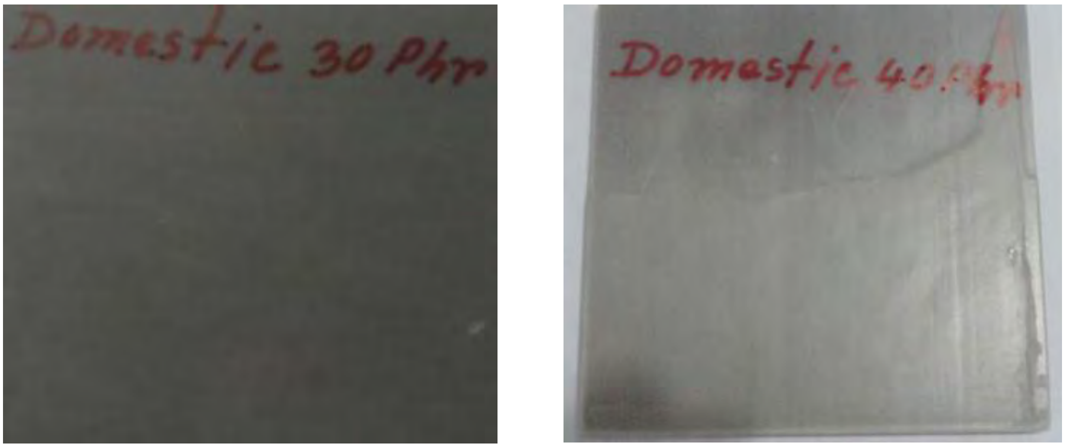
D. DS-40

E. DS-50

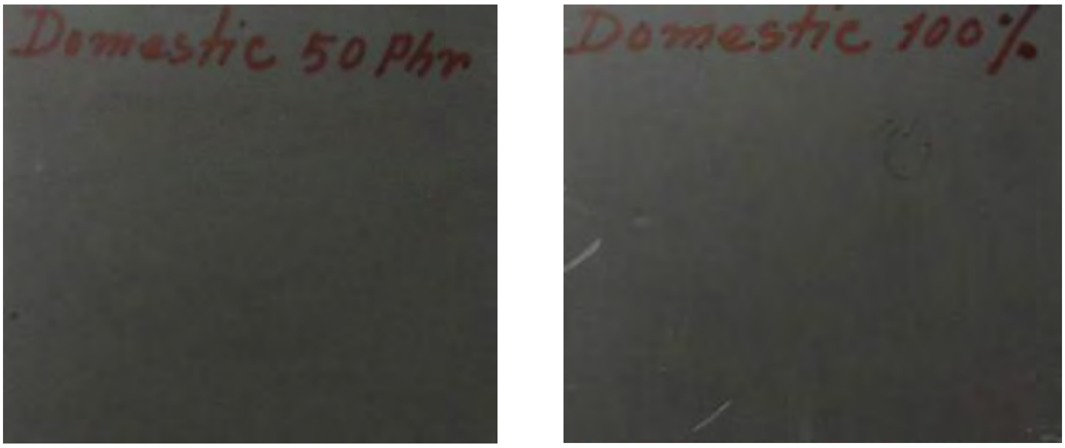
F. DS-100

Fig. 4.1.1: Camera images of the samples (A) CS-0, (B) DS-10, (C) DS-30, (D) DS-40, (E) DS-50 and (F) DS-100 before immersion in acetone reagent.

A. CS-0 B. DS-10



C. DS-30 D. DS-40



E. DS-50 F. DS-100

Fig. 4.1.2: Camera images of the samples (A) CS-0, (B) DS-10, (C) DS-30, (D) DS-40, (E) DS-50 and (F) DS-100 after immersion in acetone reagent.

The results of the acetone test performed on all the samples containing domestic and external scraps with their dimensions have been shown in the Tables 4.1.1-4.1.2: In the tables it can be seen that all the samples have passed the acetone test.

Table 4.1.1: Results of acetone test on samples containing no scrap and domestic scraps.

| Samples | Sample size | Result |
|---|---|---|
| CS-0 | 75mm×75mm×4.5mm | passed |
| DS-10 | 75mm×75mm×4.5mm | Passed |
| DS-20 | 75mm×75mm×4.5mm | Passed |
| DS-30 | 75mm×75mm×4.5mm | Passed |
| DS-40 | 75mm×75mm×4.5mm | Passed |
| DS-50 | 75mm×75mm×4.5mm | Passed |
| DS-100 | 75mm×75mm×4.5mm | Passed |

Table 4.1.2: Results of acetone test on samples containing external scraps.

| Samples | Sample Size | Result |
|---|---|---|
| ES-10 | 75mm×75mm×4.5mm | Passed |
| ES-20 | 75mm×75mm×4.5mm | Passed |
| ES-30 | 75mm×75mm×4.5mm | Passed |
| ES-40 | 75mm×75mm×4.5mm | Passed |
| ES-50 | 75mm×75mm×4.5mm | Passed |
| ES-100 | 75mm×75mm×4.5mm | Passed |

## 4.2 Density Test

Fig. 4.2.1 shows the variation of density of reference sample (CS-0) and different other samples prepared with addition of scraps both domestic and external. The density value of CS-0 sample is found to be 1.57 gm/cc. Density values show minor fluctuations. The minimum and maximum density values of domestic samples are found to decrease by 0.6% for DS-50 and increase by 5.1% for DS-100, respectively. On the other hand, the minimum and maximum densities of the samples having external scrap decrease by 0.6% for ES-10 and increase by 12.1% for ES-100, respectively. From these data, it can be concluded that density values gradually increase in both cases. It has also been found that the density of the samples containing external scrap is more pronounced than that of samples containing domestic scraps.

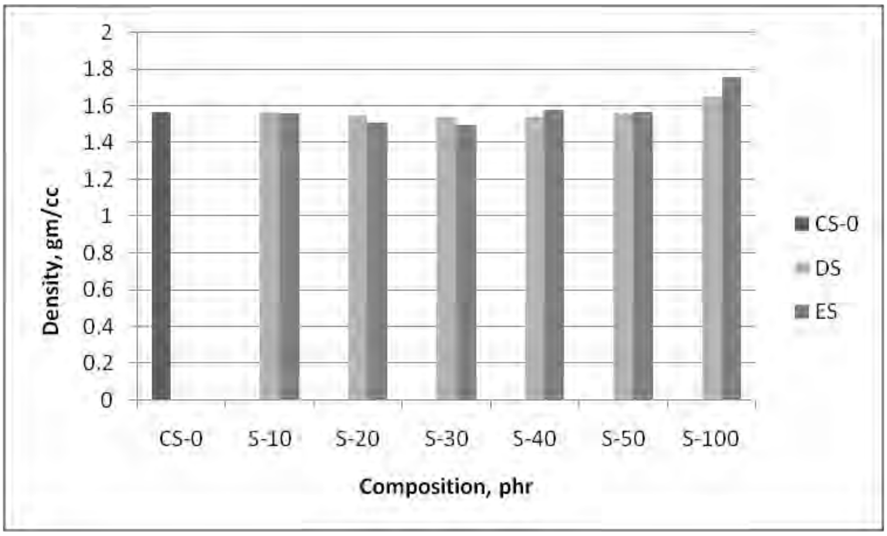


Fig. 4.2.1: Variation of density with quantity of scrap (domestic and external) in the raw material mix.

The results are in good agreement with those of Sombatsompop *et al* [2] who also found increase in density. But the change in density in this study is not significant. The density of $CaCO_3$ (2.71 gm/cc) is higher than the density of PVC resin (1.35-1.45gm/cc). In different samples the added amount of $CaCO_3$ as filler is the same. The $CaCO_3$ is supposed to be inhomogenously distributed. Therefore, a fluctuation in density change is observed. However, due to the increase of scrap content the amount of $CaCO_3$ may increase because the scrap itself contains some filler during its procuring. Due to this increased $CaCO_3$ the density of the samples increases with increasing amount of scrap.

### 4.3 Tensile Test

Figs. 4.3.1 and 4.3.2 represent how break stress (BS) and % elongation-at-break or strain% vary with composition of DS and ES. The BS value of CS-0 sample is found to be 34.1 MPa. It seems to decrease gradually with the increase of DS content. However, the minimum BS value is observed for the sample DS-20 is 30.2MPa. Thus, the estimated maximum decrease in BS is 11.4%. On the other hand, the strain% also decreases with the increase of DS content. Similarly, break stress and % elongation-at-break decrease by 38.9 and 45.8% with addition of 100% external scrap. From these data, it can be stated that the deterioration of BS and strain% for domestic scarp loaded are lower than those for external scrap loaded PVC. Break stress is strongly influenced with number of monomers present in the large molecules or the molecular weight and its distribution [3, 4]. In general, domestic scrap is less contaminated and within short time this type of scrap is consumed. On the contrary, external scrap is highly contaminated and most of the external scraps are exposed to ultraviolet ray, sun light and mechanical stress for long time. External scrap also faces weathering effect. These factors accelerate to break large molecules of scraps into smaller molecules. From the above discussion it can be stated that the decreasing in break stress and % elongation at break may be attributed to the contamination present in the scrap and breaking of large molecules into smaller molecules. However, the values obtained in break stress and % elongation at break show some fluctuations in both the sets of samples. This may be lack of compatibility or may be related to gelation of ingredients.

Both the decrease and fluctuation of BS and strain% have been investigated elsewhere [5], where the authors have found similar changes in the mechanical properties of PVC during their study on the recycling of PVC bottle compounds. This fact was also reported by Strapasson *et al.* [6] who studied tensile and impact behaviour of polypropylene/low density polyethylene blends. In their study a linear variation of the yield strength and elastic modulus with the blend composition was observed. An irregular behavior of the blend was also reported.

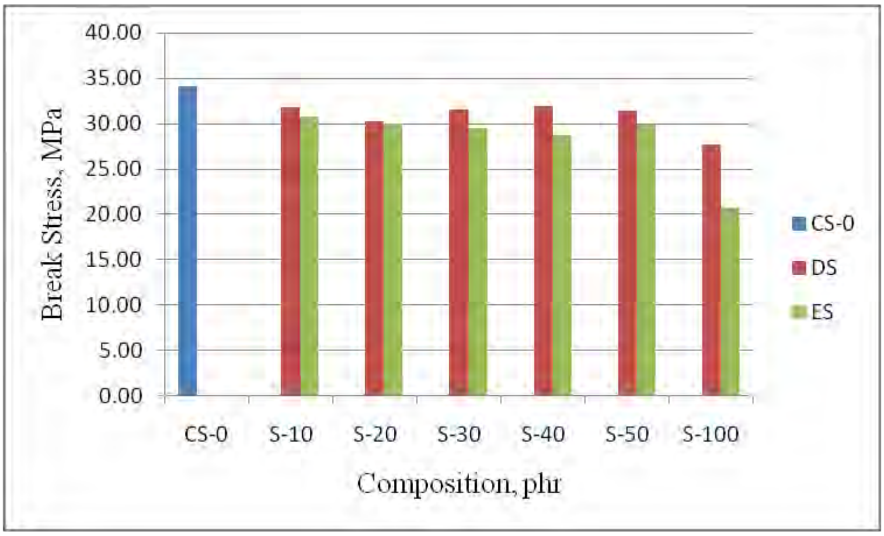


Fig. 4.3.1: Variation of break stress with addition of scrap (domestic and external) in the raw material mix.

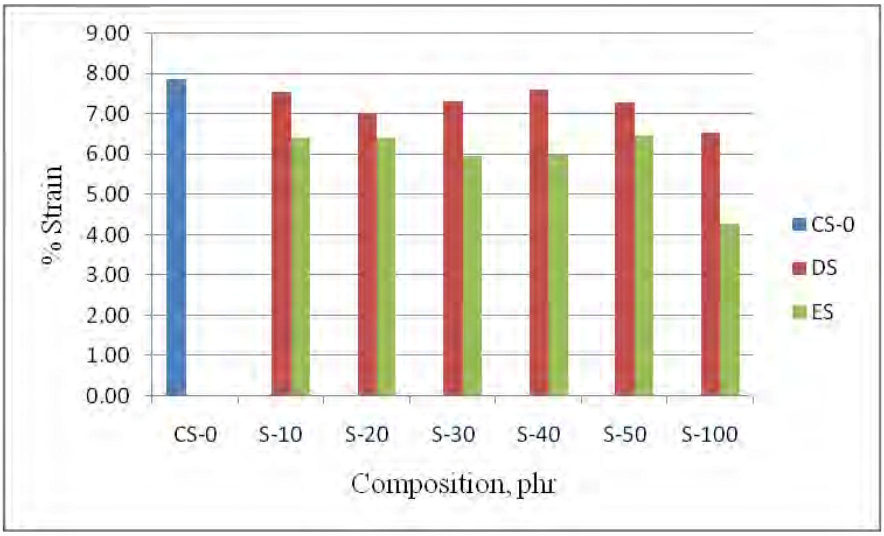


Fig.4.3.2: Variation of % elongation at break with addition of scrap (domestic and external) in the raw material mix.

Generally, with increasing BS, % elongation-at-break decreases. But from the above figs it is seen that with decreasing BS, % elongation-at-break is also decreasing. This effect is controlled with addition of the required amount of $CaCO_3$ which imparts ductility. There is also an optimum value of $CaCO_3$ addition beyond which the BS starts to decline. So optimization of BS and % elongation-at-break through proper formulation is an important issue to produce a good quality pipe products.

## 4.4 Flexural Strength

The results of flexural test are shown in Fig. 4.4.1. The flexural yield stress (FYS) value of CS-0 sample is found to be 52.7 MPa. The FYS fluctuates with addition of domestic and external scrap. The maximum increase and decrease of FYS of domestic samples are 11.3% for DS-30 and 5.8% for DS-100, respectively. On the other hand, the maximum decrease of FYS of external samples is 35.5% for ES-100. From these data, it can be mentioned that the deterioration of FYS for DS loaded is lower than that for ES loaded PVC. FYS of samples containing 20, 40 and 50 phr uPVC scrap is almost similar to the samples containing no uPVC scrap. Although there is fluctuation in flexural strength, the overall trend is decreasing in FYS with scrap addition in both cases. Basically, flexural strength is the combination of tensile strength and compressive strength. So the same reasons mentioned in tensile test may be applicable to explain deceasing and fluctuating nature in flexural strength.

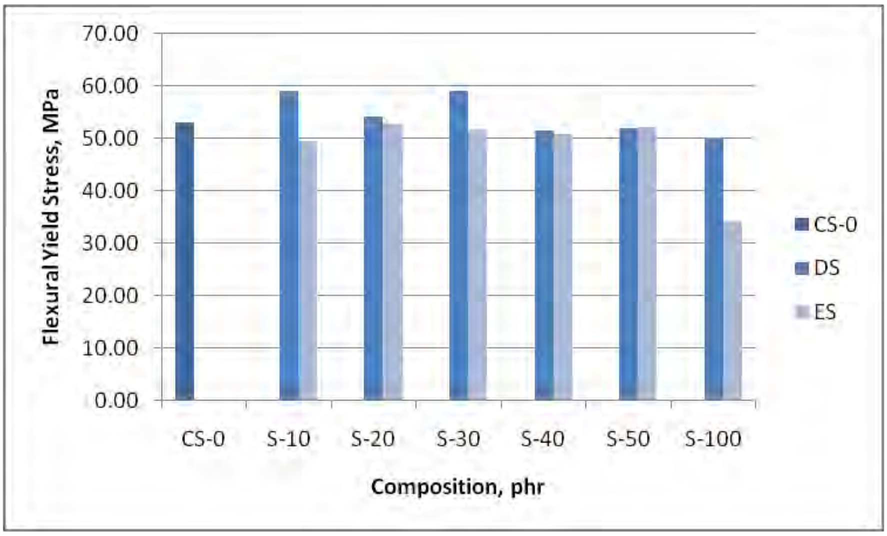


Fig. 4.4.1: Variation of flexural strength with quantity of scrap (domestic and external) in the raw material mix.

From fig. it is also observed reduction in FYS of samples having external scraps is more pronounced compared to samples containing domestic scrap. It is also seen that for samples DS-10 and DS-30, FYS has increased compared to the samples containing no scrap. This may be due to good compatibility and gelation of ingredients.

## 4.5 Impact Strength

Fig. 4.5.1 illustrates the variation of impact strength with the quantity of scrap in the raw material mix. The impact strength value of CS-0 sample is found to be 47. KJ/m$^2$. Impact strength values show some fluctuations. The minimum and maximum reduction in impact strength values of domestic samples are recorded 1.0% for DS-10 and 27.4% for DS-40, respectively, whereas the minimum and maximum decrease in impact strength values of external samples are recorded 9.6% for ES-10 and 39.2% for ES-50, respectively. It is clear that external scrap affects the impact properties to a greater extent as compared to domestic scrap. It has also been found that the impact strength value decreases by 9.6 and 35.9% with 100% domestic and external scraps, respectively. From these data, it can be concluded that impact strength of samples containing external scraps deteriorates more than that of the samples containing domestic scraps.

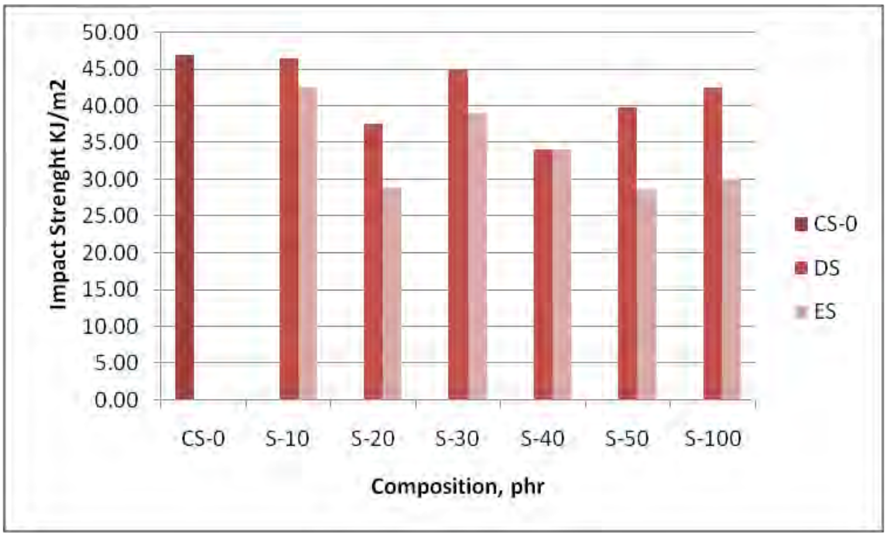


Fig. 4.5.1: Variation in impact strength with quantity of scrap (domestic and external) in the raw material mix.

This may be due to the presence of inhomogeneity, lack of compatibility and impurities in mixture. Besides, difference in sizes and shapes of filler and other additives used by different industries may be responsible for the reduction of impact values of both domestic and external samples.

The values obtained in impact strength show some fluctuations in both the sets of samples which may be attributed to difference in sizes and shapes, and amount of fillers mixed in the raw materials mix. Below the glass transition, molecular movement is restricted due to the presence of different ingredients. As a result, impact strength is reduced and sometimes fluctuates. Similar effects have been observed by L.A. Fillo *et al.* [7].

## 4.6 Hardness Test

Fig. 4.6.1 displays the variation of hardness with the quantity of scrap mixed with the PVC resin and additives. The hardness value of CS-0 sample is found to be 75.25 shore-D. Hardness values show minor fluctuations. The minimum and maximum increase in hardness values of domestic samples are recorded to be 0.07% for DS-40 and 2.8% for DS-10, respectively, whereas the minimum and maximum reduction in hardness values of external samples are recorded to be 1.2% for ES-50 and 2.2% for ES-20, respectively. It has also been found that the hardness value increases by 0.3% and decreases by 1.8% with addition of 100% domestic and external scraps, respectively. It can also be seen that the increasing effect of hardness value is more pronounced in the case of external scrap. In analyzing the increase or decrease of hardness value of the samples containing domestic and external scrap, it can be seen that the difference in hardness is low. From these data analysis it can be concluded that harness does not depend on the amount of scrap added. The small variation of hardness may be due to lack of homogenous dispersion of fillers and additives in the polymer matrix.

The results of hardness are in good agreement with Sombatsompop, *et al.* [8] who studied processability, and properties of postconsumer polyvinyl chloride scraps. He observed that hardness and density remain unaffected by addition of scraps. It is also concluded that the optimum concentration of PVC recyclates to be added to PVC resin and additives are different from one property to another and also dependent on the type of PVC resin grade.

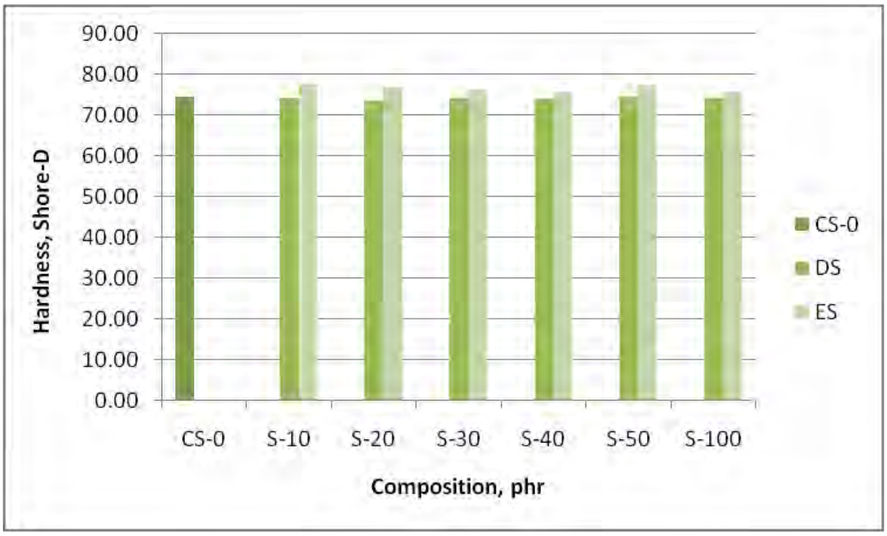


Fig. 4.6.1: Variation of hardness with quantity of scrap (domestic and external) in the raw material mix.

To explain the results obtained in tensile, flexural and impact test the following reasons may be considered.

PVC contains organic and inorganic ingredients and is a highly unstable material. To prevent degradation during transportation and storage organic additives including plasticizers are added. Different companies use formulations of filler ($CaCO_3$), processing aids and stabilizers of different types and amounts. Thus, there is a complex compositional variation in the PVC compound. The compositional variation can affect compatibility among different ingredients and thus lead to variation in properties.

Different recipe is used for different grades of pipe. Different grades of pipe are manufactured in the same industry or in different industries. During recycling different grades of pipe are cut, crushed and pulverized. So there is a possibility of variation in ingredients from different batches and also from different industry. Besides, long time exposure to the environment can contaminate the products with foreign particles. Recipe variation along with contamination has ultimately affected the mechanical properties which have been reflected as fluctuation in properties. The scrap had different prior history of processing and heating to different temperatures during processing may have caused variation in gelation or fusion. Gelation to different extents may be another cause of property variation. Since PVC is a viscoelastic organic material, its properties change with time, temperature and weathering effect. The scraps have a different prior history and there was time variation and weathering effect on the scrapped PVC which affected the nature of the scrap. This type of change in mechanical properties has also been reported by Wenguang *et al* [9] who investigated the processing and mechanical properties of recycled PVC and of homopolymer blends with virgin PVC.

Ditta *et al*. [10] carried out a study on the processing characteristics and mechanical properties of multiple recycled rigid PVC. In their investigation it was observed that for outdoor profiles, the elongation at break does not change significantly even after 20 years of service life compared to the values when new material is used. Re-extrusion of old materials gives profiles with almost the same tensile properties as for the new profiles, provided contamination is addressed. The type and amount of contaminations vary with time and environment to which the scrap was exposed. These contaminations are one of the most important causes which affect the quality of products and a variation in quantity of contaminants may cause a fluctuation in properties.

Different industries use different types of extruder. Even when the same recipes are used the quality will be different for different models of extruder. Although in this research work same extruder has been used to prepare the samples, the scrap used may not have been produced by the same type of extruder. Before blending of ingredient with scrap materials, the scrap components were shredded and pulverized. Different models of crusher and pulverizing unit are available in the world. Due to a different model of crusher and pulverizing unit the grain size of powder is also different. Even small differences can be significant, especially where fine fillers are involved. Particle size distribution is also significant. In short, it can be mentioned that the quality of used technology also affects the quality of the products. Variation in using technology may be also an important cause of decreasing the quality of products with fluctuation.

Yarahmadi *et al.* [11] investigated profiles made of rigid PVC after different numbers of repeated extrusions to check changes of properties and durability. They found an improvement of mechanical properties after the second extrusion. This was explained by an increase in the degree of gelation of the PVC material. They also found the estimated lifetime, for indoor use at room temperature; of materials that were extruded for five times was one-third of the lifetime of the materials that were extruded only once.

The crystallinity of a material influences many of its characteristics, including mechanical strength, opacity, and thermal properties. With increasing crystallinity upto a certain limit tensile increases and then decreases. With increasing crystallinity impact strength also decreases. Fluctuation in crystallinity may also affect mechanical properties.

### 4.7 Viscosity Number Determination

The variation of viscosity number with proportions of domestic and external scrap has been shown in Fig. 4.7.1. The viscosity number of CS-0 sample is 116. Fluctuations in VN of samples containing domestic and external scraps have been observed. VN varies from 105(DS-30) to 83 (DS-40) for samples containing domestic scrap and 71(ES-10/20) to 62(ES-50) for samples containing external scrap. VN of samples DS-100 and ES-100 are 66 and 51, respectively.

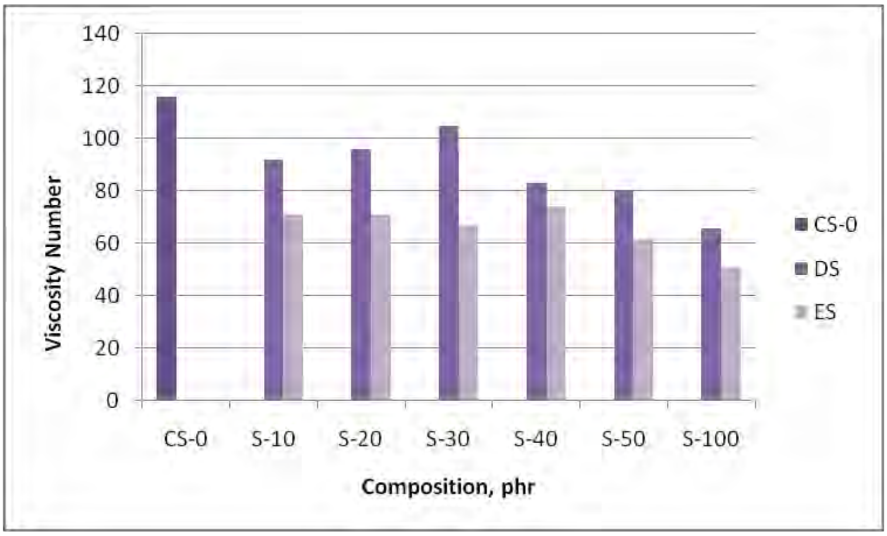


Fig. 4.7.1: Variation of viscosity number with quantity of scrap (domestic and external) in the raw material mix.

VN and its corresponding molecular weight which is expressed as k-value [k-value has been explained in **2.3**.1] have been shown in Table4.7.1

Table 4.7.1: Results of VN and its corresponding k-value found by wet analysis process on samples containing scrap and without scrap.

| Samples | VN | k-value | Samples | VN | k-value |
|---|---|---|---|---|---|
| CS-0 | 116 | 63.16 | -- | -- | -- |
| DS-10 | 92 | 57.21 | ES-10 | 71 | 51.09 |
| DS-20 | 96 | 58.25 | ES-20 | 71 | 51.09 |
| DS-30 | 105 | 60.46 | ES-30 | 67 | 50.11 |
| DS-40 | 83 | 54.75 | ES-40 | 74 | 52.06 |
| DS-50 | 80 | 53.87 | ES-50 | 62 | 48.65 |
| DS-100 | 66 | 43.56 | ES-100 | 51 | 38.24 |

(N.B: practical applicable range of k-value is 55-88)

It is seen from the table that molecular weight of samples containing 10, 20 and 30 phr domestic scrap is within the applicable range of k-value and the samples containing 40 and 50 phr and 100% domestic scrap are out of the range of k-value. Whereas all the samples containing 10, 20, 30, 40 and 50 phr and 100% external scrap are out of the range of k-value. This indicates the domestic scraps up to 30 phr could be used with PVC resin and additives safely for quality pipe production. On the contrary, the rest samples containing 40, 50phr, and 100% domestic scraps and 10, 20, 30, 40, and 50 phr, and 100% external scraps could be used for making less important pipe, electrical conduit and other less load bearing applications. It was also found that with adding scrap, viscosity number decreases, which ultimately influences mechanical properties. Viscosity number is related to molecular weight [12].

In both the cases viscosity number was found to decrease with scrap addition. Long exposure to mechanical stress, light and heat breaks the molecules to monomers. As a result, the number of monomers of PVC molecules decreases. With increasing scrap, the number of polymer molecules with decreased monomers increases in unit mass. For this reason with increasing PVC scrap in raw materials mix the viscosity decreases.

This fact has been reported elsewhere [5] who studied the effects of recycling on the mechanical properties of recycled PVC bottle compounds. Shinozaki et al. [13] studied the influence of processing parameters and molecular weight on the mechanical properties of PVC. They found that the molecular weight affects the various mechanical properties and as the molecular weight increases the mechanical properties are enhanced. Decreasing in viscosity number of samples containing external scrap is more pronounced than the decrease in viscosity number of the sample containing domestic scrap.

## 4.8 Vicat Softening Temperature

The VST is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. It is applied to materials that have no definite melting point such as plastics.

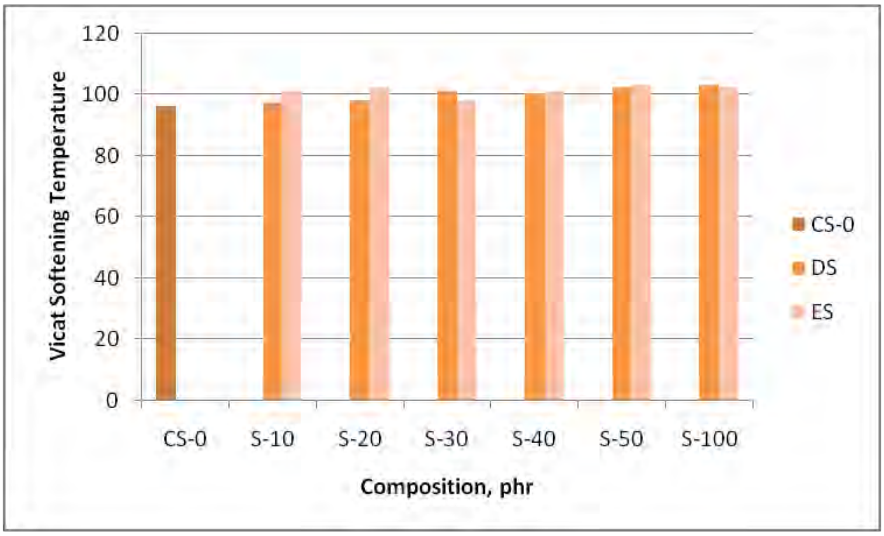


Fig. 4.8.1: Variation of vicat softening temperature with quantity of domestic and external scrap in the raw material mix.

Fig.4.8.1 shows the variations of VST with proportions of scrap incorporation. The VST of CS-0 sample is 96°C. Minor fluctuations in VST of samples containing domestic and external scraps have been revealed. The minimum and maximum VST values of samples containing domestic scraps are found to be 103°C for DS-50 and

97$^oC$ for DS-10, respectively, whereas the minimum and maximum VST values of samples containing external scraps have been found to be 98$^oC$ for DS-30 and 103 $^oC$ for ES-50, respectively. VST value of domestic and external samples gradually increases. In case of domestic samples, VST has increased from 1% to 4.1%. On the other hand, in case of external samples VST has increased from 2% to 7.3%. The VST of DS-100 and ES-100 samples have been demonstrated 103$^oC$ and 102$^oC$, respectively. The sample containing external scrap has a slightly higher resistance to heat.

In both cases the resistance to heat has increased with scrap addition. This may be due to the dispersion effect of filler and additives. The dispersed particles hinder the movement of PVC molecules. The inorganic ingredients such as $CaCO_3$, $TiO_2$ are more heat resistive. In recyclate some impurities exist, they also prevent the movement of PVC molecules. By increasing the amount of scrap the amount of dispersed inorganic particles increases, which eventually increases the resistance to heat.

Garcia *et al.* [14] found an increase in VST with the incorporation of styrenic polymers. The results are also in good agreement with those of Sombatsompop *et al* [8] who studied the rheology, morphology, mechanical and thermal properties of recycled PVC and found that VST increases with PVC loadings.

From the above discussion, it could be concluded that with the proportions of both domestic and external uPVC scraps the resistance to heat is increased with minor differences.

## 4.9 XRD data analysis

Figs. 4.9.1 and 4.9.2 exhibit the XRD profiles of PVC resin and $CaCO_3$ samples, taken with the scattering angle (2θ) ranging 10–70°. The PVC resin sample shows diffuse scatterings with two broad peaks around 18 and 26°. These results indicate that the PVC resin is a very poorly crystalline material with short range order. From the values of 2θ from the peaks, the estimated short range order shows a lattice spacing of 4.924 and 3.424 Å, respectively. On the other hand, the $CaCO_3$ sample exhibits sharp peaks at scattering angle of 29.5°. These results show a highly crystalline nature of the filler $CaCO_3$.

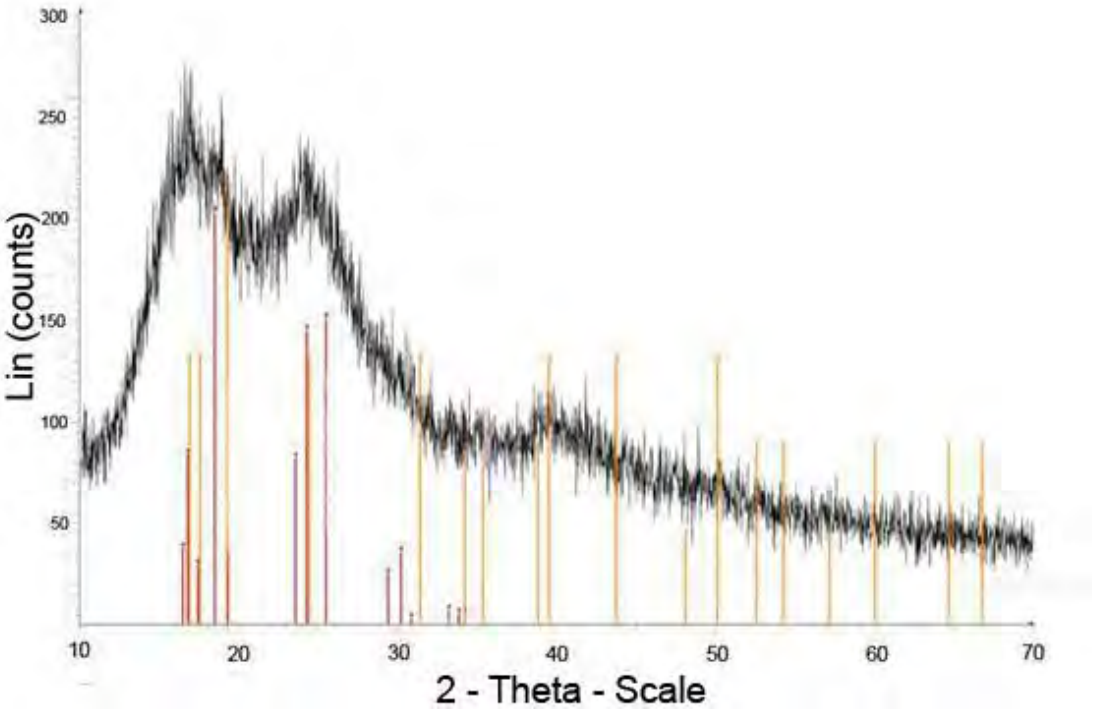


Fig. 4.9.1: An XRD profile of PVC resin.

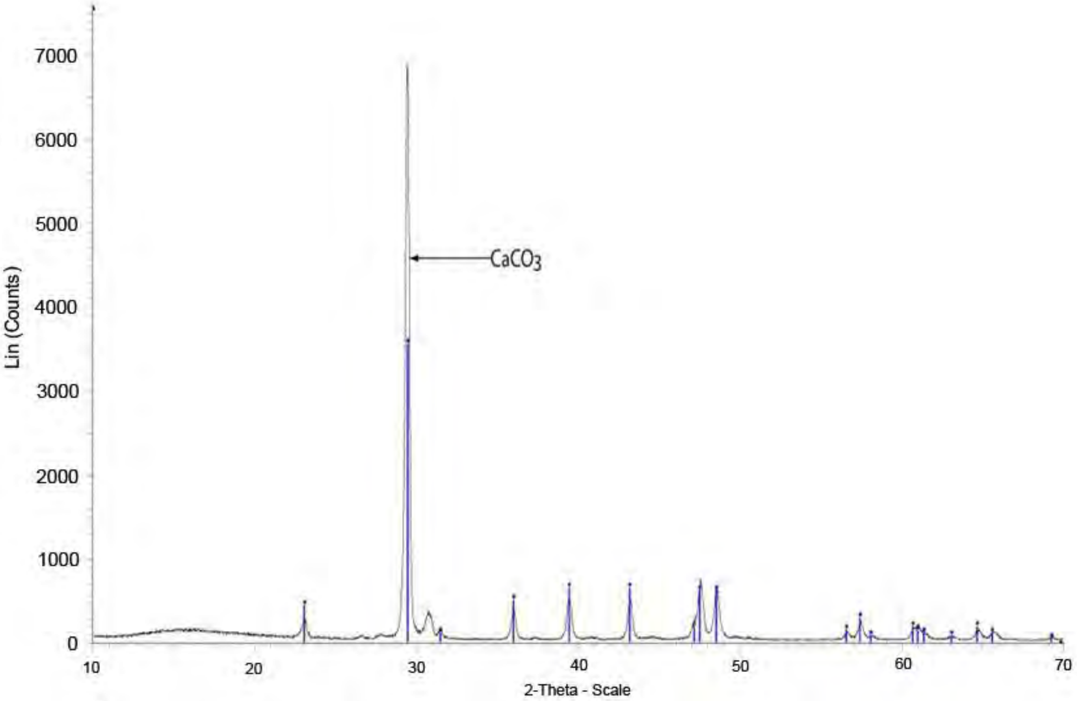


Fig. 4.9.2: An XRD profile of calcium carbonate.

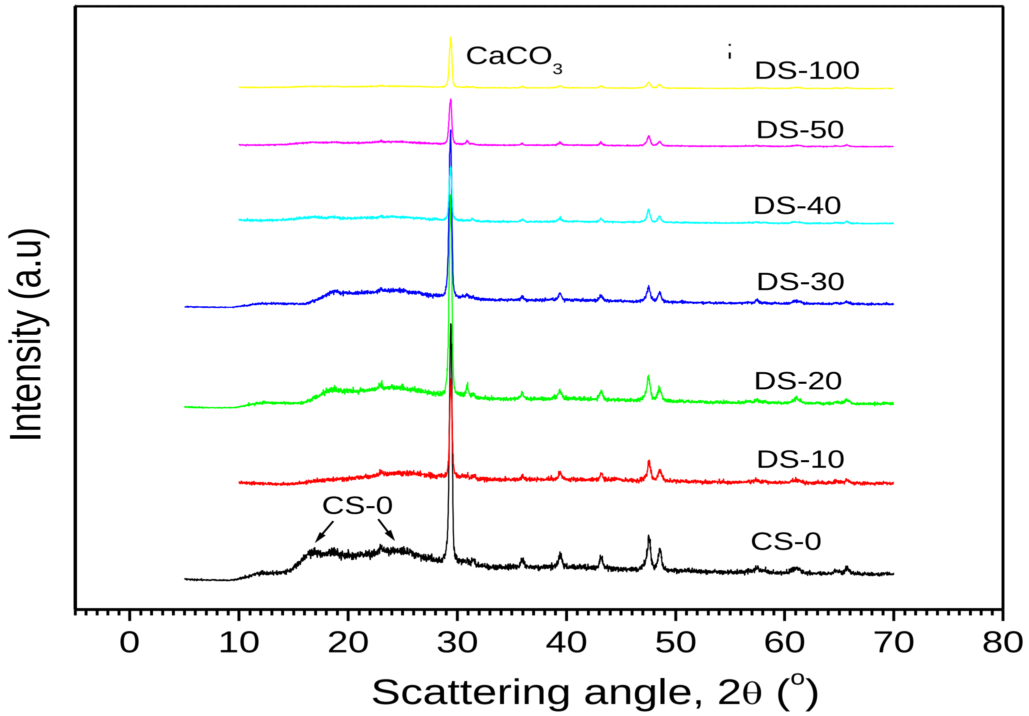


Fig. 4.9.3:Comparative XRD profiles of various samples having different proportions of domestic scrap.

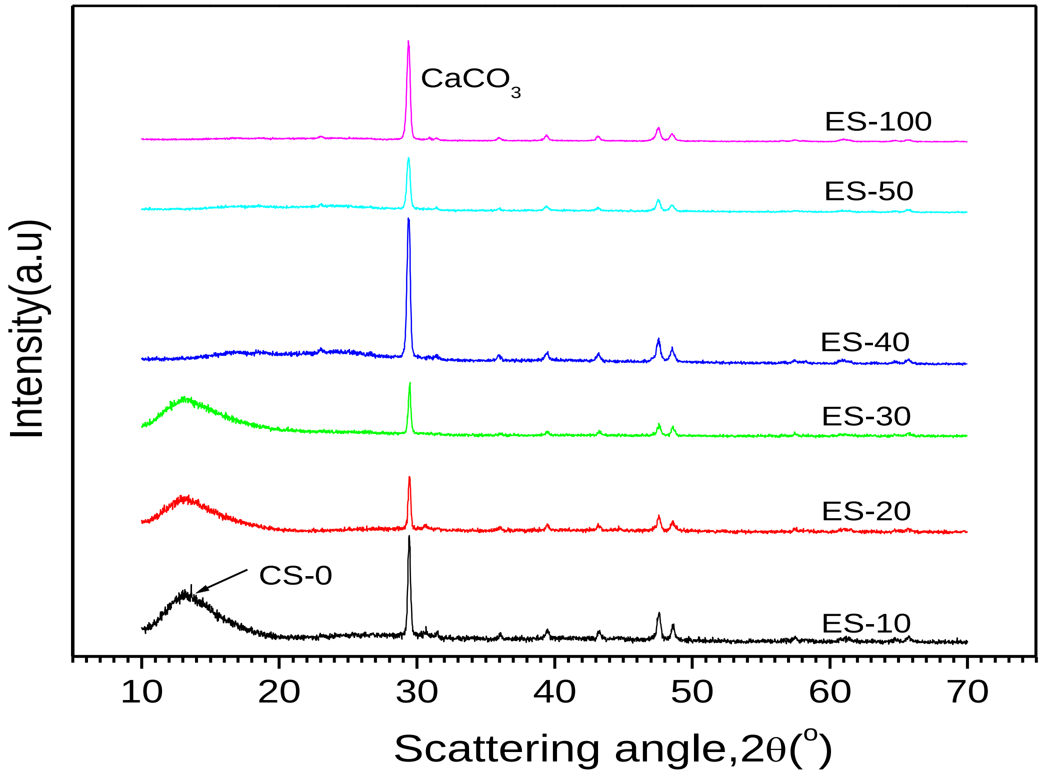


Fig. 4.9.4: Comparative XRD profiles of various samples having different proportions of external scrap.

Comparative XRD profiles of various samples with domestic and external scarps are represented in Figs. 4.9.3 and 4.9.4.

From these comparative profiles it can be seen that the location of the sharp peaks formed in all compositions are identical and can be attributed to the individual peak of $CaCO_3$ (Fig.: 4.9.1).The two peaks of PVC resin have appeared to be more isolated in the prpfiles of CS-0. The reason may be due to the inclusion of additives. It can also be noted that the relative intensities/peak shapes of different peaks for each sample are not same. From the profiles, it is obvious that the crystalline intensity of the compound increases due to the presence of filler in the scraps.

Fig. 4.9.3 shows that the hump area (amorphorous phase) of samples containing 0, 10, 20, and 30 phr is more compared to samples containing 40, 50phr and 100% domestic scrap. 30 phr is the border composition from which amorphous area has decreased and crystalline area has increased, while the peaks of $CaCO_3$ appear in the same $2\theta$ value in the profiles of external scrap (Fig.4.9.4). One peak emerges for PVC. This distinguishes the ES from DS. Analysis of X-ray diffraction patterns, thus shows that the addition of different amounts of scrap did not exhibit the formation of any new phase.

This effect has also been observed from the crystallinity graph of Fig 4.9.5. A similar effect has also been illustrated in case of external scrap of comparative fig 4.9.4 and crystallinity Fig. 4.9.6.

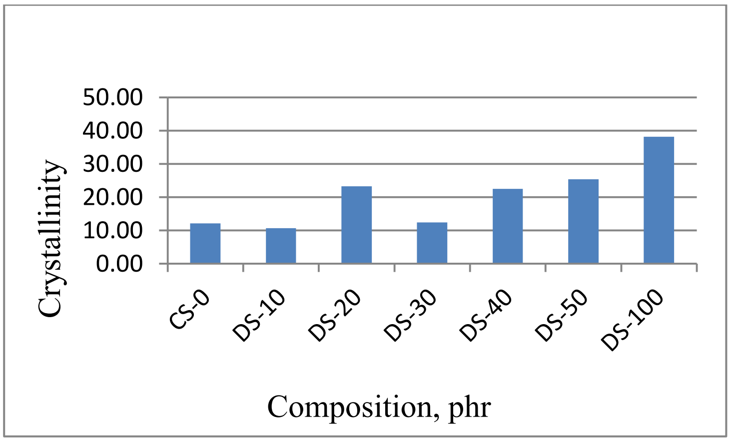


Fig. 4.9.5: Variation of crystallinity with percentage of domestic scrap in the raw material mix.

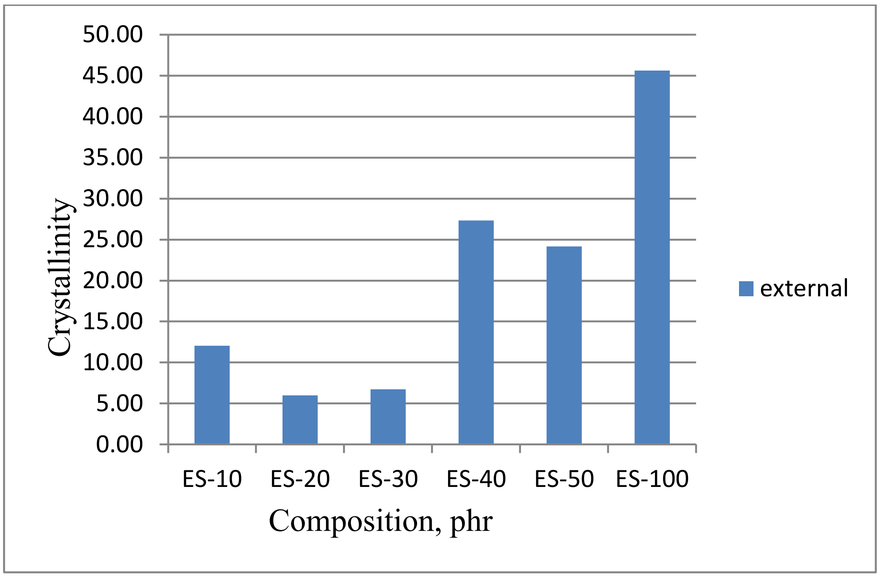


Fig. 4.9.6: Variation of crystallinity with percentage of external scrap in the raw material mix.

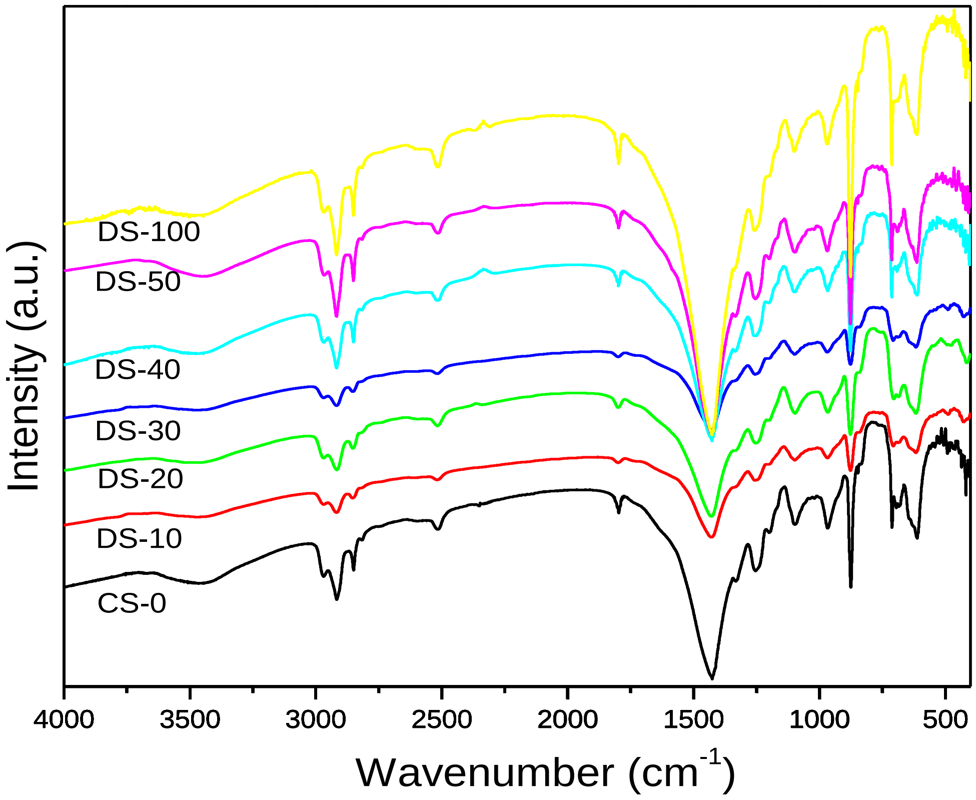
The estimated crystallinity, as according to equation$^{(c)}$ for samples with domestic and external scarps is presented in Figs. 4.9.5 and 4.9.6. The values obtained show some fluctuations in both the sets of samples. It has been observed that for 10, 20 and 30 phr of domestic and external scrap addition, crystalline formation is low, whereas from 40 and 50 phr and 100% scrap of domestic and external scraps addition increasing rate of crystallinity is more. For sample DS-100 it is 214% and for sample ES-100 it is 275 %.With increasing crystallinity, tensile strength increases at certain limit; beyond that limit tensile strength declines. On the other hand, with increasing crystallinity impact strength decreases. The higher the crystallinity, the lower the impact value. So there is an optimum value of scrap addition. This value may be 30 phr of domestic and external scrap. The cause of increasing crystallinity with scrap addition may be due to increasing crystalline inorganic recipes of $CaCO_3$, $TiO_2$ and chilling effect after extrusion.

## 4.10 Fourier Transform Infrared Test

The formation of new organic compounds from samples containing domestic and external scrap was investigated by fourier transform infrared spectroscopy. The results are shown in Figs. 4.10.1- 4.10.2 and in Tables 4.10.1 - 4.10.2.

From Fig. 4.10.1 it can be seen that peaks formed by samples of CS-0, DS-10, DS-20, DS-30, DS-40, DS-50 and DS-100 are within the range of standard peak. Little variation is observed in intensity of the peaks. Intensity variation may be due to the presence of other ingredients. It is here noted that no peak is observed at wavenumber 712, 2515, 2955 for DS-30, 2955 for DS-40, 2955 for DS-50 and 2955, 3200-3500 for DS-100. No degraded peak or new functional group is seen in any sample.

The typical peaks related to PVC are CH3, CH2, CH2-Cl, C=O, C-O, aromatic bonds (for phthalate as plasticizer), calcium carbonate (as a filler), and C=C for the degraded samples. The character m for medium, s for strong and b for broad has been used in the FTIR table.



Fig, 4.10.1: Comparative FTIR spectra of samples containing domestic-scraps.

Table 4.10.1: Results of FTIR test on samples containing domestic scraps.

| Band | Wavenumber ($cm^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ref. value($cm^{-1}$) | CS-0 | DS-10 | DS-20 | DS-30 | DS-40 | DS-50 | DS-100 |
| C–Cl stretch | 850–550 (m) | 876 | 876 | 876 | 877 | 877 | 877 | 877 |
| C–H "oop"(s) | 900–675 (s) | 967 | 968 | 966 | | 966 | 968 | 969 |
| C–N stretch | 1250–1020 (m) | 1097 | 1097 | 1096 | 1100 | 1100 | 1097 | 1100 |
| C-O(phthalate, PVC) | 1283 | 1254 | 1255 | 1252 | 1255 | 1252 | 1254 | 1257 |
| $CaCO_3$/$CH_2$-Cl | 1422/1429 | 1426 | 1428 | 1428 | 1430 | 1431 | 1431 | 1427 |
| C=O(phthalate, PVC) | 1725 | 1797 | 1798 | 1798 | 1798 | 1798 | 1798 | 1798 |
| H–C=O: C–H stretch | 2830–2695 (m) | 2515 | 2517 | 2516 | | 2516 | 2514 | 2516 |
| C–H stretch | 3000–2850 (m) | 2849 | 2852 | 2851 | 2854 | 2850 | 2850 | 2850 |
| $CH_2$(PVC) | 2923 | 2917 | 2917 | 2916 | 2919 | 2917 | 2917 | 2917 |
| $CH_3$(PVC) | 2955 | 2969 | 2968 | 2968 | | | | |
| O–H stretch, H–bonded | 3500–3200 (s,b) | 3455 | 3464 | 3454 | 3454 | 3458 | 3435 | |

From Fig. 4.10.2 it can also be seen that peaks formed on samples ES-10, ES -20, ES -30, ES -40, ES -50 and ES -100 are within the range of standard peak. Little variation is observed in the intensity. Intensity variation may be due to the presence of other ingredients. It is also remarkable that no peak is observed at wave number 2955 for ES-10, ES-40 and ES-100. No degraded peak or new functional group was seen in any of the samples.

The chemical structure for the samples with or without scrap is similar, as there is no difference in the important peaks and their strength. Such fact was reported by Sombatsompop [8] who studied postconsumer polyvinyl chloride bottles and cables and found no color change by adding recycled cable to virgin PVC cable and recycled bottle to virgin PVC pipe and virgin bottle.

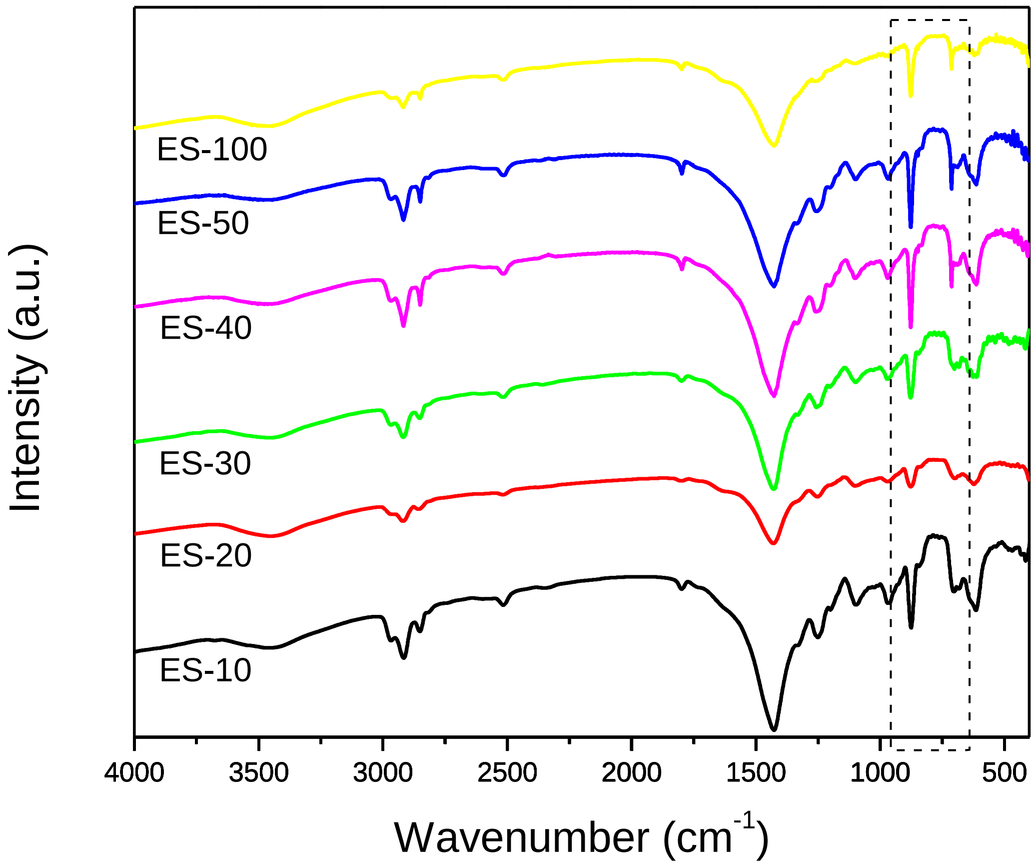


Fig. 4.10.2: Comparative FTIR spectra of samples containing external scrap.

Table 4.10.2: Results of FTIR test on samples containing external scrap.

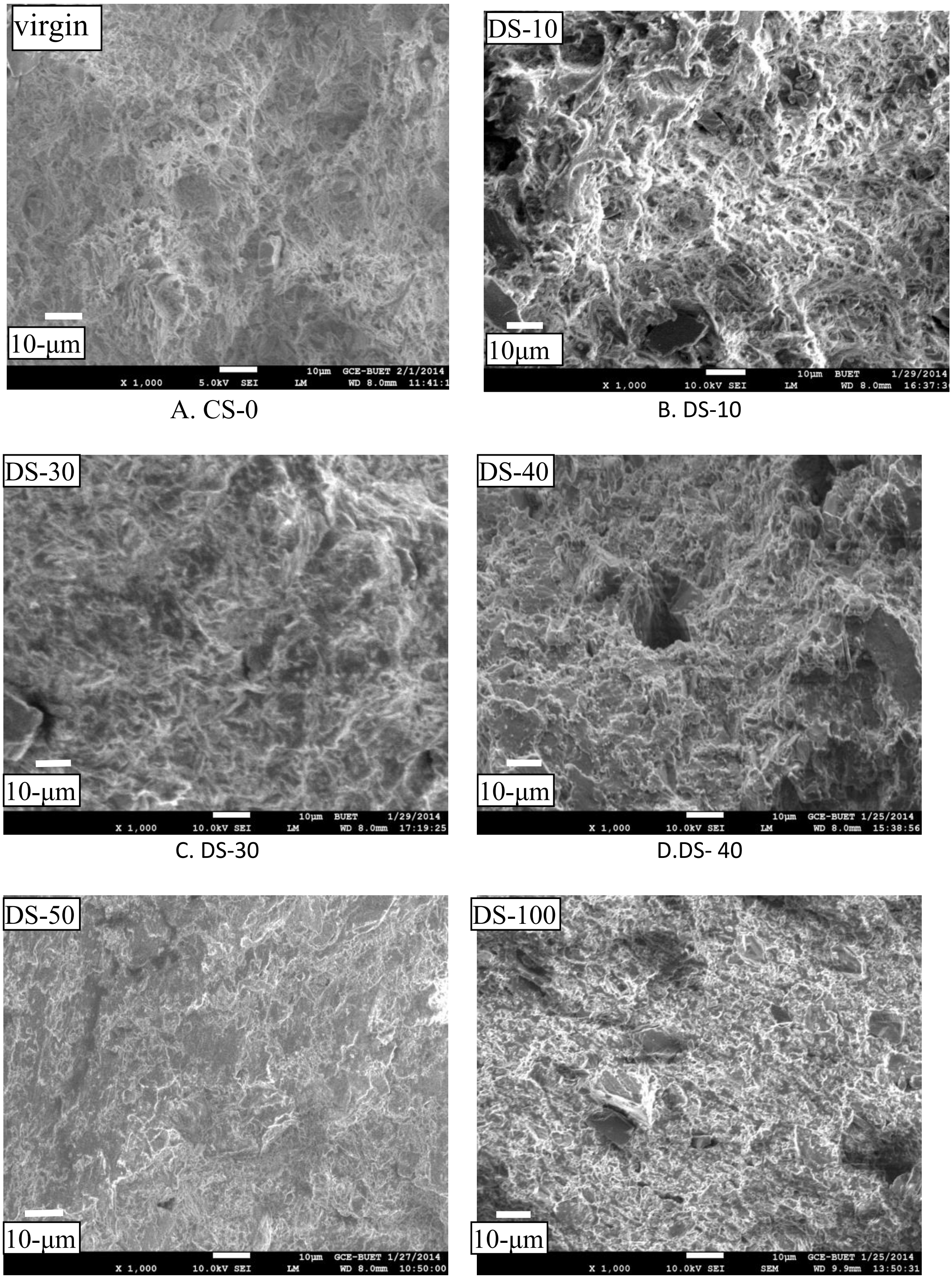
| Band | Wavenumber ($cm^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ref. value ($cm^{-1}$) | ES-10 | ES-20 | ES-30 | ES-40 | ES-50 | ES-100 |
| C–Cl stretch | 850–550 (m) | 876 | 877 | 876 | 876 | 876 | 877 |
| C–H "oop" | 900–675 (s) | 968 | 970 | 968 | 969 | 966 | |
| C–N stretch | 1250–1020 (m) | 1100 | 1097 | 1099 | 1100 | 1097 | |
| C-O(phthalate, PVC) | 1283 | 1251 | 1255 | 1255 | 1257 | 1255 | 1251 |
| $CaCO_3/CH_2$-Cl | 1422/1429 | 1429 | 1426 | 1428 | 1431 | 1426 | 1426 |
| C=O (phthalate, PVC) | 1725 | 1799 | 1798 | 1797 | 1797 | 1796 | 1797 |
| H–C=O: C–H stretch | 2830–2695 (m) | 2517 | 2516 | 2516 | 2515 | 2513 | 2514 |
| C–H stretch | 3000–2850 (m) | 2856 | 2852 | 2850 | 2849 | 2849 | 2850 |
| $CH_2$(PVC) | 2923 | 2919 | 2917 | 2916 | 2917 | 2917 | 2917 |
| $CH_3$(PVC) | 2955 | | 2967 | 2969 | | | |
| O–H stretch, H–bonded | 3500–3200 (s,b) | 3451 | 3448 | 3437 | 3467 | 3442 | 3457 |

## 4.11 Surface Morphology and Elemental Analysis.

### 4.11.1 Surface Morphology

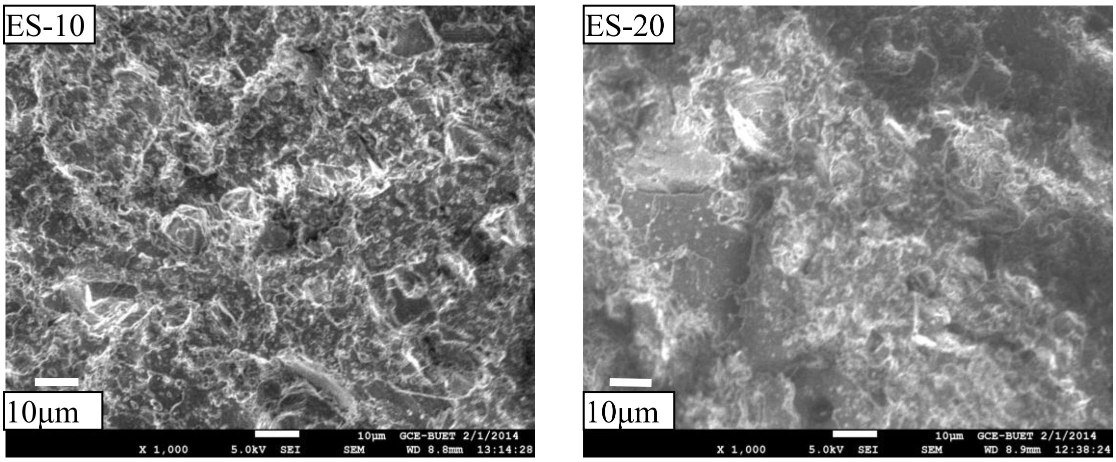
SEM was used to investigate the morphological properties of the fractured surface of CS-0, DS-10, DS-20, DS-30, DS-40, DS-50, DS-100, ES-10, ES -20, ES -30, ES -40, ES -50 and ES-100. The results of SEM of the fracture surfaces are illustrated in Figs. 4.11.1- 4.11.2:

During testing the samples CS-0, DS-10, DS-20, DS-30, DS-40, DS-50 and DS-100 shows ductile to brittle fracture with descending order. Ductile fractured samples exhibit white appearance and necking during failure. On the other hand, the brittle fractured surface does not show any white appearance. A similar effect was observed during testing the samples of ES-10, ES -20, ES -30, ES -40, ES -50 and ES-100. Whitening effect was more pronounced in case of domestic scrap. More numbers of domestic samples showed a ductile fracture and whitening effects. On the contrary, external samples demonstrated ductile fracture on minimum number of samples. Before the SEM examination, platinum sputtering was done to minimize the charging effect of organic materials such as PVC. During examination of different samples black and white area, different phases, phase interaction area and phase distribution style are observed. White area of the images indicates the tip of protruded surface and black area of images indicates the area of valley of fracture surfaces. External fracture surface shows the more black area in descending order from CS-0, DS-10 and so on. Different phases and interfaces were observed in both sets of samples. Variation in the distribution of phases and interfaces is also observed. No void is detected. Similar results have also been reported elsewhere [15]. Phases and interfaces differences in the same sample or in different samples of fracture surface have been exhibited during SEM observation [Figs. 4.11.1- 4.11.2]. For polymeric materials phase distribution is an important factor. This phase distribution is related to mechanical properties. Lack of uniform phase distribution is one of the causes of fluctuation of mechanical properties. Again the phase distribution is related to processing technology of products. During investigation it was found that break stress along longitudinal direction is more comparable to transverse direction.

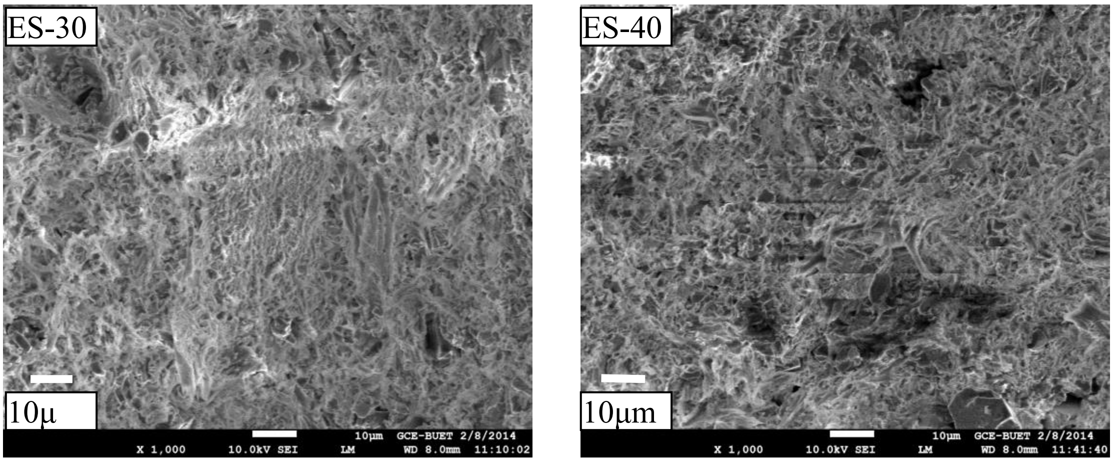


A. CS-0
B. DS-10
C. DS-30
D.DS- 40
E. DS-50
F. DS-100

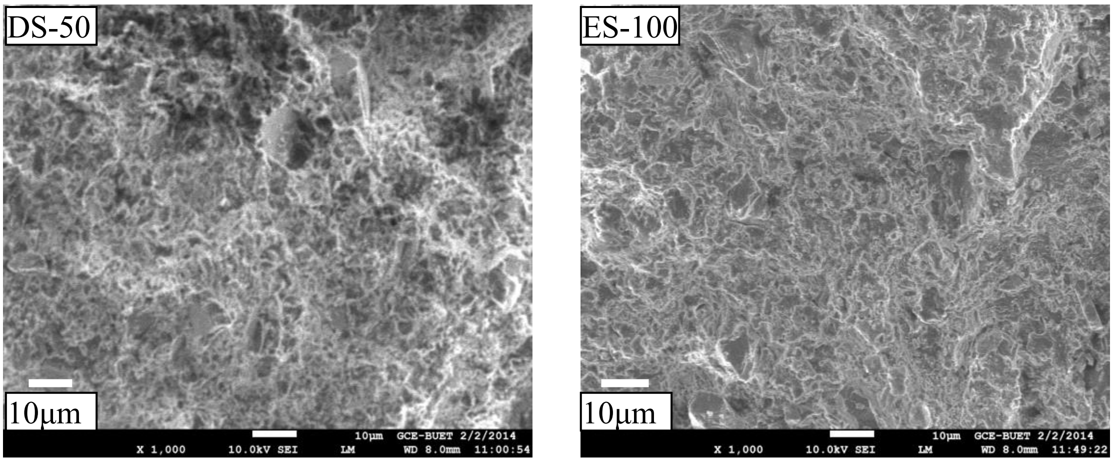
Fig. 4.11.1.1: SEM micrograph of the fractured surface of samples (A) CS-0, (B) DS-10, (C) DS-30, (D) DS-40, (E) DS-50 and (F) DS-100.



A.ES-10 B. ES-20



C. ES-30 D. ES-40



E.ES- 50 F. ES-100

Fig. 4.11.1.2: SEM micrograph of the fractured surface of samples (A) ES-10, (B) ES-20, (C) ES-30, (D) ES-40, (E) ES-50 and (F) ES-100.

### 4.11.2 Elemental Analysis

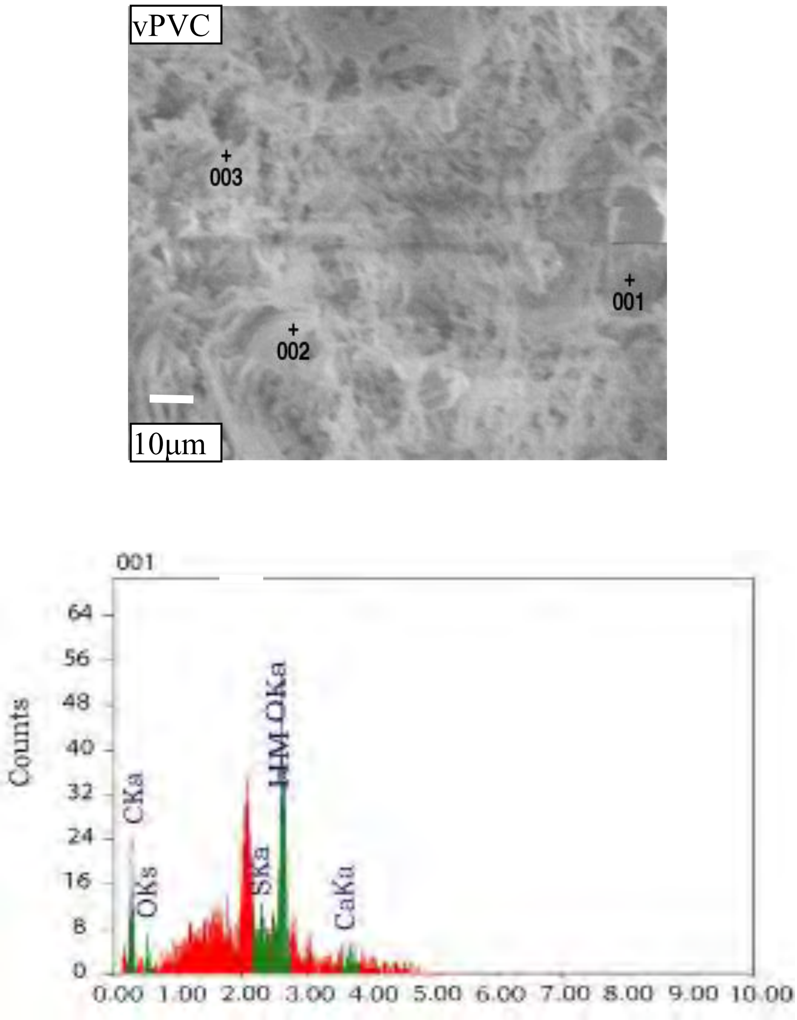
Elemental analysis was performed on different points of the fracture surface of the samples CS-0, DS-10, DS-20, DS-30, DS-40, DS-50, DS-100, ES-10, ES -20, ES -30, ES -40, ES -50 and ES-100 for elemental information. The results of the elements obtained in energy dispersive x-ray technique have been shown in Tables 4.11.2.2-4.11.2.14. The spectra as well as the relevant SEM images of the mentioned samples have also been illustrated in Figs. 4.11.2.1- 4.11.2.13.

Variation in spectrum of different elements in different samples containing domestic and external scrap has been observed [Figs. 4.11.2.1- 4.11.2.13]. Compositional variations in different phases and interfaces of different samples have also been detected by EDS spot analysis [Tables 4.11.2.2- 4.11.2.14]. This type of variation may be due to density difference of the elements, fusion of ingredients during hot and cold mixing, elements detecting technology and extrusion technology. In-homogeneity has also been reported by D. Braun [16]. Attempts were taken to make a homogenous compound by blending the ingredients in a high speed rotating drum of 3500 rpm followed by low speed rotating drum of 200 rpm. The mixture was then sent to the extrusion process. Over there the ingredients were also mixed and extruded as a pipe. Still inhomogeneity has been detected by EDS analysis. The range of elements found by EDS analysis are shown in table 4.11.2.1.

Table 4.11.2.1: Summary of EDS spot analysis results performed on 13 different samples containing domestic and external scraps.

| Elements | Range (%) | Elements | Range (%) | Elements | Range (%) |
|---|---|---|---|---|---|
| C | 3.45-87.74 | Cl | 0.03-55.13 | O | 0.69-56.23 |
| Ca | 0.03-42.51 | Cd | 2.16-5.49 | S | 0.03-3.21 |
| Sb | 0.02-8.34 | Pb | 0.26-31.81 | Sn | 0.75-8.96 |
| Si | 0.01-0.29 | Zn | 1.14-25.05 | Ba | 0.18-2.67 |
| Fe | 1.84 | Al | 0.03-0.19 | Ti | 0.92-1.73 |

From the above table it is seen that there are large gap in the range of elements. Besides, some elements such as Si, Fe, Al generally do not present in the polymeric compound. Big gap and present of unexpected elements may be due to technological limitation and the presence of impurities.

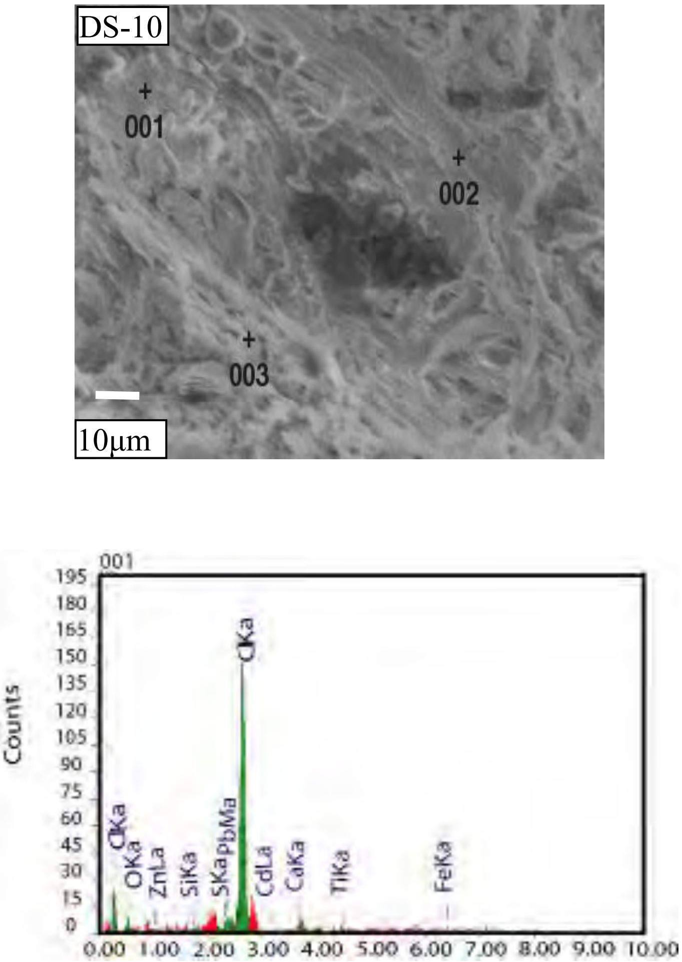


Spot 1

Fig.4.11.2.1: EDS analysis of a fractured surface of the sample containing zero scrap.

Table 4.11.2.2: Results of spot analysis performed by EDS on sample containing zero scrap.

| Spot no | C | S | Cl | Ca | Cd | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|
| 1 | 27.45 | 3.21 | 54.51 | 8.40 | - | - | - | 4.57 |
| 2 | 9.59 | - | 51.49 | - | 5.49 | - | - | 31.81 |
| 3 | 3.45 | - | 13.93 | 39.43 | - | 8.96 | 7.89 | 24.29 |

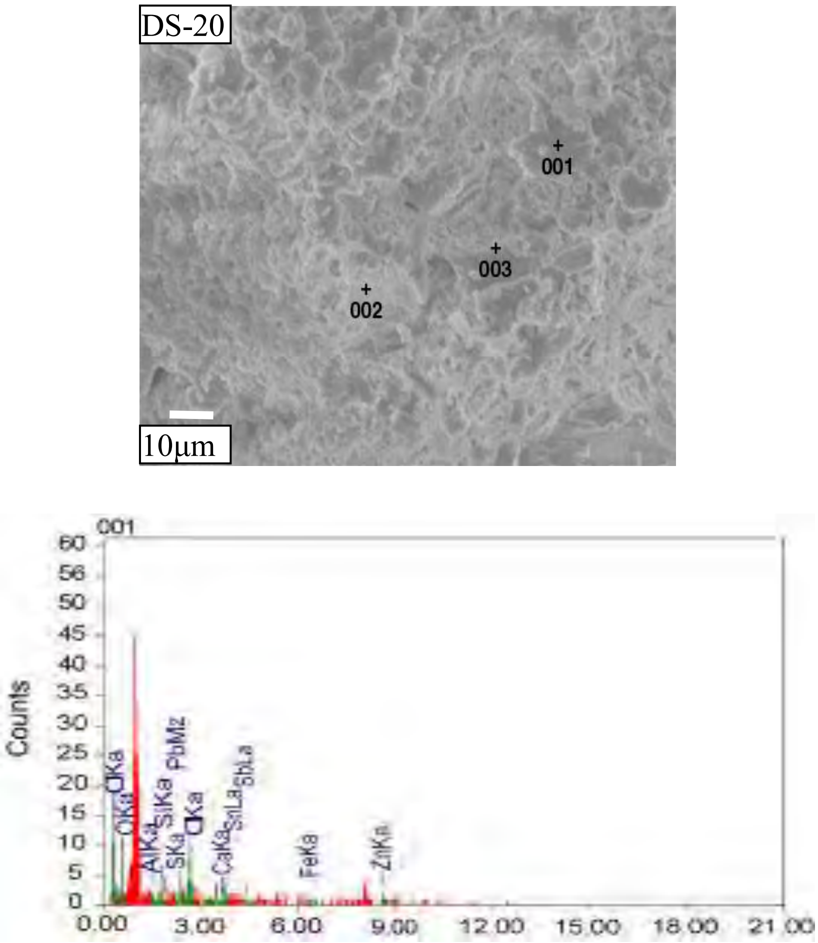


Spot-1

Fig. 4.11.2.2: EDS analysis of a fractured surface of a sample containing 10 per domestic scrap.

Table 4.11.2.3: Results of spot analysis performed by EDS on sample containing 10 phr domestic scrap.

| Spot no | C | O | Si | Cl | Ca | Zn | Sn | Pb |
|---|---|---|---|---|---|---|---|---|
| 1 | 43.80 | 3.59 | 0.06 | 40.54 | 3.80 | 1.14 | - | 5.51 |
| 2 | 31.08 | 2.20 | 0.03 | 55.13 | 4.05 | - | 1.64 | 5.75 |
| 3 | 20.73 | 2.04 | 0.29 | 27.54 | 37.27 | 6.01 | - | 5.47 |

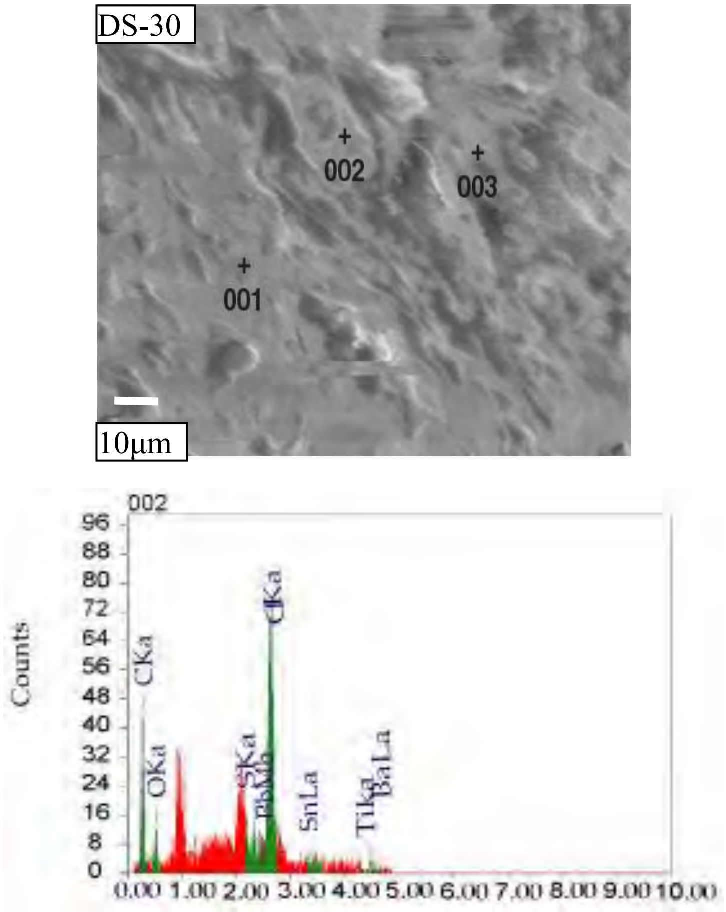


Spot: 1

Fig. 4.11.2.3: EDS analysis of a fractured surface of a sample containing 20 per domestic scrap.

Table 4.11.2.4: Results of spot analysis performed by EDS on sample containing 20 phr domestic scrap.

| Spot no | C | O | S | Cl | Ca | Zn | Sn | Pb |
|---|---|---|---|---|---|---|---|---|
| 1 | 64.57 | 4..59 | 0.04 | 5.45 | 1..31 | 14.66 | 0.75 | 5.96 |
| 2 | 73.15 | 12.24 | 0.29 | 6..30 | 1.08 | 2.37 | 1.27 | 2.15 |
| 3 | 67.42 | 5.70 | 0.28 | 7.11 | 3.44 | 1.81 | 4.56 | 8.01 |

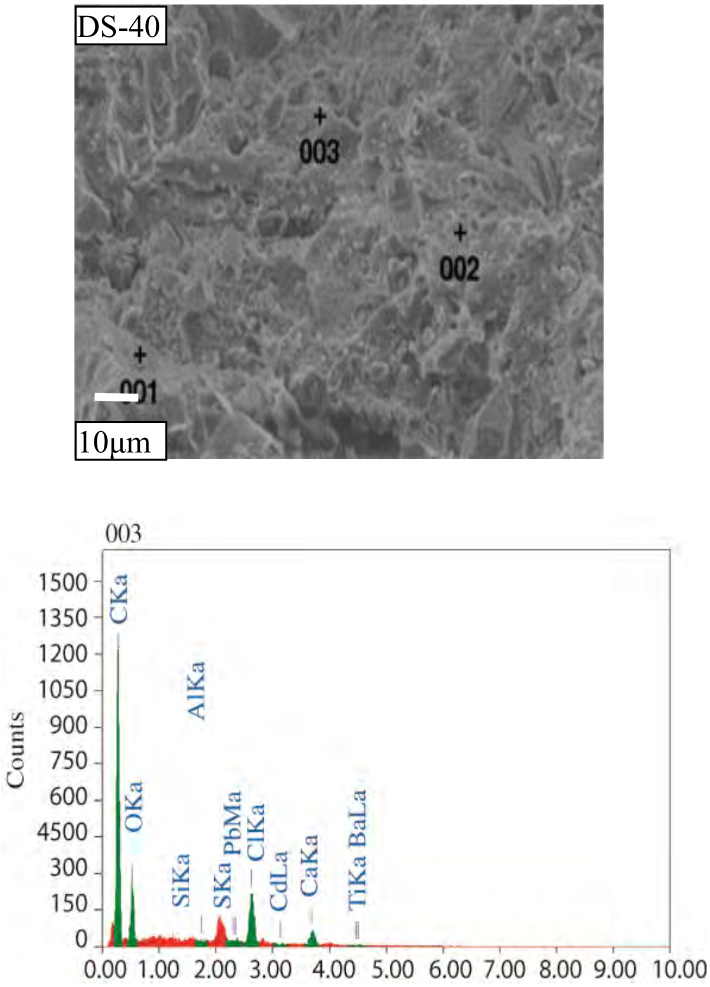


Spot No-2

Fig. 4.11.2.4: EDS analysis of a fractured surface of a sample containing 30 per domestic scrap.

Table 4.11.2.5: Results of spot analysis performed by EDS on sample containing 30 phr domestic scrap.

| Spot no | C | O | S | Cl | Ca | Ba | Pb |
|---|---|---|---|---|---|---|---|
| 1 | 60.92 | 10.85 | 0.48 | 19.40 | 1.37 | 1.48 | 4.71 |
| 2 | 41.20 | 5.79 | 1.56 | 24.85 | - | 1.11 | 3.70 |
| 3 | 66.98 | 7.32 | 0.21 | 16.22 | 1.85 | - | 4.66 |

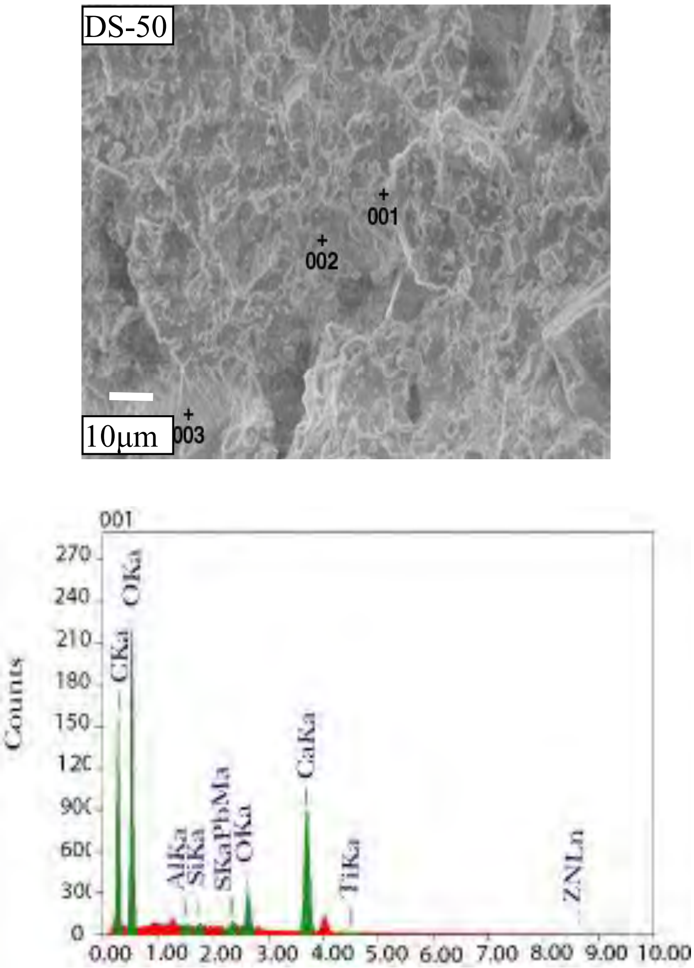


Spot No-3

Fig. 4.11.2.5: EDS analysis of a fractured surface of a sample containing 40 per domestic scrap.

Table 4.11.2.6: Results of spot analysis performed by EDS on sample containing 40 phr domestic scrap.

| Spot no | C | O | Cl | Ca | Sb | Pb |
|---|---|---|---|---|---|---|
| 1 | 24.35 | 56.23 | 1.85 | 6.44 | 8.34 | - |
| 2 | 73.27 | 12.36 | 8.71 | 1.03 | - | 3.49 |
| 3 | 69.28 | 16.43 | 7.72 | 3.94 | - | 1.81 |

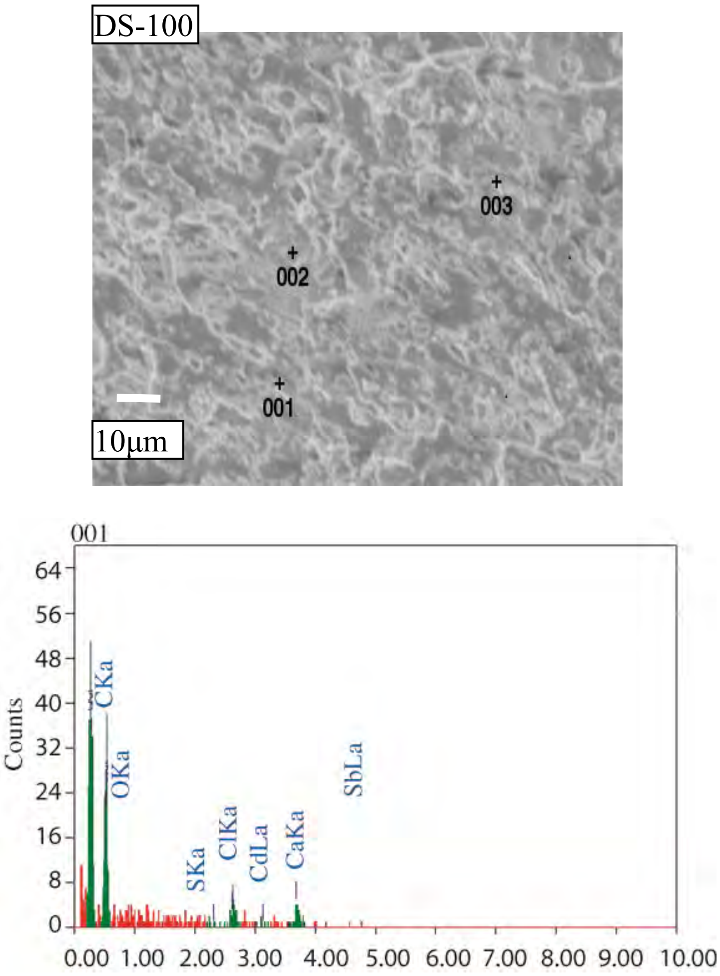


Spot-1

Fig. 4.11.2.6: EDS analysis of a fractured surface of a sample containing 50 per domestic scrap

Table 4.11.2.7: Results of spot analysis performed by EDS on sample containing 50 phr domestic scrap.

| Spot No | C | O | Si | Cl | Ca | Pb |
|---|---|---|---|---|---|---|
| 1 | 51.01 | 28.88 | 0.16 | 2.68 | 15.06 | 1.81 |
| 2 | 77.36 | 13.53 | 0.06 | 2.47 | 5.00 | 1.27 |
| 3 | 80.98 | 10.52 | 0.01 | 3.72 | 3.73 | 0.84 |

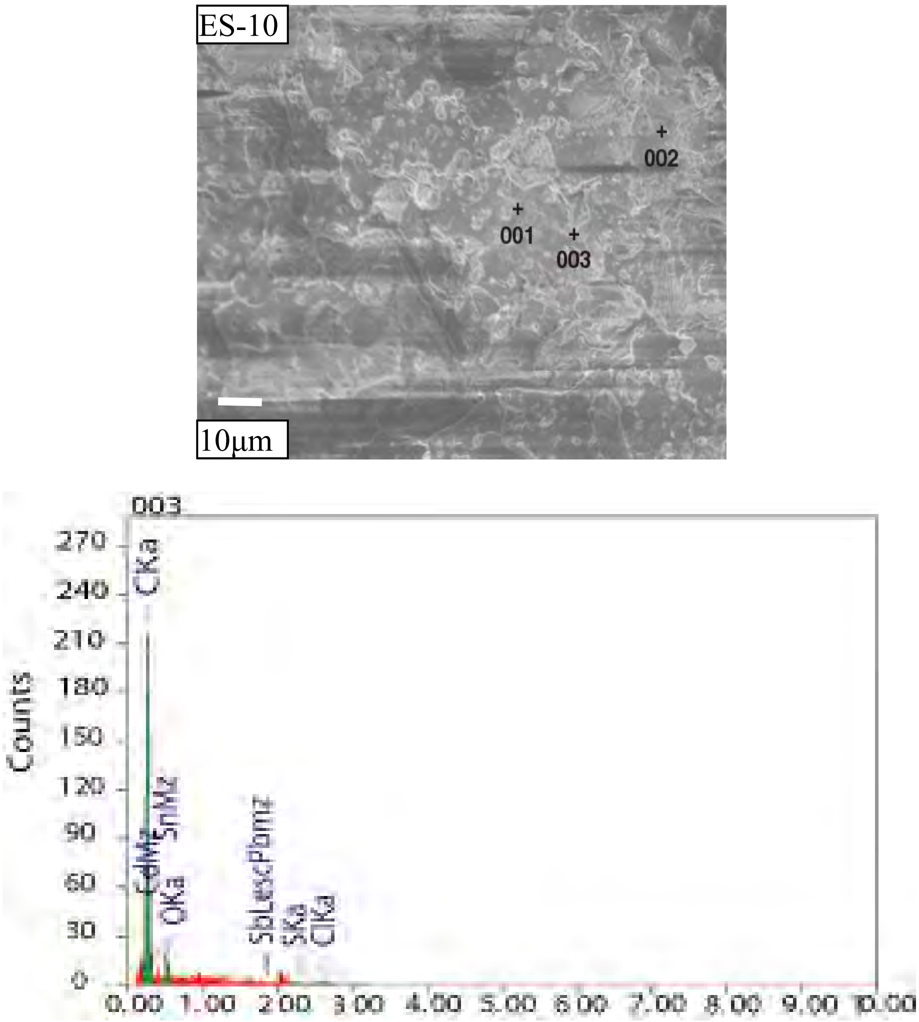


Spot-1

Fig. 4.11.2.7: EDS analysis of different points of the fractured surface of a sample containing 100% domestic scrap.

Table 4.11.2.8: Results of spot analysis performed by EDS on sample containing 100% domestic scrap.

| Spot no | C | O | Cl | Ca | Fe | Zn | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 52.31 | 38.48 | 3.77 | 3.65 | - | - | - | - | - |
| 2 | 65.27 | 11.98 | 7.65 | 2.70 | - | - | - | 6.26 | 4.29 |
| 3 | 40.76 | 20.97 | 3.94 | 3.02 | 1.84 | 25.05 | 0.90 | 0.66 | 1.83 |

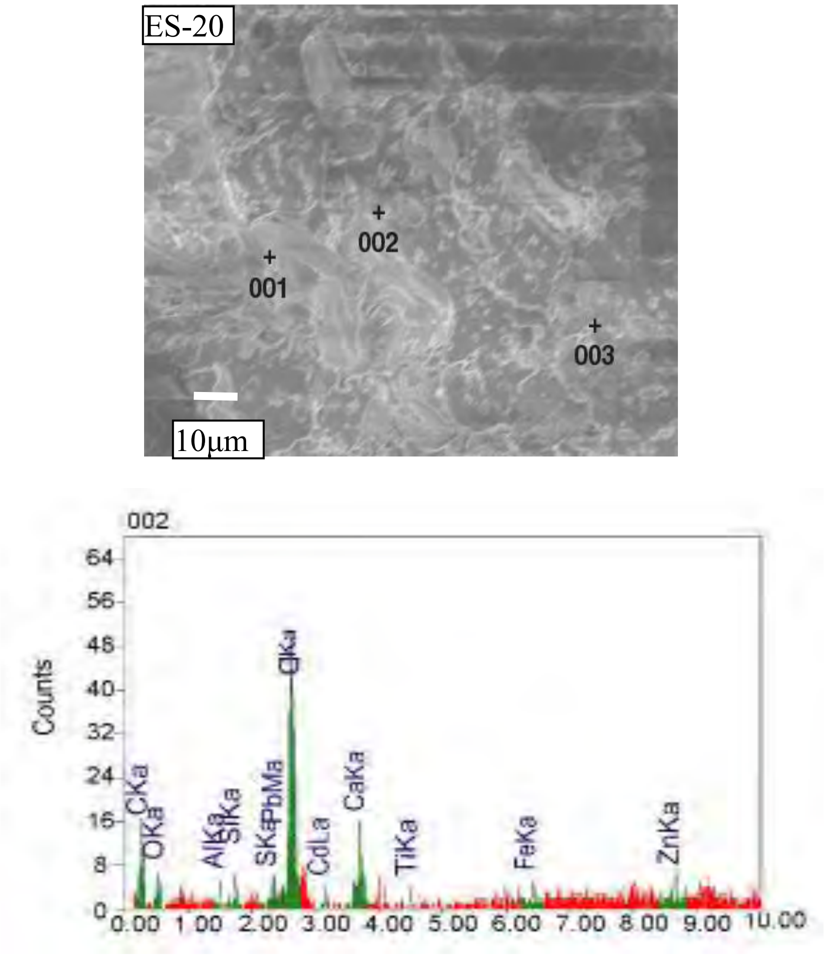


Spot -3

Fig. 4.11.2.8: EDS analysis of a fractured surface of a sample containing 10 per external scrap.

Table 4.11.2.9: Results of spot analysis performed by EDS on sample containing 10 phr external scrap.

| Spot no | C | O | Cl | Ca | Sb | Pb |
|---|---|---|---|---|---|---|
| 1 | 79.57 | 10.24 | 0.68 | 0.07 | 2.51 | 6.86 |
| 2 | 43.83 | 54.83 | 0.40 | - | 0.02 | 0.26 |
| 3 | 87.74 | 7.10 | 2.23 | - | 0.27 | 0.28 |

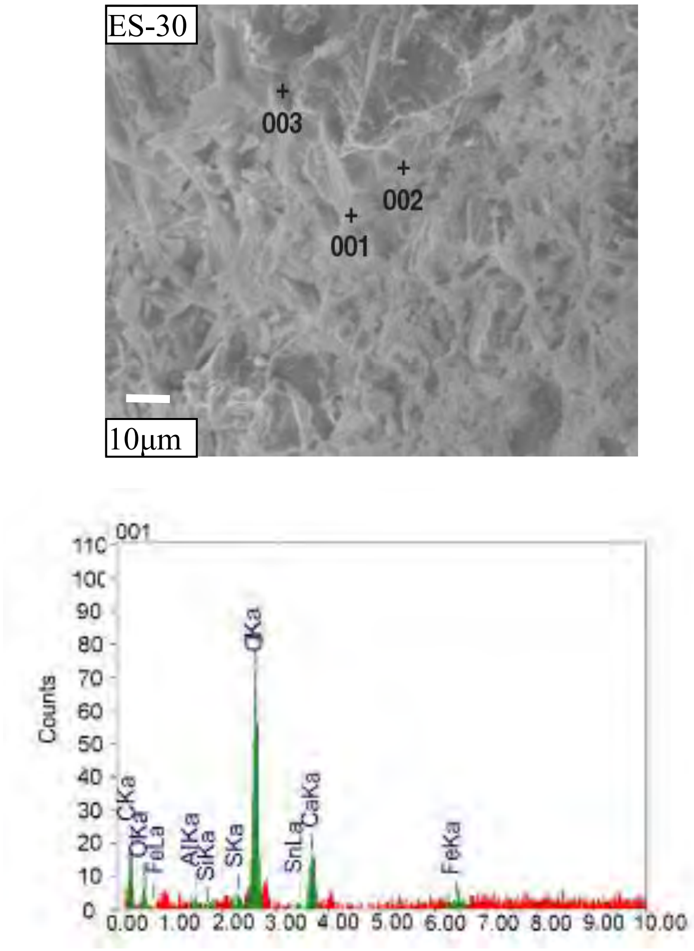


Spot -2

Fig. 4.11.2.9: EDS analysis of a fractured surface of a sample containing 20 per external scrap.

Table 4.11.2.10: Results of spot analysis performed by EDS on sample containing 20 phr external scrap.

| Spot no | C | O | S | Cl | Ca | Zn | Cd | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 48.97 | 42.29 | 1.27 | 0.57 | 0.05 | 1.67 | - | - | - | 4.22 |
| 2 | 78.27 | 10.73 | - | 0.83 | 0.03 | - | - | 1.57 | 1.51 | 5.35 |
| 3 | 50.42 | 45.03 | 1.49 | 0.03 | - | - | 2.16 | 0.76 | - | - |

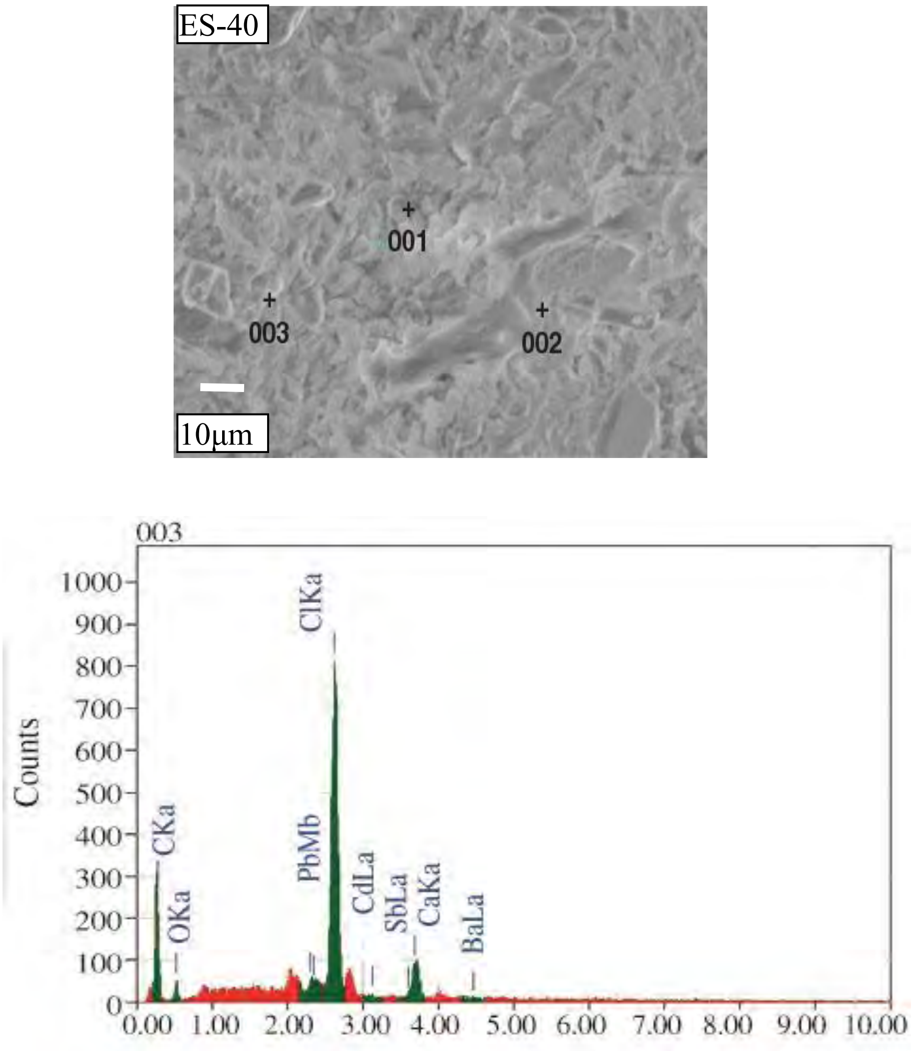


Spot-1

Fig. 4.11.2.10: EDS analysis of a fractured surface of a sample containing 30 per external scrap.

Table 4.11.2.11: Results of spot analysis performed by EDS on sample containing 30 phr external scrap.

| Spot No | C | O | S | Cl | Ca | Zn | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 56.90 | 3.96 | 0.03 | 21.98 | 10.68 | - | 2.42 | 2.94 | - |
| 2 | 54.91 | 2.64 | 0.27 | 16.89 | 6.26 | 12.40 | - | 1.84 | 3.46 |
| 3 | 61.77 | 4.11 | 0.39 | 19.19 | 6.45 | 4.78 | - | - | 2.80 |

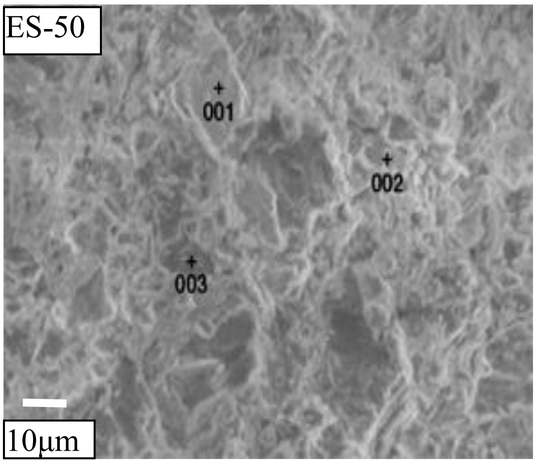


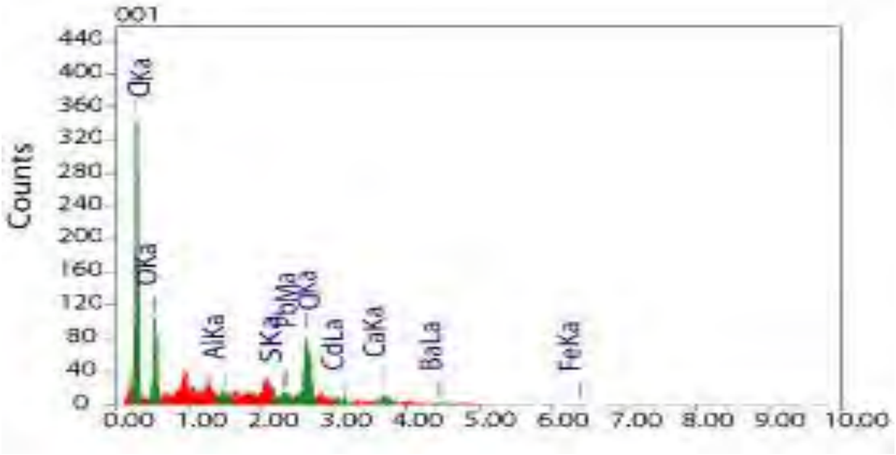
Spot-3

Fig. 4.11.2.11: EDS analysis of fractured surface of sample containing 40 phr external scrap.

Table 4.11.2.12: Results of spot analysis performed by EDS on sample containing 40 phr external scrap.

| Spot no | C | O | S | Cl | Ca | Ba | Pb |
|---|---|---|---|---|---|---|---|
| 1 | 30.61 | 0.69- | 0.28 | 42.27 | 11.93 | 0.18 | 11.67 |
| 2 | 55.92 | 1.18 | 0.35 | 33.77 | 4.28 | - | 3.87 |
| 3 | 71.47 | 1.59 | 0.18 | 19.00 | 4.23 | 2.67 | - |



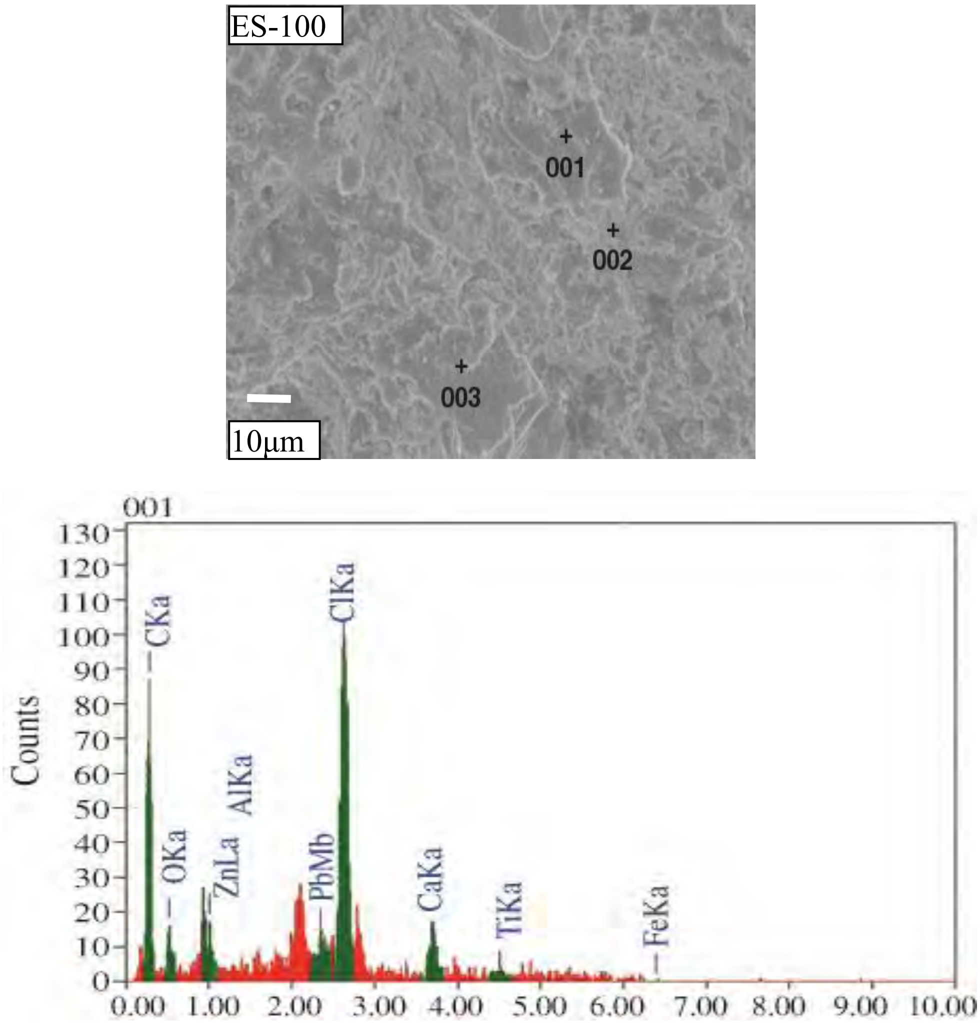


Spot-1

Fig. 4.11.2.12: EDS analysis of fractured surface of sample containing 50 phr external scrap.

Table 4.11.2.13: Results of spot analysis performed by EDS on sample containing 50 phr external scrap.

| Spot no | C | O | Al | Cl | Ca | Pb |
|---|---|---|---|---|---|---|
| 1 | 65.82 | 19.78 | 0.19 | 7.63 | 1.89 | 2.50 |
| 2 | 55.89 | 31.13 | 0.05 | 3.46 | 5.60 | 3.05 |
| 3 | 24.13 | 24.11 | 0.03 | 4.37 | 42.51 | 3.65 |



Spot-1

Fig. 4.11.2.13: EDS analysis of a fractured surface of a sample containing 100% external scrap.

Table 4.11.2.14: Results of spot analysis performed by EDS on sample containing 100% external scrap.

| Spot No | C | O | S | Cl | Ca | Ti | Pb |
|---|---|---|---|---|---|---|---|
| | 59.86 | 5.60 | - | 21.83 | 5.41 | 0.92 | 5.72 |
| | 44.78 | 22.69 | - | 19.46 | 8.50 | - | 2.38 |
| | 39.75 | 9.90 | 1.30 | 16.21 | 26.84 | 1.73 | 3.27 |

### 4.12 X ray Fluorescence Analysis

XRF analysis was performed to identify and quantify the cumulative elements` concentrations present in PVC resin, uPVC scraps and additives (fillers, stabilizers, pigments, lubricants etc). The results of XRF are shown in Tables 4.12.1- 4.12.2.

Table 4.12.1: Results of x-ray fluorescence analysis done on samples containing zero and domestic scrap.

| Samples. | C | Cl | Ca | Pb | Ti | S |
|---|---|---|---|---|---|---|
| CS-0 | 47.92 | 42.56 | 9.19 | 0.27 | 0.05 | 0.01 |
| DS-10 | 46.80 | 43.67 | 9.16 | 0.30 | 0.04 | 0.03 |
| DS-20 | 45.90 | 44.35 | 9.42 | 0.26 | 0.05 | 0.02 |
| DS-30 | 41.76 | 48.07 | 9.88 | 0.23 | 0.07 | -- |
| DS-40 | 42.59 | 47.47 | 9.35 | 0.59 | -- | -- |
| DS-50 | 40.48 | 47.03 | 11.89 | 0.57 | 0.04 | -- |
| DS-100 | 40.87 | 42.98 | 15.65 | 0.43 | 0.07 | -- |

Table 4.12.2: Results of x-ray fluorescence analysis done on samples containing external scrap.

| Samples | C | Cl | Ca | Pb | Ti | S |
|---|---|---|---|---|---|---|
| ES-10 | 48.47 | 44.20 | 6.75 | 0.57 | -- | 0.02 |
| ES-20 | 51.98 | 41.61 | 5.78 | 0.59 | 0.03 | 0.02 |
| ES-30 | 49.51 | 43.61 | 6.26 | 0.60 | 0.04 | -- |
| ES-40 | 41.54 | 44.45 | 13.33 | 0.64 | 0.04 | -- |
| ES-50 | 41.86 | 46.44 | 11.02 | 0.62 | 0.06 | -- |
| ES-100 | 38.92 | 37.82 | 22.27 | 0.85 | 0.13 | -- |

XRF technique was done on the solid surface of the samples. It can be seen from the tables that the percentage of carbon decreases, the percentage of calcium, titanium and lead increases while the percentage of sulfur and chlorine fluctuates. The amount of lead increased with the addition of scrap. PVC articles are susceptible to degradation at almost all stages of their lifetime: production, storage, processing, transportation and end-use. Several possible influences, which can be hostile to polymers, are heat, light, oxygen and mechanical stress. Therefore, the stable system is partially consumed during the service life of PVC products. So, the recycling of PVC waste offers a lot of problems due to the limited thermal stability which requires, in most cases, the addition of new stabilizer. The use of new heat stabilizers for this purpose is related with some difficulties. First, it is necessary to determine the stabilizer in the PVC waste because some stabilizers are not compatible with others. The use of heavy metals in stabilizers might be forbidden in a year by the government of some countries because of their toxicity. If this happens, every processing company will face the problem to stabilize old PVC products if materials recycling are desired. In Bangladesh most of the manufacturers use lead compound as a heat stabilizer as it is cheap.

Gradual increase in the quantity of lead is a vulnerable matter. Lead is a very harmful element for human body. It creates fatal diseases like cancer. So use of pipes containing recycled scraps should be totally stopped in pipelines to supply drinking water. Even in the sewage system. Because by leaching lead comes out from uPVC pipe [17] and goes into the soil and water which deteriorates the environment. Lead compound is a powerful heat stabilizing additive for PVC processing. Without heat stabilizer, it is difficult to process uPVC. Lead compounds are cheap and the manufacturers sometime use lead compounds to prevent degradation of PVC products. This should be stopped and use of environment friendly heat stabilizers, such as tin base, zinc base, organic base or organo-tin base compounds, should be encouraged.

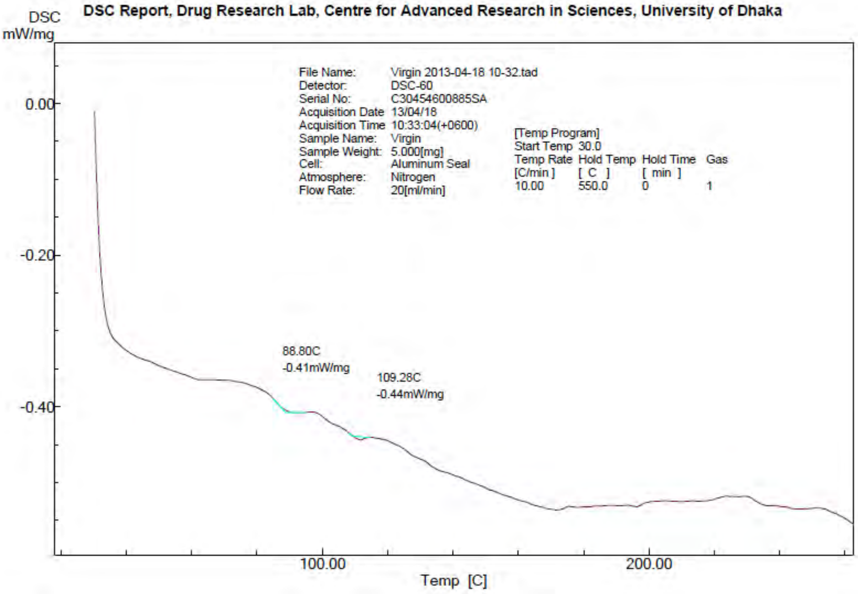
Sulfur in significant quantity was not found in samples containing scrap. Only trace amount of sulfur was detected in domestic samples of CS-0, DS-10, DS-20 and external samples of ES-10, ES-20 and ES-30. Sulfur is also harmful for environment. The rates of change of elements in the samples containing external scrap are higher. This is especially true for calcium and lead. This fact also merits serious consideration.

## 4.13 Differential Scanning Calorimetry

In this study, differential scanning caloriemetry was used on the samples containing zero scrap, domestic and external uPVC scrap to measure glass transition temperature. The results of differential scanning calorimetry are shown in Figs.: 4.13.1- 4.13.6 and in Tables 4.13.1- 4.13.2.

In DSC thermo-graphs two glass transitions ($T_g$) temperatures have been observed. According to Balart et al. [18] if the system were immiscible, $T_g$ values of individual polymers would not change. On the other hand, a completely miscible system would have displayed only one $T_g$. This system shows an intermediate behavior, since two changing $T_g$ values in the whole composition range are observed. This partial miscibility, together with the small degradation of the elastomeric component, contributes to a low interaction promoting a decrease on mechanical performance.

In this investigation, the obtained $T_g$ values are different from individual polymer. In each sample two $T_g$ values have been seen. This indicates intermediate behavior of composition which can be attributed to incompatability among the ingredients. This incompatability may be reduced by changing internal lubricant or adjusting the ingredients or adding compatibilizer.



DSC Report, Drug Research Lab, Centre for Advanced Research in Sciences, University of Dhaka

File Name: Virgin 2013-04-18 10-32.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/04/18
Acquisition Time 10:33:04(+0600)
Sample Name: Virgin
Sample Weight: 5.000[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate [C/min ] | Hold Temp [ C ] | Hold Time [ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 0 | 1 |

Fig.: 4.13.1: DSC analysis on the sample containing zero scraps

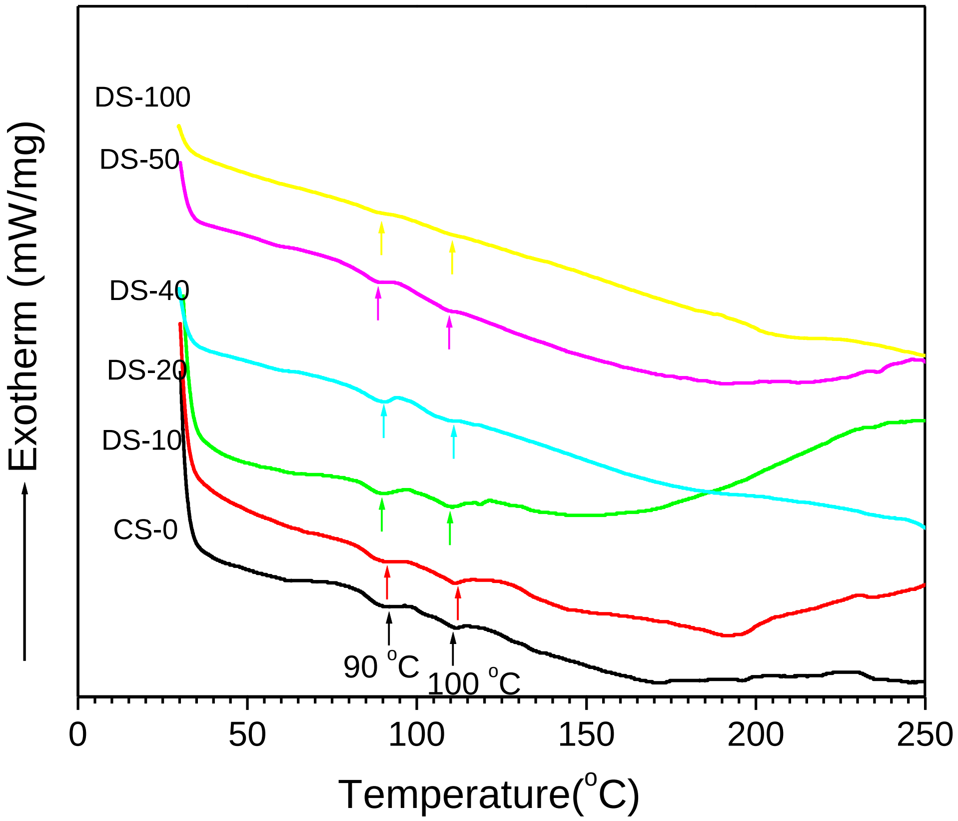


Fig. 4.13.2: Comparative DSC analysis on the samples containing domestic scrap with vPVC.

Table 4.13.1: Glass transition temperature of samples containing domestic scraps.

| Samples | 1st glass transition temperature °C | 2nd glass transition temperature °C |
|---|---|---|
| CS-0 | 88.80 | 109.28 |
| DS-10 | 88.50 | 111.44 |
| DS-20 | 89.28 | 110.57 |
| DS-30 | 90.68 | 100.35 |
| DS-40 | 90.78 | 108.81 |
| DS-50 | 88.25 | 109.32 |
| DS-100 | 89.08 | 110.04 |

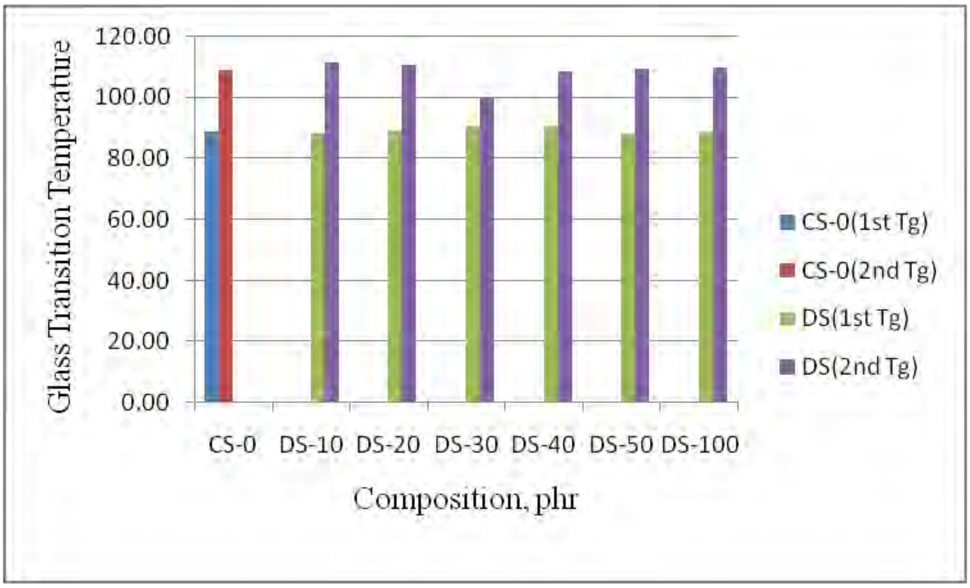


Fig. 4.13.3: Variation of glass transition temperature with quantity of domestic uPVC scraps in the raw material mix.

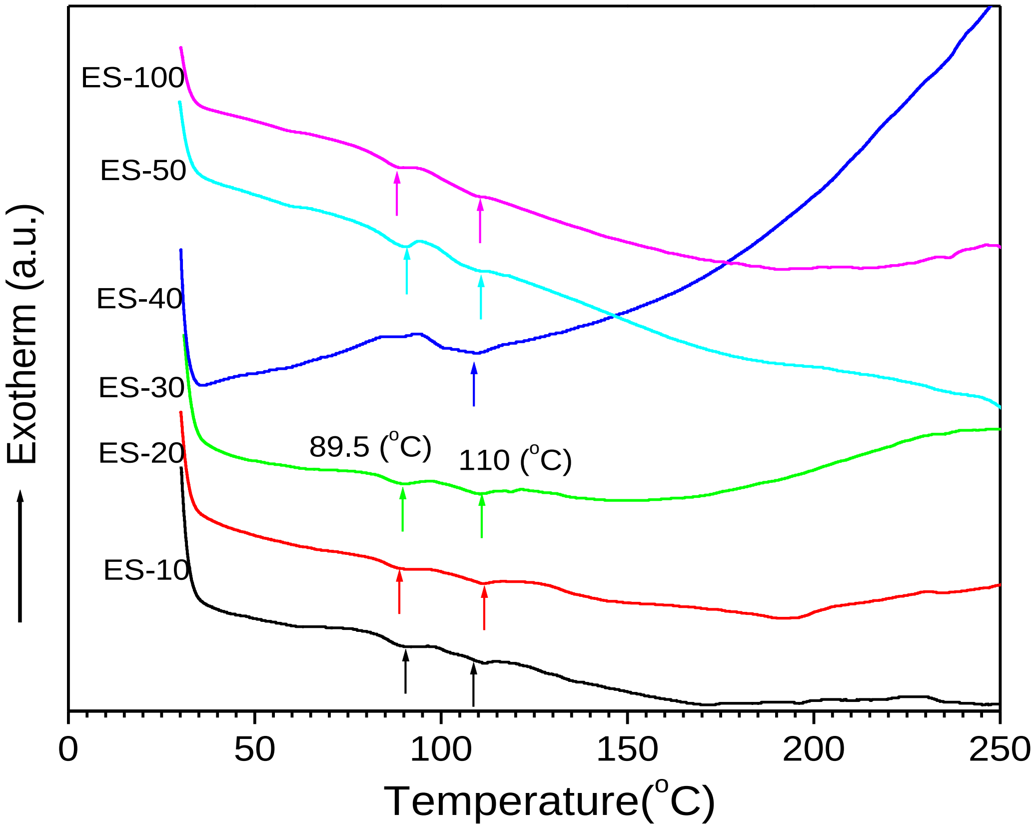


Fig. 4.13.4: Comparative DSC analysis on the samples containing external scrap

Table 4.13.2: Glass transition temperature of samples containing external scrap.

| Samples | 1st glass transition temperature °C | 2nd glass transition temperature °C |
|---|---|---|
| ES-10 | 97.86 | 108.18 |
| ES-20 | 93.74 | 108.54 |
| ES-30 | 90.53 | 109.68 |
| ES-40 | 88.81 | 109.82 |
| ES-50 | 88.10 | 109.65 |
| ES-100 | 86.45 | 109.45 |

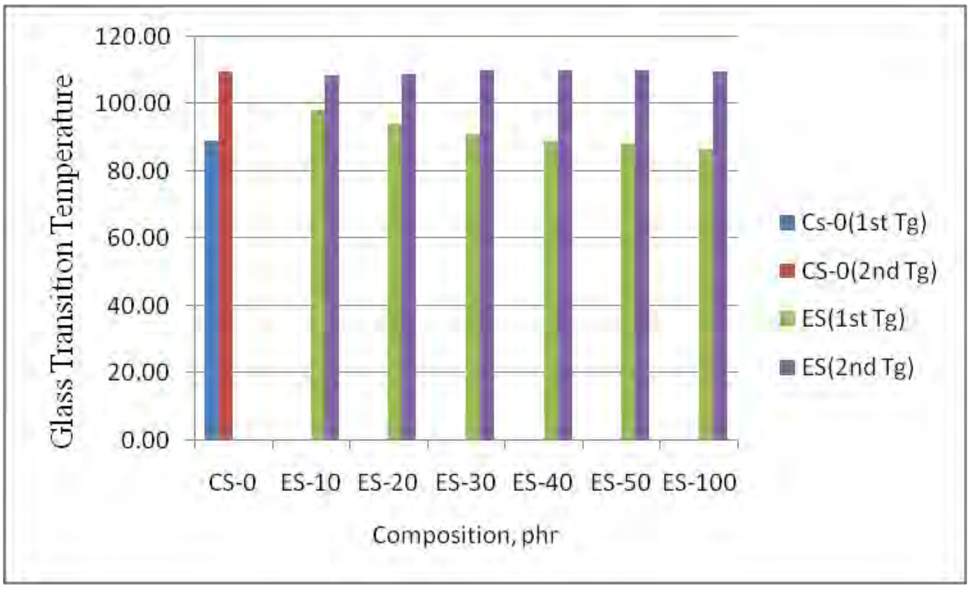


Fig. 4.13.5: Variation of glass transition temperature with quantity of external uPVC scraps in the raw material mix.

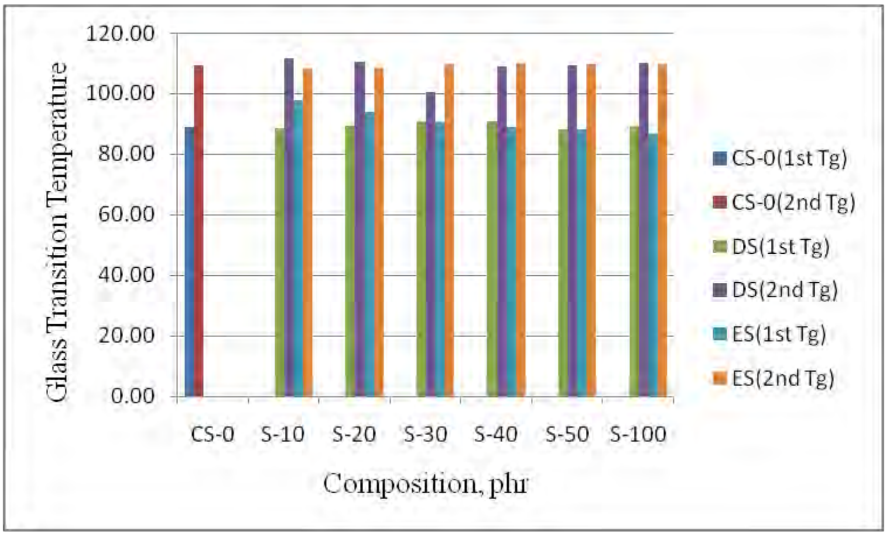


Fig.4.13.6: Variation of glass transition temperature with quantity of domestic and external uPVC scrap in the raw material mix.

## 4.14 Thermo-Mechanical Analysis

Thermo-Mechanical Analysis provides valuable characterization information on the dimensional properties of a wide range of materials. Results of TMA are shown in Figs 4.14.1- 4.14.2 and Tables 4.14.1 - 4.14.3.

From these thermo-graphs two types of information have been recorded. One type of information is the $T_g$ of samples having domestic and external scrap [Table: 4.14.1]. From the table it can be observed that the $T_g$ of samples containing domestic and external scrap are close to each other. Nevertheless, more fluctuation of glass transition in domestic scrap occurred compared to external scrap. Another type of information is CTE and it has been shown in Tables 4.14.2- 4.14.3. It can be observed that there is fluctuation in CTE among different compositions.

The CTE of samples containing domestic and external scrap gradually increases with the amount of scrap in the sample. Before glass transition molecules in the specimens exist rigidly. Dispersed particles of fillers, pigment and other additives in the PVC polymer matrix provide obstacle to the movement of polymeric molecules. The size and shape and amount of these dispersed particles vary and as a result, coefficient of thermal expansion also fluctuates.

With increasing temperature the molecules absorb more energy and their movement is increased. After reaching their $T_g$, the CTE decreases. Because $T_g$ molecules are free to move easily. Then they do not stay in solid state. In this stage the CTE is not considerd.

In TMA study the variation of thermal expansion or contraction was seen which was attributed to difference in CTE. For samples containing both domestic and external scrap the CTE increased before the $T_g$ but after the glass transition the CTE decreased. This phenomenon is very important where hot fluid is transferred from one place to another.

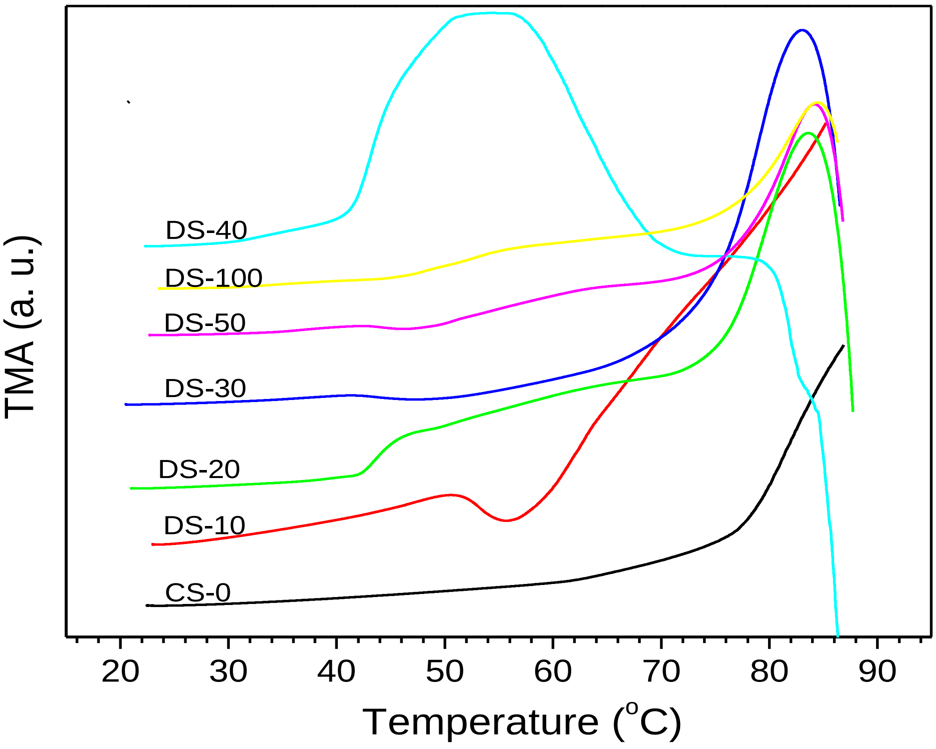


Fig. 4.14.1: Comparative TMA thermo graph the samples containing domestic scrap with CS-0.

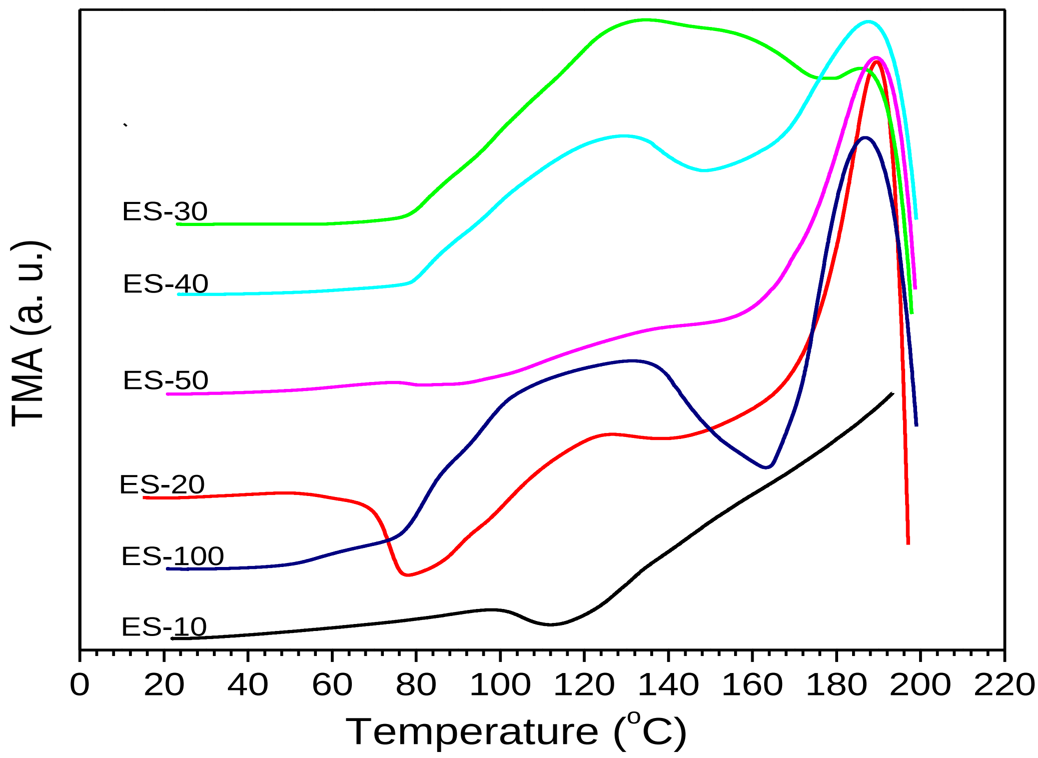


Fig. 4.14.2: Comparative TMA thermo graph on the samples containing external scrap.

Table: 4.14.1 Determination of glass transition ($T_g$) temperature by TMA.

| Particulars | Glass transition temperature (°C) | Particulars | Glass transition temperature (°C) |
|---|---|---|---|
| CS-0 | 77.6 | | |
| DS-10 | 77.2 | ES-10 | 79.6 |
| DS-20 | 81.8 | ES -20 | 75.9 |
| DS-30 | 79.8 | ES -30 | 75.8 |
| DS-40 | 79.7 | ES -40 | 78.8 |
| DS-50 | 74.3 | ES -50 | 75.3 |
| DS-100 | 94.5 | ES -100 | 76.7 |

Table 4.14.2: Determination of coefficient of thermal expansion of samples containing zero and domestic scraps.

| Particulars | Temperature Range ($^oC$) | CTE ($\times 10^{-5}$) |
|---|---|---|
| CS-0 | 31.18-51.31 | 4.91 |
|  | 80.96-85.01 | 0.02 |
| DS-10 | 29.80-65.60 | 5.94 |
|  | 91.50-119.90 | 0.47 |
| DS-20 | 38.9-55.1 | 4.98 |
|  | 100.30-113.20 | 0.32 |
| DS-30 | 36.50-62.70 | 5.75 |
|  | 97.70-112.10 | 0.15 |
| DS-40 | 38.70-61.80 | 0.13 |
|  | 81.60-89.40 | 0.03 |
| DS-50 | 31.50-74.30 | 0.10 |
|  | 95.50-125.60 | 0.51 |
| DS-100 | 43.00-68.60 | 0.13 |
|  | 106.50-118.00 | 0.67 |

Table 4.14.3: Determination of coefficient of thermal expansion of samples containing external scraps.

| Particulars | Temperature Range ($^oC$) | CTE ($\times 10^{-5}$) |
|---|---|---|
| ES-10 | 38.90-56.20 | 4.27 |
|  | 83.80-88.60 | 0.04 |
| ES-20 | 30.50-52.80 | 1.88 |
|  | 97.10-116.40 | 0.37 |
| ES-30 | 31.70-54.60 | 14.05 |
|  | 89.70-98.80 | 0.01 |
| ES-40 | 32.10-50.10 | 3.85 |
|  | 89.10-102.90 | 0.01 |
| ES-50 | 36.00-61.10 | 7.67 |
|  | 97.60-114.80 | 0.42 |
| ES-100 | 29.80-44.40 | 4.45 |
|  | 84.40-99.00 | 0.014 |

## 4.15 Thermo-Gravimetric Analysis

Results of TGA are shown in Figs 4.15.1 - 4.15.3 and Tables 4.15-14.15.2. From the comparative TGA thermograph, it can be seen that samples CS-0, DS-10, DS-20, DS-30 follow almost similar path and samples DS-40, DS-50 and DS-100 follow another similar path. On the contrary, samples ES-10, ES-20, ES-30 show almost similar path and ES-40, ES-50 and ES-100 show another similar path.

Alternatively, it can be described that samples CS-0, DS-10, DS-20, DS-30 demonstrate similar heat and mass change and the samples DS-40, DS-50 and DS-100 demonstrate another similar heat and mass change. Similarly, samples ES-10, ES-20, ES-30 exhibit similar heat and mass change and ES-40, ES-50 and ES-100 exhibit another similar heat and mass change. Different amounts of weight percentage have been recorded at different stages. Especially different amounts of residue have been found at 1000°C for different proportions of uPVC scraps.

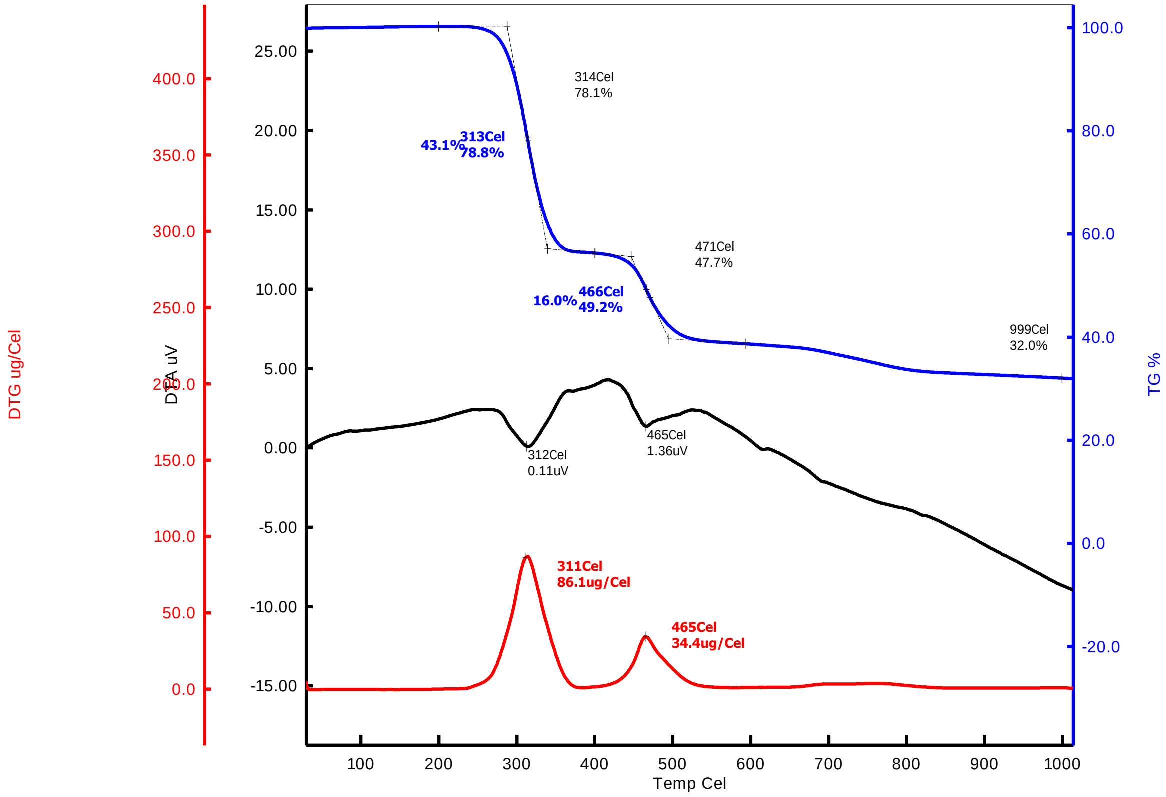


Fig. 4.15.1 TGA thermo graph of sample containing zero scrap.

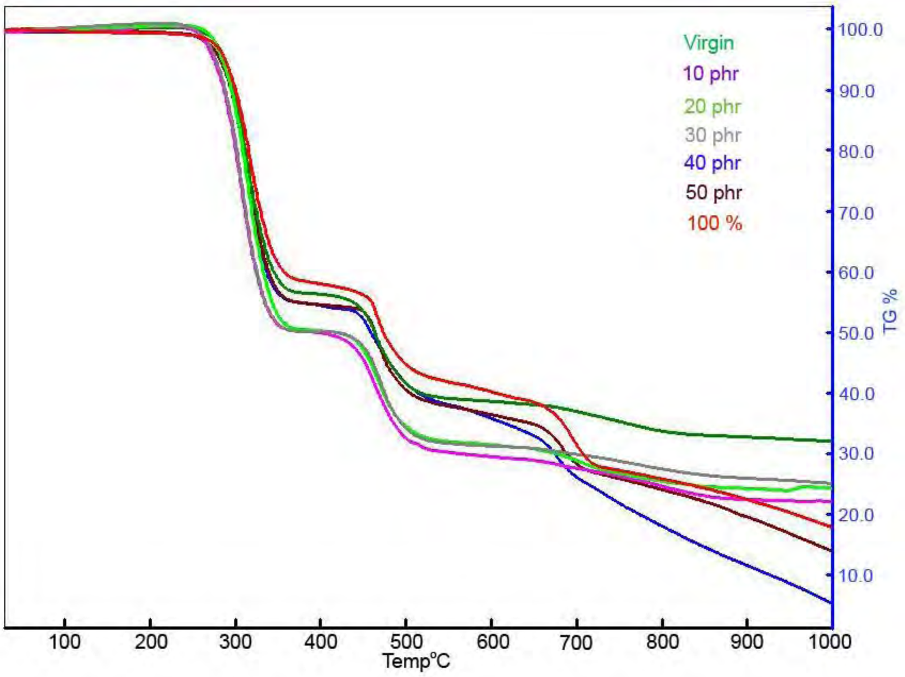


Fig. 4.15.2: Comparative TGA thermo-graph of samples containing zero and domestic scrap.

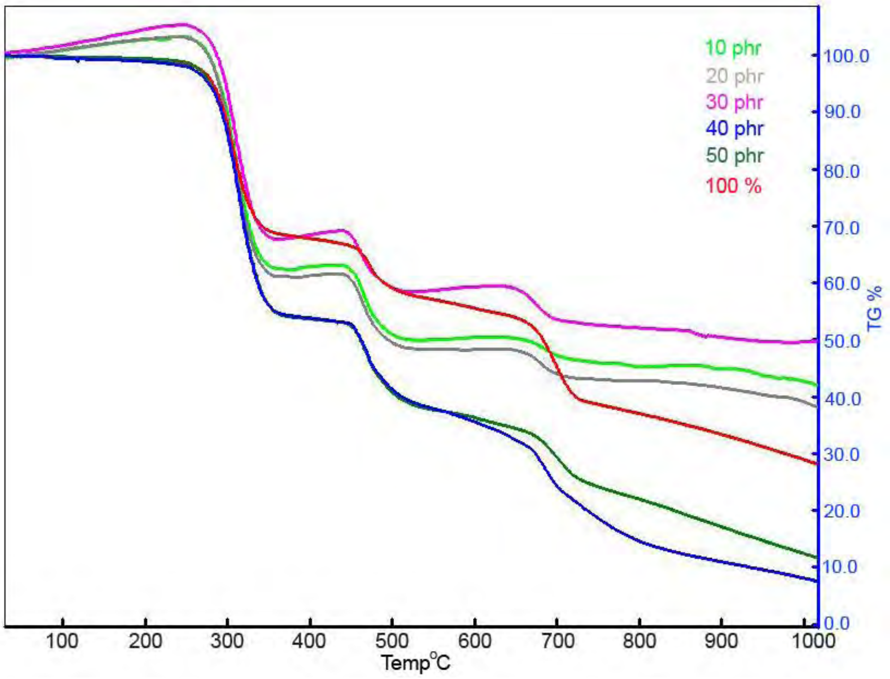


Fig. 4.15.3: Comparative TGA thermo-graph of samples containing external scrap.

Table 4.15.1: TGA data of samples containing domestic scraps.

| Code No. | 1st Stage | | 2nd Stage | | 3rd Stage | | Rest Weight | |
|---|---|---|---|---|---|---|---|---|
| | Temp. °C | weight % | Temp. °C | weight % | Temp. °C | weight % | Temp. °C | weight % |
| CS-0 | 298 | 83.6 | 475 | 53.00 | 674 | 44.00 | 1001 | 36.00 |
| DS-10 | 305 | 76.2 | 465 | 40.90 | 778 | 35.40 | 1000 | 22.10 |
| DS-20 | 313 | 75.9 | 470 | 41.20 | 676 | 46.30 | 1002 | 24.30 |
| DS-30 | 306 | 75.8 | 473 | 41.00 | -- | -- | 1002 | 25.10 |
| DS-40 | 316 | 76.5 | 460 | 49.00 | 689 | 29.30 | 1004 | 13.60 |
| DS-50 | 313 | 77.4 | 466 | 49.2 | 682 | 31.20 | 1000 | 13.90 |
| DS-100 | 317 | 79.1 | 471 | 51.00 | 694 | 32.90 | 1000 | 18.00 |

Table 4.15.2 TGA data of samples containing external scraps.

| Code No. | 1st Stage | | 2nd Stage | | 3rd Stage | | Rest Weight | |
|---|---|---|---|---|---|---|---|---|
| | Temp. °C | weight % | Temp. °C | weight % | Temp. °C | weight % | Temp. °C | weight % |
| ES-10 | 308 | 83.40 | 466 | 57.80 | 683 | 48.60 | 999 | 42.70 |
| ES-20 | 307 | 82.40 | 462 | 57.1 | 676 | 46.30 | 1001 | 39.00 |
| ES-30 | 308 | 87.20 | 461 | 65.40 | 671 | 56.70 | 1001 | 49.60 |
| ES-40 | 311 | 77.60 | 471 | 46.90 | 678 | 29.00 | 1003 | 8.00 |
| ES-50 | 312 | 76.60 | 463 | 49.30 | 702 | 28.90 | 1003 | 12.30 |
| ES-100 | 306 | 84.20 | 473 | 62.90 | 696 | 46.50 | 1003 | 28.80 |

TGA thermograms for PVC shows 5 onsets related to plasticizer, HCl releasing, polyene chain degradation and filler. The first onset is the maximum temperature between 240 – 250°C. This is related to the phthalate [19]. The samples under investigation were made of uPVC which does not normally contain plasticizer, first onset was not observed in these experimentations. Second onset which is in the range of 270-300°C is related to HCl release and polyene chain production. Released HCl at this stage corrodes the mold or dies and also attacks the surrounding steel components. The fume of HCl is harmful for workforce as well as for environment.

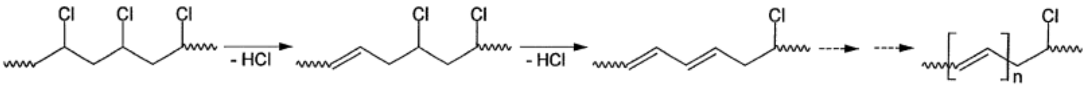


Fig. 4.15.4: Scheme diagram of dehydrochlorination.

In all samples under investigation the same trend has been observed with minor non-systematic deviation from sample to sample. The third and the forth onsets are related to breaking of polyene chain which is stated around 460 – 470$^{o}$C [20]. This effect has also been revealed with little deviation in all these experimentations. As PVC samples have $CaCO_3$ as filler, the range of calcium carbonate decomposition ($CaCO_3 \rightarrow CaO + CO_2$) is around 580-875$^{o}$C [21]. In all samples under investigation the endsets of temperature was 1000$^{o}$C to complete the decomposition reaction. The amounts of residue obtained have been shown in Tables 4.15.1- 4.15.2.

The maximum processing temperature of all the samples under investigation was 180$^{o}$C. On the other hand, from the Tables 4.15.1-4.15.2 it can be seen that the degradation temperature of sample containing virgin ingradients is 298$^{o}$C and the degradation temperature of other samples is higher than the virgin sample. Since the degradation temperature of samples having virgin as well as scrap is higher than the processing temperature, it can be concluded that no degradation has been occurred in the investigated samples at processing temperature. This has also been varified by FTIR analysis where no new compound was detected.

It is also observed from Tables 4.15.1 - 4.15.2 that the trend of degradation temperature is higher with amount of scrap addition. Fluctuation of degradation temperature has also been observed. Due to the presence of higher amount of heat stabilizer and filler materials (results of XRF) the degradation temperature has increased. This fact has also been observed by Samira *et al.*[22] who studied thermal and mechanical properties of PVC and PVC-HDPE Blends. The heat stability effect of filler $CaCO_3$ was studied by Braun [23] who found with increasing filler heat stability increases.

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# CHAPTER FIVE

## 5. Conclusions and Recommendation

### 5.1 Conclusions

Effects of the quantity of domestic and external scraps on the properties of recycled uPVC products have been investigated by acetone, tensile, flexural, impact, and hardness and density test, VN, VST, XRD, FTIR, SEM-EDS, XRF, DSC, TMA and TGA. From the results obtained, the following conclusion can be addressed.

1. All the samples containing different proportions of domestic and external uPVC scrap have passed the acetone test.
2. The density increases with addition of domestic and external scrap. The effect is lower in the samples of external scrap.
3. The mechanical properties, such as break stress, % elongation at break, flexural strength and impact strength decrease with the increase of domestic and external scrap. It is notable that observed values show a little fluctuation, which has been attributed to incompatibility, inhomogeneity, varying molecular weight and impurities. Deterioration in mechanical properties is found to be more in the samples containing external scrap than that containing domestic scrap.
4. The hardness value of the samples does not depend on the quantity of scrap mixed.
5. It is also found that with the amount of scrap addition the viscosity number decreases which ultimately affects the mechanical properties. The molecular weight obtained from viscosity number of samples containing 10, 20 and 30 phr domestic scrap is within the range of k-value. The molecular weight of other samples is out of the range of k-value.
6. The resistance to heat of samples containing domestic scrap increases with the scrap addition, while the resistance to heat of samples containing external scrap remains unchanged.
7. The crystallinity found in samples containing both domestic and external scrap is almost similar up to 30 phr scrap and then increases.
8. No new functional group has been detected due to the addition of different proportions of scraps. Only intensity variation has been observed.

9. SEM shows variation of shape and distribution of different phases. The differences in interfaces are also observed. Variation in the quantities of elements is also observed by EDS spot analysis.
10. XRF analysis has shown that the percentage of carbon decreases whereas that of calcium, titanium and lead increases and that of sulfur and chlorine fluctuates. In both cases, the amount of lead increases with the quantity of scrap added and this increase is dangerous for human being.
11. Two different glass transition temperatures are observed which indicates the incompatibility among the ingredients used in the samples preparation.
12. In both the sets of samples, the coefficient of thermal expansion increases before the glass transition but after the glass transition the coefficient of thermal expansion decreases. This information is valuable for hot fluid flow in the pipe of recycled products.
13. A big gap between processing temperature and degrading temperature has been noted. The amount of residue found at $1000^{o}$C is observed different for different proportions of scrap.
14. Samples containing only up to 30 phr of domestic scrap are within the practical range of k-value. Besides, crystallinity increases abruptly in samples containing more than 30 phr scrap. Higher crystallinity affects mechanical properties, particularly impact strength. In FTIR spectra samples containing 30 phr domestic scrap show a boundary spectrum. TGA thermograph also illustrates similar heat and mass change up to samples containing 30 phr domestic scrap.

It can therefore be concluded that up to 30 phr domestic scrap could be used for making better quality pipes while the other proportions of scrap investigated may be used for less important applications.

From the above discussion it can be concluded that up to 30 phr domestic scrap could be used for making pressure pipe that could be used before glass transition temperature and other proportions of scrap may be used for making non-pressure pipe or other less important applications.

## 5.2 Recommendations for Future Work

1. Optimization of
   (i) Lead base and lead free stabilizers
2. Characterization of
   (i) Blended post consumer uPVC products with scrap plastics of polyolefin group (polyethylene or polypropylene).
   (ii) Repeated recycling of uPVC products containing different proportions of domestic and external scrap.
3. Effect of proportion of different fillers in the raw material mixture on mechanical and thermal properties of products.
4. Comparative study of
   (i) Environmental
   (ii) Tacticity effect

   of uPVC containing domestic and external scrap without adding make up heat stabilizer.
5. Study on
   (i) Quenching
   (ii) Particle size
   (iii) Ageing
   (iv) Degree of gelation
   (v) Melt flow index

   on the properties of recycled products containing domestic and external scrap.

# APPENDIX-A

## LIST OF TABLES

1.1 Tensile strength test results of domestic scrap.

| Samples | Max load KN | Max stress MPa | Break stress MPa | Modulus MPa | 0.2% YD stress MPa | Max %strain |
|---|---|---|---|---|---|---|
| CS-0 | 1.86 | 39.01 | 34.12 | 1793.84 | 17.64 | 7.88 |
| DS-10 | 1.81 | 37.47 | 31.80 | 1813.87 | 17.20 | 7.54 |
| DS-20 | 1.75 | 36.56 | 30.23 | 1814.77 | 17.16 | 7.00 |
| DS-30 | 1.89 | 40.10 | 31.60 | 1750.73 | 18.08 | 7.32 |
| DS-40 | 1.38 | 35.80 | 31.93 | 1841.36 | 14.72 | 7.61 |
| DS-50 | 1.27 | 34.82 | 31.43 | 1840.57 | 15.32 | 7.28 |
| DS-100 | 1.14 | 30.64 | 27.68 | 2129.29 | 15.89 | 6.53 |

1.2 Tensile strength test results of external scrap.

| Samples | Max load KN | Max stress MPa | Break stress MPa | Modulus MPa | 0.2% YD stress MPa | Max %strain |
|---|---|---|---|---|---|---|
| ES-10 | 1.12 | 35.93 | 31.41 | 1751.24 | 15.40 | 6.94 |
| ES-20 | 1.13 | 34.72 | 30.72 | 1813.59 | 22.24 | 6.41 |
| ES-30 | 1.15 | 33.68 | 29.95 | 1786.70 | 15.62 | 6.42 |
| ES-40 | 1.08 | 31.76 | 29.46 | 1806.64 | 15.16 | 5.95 |
| ES-50 | 1.12 | 31.00 | 28.76 | 1896.79 | 14.15 | 6.00 |
| ES-100 | 1.25 | 33.27 | 29.82 | 1850.00 | 15.20 | 6.48 |
| ES-10 | 0.79 | 22.24 | 20.83 | 2699.36 | 14.82 | 4.27 |

2.1 Flexural strength test results of domestic scrap.

| Samples | Yl D. Load KN | YlD.STR MPa | Modulus MPa | Slope N/mm |
|---|---|---|---|---|
| CS-0 | 0.14 | 52.79 | 2813.00 | 35.22 |
| DS-10 | 0.15 | 58.96 | 3750.20 | 47.66 |
| DS-20 | 0.15 | 53.95 | 3236.00 | 40.87 |
| DS-30 | 0.15 | 58.80 | 3063.00 | 38.66 |
| DS-40 | 0.12 | 51.36 | 3240.20 | 41.36 |
| DS-50 | 0.10 | 51.70 | 3291.90 | 42.15 |
| DS-100 | 0.10 | 49.68 | 3954.00 | 50.09 |

2.2 Flexural strength test results of external scrap.

| Samples | Yl D. Load KN | YlD.STR MPa | Modulus MPa | Slope N/mm |
|---|---|---|---|---|
| ES-10 | 0.09 | 49.43 | 2777.00 | 35.26 |
| ES-20 | 0.10 | 52.65 | 3172.20 | 40.39 |
| ES-30 | 0.10 | 51.54 | 3363.70 | 42.58 |
| ES-40 | 0.18 | 50.57 | 2988.50 | 37.84 |
| ES-50 | 0.10 | 52.06 | 3302.50 | 42.26 |
| ES-100 | 0.07 | 34.04 | 4462.00 | 57.49 |

3.1 Impact strength (IS) test results of domestic scrap.

| Samples | IS (kJ/m$^2$) | Samples | IS (kJ/m$^2$) |
|---|---|---|---|
| CS-0 | 47.03 | | |
| DS-10 | 46.55 | ES-10 | 42.48 |
| DS-20 | 37.63 | ES-20 | 28.96 |
| DS-30 | 44.95 | ES-30 | 39.09 |
| DS-40 | 34.10 | ES-40 | 34.19 |
| DS-50 | 39.87 | ES-50 | 28.60 |
| DS-100 | 42.50 | ES-100 | 30.13 |

4.1 Hardness test results of domestic and external scrap.

| Samples | Hardness (Shore-D) | Samples | Hardness (Shore-D) |
|---|---|---|---|
| CS-0 | 75.25 | | |
| DS-10 | 77.40 | ES-10 | 74.00 |
| DS-20 | 76.47 | ES-20 | 73.53 |
| DS-30 | 75.90 | ES-30 | 74.07 |
| DS-40 | 75.30 | ES-40 | 73.80 |
| DS-50 | 77.07 | ES-50 | 74.33 |
| DS-100 | 75.47 | ES-100 | 73.87 |

5.1 Density test results of domestic and external scrap.

| Samples | Density(gm/cc) | Samples | Density(gm/cc) |
|---|---|---|---|
| CS-0 | 1.57 | | |
| DS-10 | 1.57 | ES-10 | 1.56 |
| DS-20 | 1.55 | ES-20 | 1.51 |
| DS-30 | 1.54 | ES-30 | 1.50 |
| DS-40 | 1.54 | ES-40 | 1.58 |
| DS-50 | 1.56 | ES-50 | 1.57 |
| DS-100 | 1.65 | ES-100 | 1.76 |

6.1 Viscosity number (VN)/ k-value of domestic and external scrap.

| Samples | VN | K-value | Samples | VN | K-value |
|---|---|---|---|---|---|
| CS-0 | 126 | 63.16 | | | |
| DS-10 | 92 | 57.21 | ES-10 | 71 | 51.09 |
| DS-20 | 96 | 58.25 | ES-20 | 71 | 51.09 |
| DS-30 | 105 | 60.46 | ES-30 | 67 | 50.12 |
| DS-40 | 83 | 54.75 | ES-40 | 74 | 52.06 |
| DS-50 | 80 | 53.87 | ES-50 | 62 | 48.65 |
| DS-100 | 66 | 43.56 | ES-100 | 51 | 38.24 |

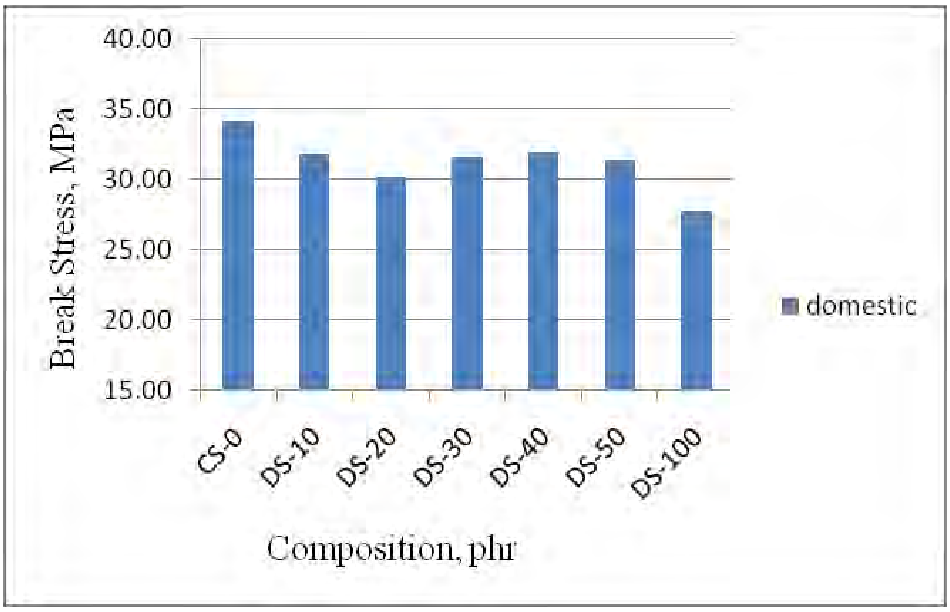
7.1 Vicat softening temperature (VST) of domestic and external scrap.

| Samples | VST | Samples | VST |
|---|---|---|---|
| CS-0 | 96 | | |
| DS-10 | 97 | ES-10 | 105 |
| DS-20 | 98 | ES-20 | 102 |
| DS-30 | 101 | ES-30 | 98 |
| DS-40 | 100 | ES-40 | 101 |
| DS-50 | 102 | ES-50 | 103 |
| DS-100 | 103 | ES-100 | 102 |

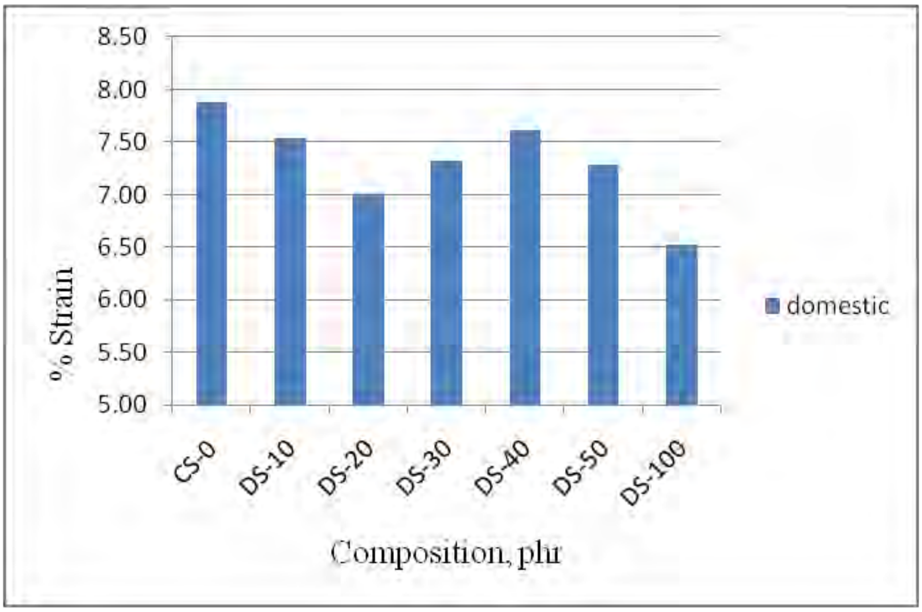
# APPENDIX – B

# LIST OF FIGURES

## 1. Tensile Strength



*.Fig. 1.1 Variation of tensile break stress with addition of scrap (domestic) in the raw material mix.*



*.Fig. 1.2 Variation of elongation at break with addition of scrap (domestic) in the raw material mix.*

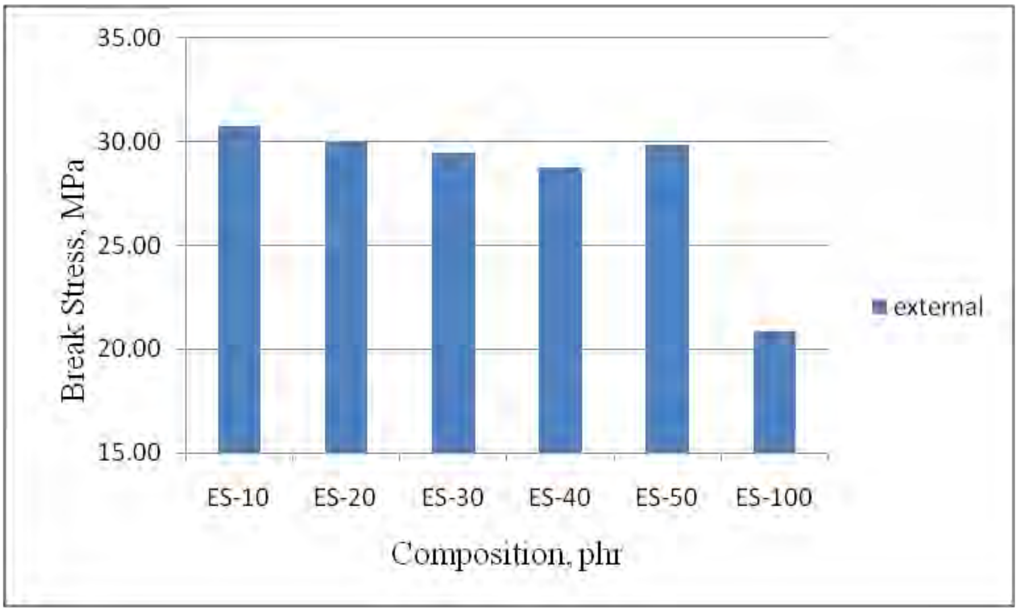
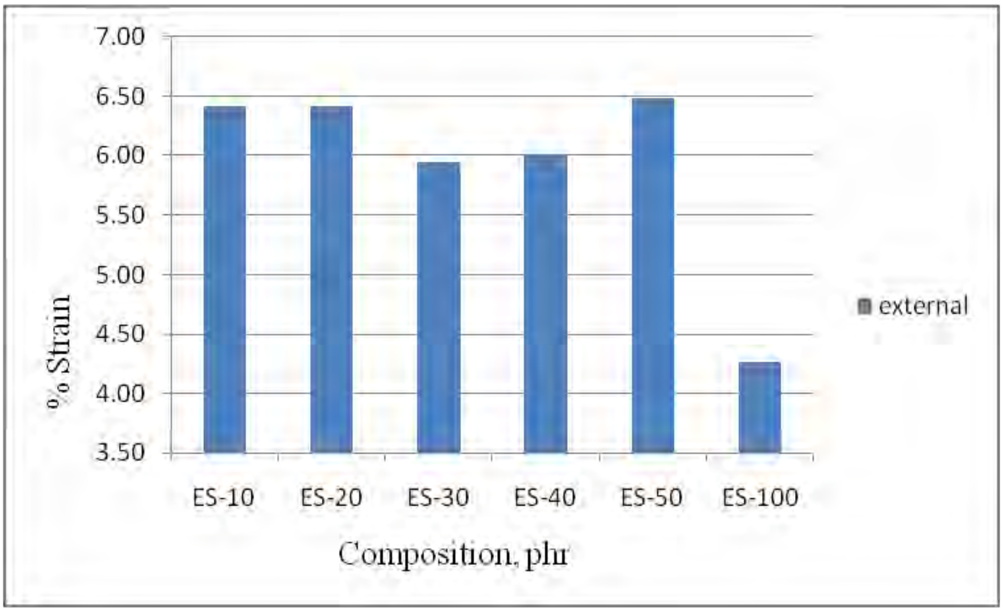


*Fig. 1.3 Variation of tensile break stress with* addition of *scrap (external) in the raw material mix.*



*.Fig. 1.4 Variation of elongation at break with* addition of *scrap (external) in the raw material mix.*

## 2. Flexural Strength

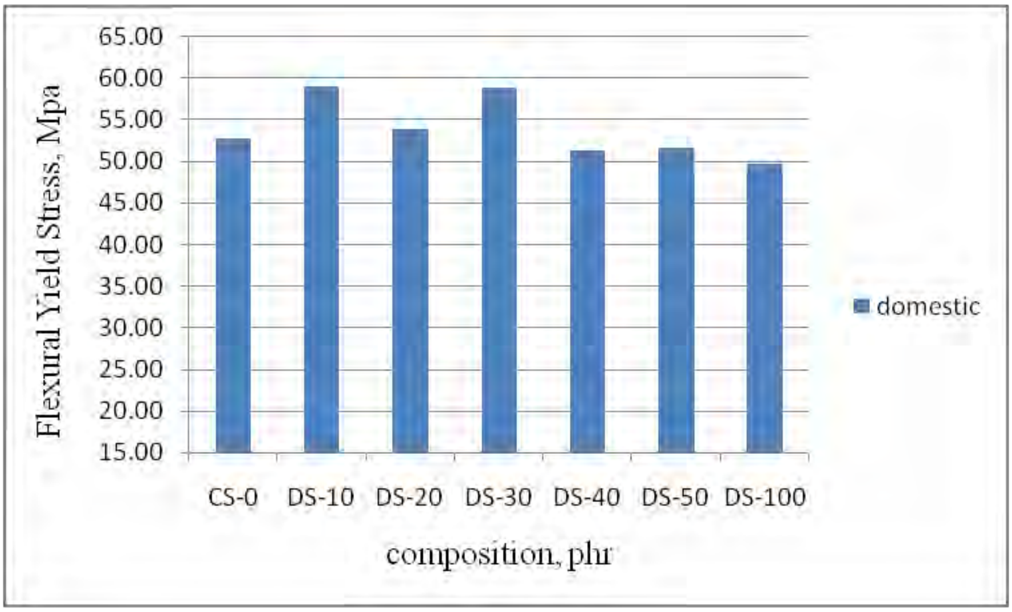


*Fig. 2.1 Variation of Flexural strength with quantity of scrap (domestic) in the raw material mix.*

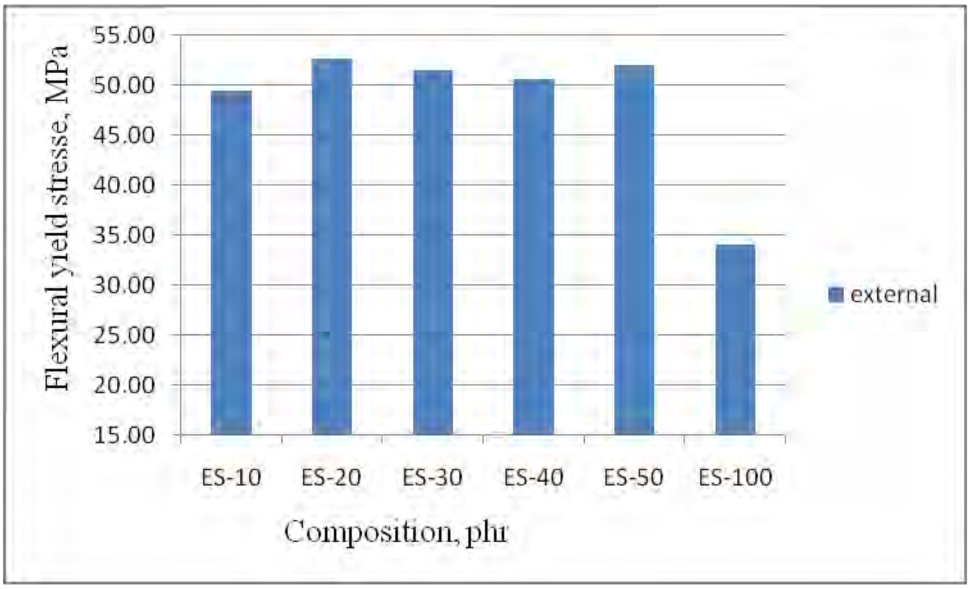


*Fig. 2.2 Variation of Flexural strength with quantity of scrap (external) in the raw material mix.*

### 3. Impact Strength

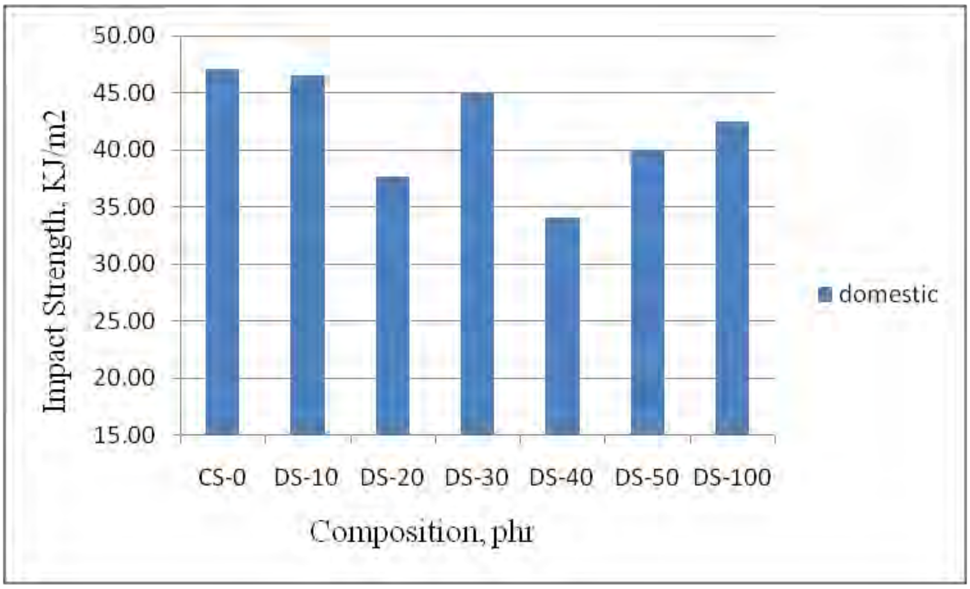


*Fig. 3.1 Variation in impact strength with quantity of scrap (domestic) in the raw material mix.*

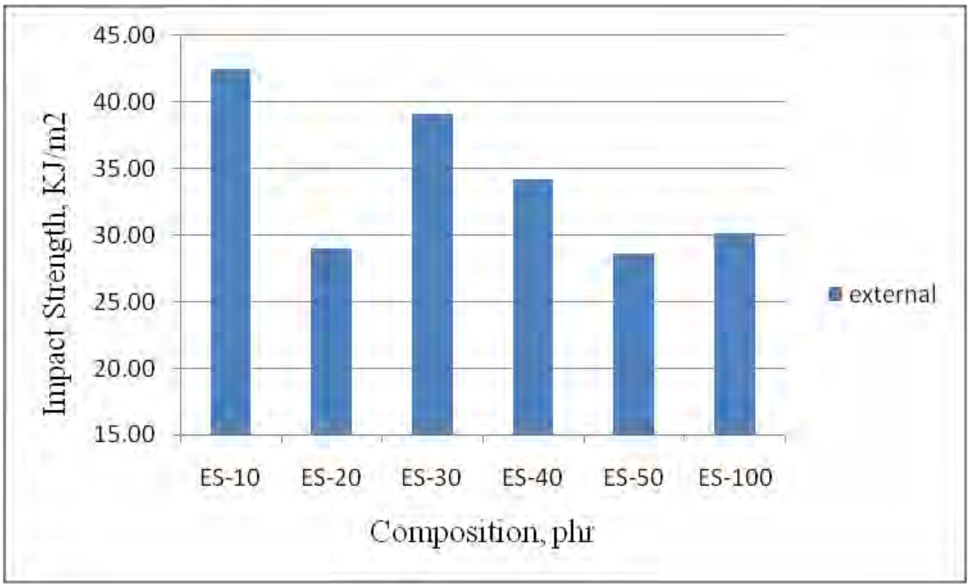


*Fig. 3.2 Variation in impact strength with quantity of scrap (external) in the raw material mix.*

## 4. Hardness Test

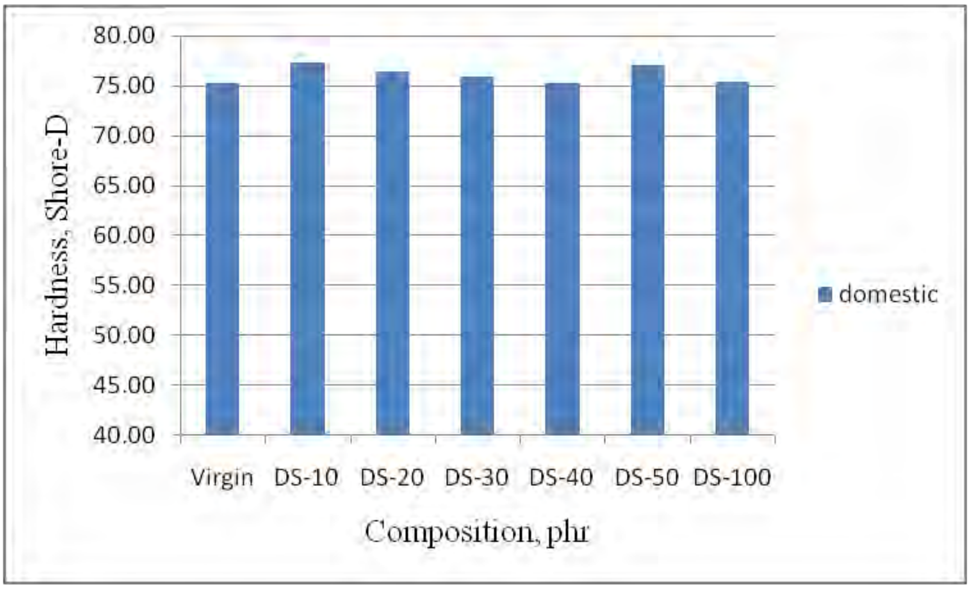


*Fig. 4.1: Variation of hardness with quantity of scrap(domestic) in the raw material mix*

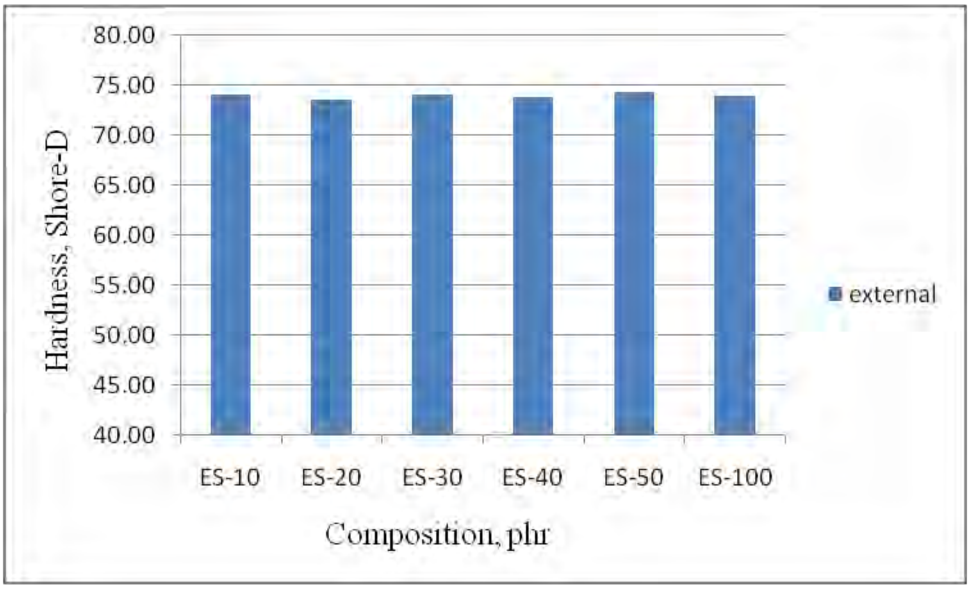


*Fig. 4.2 Variation of hardness with quantity of scrap (external) in the raw material mix*

## 5. Density Test

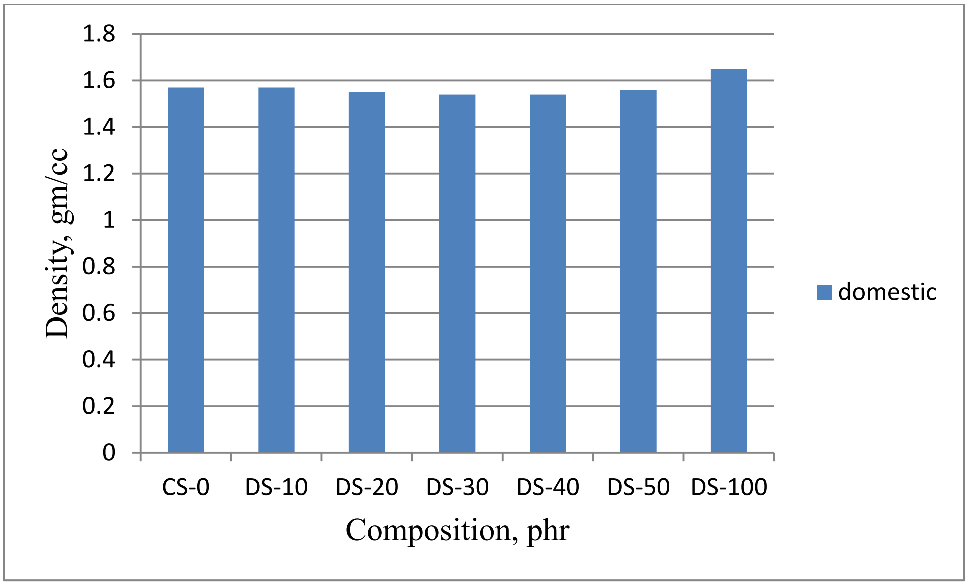


*Fig. 5.1 Variation of density with quantity of scrap (domestic) in the raw material mix*

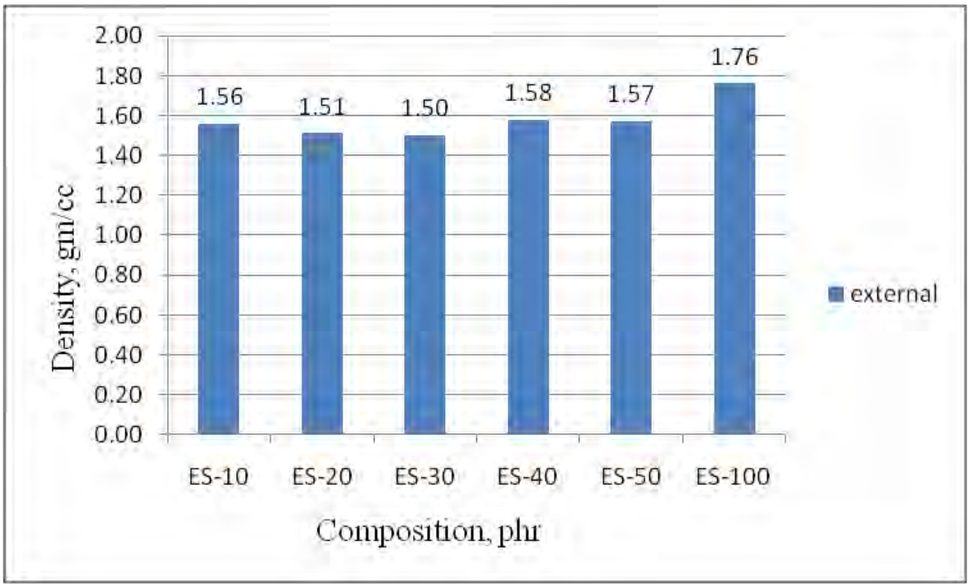


*Fig. 5.2: Variation of density with quantity of scrap (external) in the raw material mix*

## 6. Viscosity Number (VN) Determination

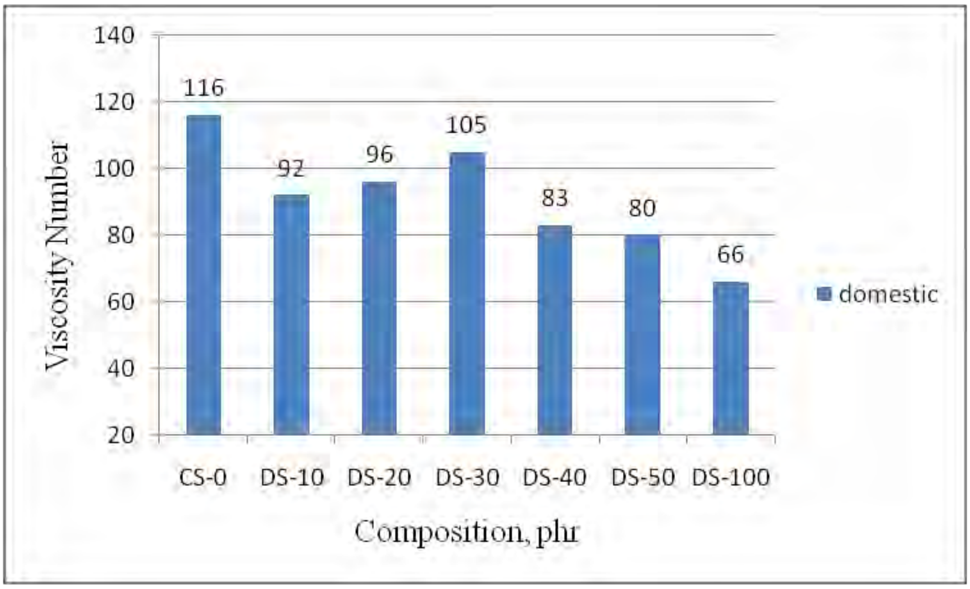


*Fig. 6.1Variation of* viscosity number *with quantity of scrap (domestic) in the raw material mix.*

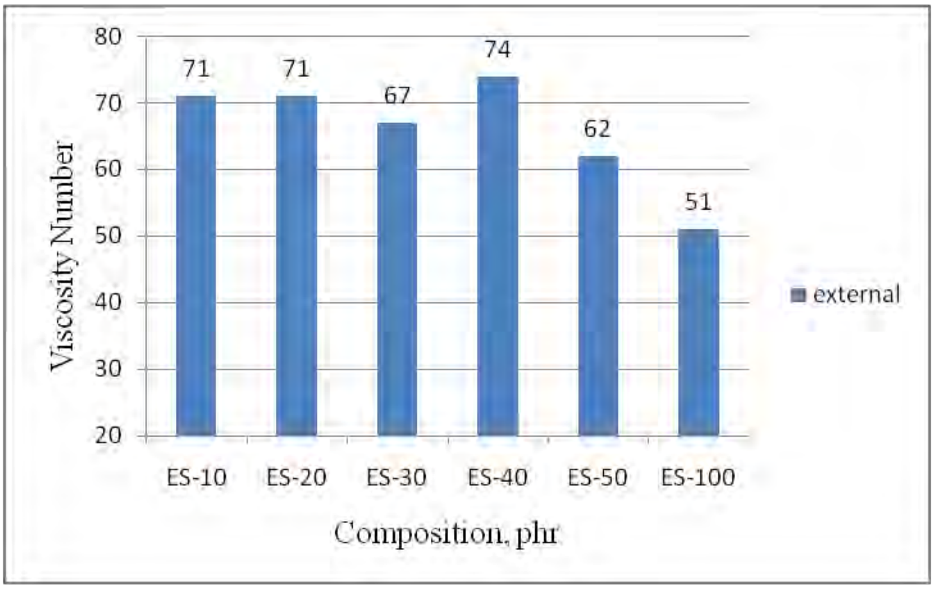


*Fig. 6.2 Variation of* viscosity number *with quantity of scrap (external) in the raw material mix*

## 7. Vicat Softening Temperature (VST)

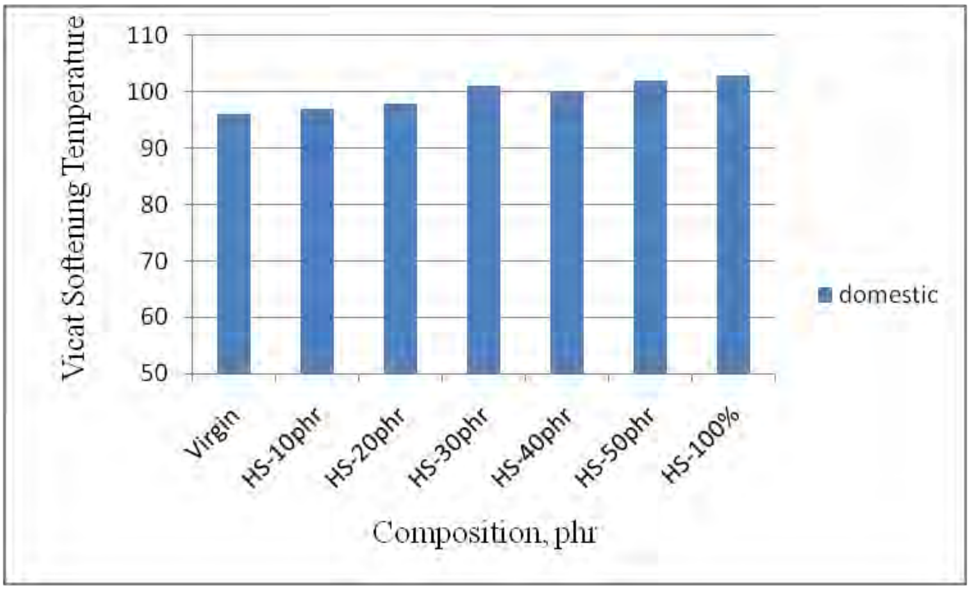


*Fig. 7.1 Variation of VST with quantity of scrap (domestic) in the raw material mi*

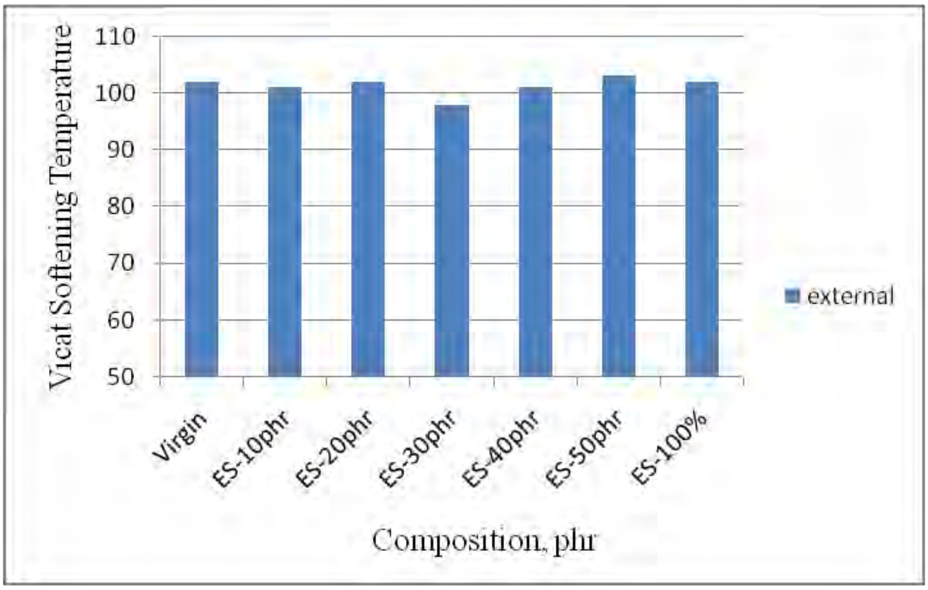


*Fig. 7.2 Variation of VST with quantity of scrap (external) in the raw material mix*

## 8. X-ray Diffraction (XRD)

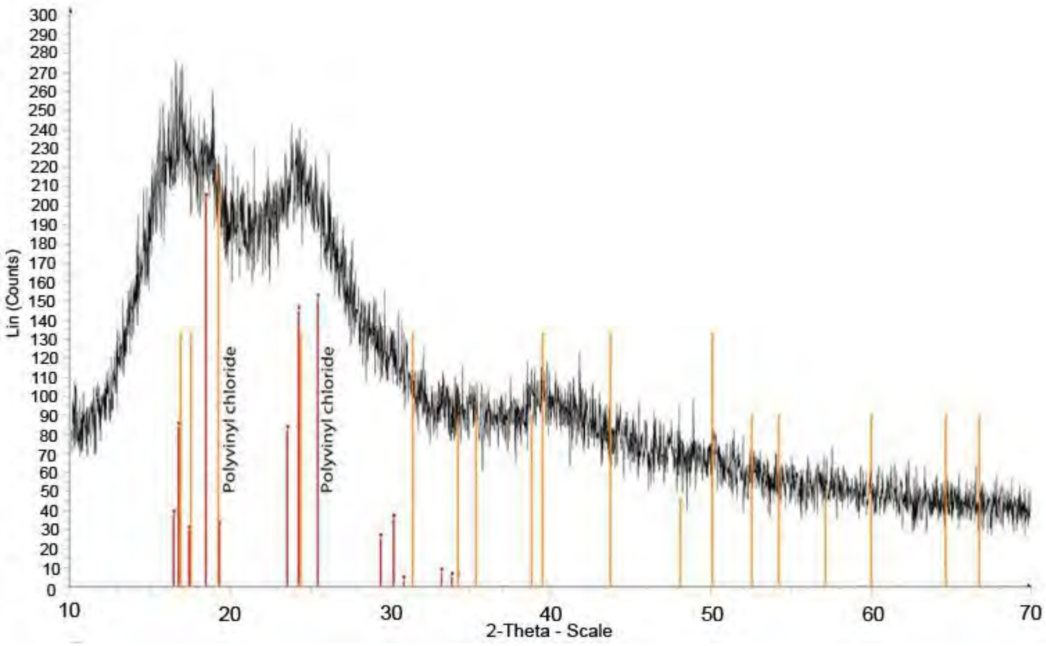


*Fig. 8.1: X-ray Diffraction pattern of PVC resin*

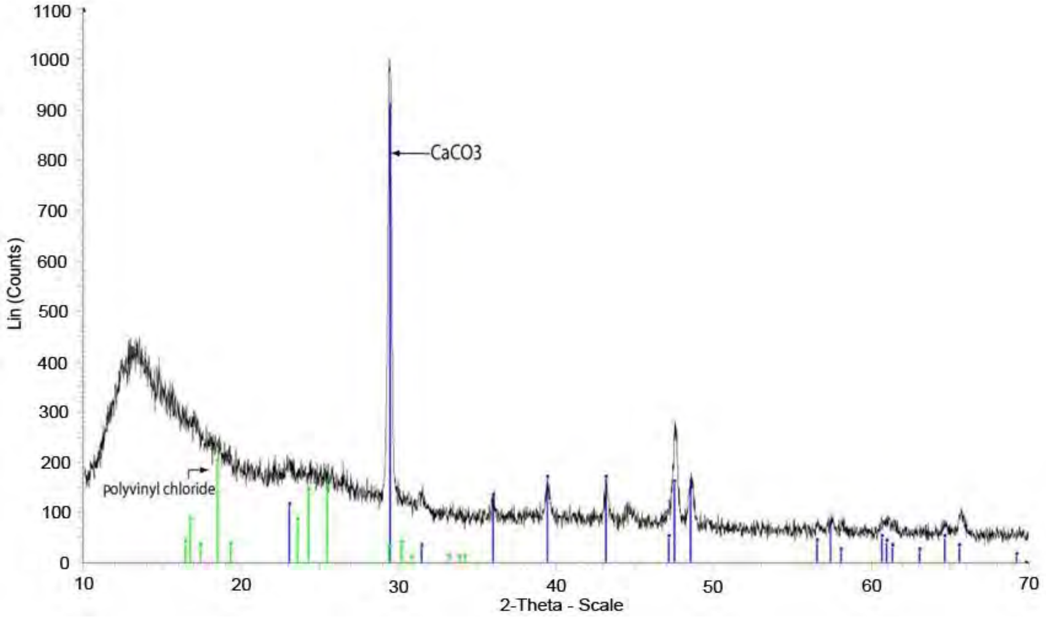


*Fig. 8.2: X-ray Diffraction pattern of PVC (-CH2CHCl-)n without additives*

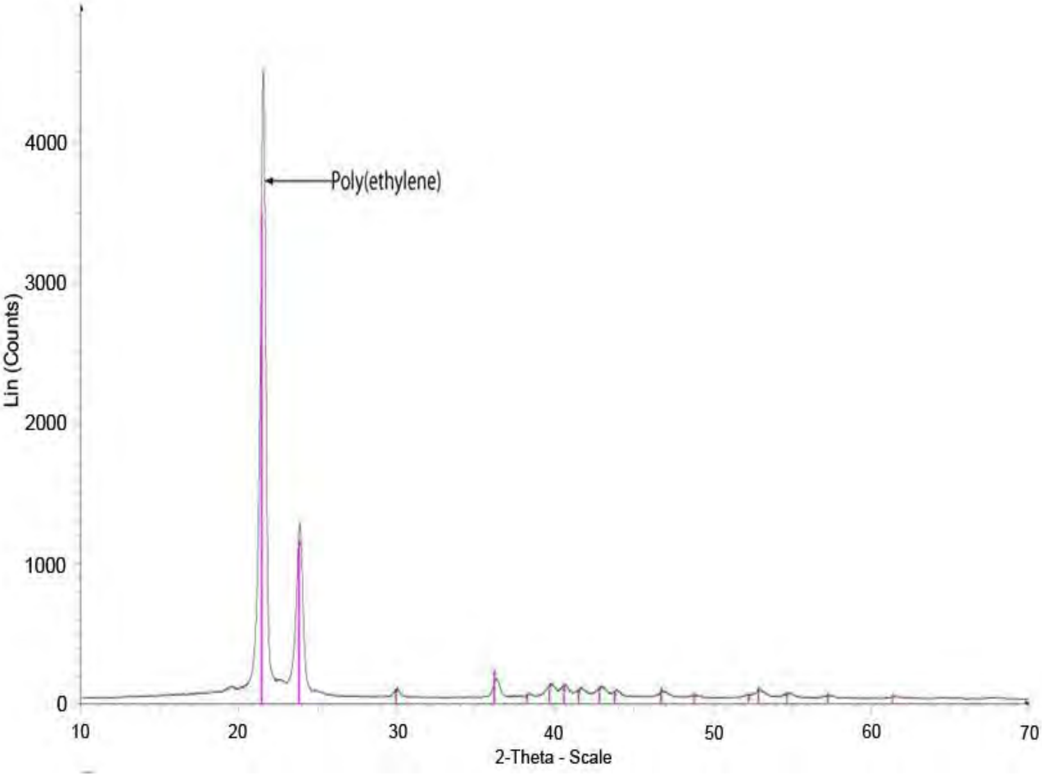


*Fig. 8.3: X-ray Diffraction (XRD) pattern of Stearic acid ($C_{17}H_{35}COOH$)*

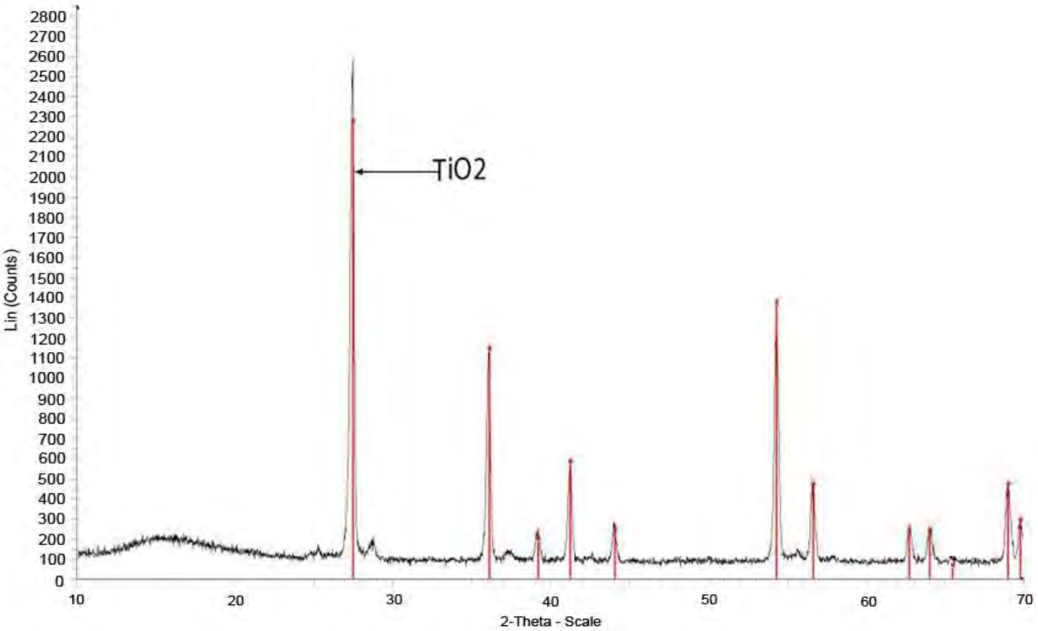


*Fig. 8.4: X-ray Diffraction pattern of titanium dioxide ($TiO_2$)*

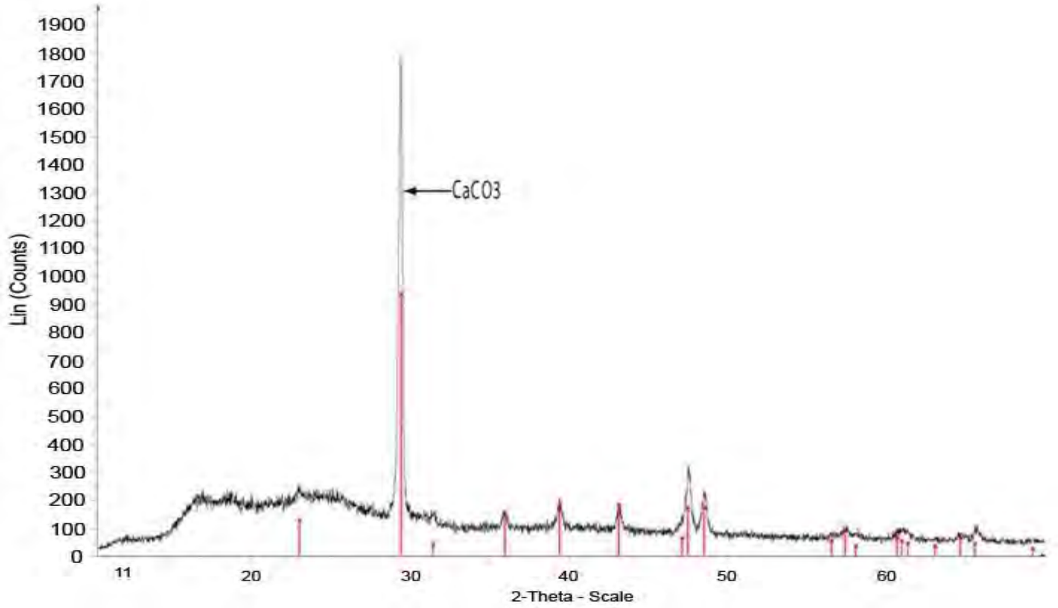


*Fig. 8.5: X-ray Diffraction pattern of virgin uPVC*

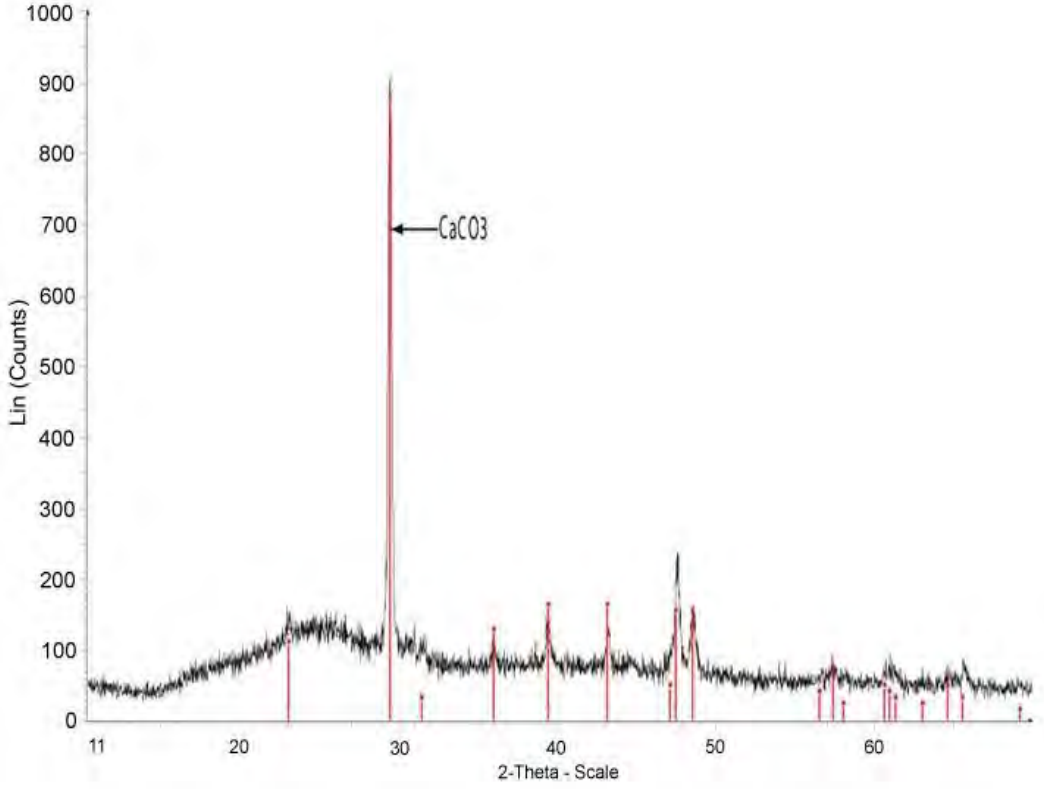


*Fig. 8.6: X-ray Diffraction pattern of sample containing 10 phr domestic scrap*

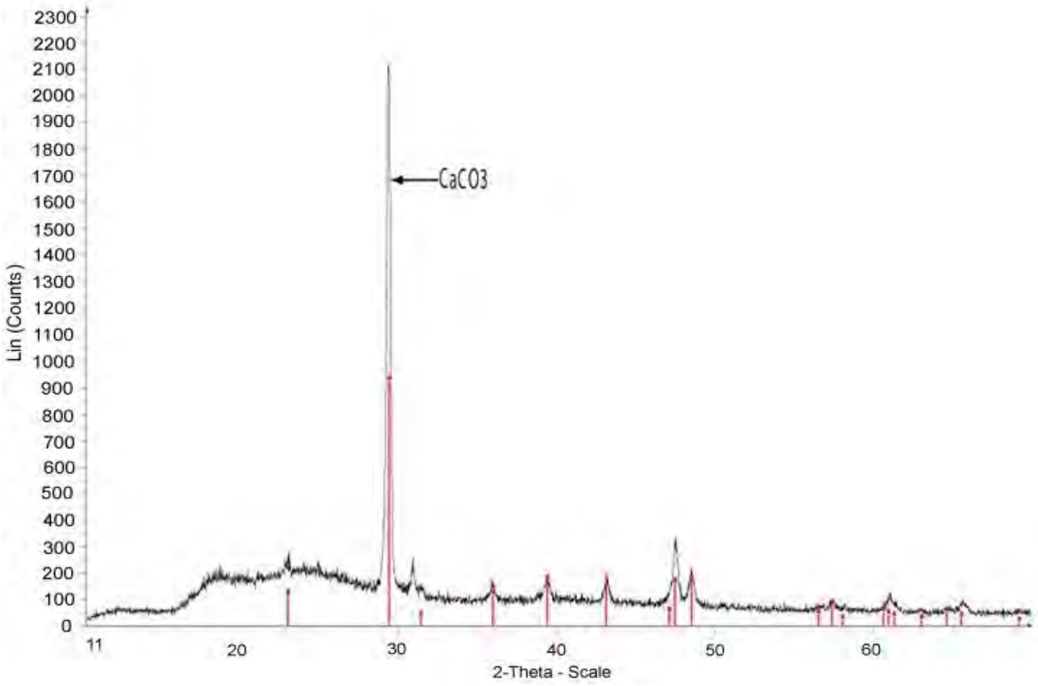


*Fig. 8.7: X-ray Diffraction pattern of sample containing 20 phr domestic scrap*

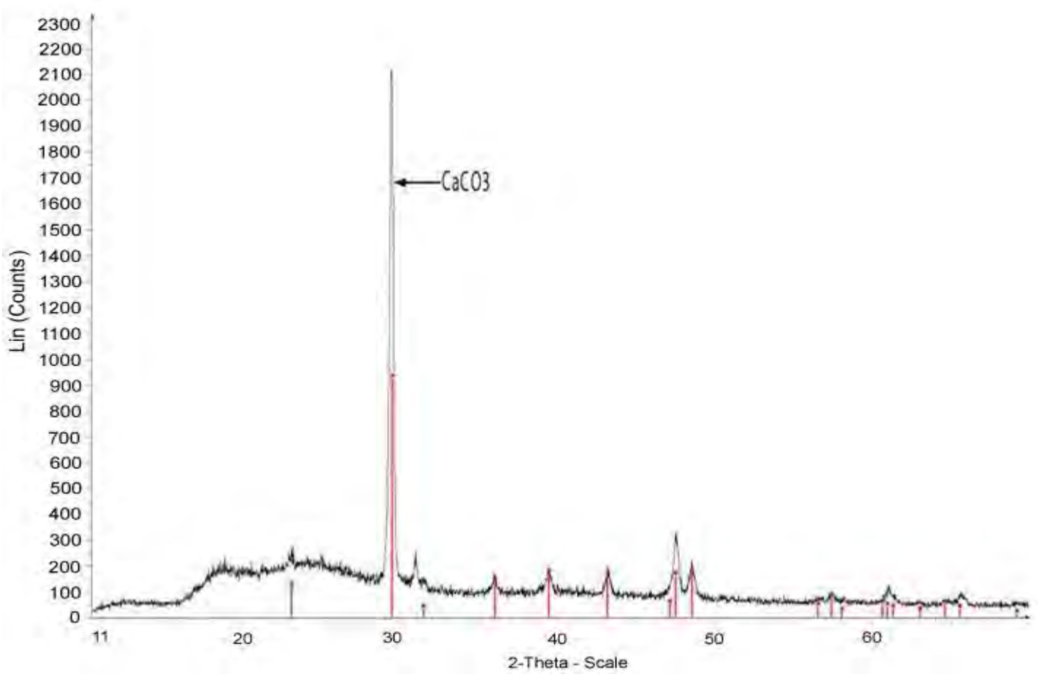


*Fig. 8.8: X-ray Diffraction pattern of sample containing 30 phr domestic scrap*

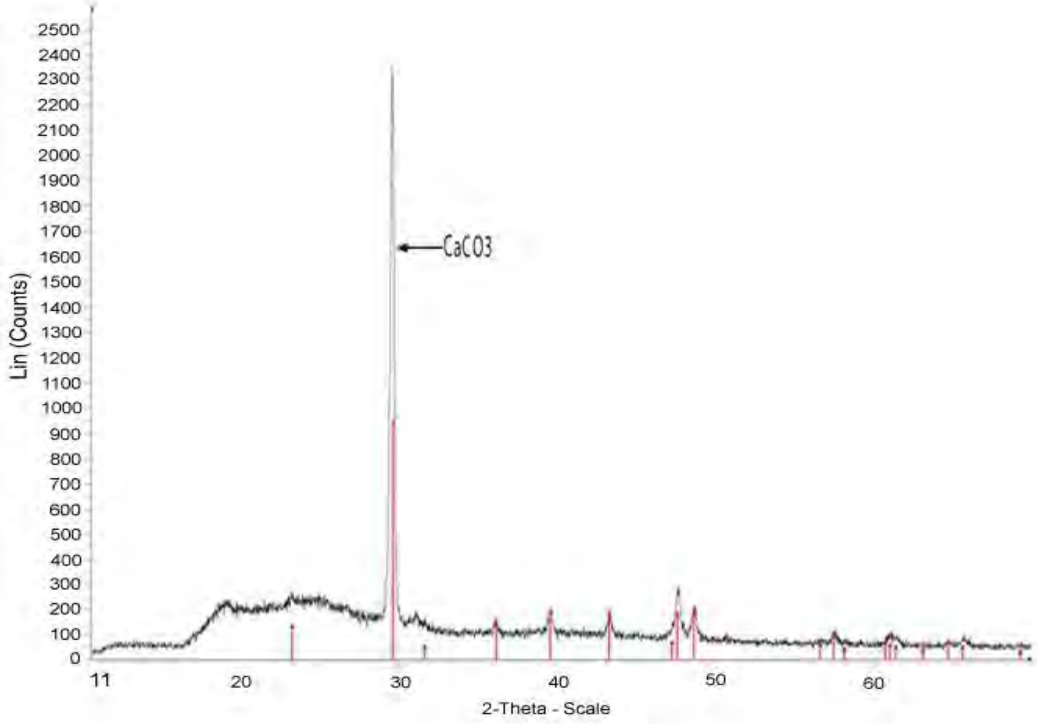


*Fig. 8.9: X-ray Diffraction pattern of sample containing 40 phr domestic scrap*

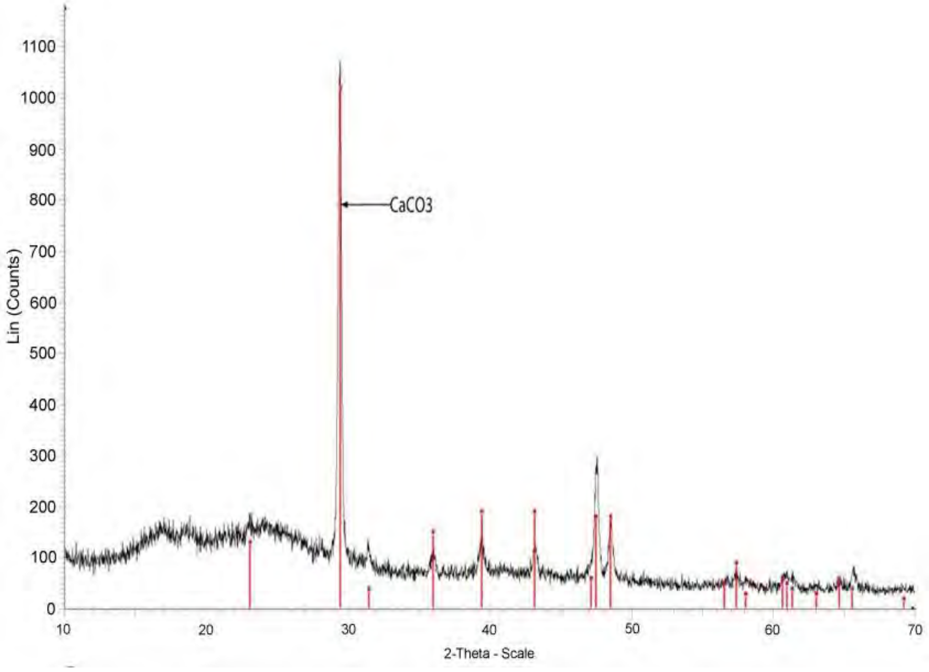


*Fig. 8.10: X-ray Diffraction pattern of sample containing 50 phr domestic scrap*

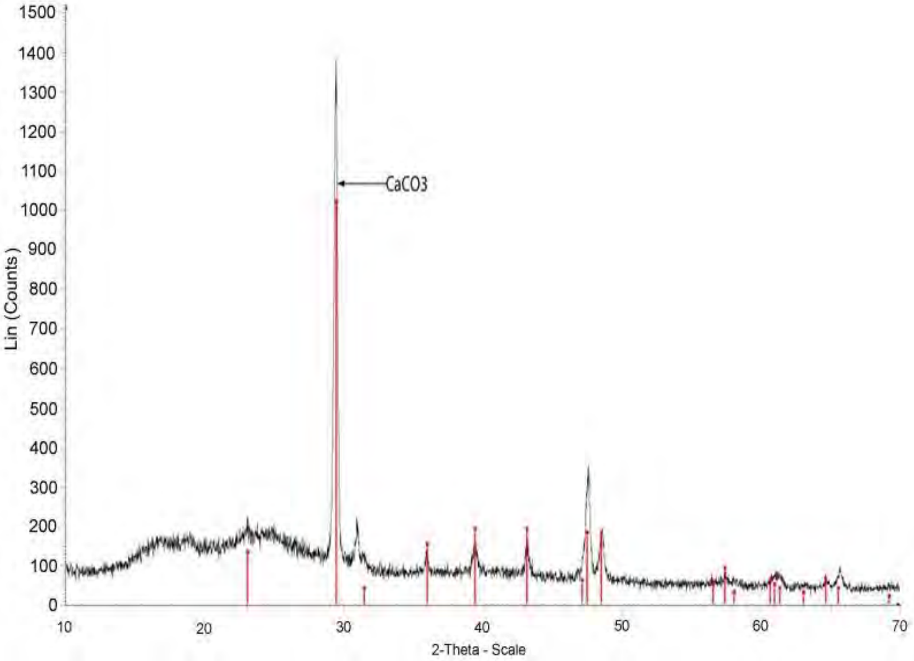


*Fig. 8.11: X-ray Diffraction pattern of sample containing 100% domestic scrap*

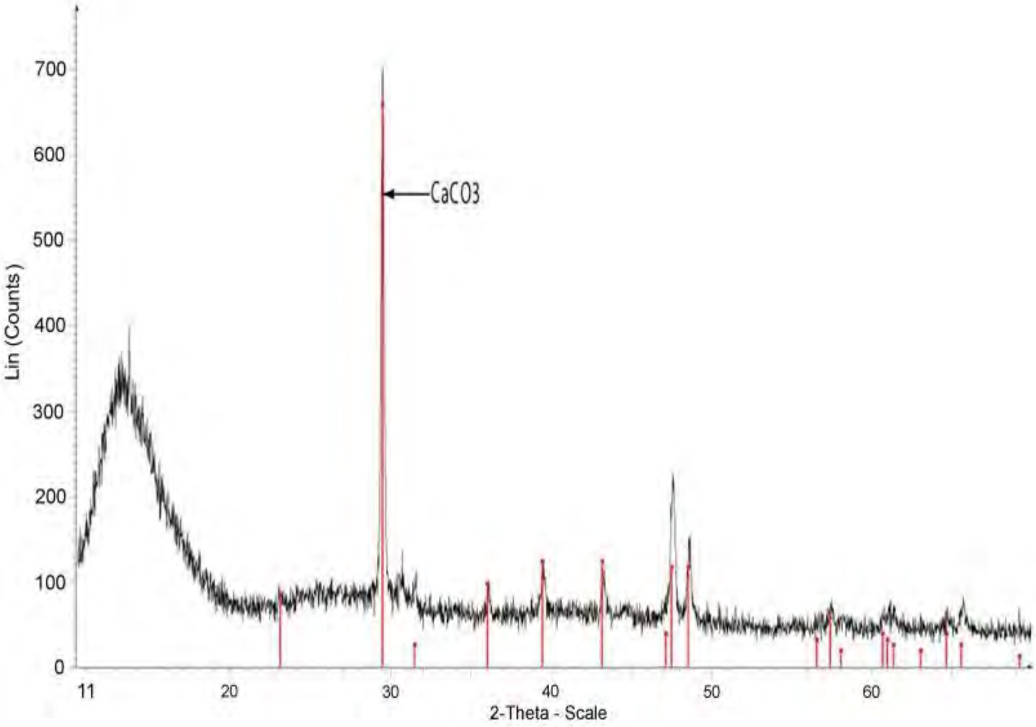


*Fig. 8.12: X-ray Diffraction pattern of sample containing10 phr external scrap*

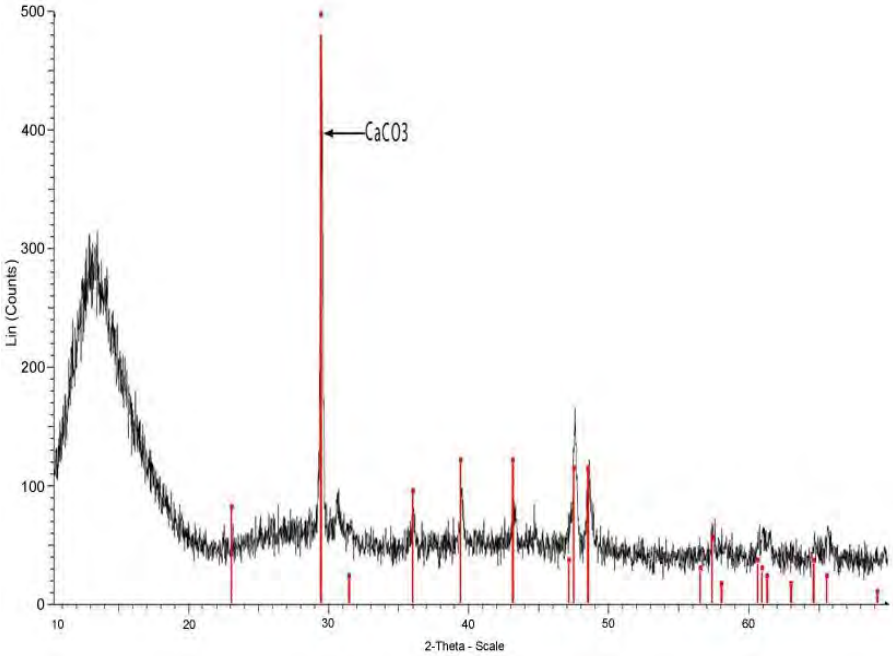


*Fig. 8.13: X-ray Diffraction pattern of sample containing 20 phr external scrap*

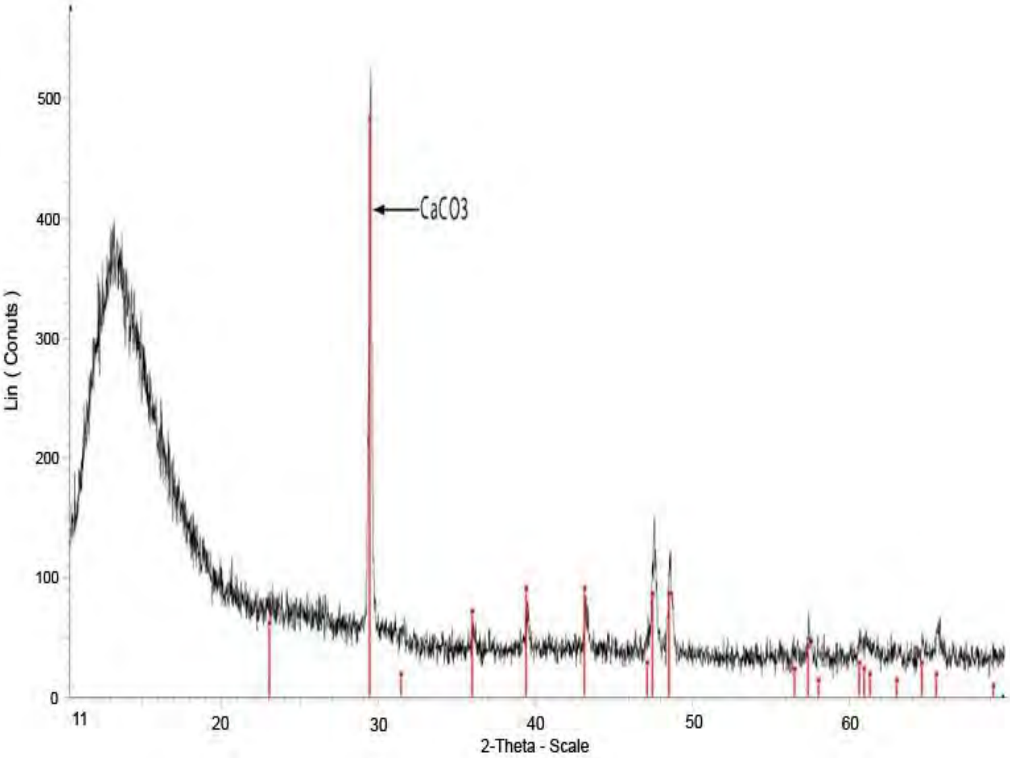


*Fig. 8.14: X-ray Diffraction pattern of sample containing 30 phr external scrap*

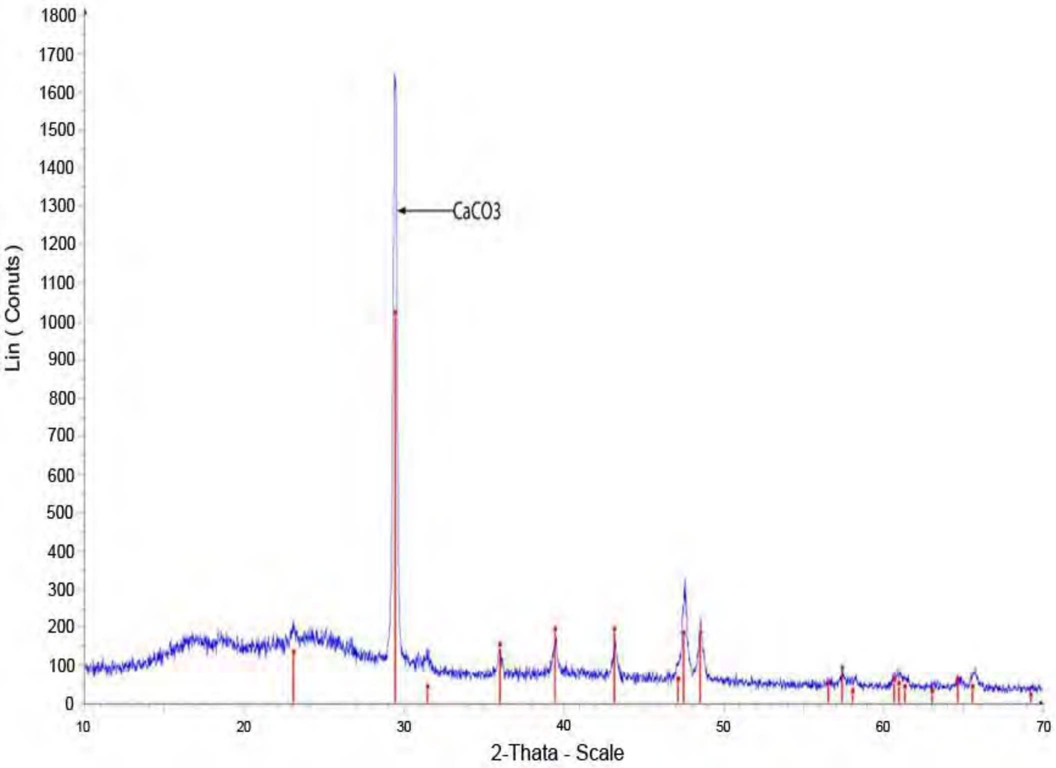


*Fig. 8.15: X-ray Diffraction pattern of sample containing 40 phr external scrap*

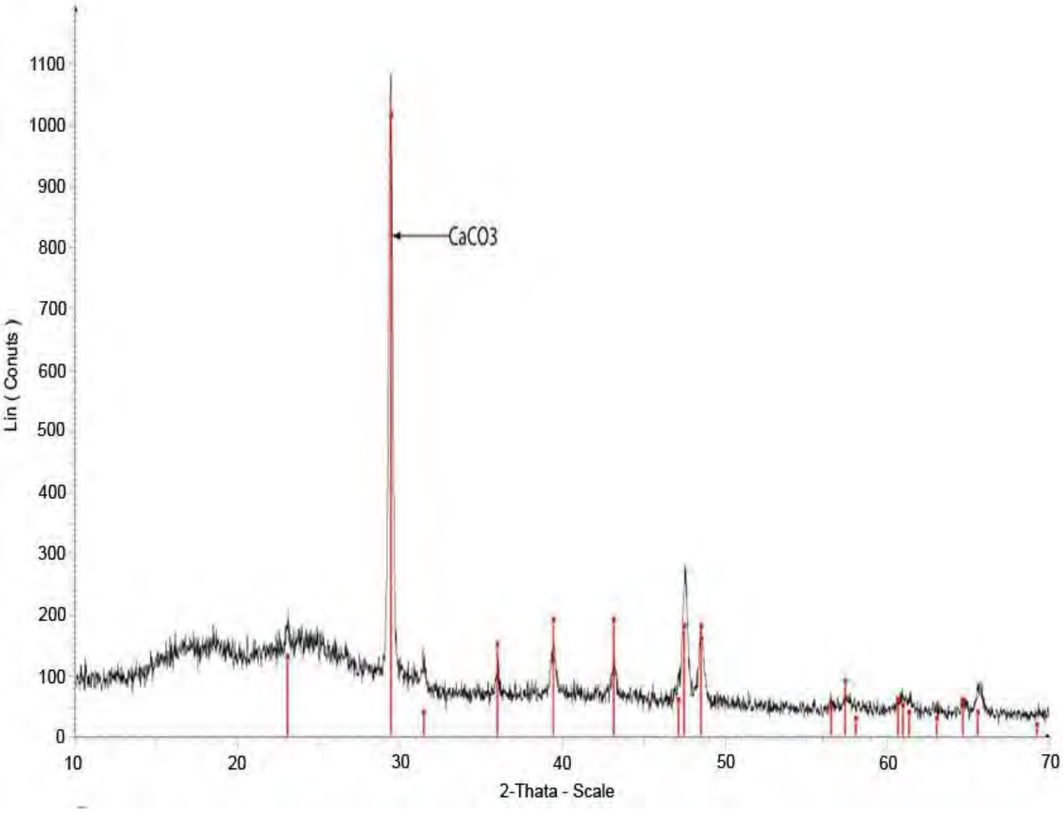


*Fig. 8.16: X-ray Diffraction pattern of sample containing 50 phr external scrap*

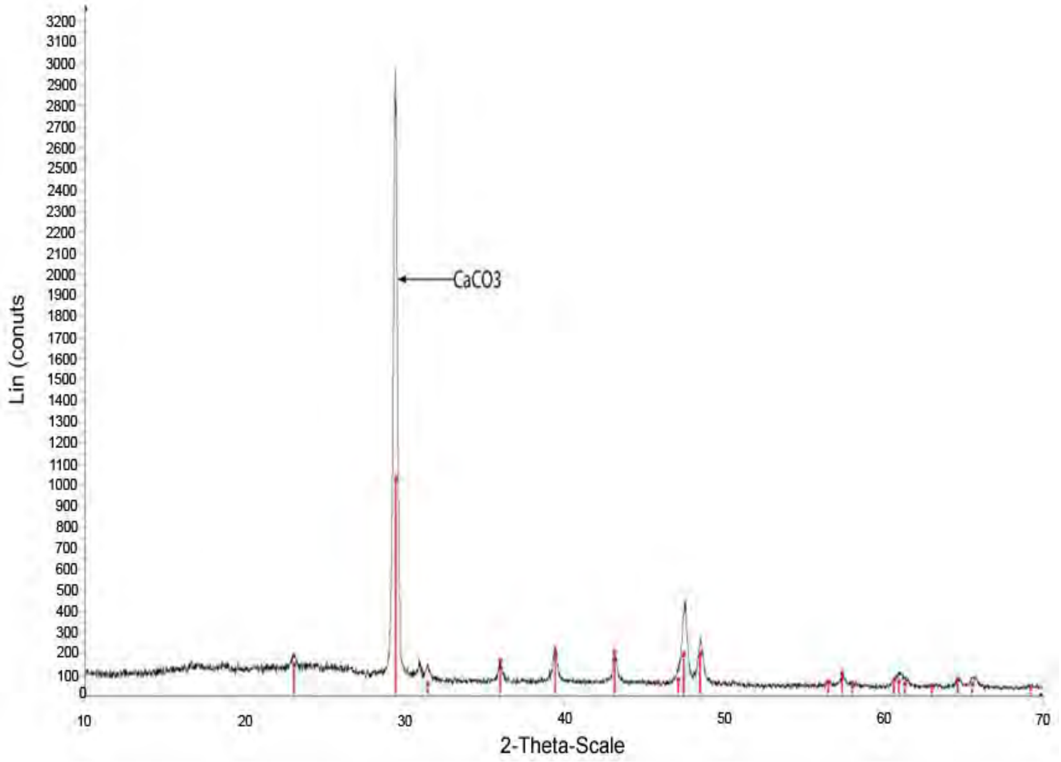


*Fig.8.17: X-ray Diffraction pattern of sample containing 100% external scrap*

## 9. Fourier Transform Infrared (FTIR)

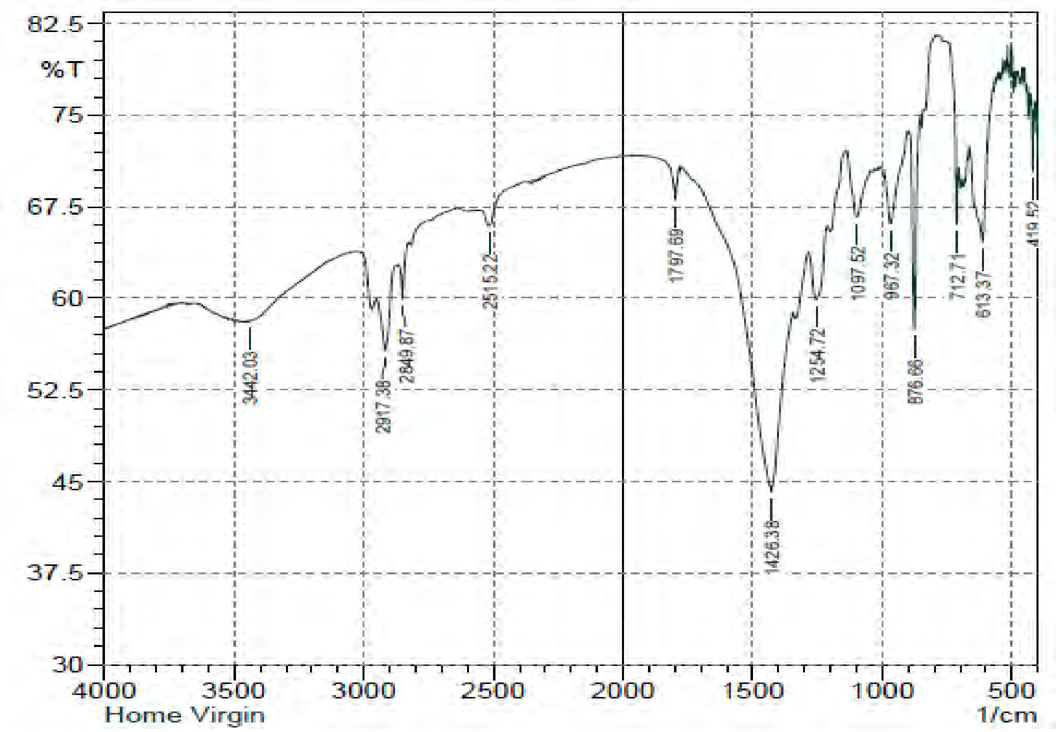


*Fig. 9.1 FTIR curve for uPVC of virgin compound.*

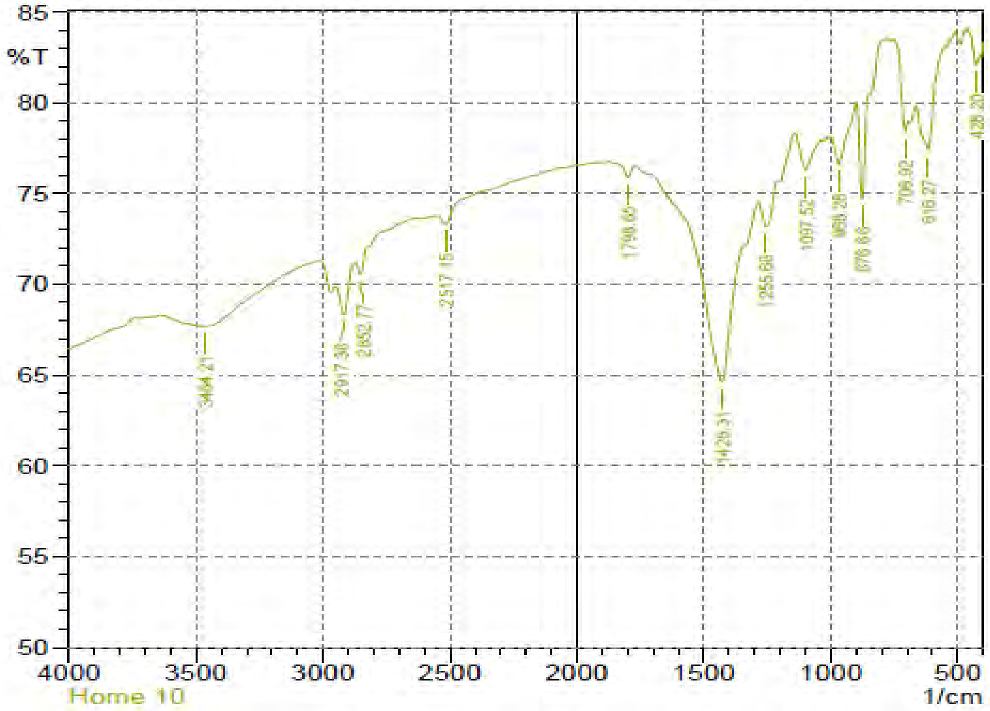


*Fig. 9.2 FTIR curve  for uPVC of 10 phr (domestic-scrap).*

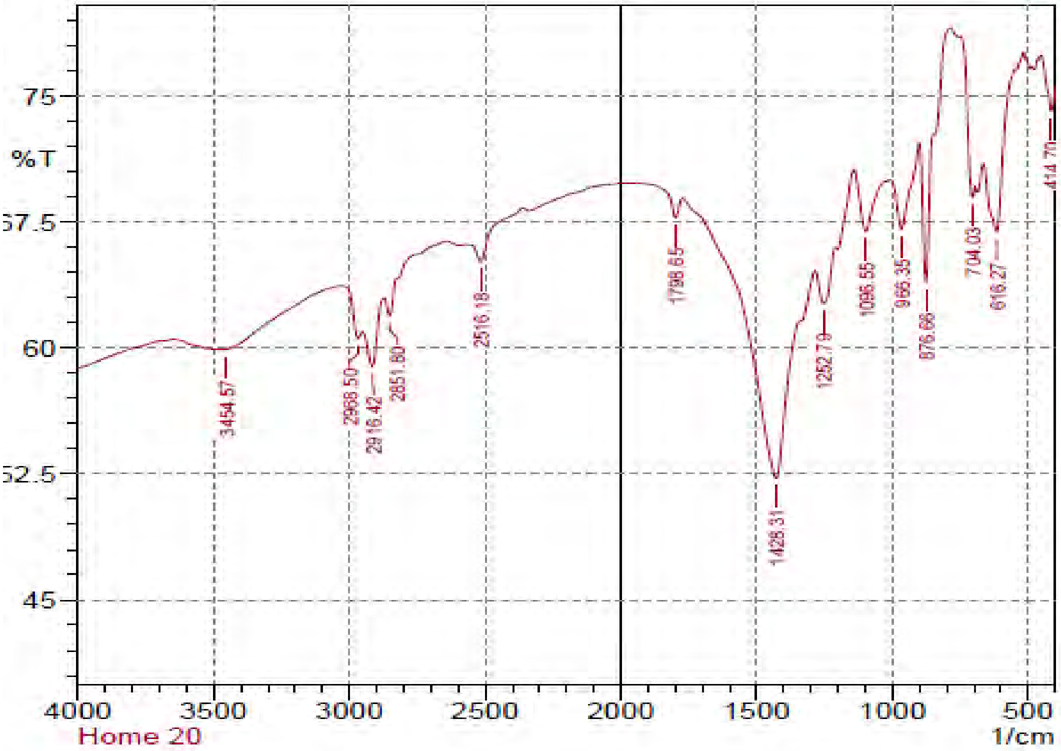


*Fig. 9.3 FTIR curve  for uPVC of 20 phr (domestic-scrap).*

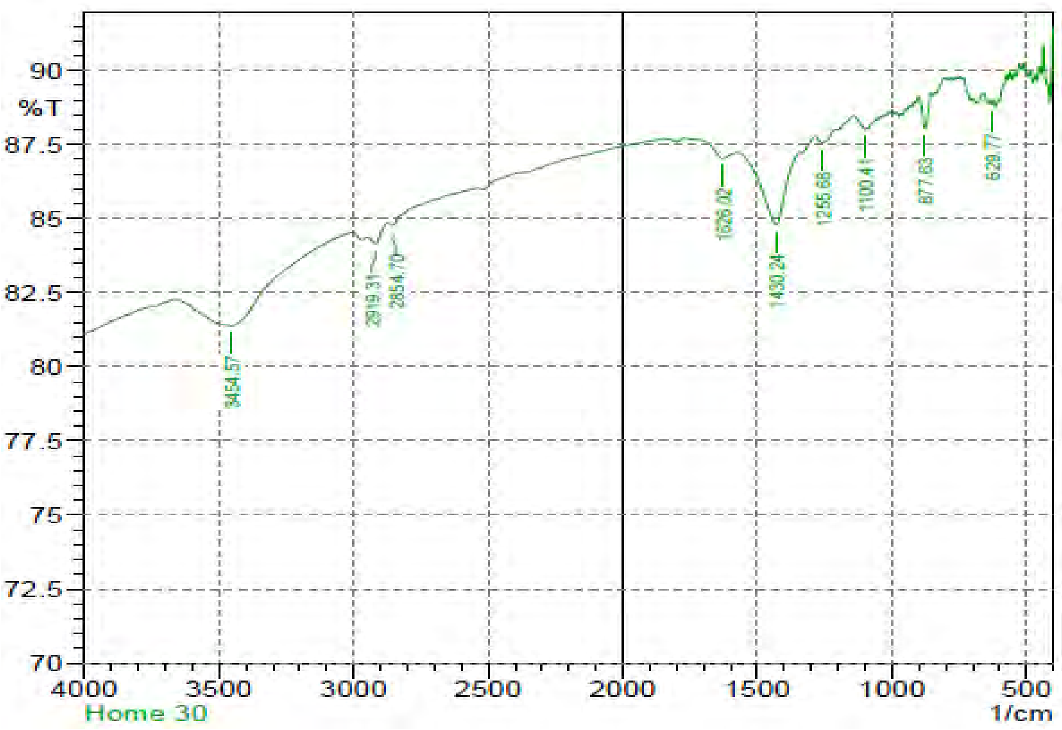


*Fig. 9.4 FTIR curve for uPVC of 30 phr (domestic-scrap).*

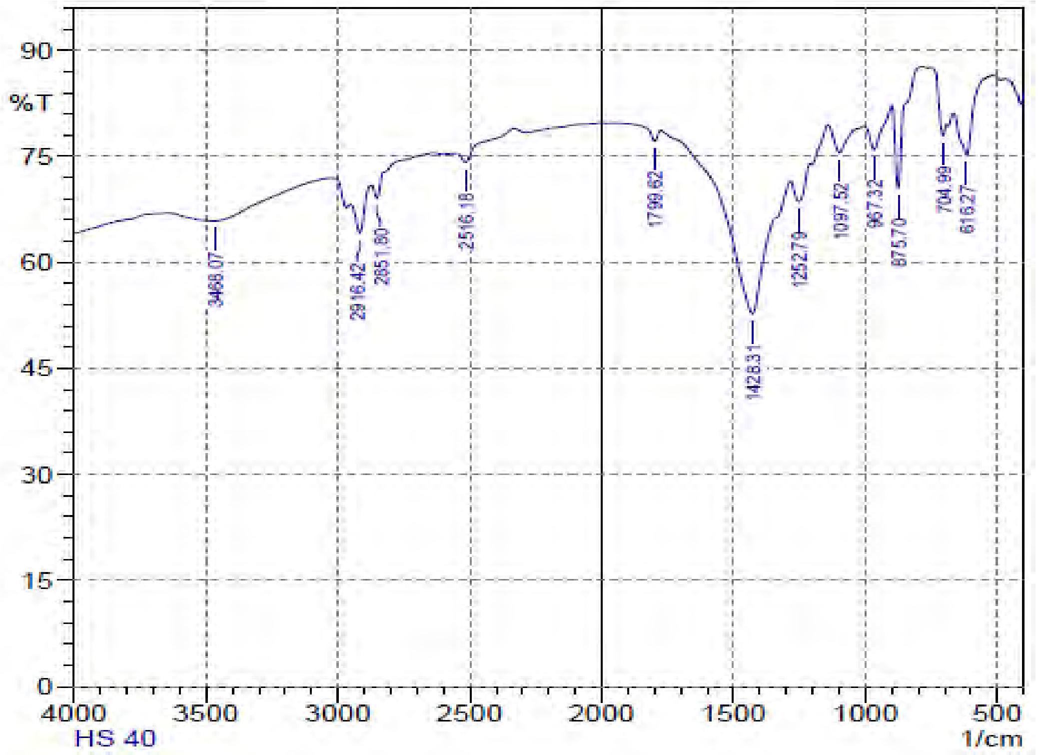


*Fig. 9.5 FTIR curve for uPVC of 40 phr (domestic-scrap).*

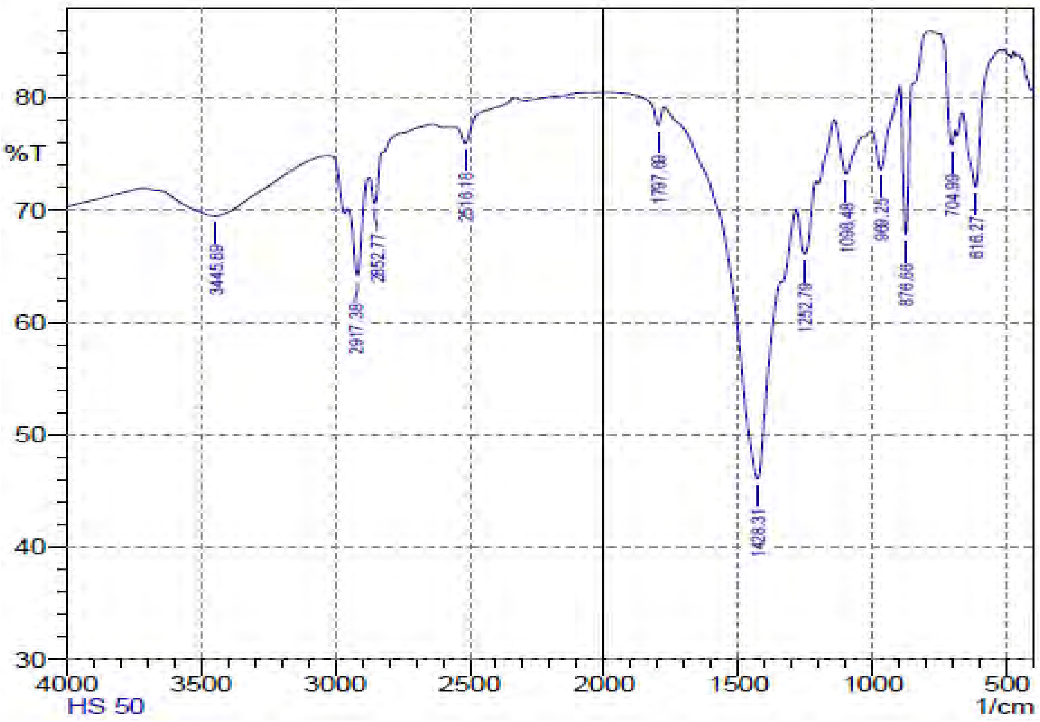


*Fig. 9.6 FTIR curve for uPVC of 50 phr (domestic-scrap).*

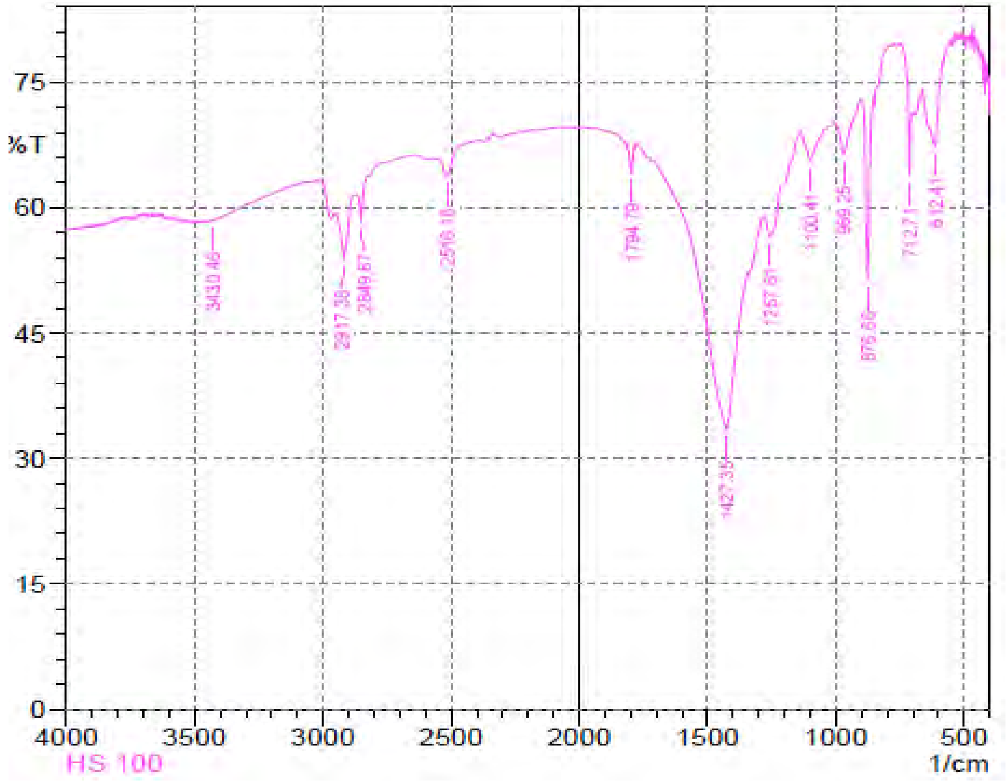


***Fig. 9.7 FTIR curve for uPVC of 100% scrap (domestic-scrap).***

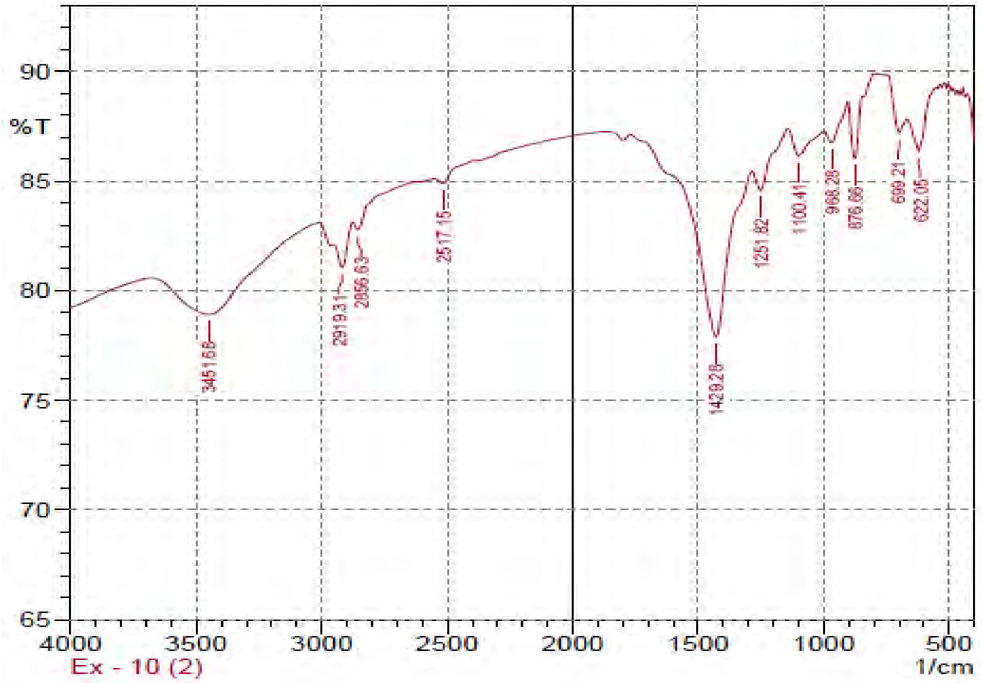


*Fig. 9.8 FTIR curve for uPVC of 10 phr (external scrap).*

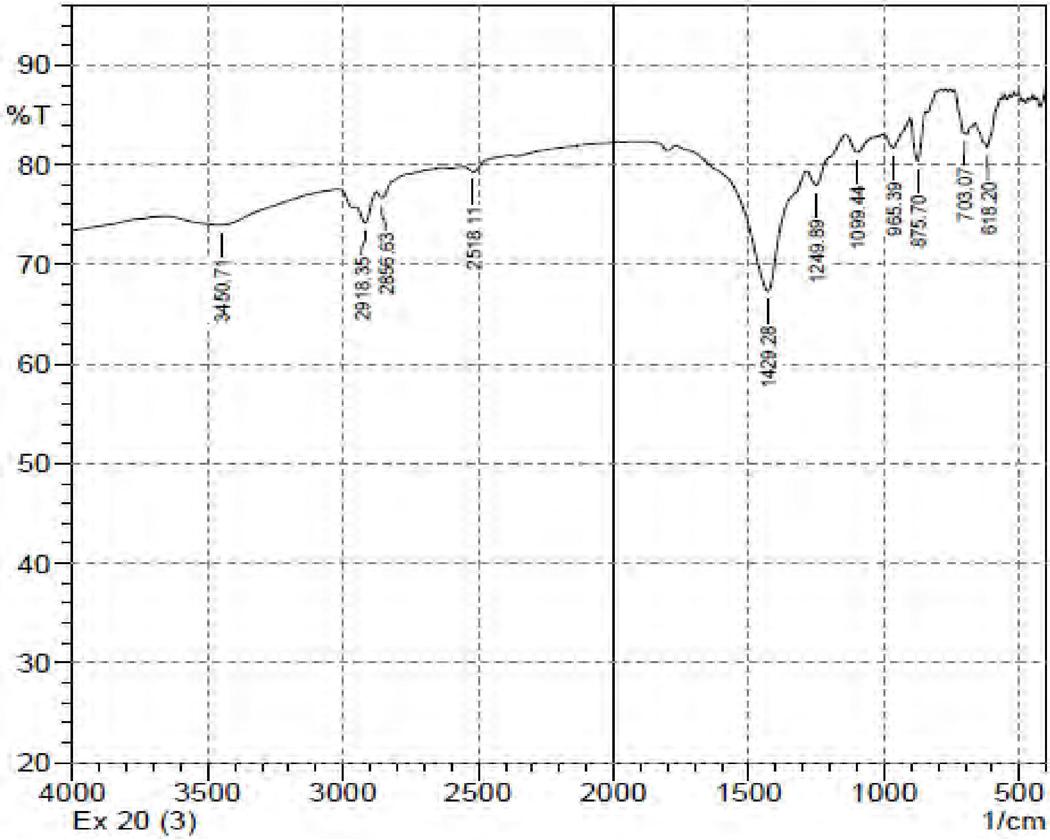


*Fig. 9.9 FTIR curve for uPVC of 20 phr (external scrap).*

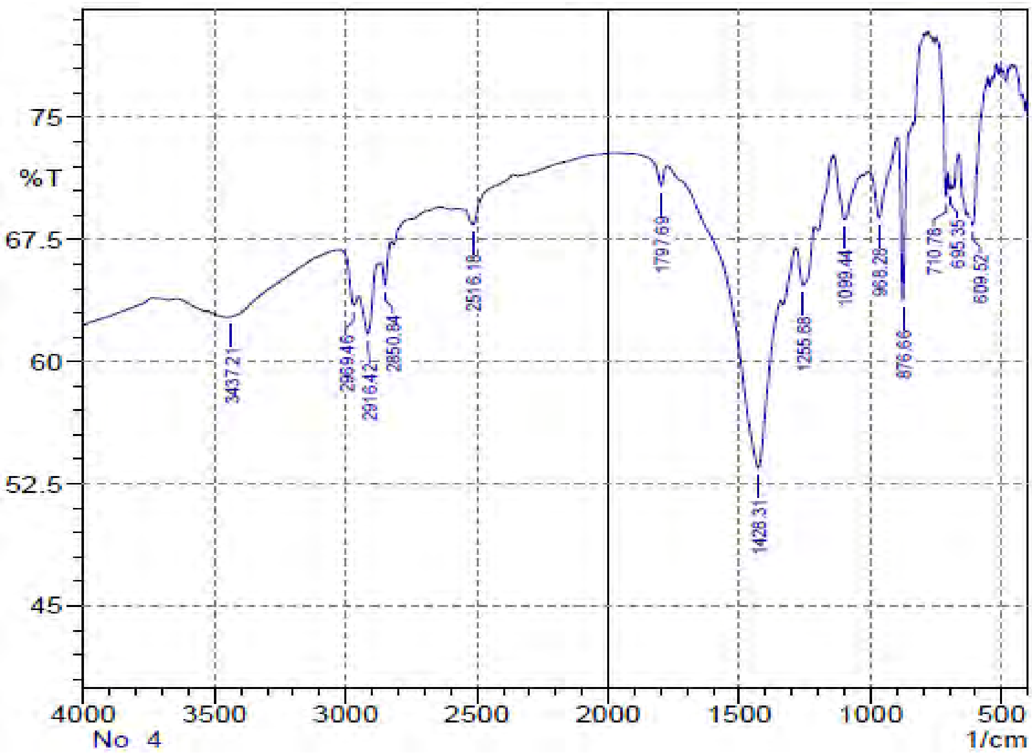


*Fig. 9.10 FTIR curve for uPVC of 30 phr (external scrap).*

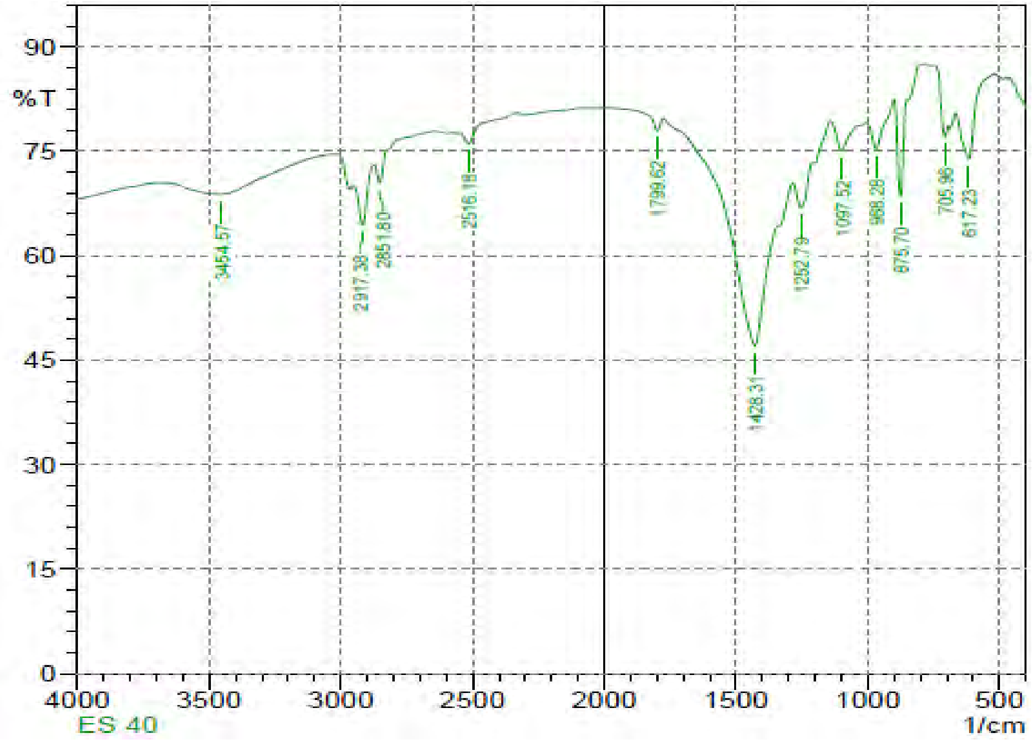


*Fig. 9.11 FTIR curve for uPVC of 40 phr (external scrap).*

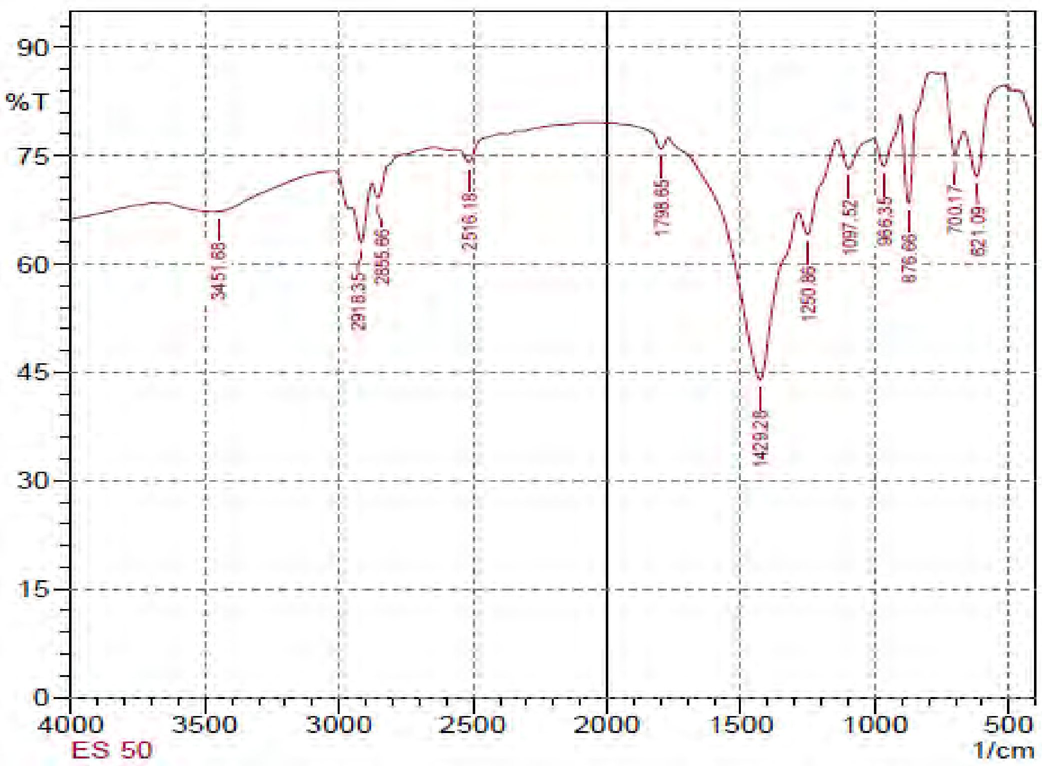


*Fig. 9.12 FTIR curve for uPVC of 50 phr (external scrap).*

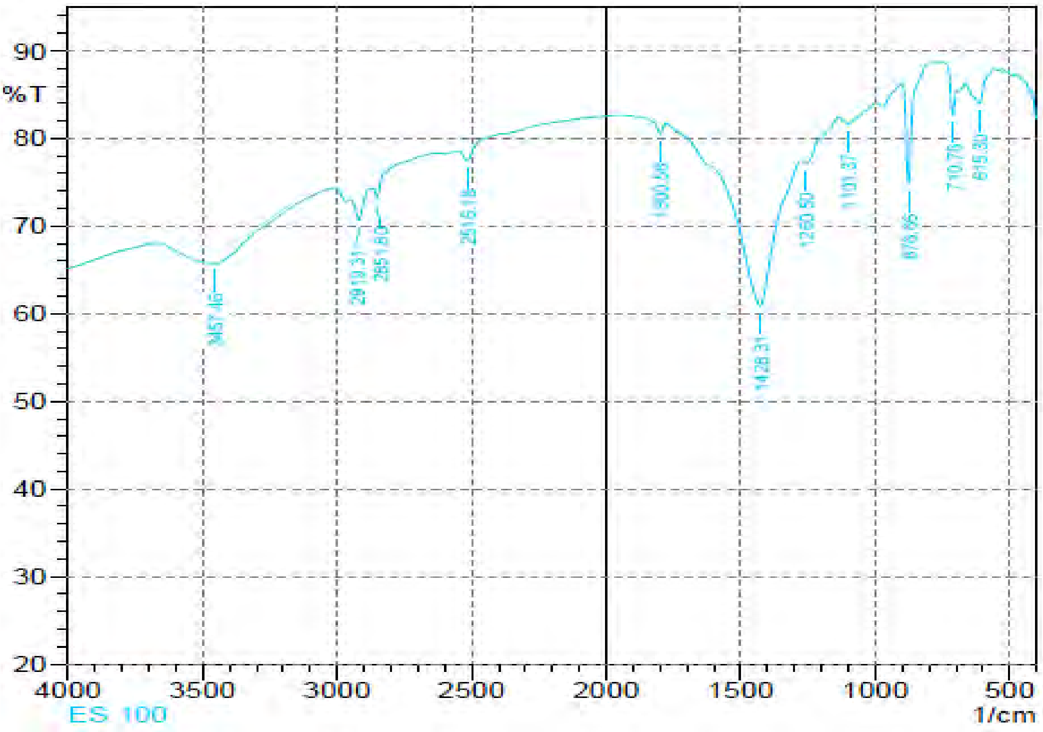
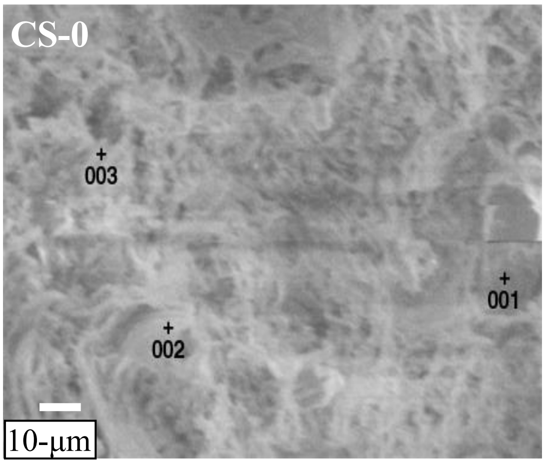


*Fig. 9.13 FTIR curve for uPVC of 100% (external scrap).*

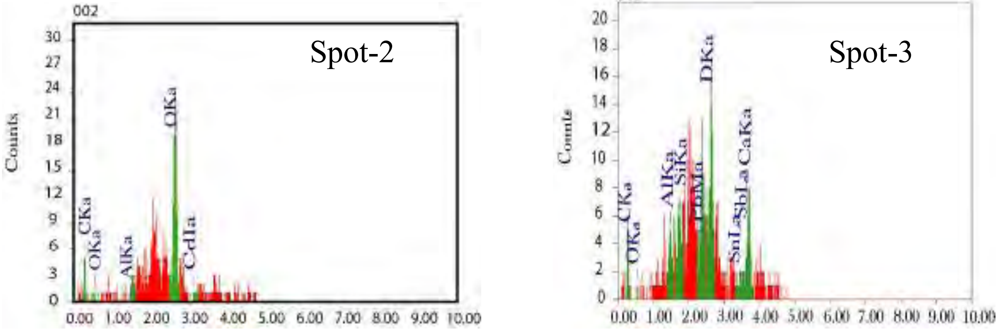
## 10. Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) Analysis

Table: 10.1: Results of energy dispersive spectroscopic spot analysis on samples containing virgin domestic scrap.

| Spot No | C | O | Si | S | Cl | Ca | Cd | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 27.45 | 1.86 | - | 3.21 | 54.51 | 8.40 | - | - | - | 4.57 |
| 2 | 9.59 | 0.46 | - | - | 51.49 | - | 5.49 | - | - | 31.81 |
| 3 | 3.45 | 0.13 | 1.06 | - | 13.93 | 39.43 | - | 8.96 | 7.89 | 24.29 |



(a) SEM Micrograph showing morphology of the fractured surface

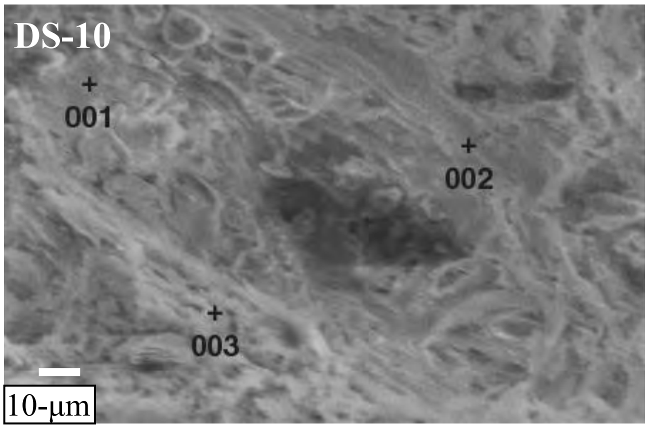


(b) EDS analysis showing peaks of different elements

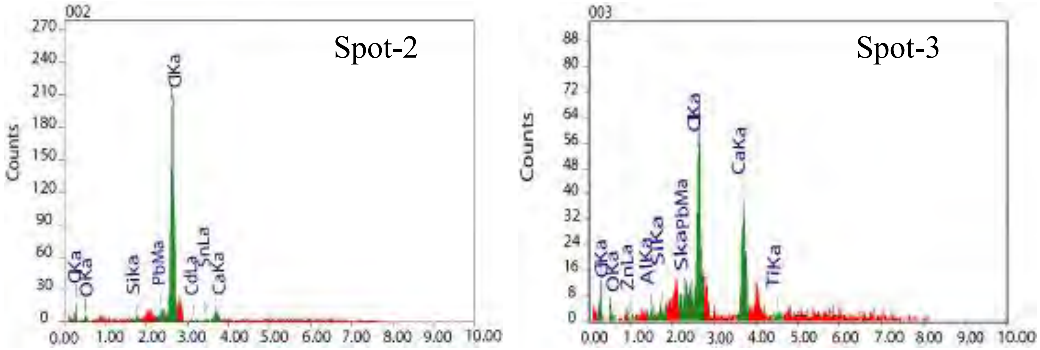
*Fig. 10.1: EDS analysis of different points of fractured surface of sample containing virgin domestic scrap*

Table: 10.2: Results of energy dispersive spectroscopic spot analysis on sample containing 10 phr domestic scrap

| Spot No | C | O | S | Cl | Ca | Zn | Cd | Sn | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 43.80 | 3.59 | 0.10 | 40.54 | 3.80 | 1.14 | 0.75 | - | 5.51 |
| 2 | 31.08 | 2.20 | - | 55.13 | 4.05 | - | 0.12 | 1.64 | 5.75 |
| 3 | 20.73 | 2.04 | 0.31 | 27.54 | 37.27 | 6.01 | - | - | 5.47 |



(a) SEM Micrograph showing morphology of the fractured surface

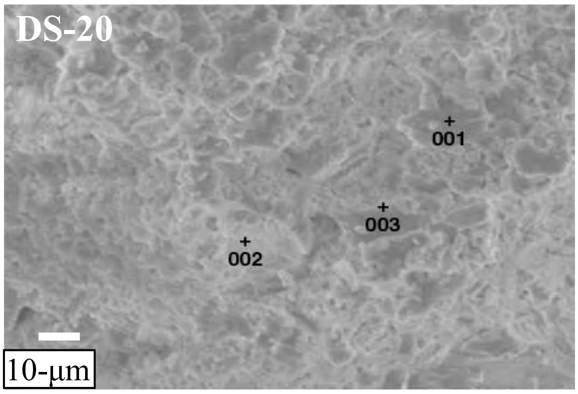


(b) EDS analysis showing peaks of different elements

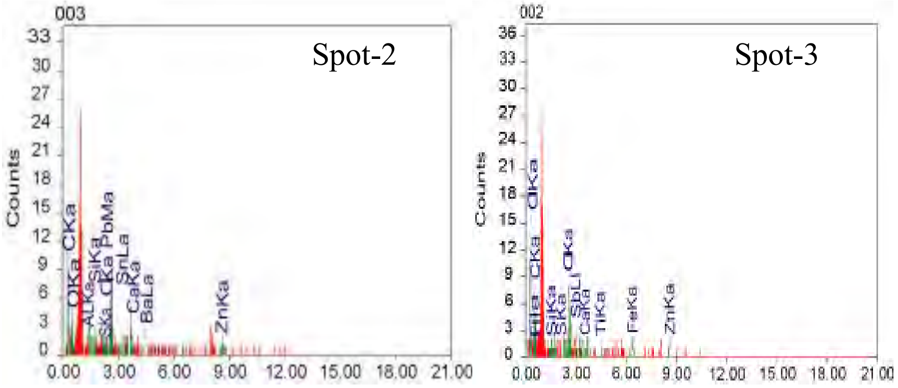
*Fig. 10.2: EDS analysis of different points of fractured surface of sample containing 10 phr domestic scrap*

Table: 10.3: Results of energy dispersive spectroscopic spot analysis on sample containing domestic scrap (20 phr)

| Spot No | C | O | Cl | Ca | Ti | Fe | Zn | Sn | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 64.57 | 4..59 | 5.45 | 1..31 | - | 0.89 | 14.66 | 0.75 | 5.96 |
| 2 | 73.15 | 12.24 | 6..30 | 1.08 | 0.02 | - | 2.37 | 1.27 | 2.15 |
| 3 | 67.42 | 5.70 | 7.12 | 3.44 | - | - | 1.81 | 4.56 | 8.01 |



(a) SEM Micrograph showing morphology of the fractured surface

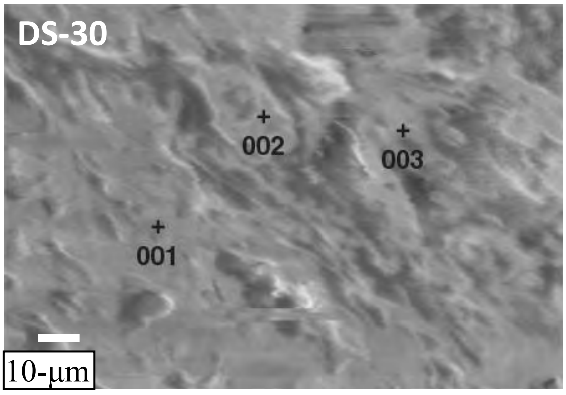


(b) EDS analysis showing peaks of different elements

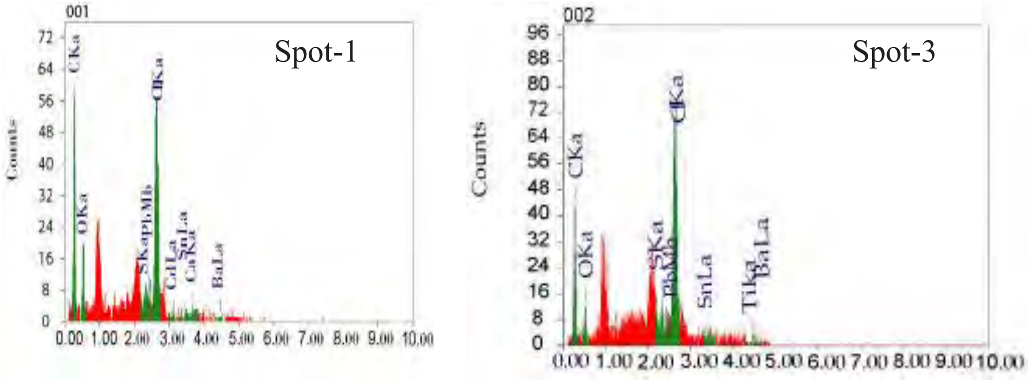
*Fig. 10.3: EDS analysis of different points of fractured surface of sample containing 20 phr domestic scrap*

Table: 10.4: Results of energy dispersive spectroscopic spot analysis on sample containing domestic scrap (30 phr)

| Spot No | C | O | S | Cl | Ca | Ti | Cd | Sn | Ba | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 60.92 | 10.85 | 0.48 | 19.40 | 1.37 | - | 0.77 | 0.03 | 1.48 | 4.71 |
| 2 | 41.20 | 5.79 | 1.56 | 24.85 | - | 0.87 | - | 0.93 | 1.12 | 3.70 |
| 3 | 66.98 | 7.32 | 0.21 | 16.22 | 1.85 | 0.72 | 0.00 | 1.08 | - | 4.66 |



(a) SEM Micrograph showing morphology of the fractured surface

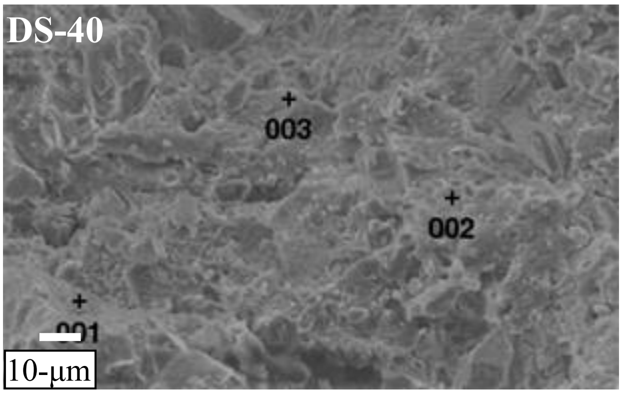


(b) EDS analysis showing peaks of different elements

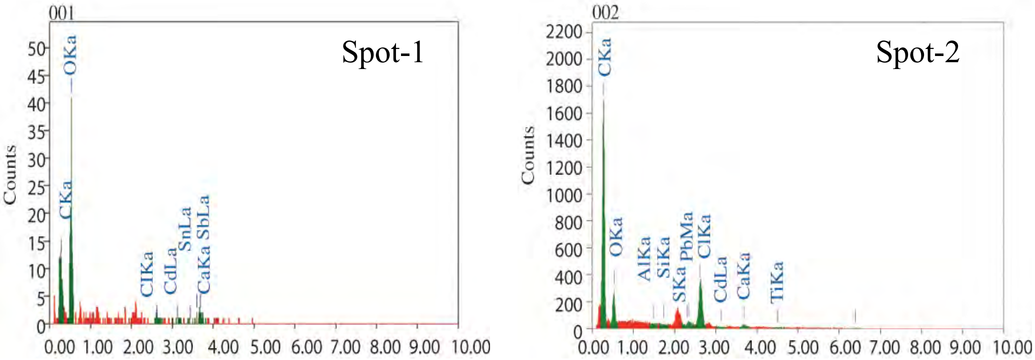
*Fig. 10.4: EDS analysis of different points of fractured surface of sample containing 30 phr domestic scrap*

Table: 10.5: Results of energy dispersive spectroscopic spot analysis on samples containing domestic scrap (40 phr

| Spot No | C | O | Cl | Ca | Ti | Fe | Cd | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 24.35 | 56.23 | 1.85 | 6.44 | - | - | 1.40 | 1.40 | 8.34 | - |
| 2 | 73.27 | 12.36 | 8.71 | 1.03 | 0.13 | 0.63 | 0.15 | - | - | 3.49 |
| 3 | 69.28 | 16.43 | 7.72 | 3.94 | 0.16 | - | 0.20 | - | - | 1.81 |



(a) SEM Micrograph showing morphology of the fractured surface

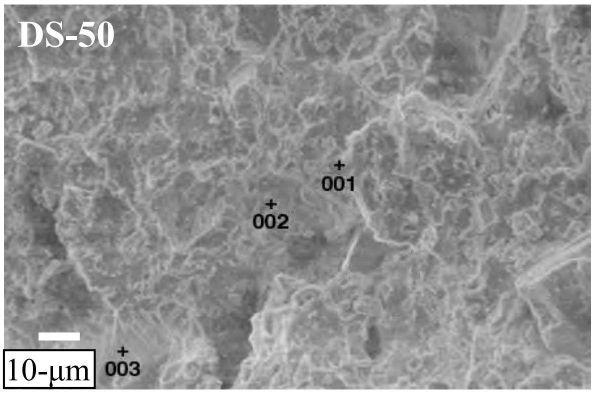


(b) EDS analysis showing peaks of different elements

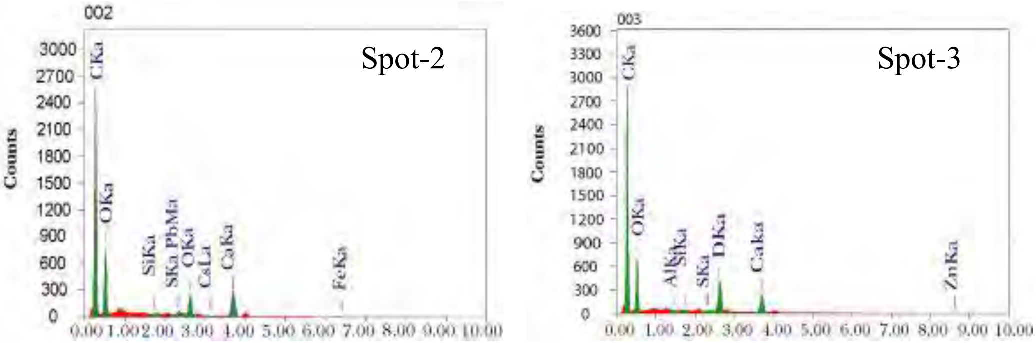
*Fig. 10.5: EDS analysis of different points of fractured surface of sample containing 40 phr domestic scrap*

Table: 10.6: Results of energy dispersive spectroscopic spot analysis on samples containing domestic scrap (50 phr)

| Spot No | C | O | Si | Cl | Ca | Ti | Cd | Pb |
|---|---|---|---|---|---|---|---|---|
| 1 | 51.01 | 28.88 | 0.16 | 2.68 | 15.06 | 0.06 | - | 1.81 |
| 2 | 77.36 | 13.53 | 0.06 | 2.47 | 5.00 | - | 0.12 | 1.27 |
| 3 | 80.98 | 10.52 | 0.01 | 3.72 | 3.73 | - | - | 0.84 |



(a) SEM Micrograph showing morphology of the fractured surface

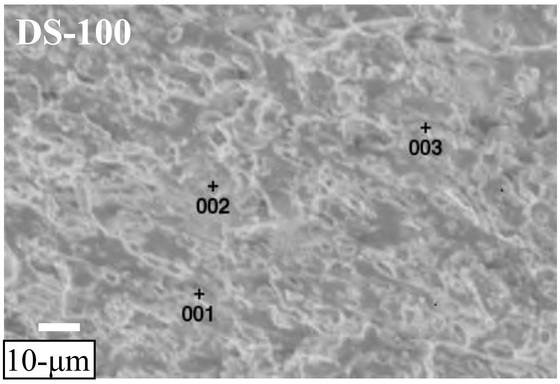


(b) EDS analysis showing peaks of different elements

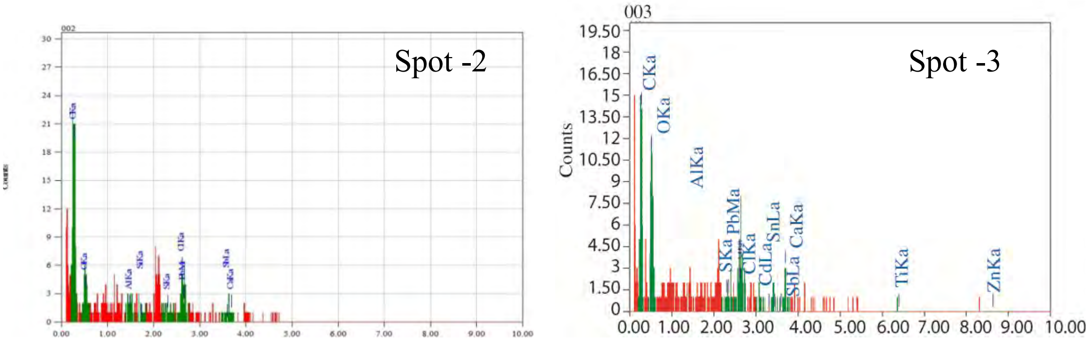
*Fig. 10.6: EDS analysis of different points of fractured surface of sample containing 50 phr domestic scrap*

Table: 10.7: Results of energy dispersive spectroscopic spot analysis on samples containing domestic scrap (100%)

| Spot No | C | O | Cl | Ca | Fe | Zn | Cd | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 52.31 | 38.48 | 3.77 | 3.65 | - | - | 1.74 | - | - |
| 2 | 65.27 | 12.98 | 7.65 | 2.70 | - | - | - | 6.26 | 4.29 |
| 3 | 40.76 | 20.97 | 3.94 | 3.02 | 1.84 | 25.05 | 0.38 | 0.66 | 1.83 |



(a) SEM Micrograph showing morphology of the fractured surface

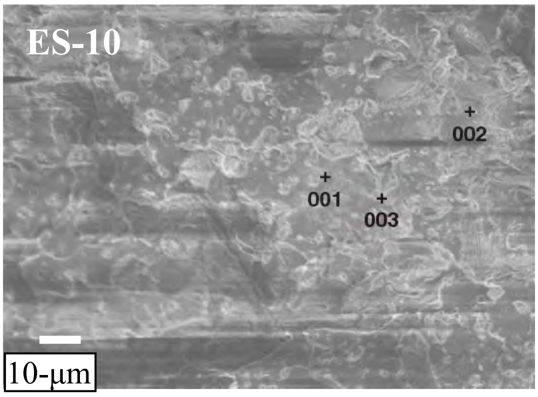


(b) EDS analysis showing peaks of different elements

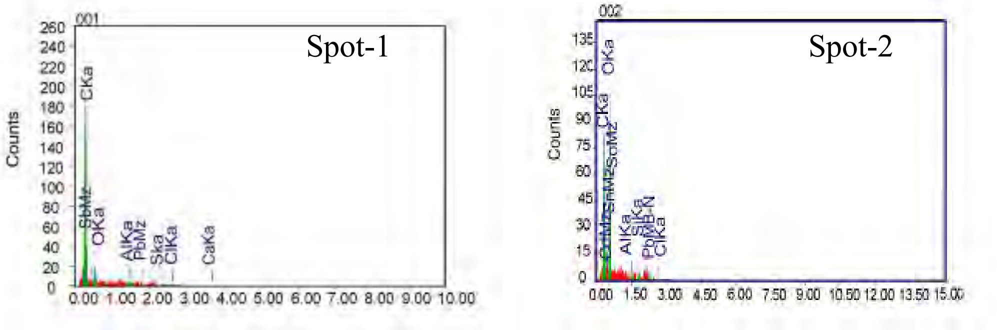
*Fig. 10.7: EDS analysis of different points of fractured surface of sample containing 100% domestic scrap*

Table: 10.8: Results of energy dispersive spectroscopic spot analysis on samples containing 10 phr external scrap.

| Spot No | C | O | Si | Cl | Ca | Cd | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 79.57 | 10.24 | - | 0.68 | 0.07 | - | - | 2.51 | 6.86 |
| 2 | 43.83 | 54.83 | 0.26 | 0.40 | - | 0.09 | 0.06 | 0.02 | 0.26 |
| 3 | 87.74 | 7.10 | - | 2.23 | - | 1.09 | 0.42 | 0.27 | 0.28 |



(a) SEM Micrograph showing morphology of the fractured surface

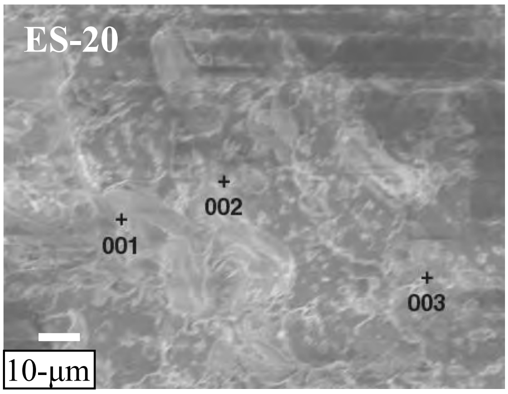


(b) EDS analysis showing peaks of different elements

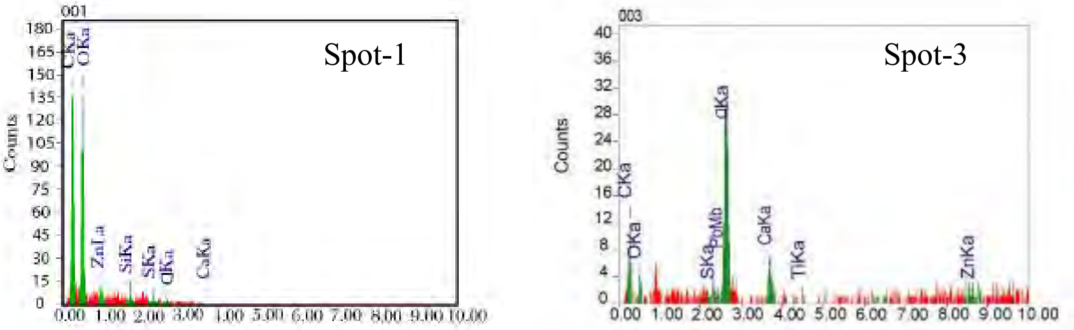
*Fig. 10.8: EDS analysis of different points of fractured surface of sample containing 10 phr external scrap*

Table: 10.9: Results of energy dispersive spectroscopic spot analysis on samples containing 20 phr external scrap

| **Spot No** | C | O | Cl | Ca | Zn | Cd | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 48.97 | 42.29 | 0.57 | 0.05 | 1.67 | - | - | - | 4.22 |
| **2** | 78.27 | 10.73 | 0.83 | 0.03 | - | - | 1.57 | 1.51 | 5.35 |
| **3** | 50.42 | 45.03 | 0.03 | - | - | 2.16 | 0.76 | - | - |



(a) SEM Micrograph showing morphology of the fractured surface

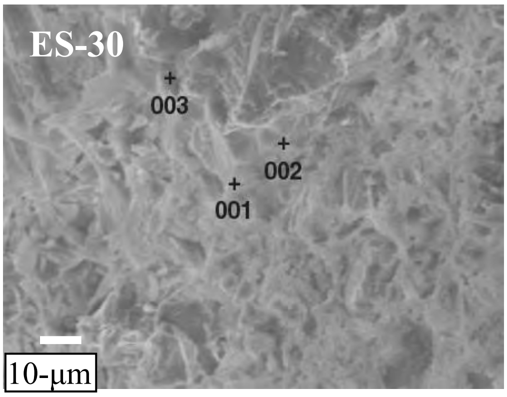


(b) EDS analysis showing peaks of different elements

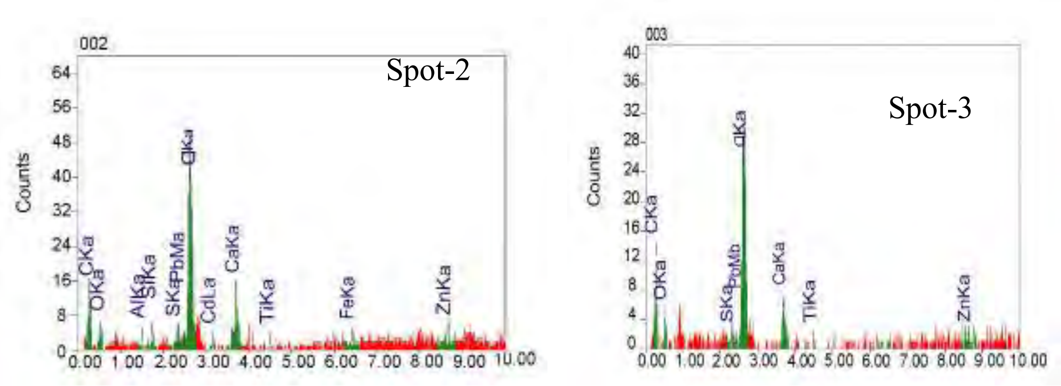
*Fig. 10.9: EDS analysis of different points of fractured surface of sample containing 20 phr external scrap*

Table: 10.10: Results of energy dispersive spectroscopic spot analysis on samples containing external scrap (30 phr)

| Spot No | C | O | Cl | Ca | Ti | Zn | Sn | Sb | Pb |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 56.90 | 3.96 | 21.98 | 10.68 | - | - | 2.42 | 2.94 | - |
| 2 | 54.91 | 2.64 | 16.89 | 6.26 | 0.20 | 12.40 | - | 1.84 | 3.46 |
| 3 | 61.77 | 4.12 | 19.19 | 6.45 | 0.52 | 4.78 | - | - | 2.80 |



(a) SEM Micrograph showing morphology of the fractured surface

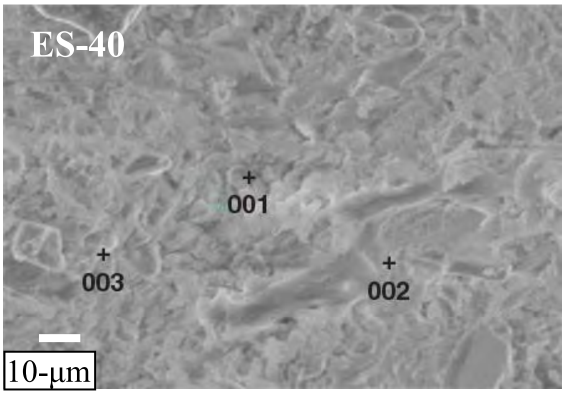


(b) EDS analysis showing peaks of different elements

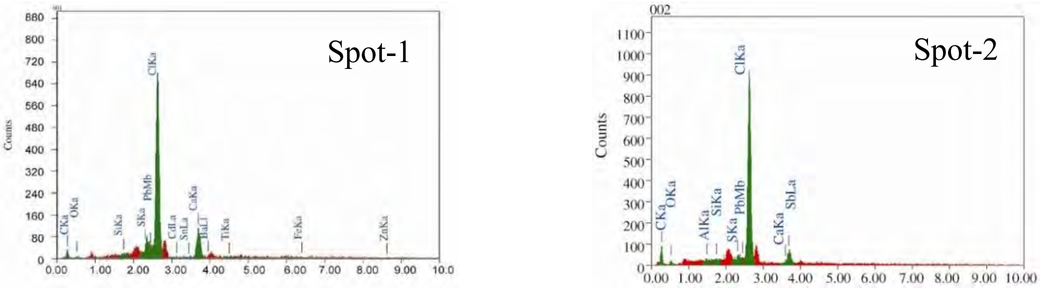
*Fig. 10.10: EDS analysis of different points of fractured surface of sample containing 30 phr external scrap*

Table: 10.11: Results of energy dispersive spectroscopic spot analysis on samples containing 40 phr external scrap

| Spot No | C | O | S | Cl | Ca | Ba | Pb |
|---|---|---|---|---|---|---|---|
| 1 | 30.61 | 0.69- | 0.28 | 42.27 | 12.93 | 0.18 | 12.67 |
| 2 | 55.92 | 1.18 | 0.35 | 33.77 | 4.28 | - | 3.87 |
| 3 | 71.47 | 1.59 | 0.18 | 19.00 | 4.23 | 2.67 | - |



(a) SEM Micrograph showing morphology of the fractured surface

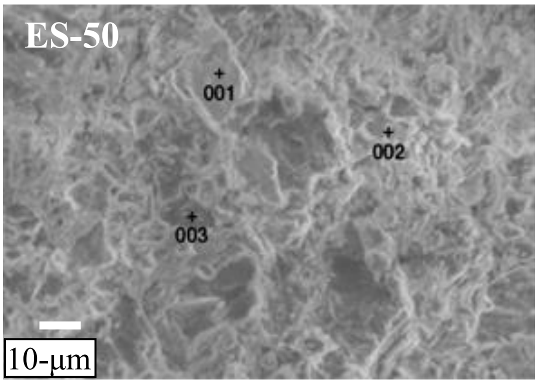


(b) EDS analysis showing peaks of different elements

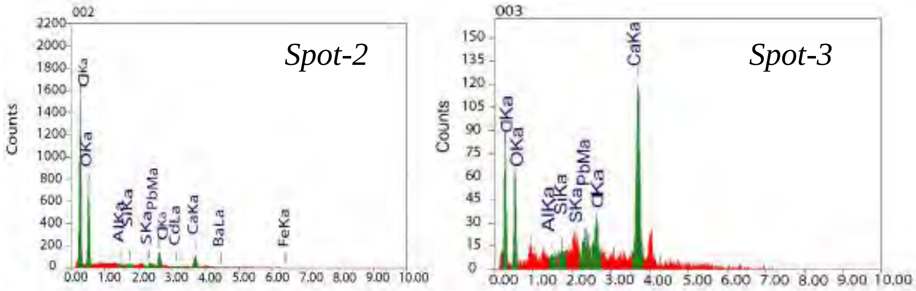
*Fig. 10.12: EDS analysis of different points of fractured surface of sample containing 40 phr external scrap*

Table: 10.12: Results of energy dispersive spectroscopic spot analysis on samples containing external scrap (50 phr)

| Spot No | C | O | Cl | Ca | Pb |
|---|---|---|---|---|---|
| 1 | 65.82 | 19.78 | 7.63 | 1.89 | 2.50 |
| 2 | 55.89 | 31.13 | 3.46 | 5.60 | 3.05 |
| 3 | 24.13 | 24.12 | 4.37 | 42.51 | 3.65 |



(a) SEM Micrograph showing morphology of the fractured surface

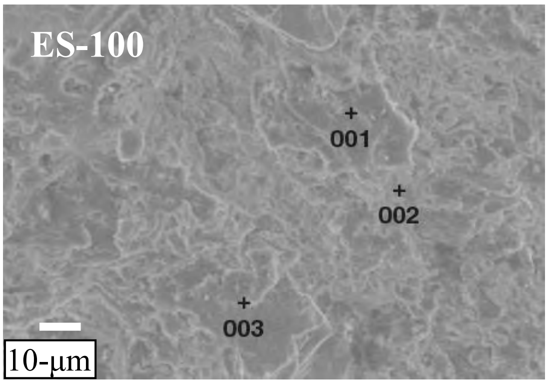


(b) EDS analysis showing peaks of different elements

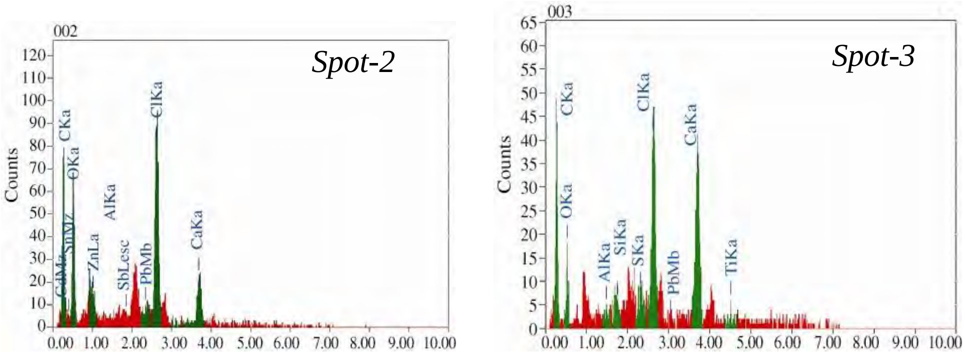
*Fig. 10.12: EDS analysis of different points of fractured surface of sample containing 50 phr external scrap*

Table: 10.13: Results of Energy Dispersive Spectroscopic Spot Analysis on samples containing External Scrap (100%)

| Spot No | C | O | S | Cl | Ca | Ti | Pb |
|---|---|---|---|---|---|---|---|
| 1 | 59.86 | 5.60 | - | 21.83 | 5.41 | 0.92 | 5.72 |
| 2 | 44.78 | 22.69 | - | 19.46 | 8.50 | - | 2.38 |
| 3 | 39.75 | 9.90 | 1.30 | 16.21 | 26.84 | 1.73 | 3.27 |



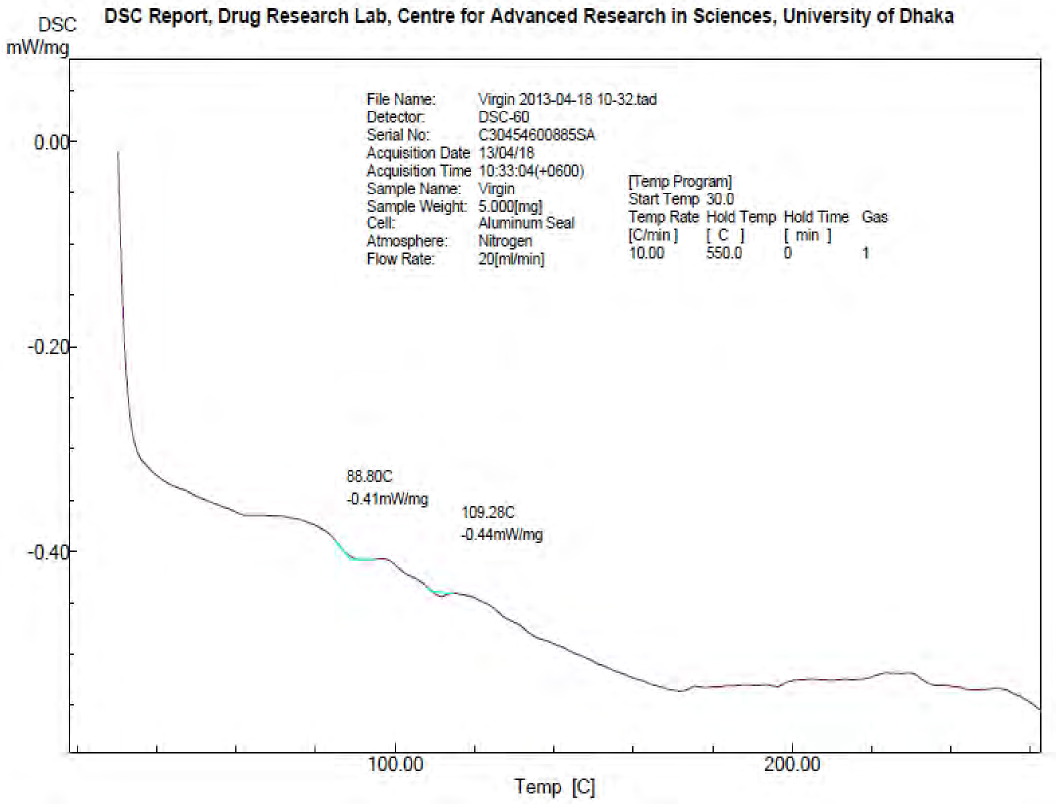
(a) SEM Micrograph showing morphology of the fractured surface



(b) EDS analysis showing peaks of different elements

*Fig. 10.13: EDS analysis of different points of fractured surface of sample containing 100% external scrap*

## 11. Differential Scanning Calorimetric (DSC)

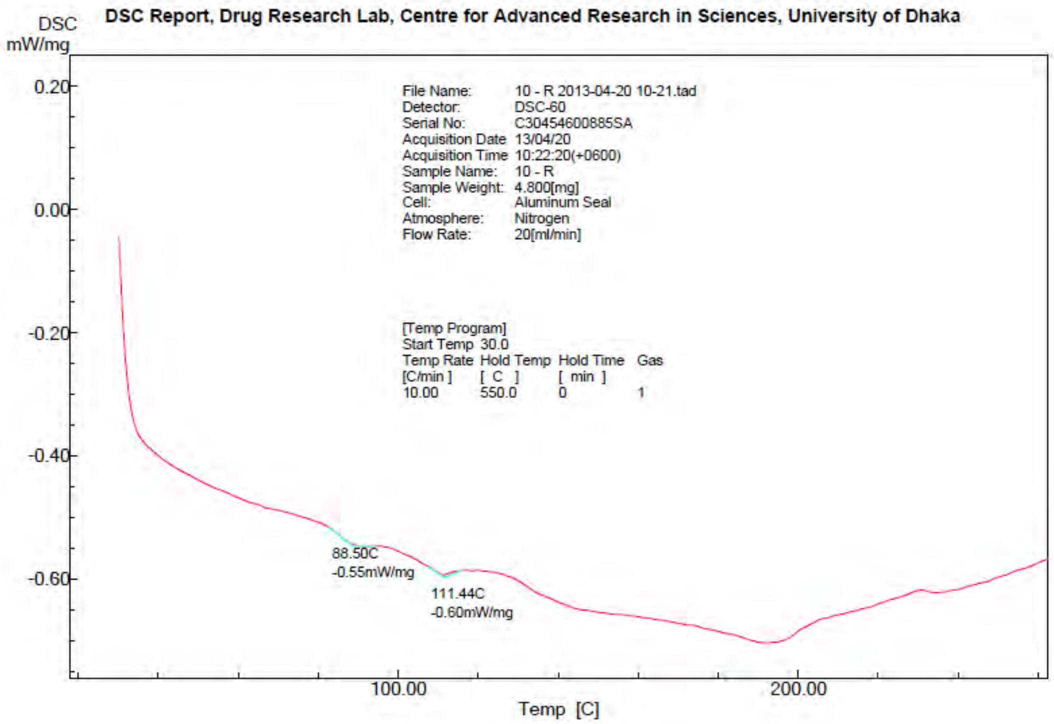


File Name: Virgin 2013-04-18 10-32.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/04/18
Acquisition Time 10:33:04(+0600)
Sample Name: Virgin
Sample Weight: 5.000[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate [C/min ] | Hold Temp [ C ] | Hold Time [ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 0 | 1 |

*Fig. 11.1 DSC curve of uPVC (no scrap addition)*

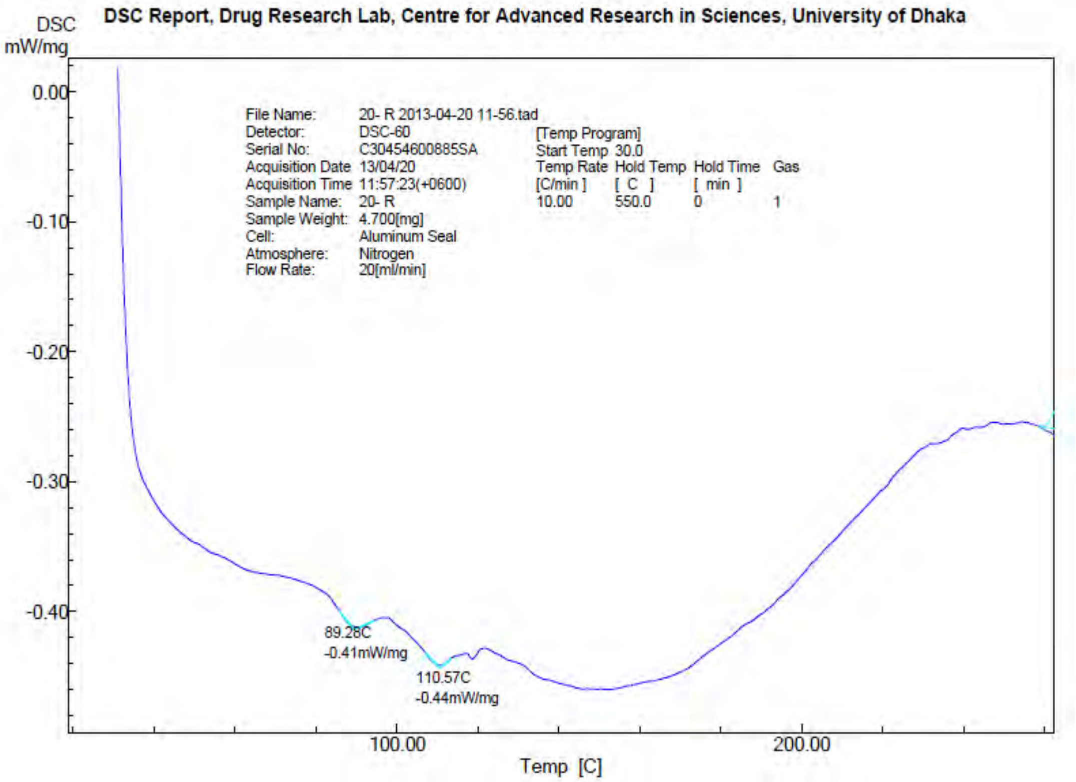


File Name: 10 - R 2013-04-20 10-21.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/04/20
Acquisition Time 10:22:20(+0600)
Sample Name: 10 - R
Sample Weight: 4.800[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate [C/min ] | Hold Temp [ C ] | Hold Time [ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 0 | 1 |

*Fig. 11.2 DSC curve of recycled uPVC (10 phr domestic scrap)*

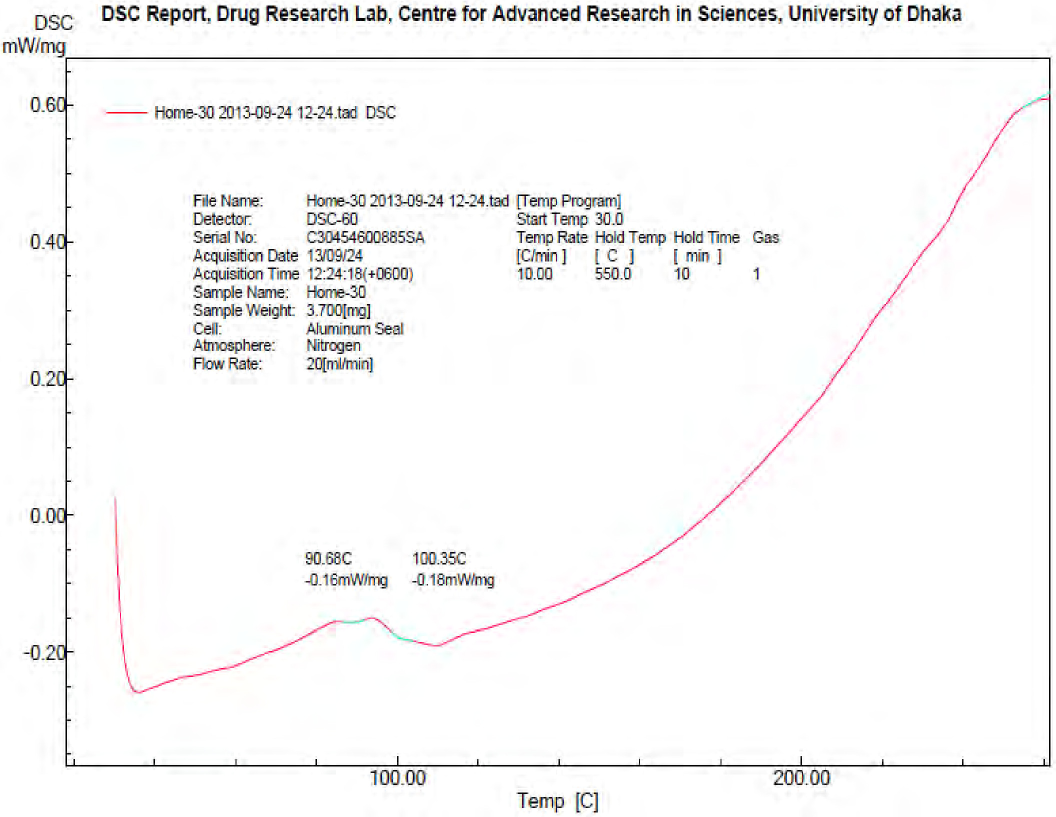


File Name: 20- R 2013-04-20 11-56.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/04/20
Acquisition Time 11:57:23(+0600)
Sample Name: 20- R
Sample Weight: 4.700[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate [C/min ] | Hold Temp [ C ] | Hold Time [ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 0 | 1 |

*Fig. 11.3 DSC curve of recycled uPVC (20 phr domestic scrap)*



File Name: Home-30 2013-09-24 12-24.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/09/24
Acquisition Time 12:24:18(+0600)
Sample Name: Home-30
Sample Weight: 3.700[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate [C/min ] | Hold Temp [ C ] | Hold Time [ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 10 | 1 |

*Fig. 11.4 DSC curve of recycled uPVC (30 phr domestic scrap)*

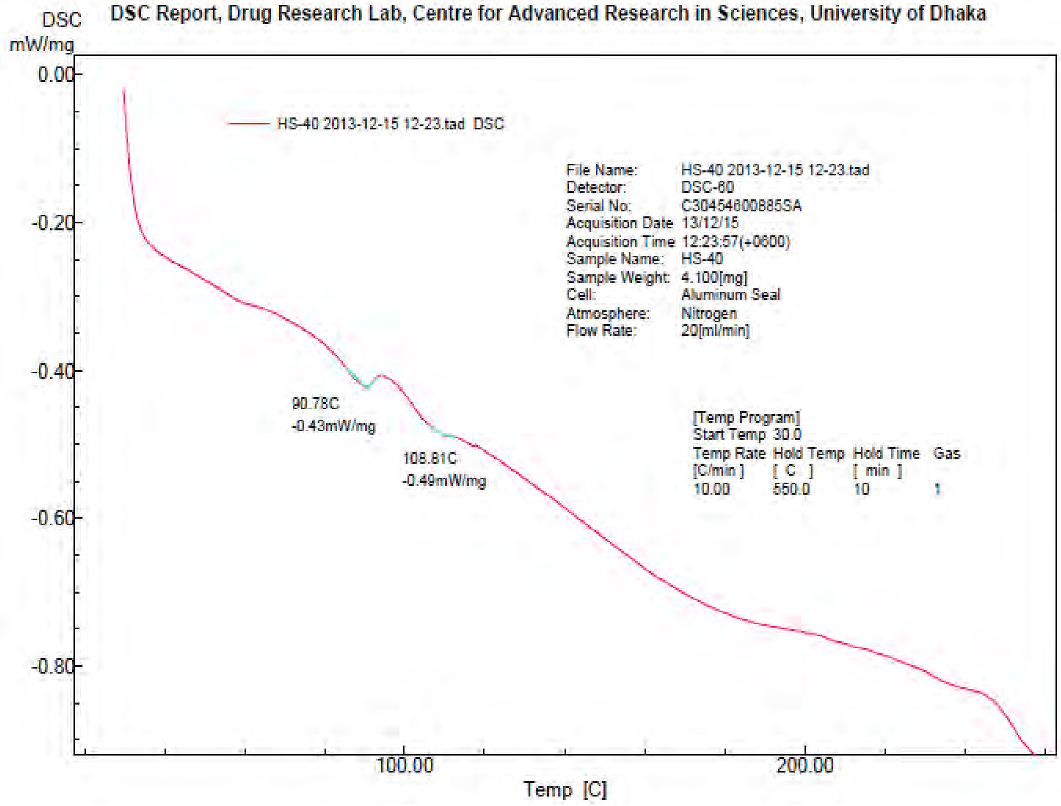
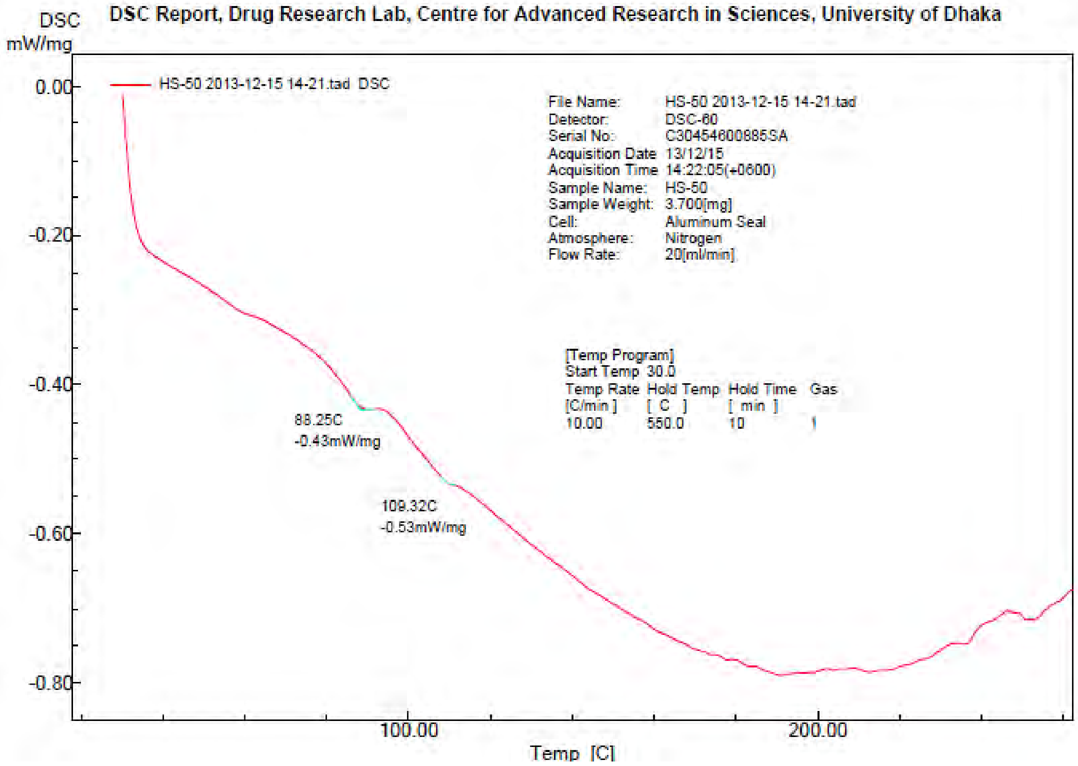


*Fig. 11.5 DSC curve of recycled uPVC (40 phr domestic scrap)*



*ig. 11.6 DSC curve of recycled uPVC (50 phr domestic scrap)*

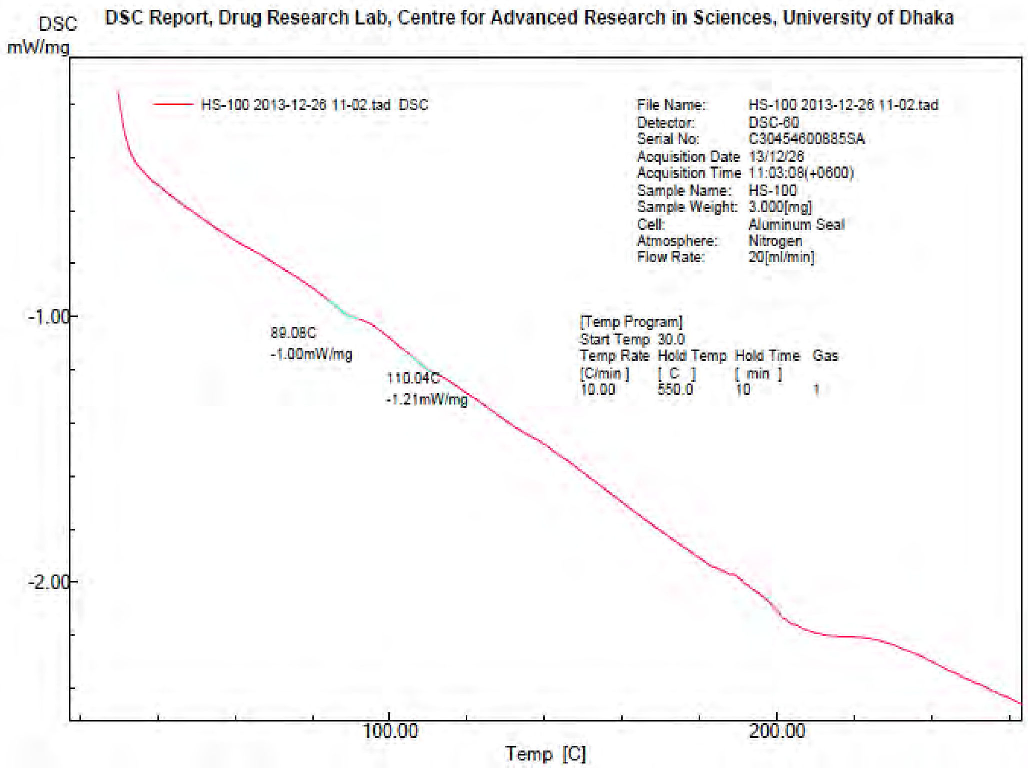


*Fig. 11.7 DSC curve of recycled uPVC (100% domestic scrap)*

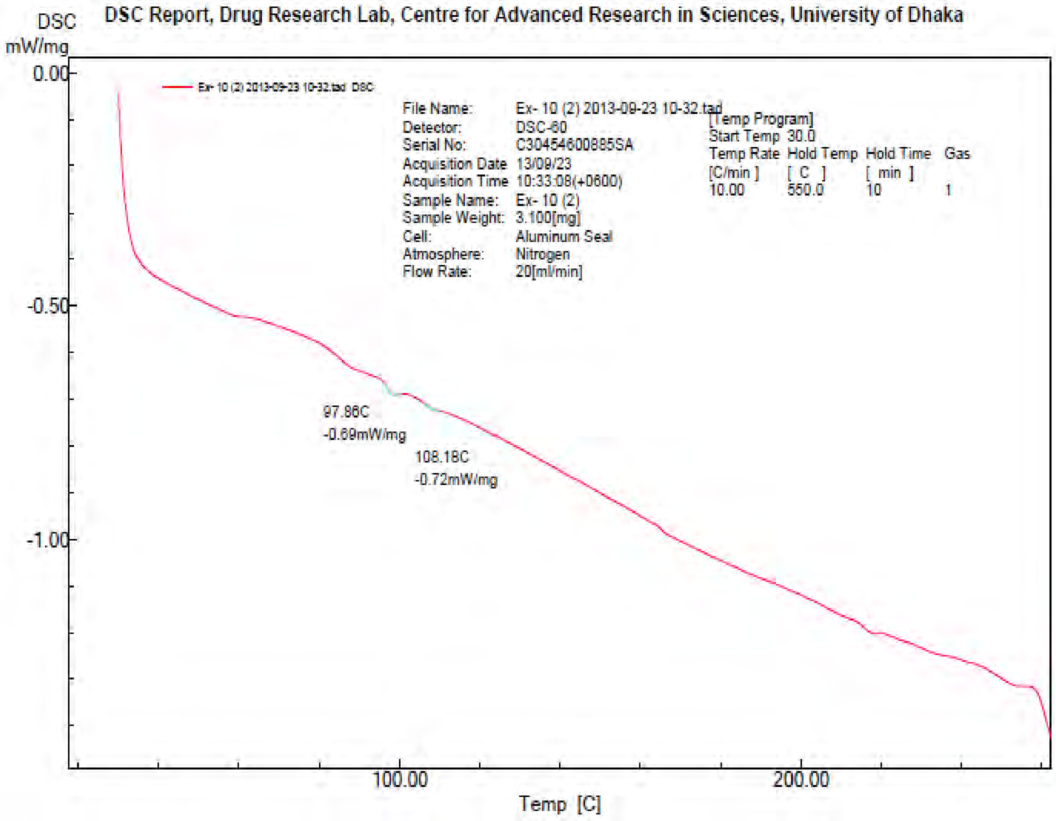


*Fig. 11.8 DSC curve for uPVC having 10phr scrap (external)*

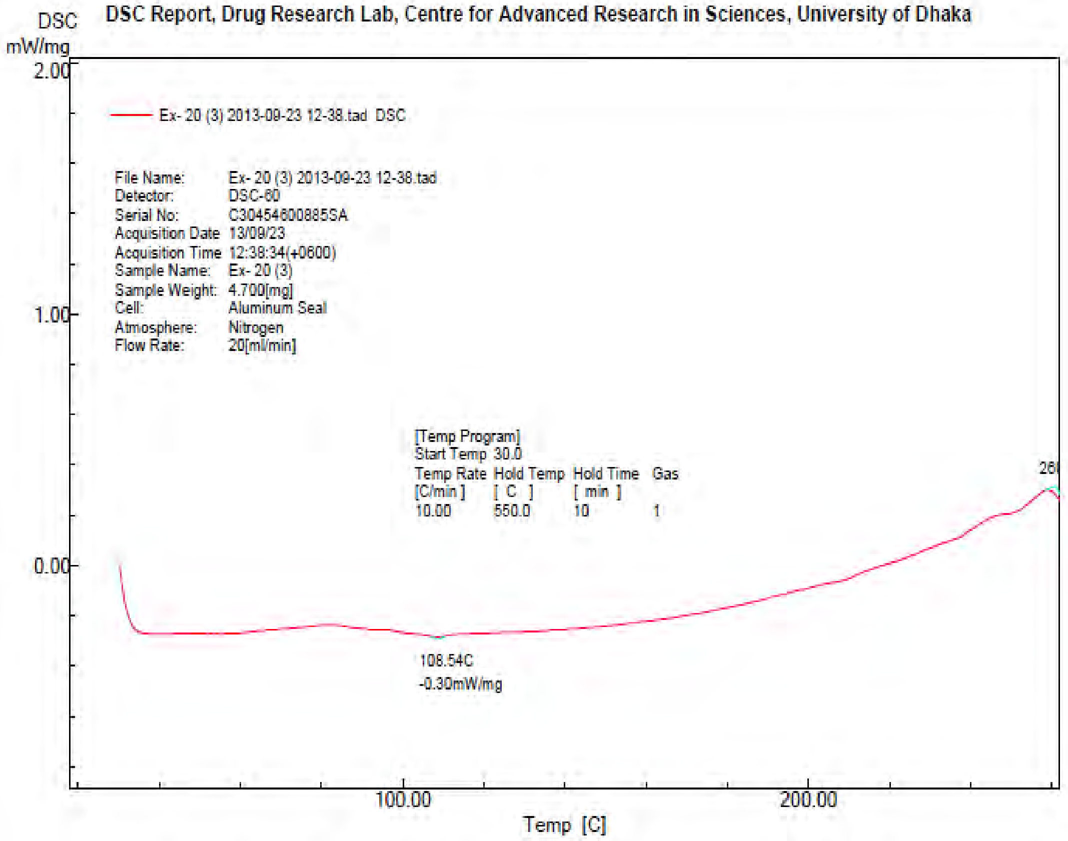


*Fig. 11.9 DSC curve for uPVC having 20phr scrap (external)*

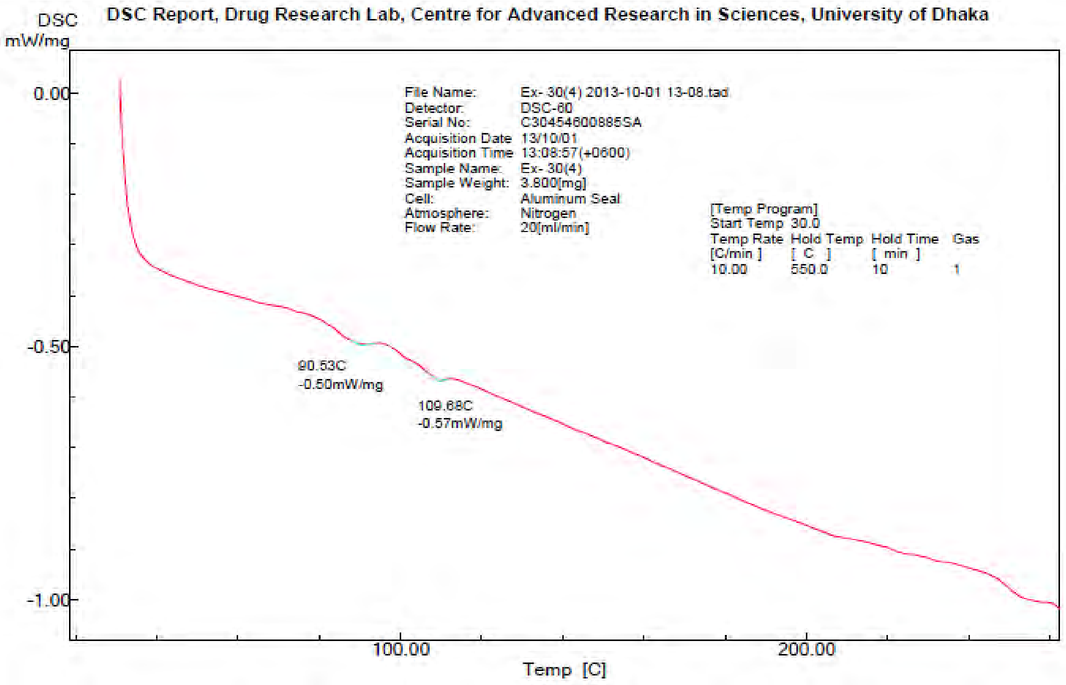
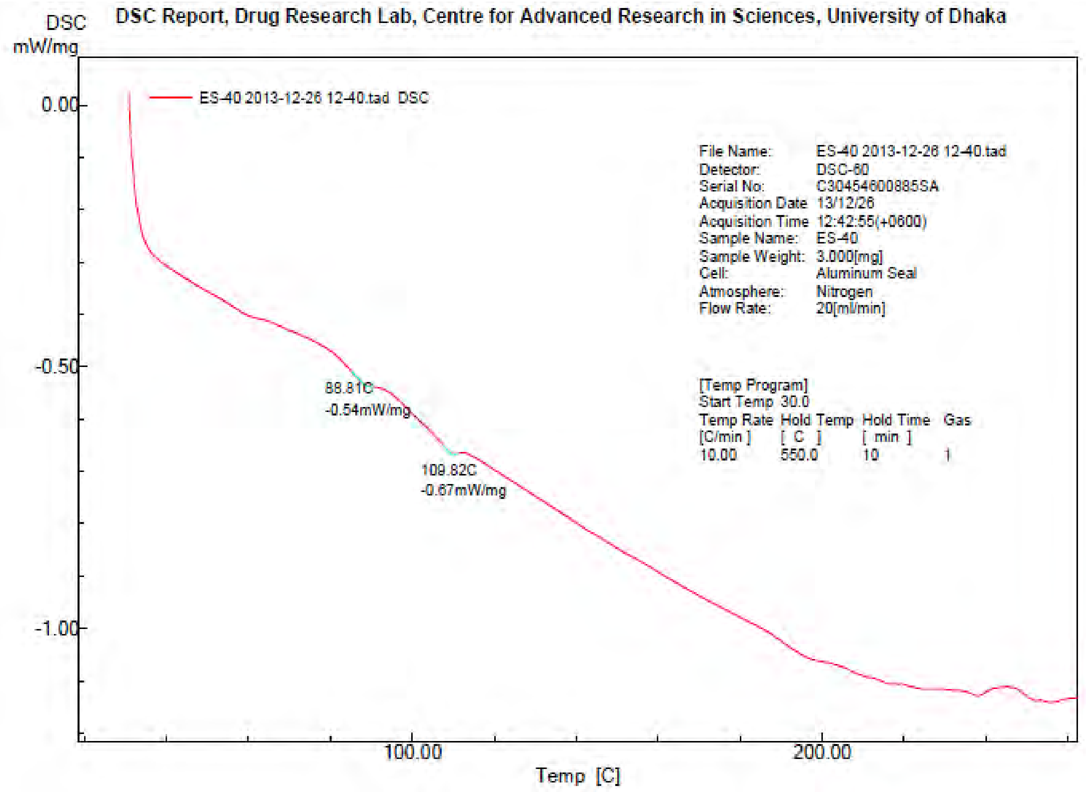


*Figure 11.10 DSC curve for uPVC having 30phr scrap (external)*

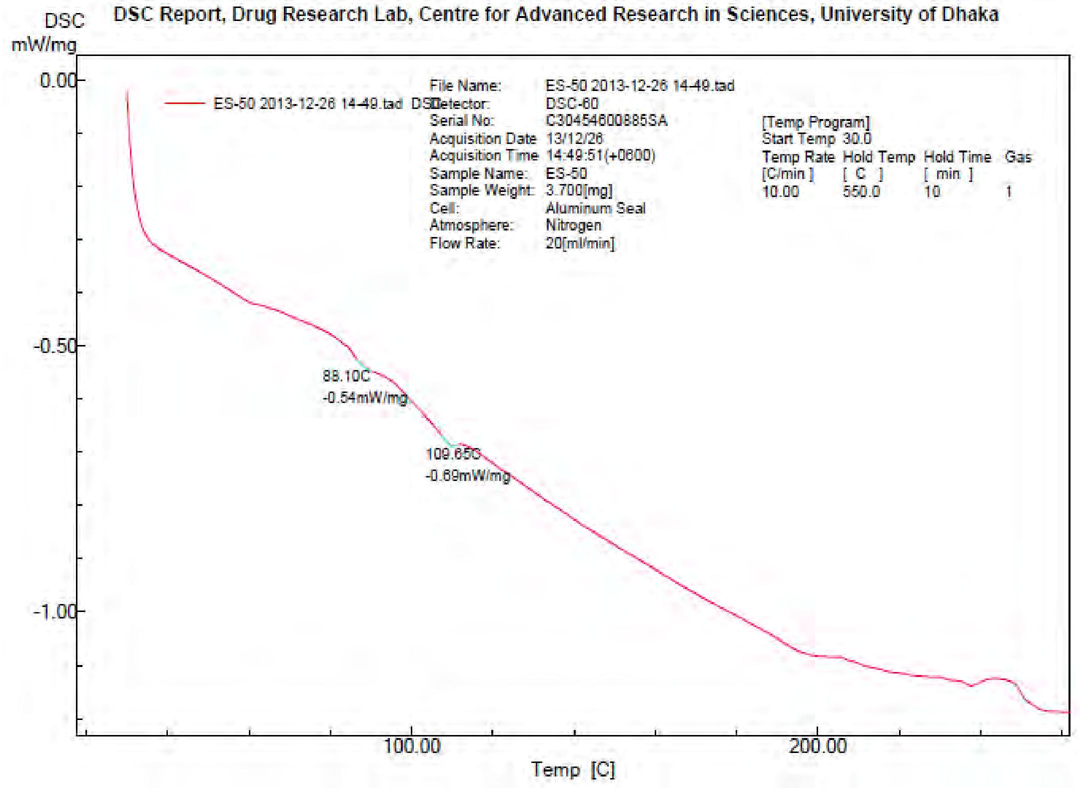


File Name: ES-40 2013-12-26 12-40.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/12/26
Acquisition Time 12:42:55(+0600)
Sample Name: ES-40
Sample Weight: 3.000[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate<br>[C/min ] | Hold Temp<br>[ C ] | Hold Time<br>[ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 10 | 1 |

*Figure 11.11 DSC curve for uPVC having 40phr scrap (external)*

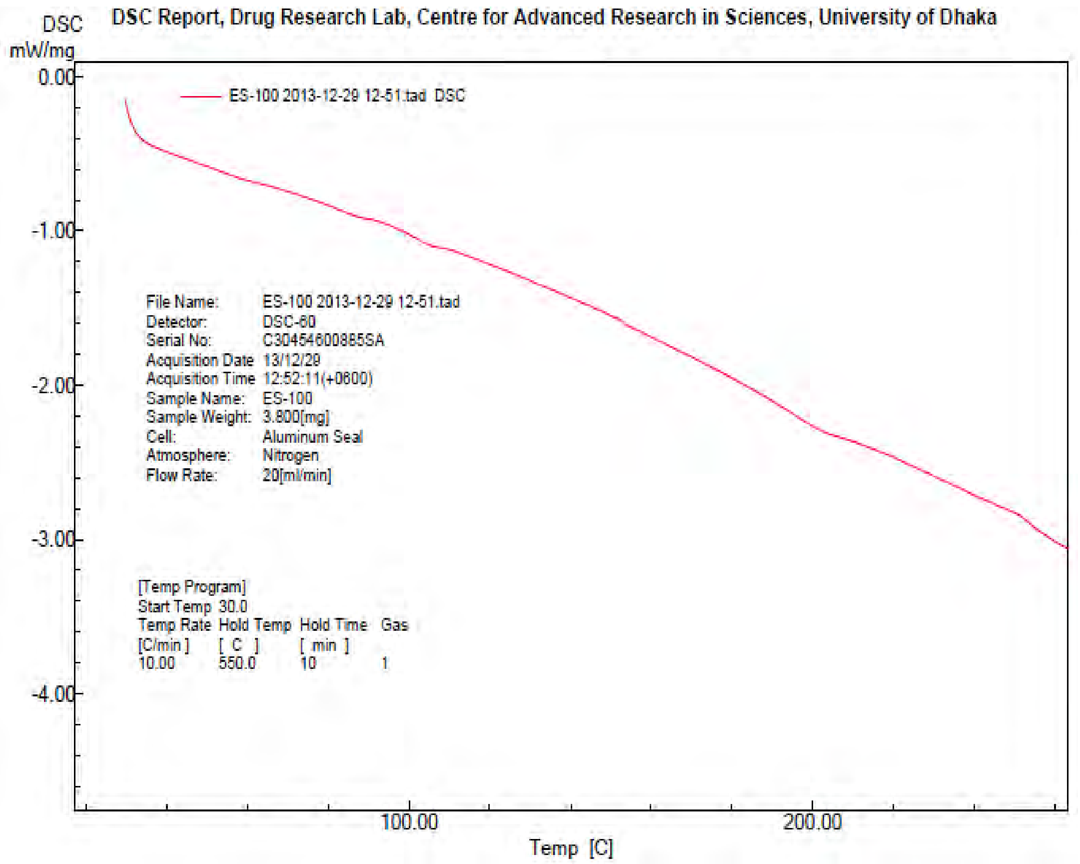


File Name: ES-50 2013-12-26 14-49.tad
Detector: DSC-60
Serial No: C30454600885SA
Acquisition Date 13/12/26
Acquisition Time 14:49:51(+0600)
Sample Name: ES-50
Sample Weight: 3.700[mg]
Cell: Aluminum Seal
Atmosphere: Nitrogen
Flow Rate: 20[ml/min]

[Temp Program]
Start Temp 30.0

| Temp Rate<br>[C/min ] | Hold Temp<br>[ C ] | Hold Time<br>[ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 10 | 1 |

*Figure 11.12 DSC curve for uPVC having 50phr scrap (external)*



| | |
|---|---|
| File Name: | ES-100 2013-12-29 12-51.tad |
| Detector: | DSC-60 |
| Serial No: | C30454600885SA |
| Acquisition Date | 13/12/29 |
| Acquisition Time | 12:52:11(+0600) |
| Sample Name: | ES-100 |
| Sample Weight: | 3.800[mg] |
| Cell: | Aluminum Seal |
| Atmosphere: | Nitrogen |
| Flow Rate: | 20[ml/min] |

[Temp Program]
Start Temp 30.0

| Temp Rate [C/min ] | Hold Temp [ C ] | Hold Time [ min ] | Gas |
|---|---|---|---|
| 10.00 | 550.0 | 10 | 1 |

*Figure 11.13 DSC curve for uPVC having 100% scrap (external)*

## 12. Thermo-mechanical Analysis (TMA)

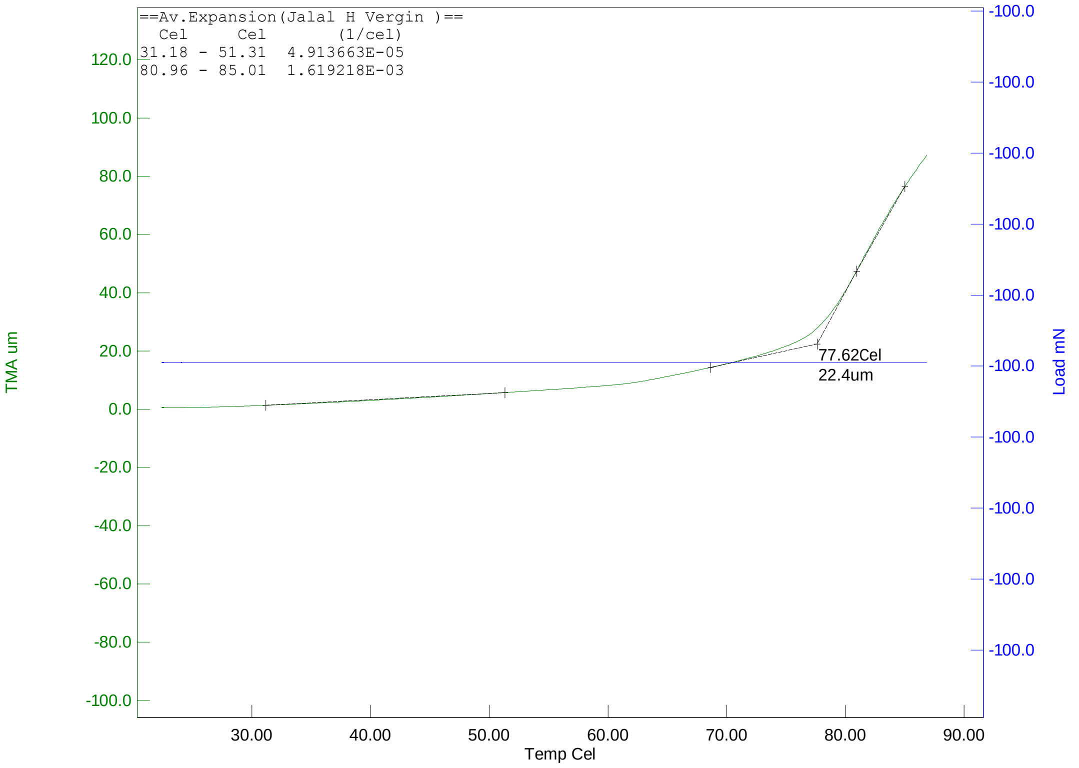


*Fig.12.1 TMA curve of virgin uPVC*

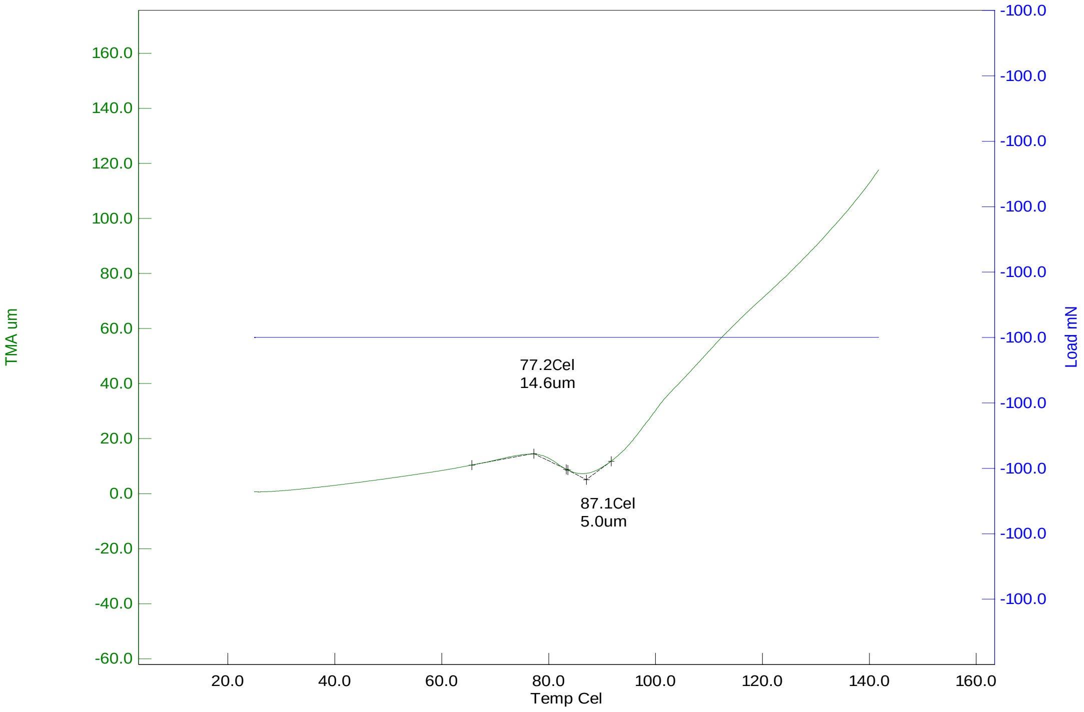
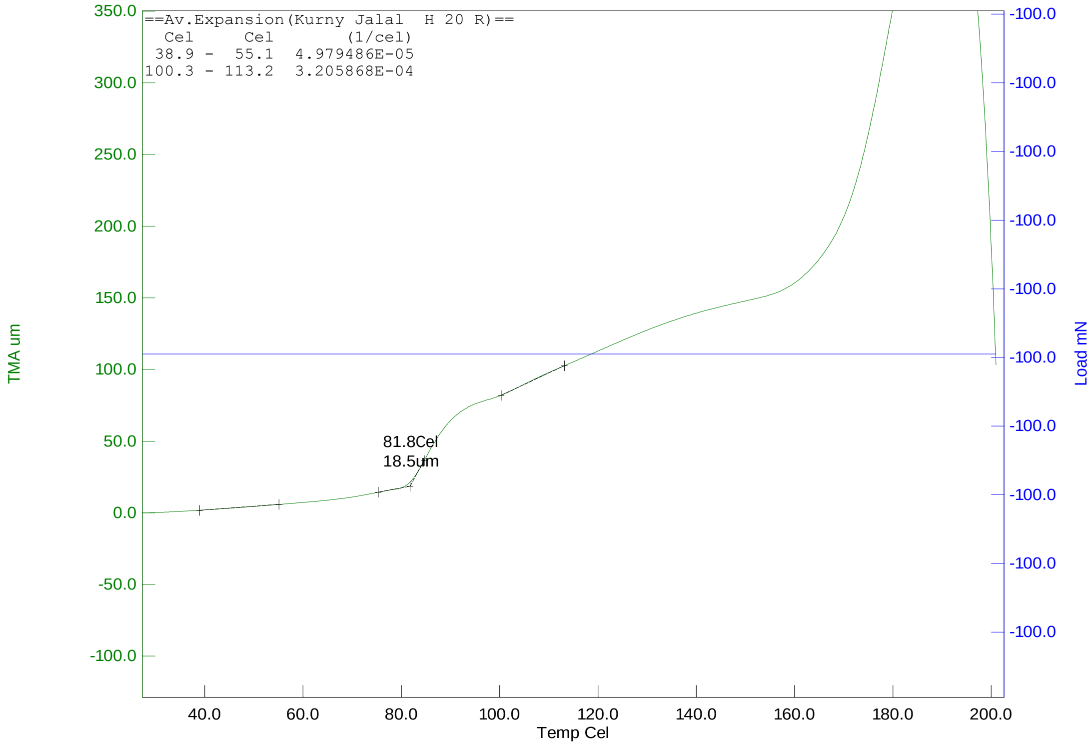
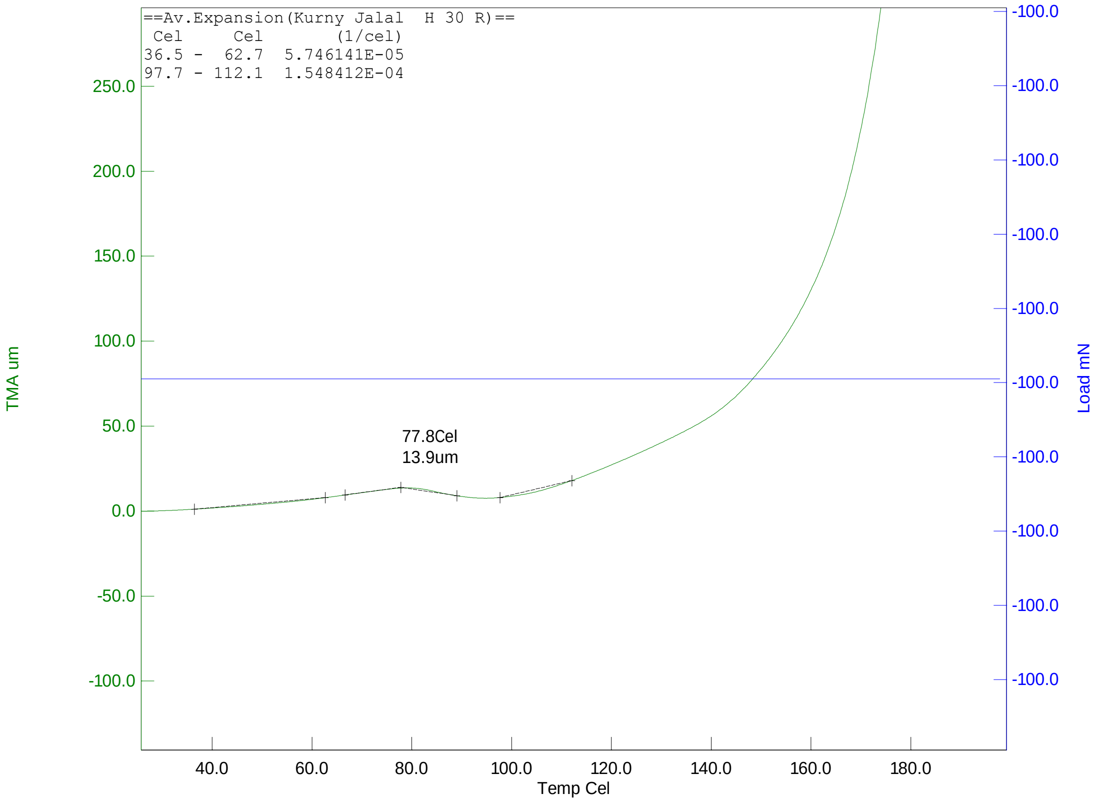


*Fig.12.2 TMA curve of recycled uPVC (10 phr domestic scrap)*



```
==Av.Expansion(Kurny Jalal  H 20 R)==
  Cel      Cel        (1/cel)
 38.9 -   55.1  4.979486E-05
100.3 - 113.2  3.205868E-04
```

*Fig.12.3 TMA curve of recycled uPVC (20 phr domestic scrap)*



```
==Av.Expansion(Kurny Jalal  H 30 R)==
 Cel      Cel        (1/cel)
36.5 -   62.7  5.746141E-05
97.7 - 112.1  1.548412E-04
```

*Fig.12.4 TMA curve of recycled uPVC (30 phr domestic scrap)*

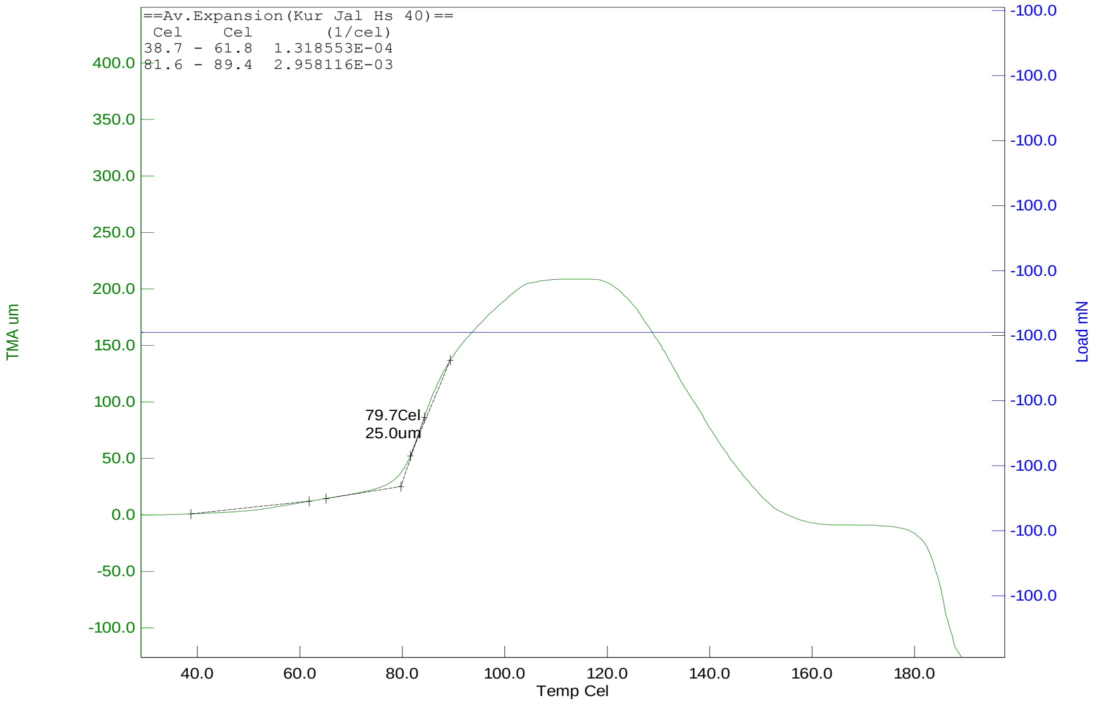


*Fig.12.5 TMA curve of recycled uPVC (40 phr domestic scrap)*

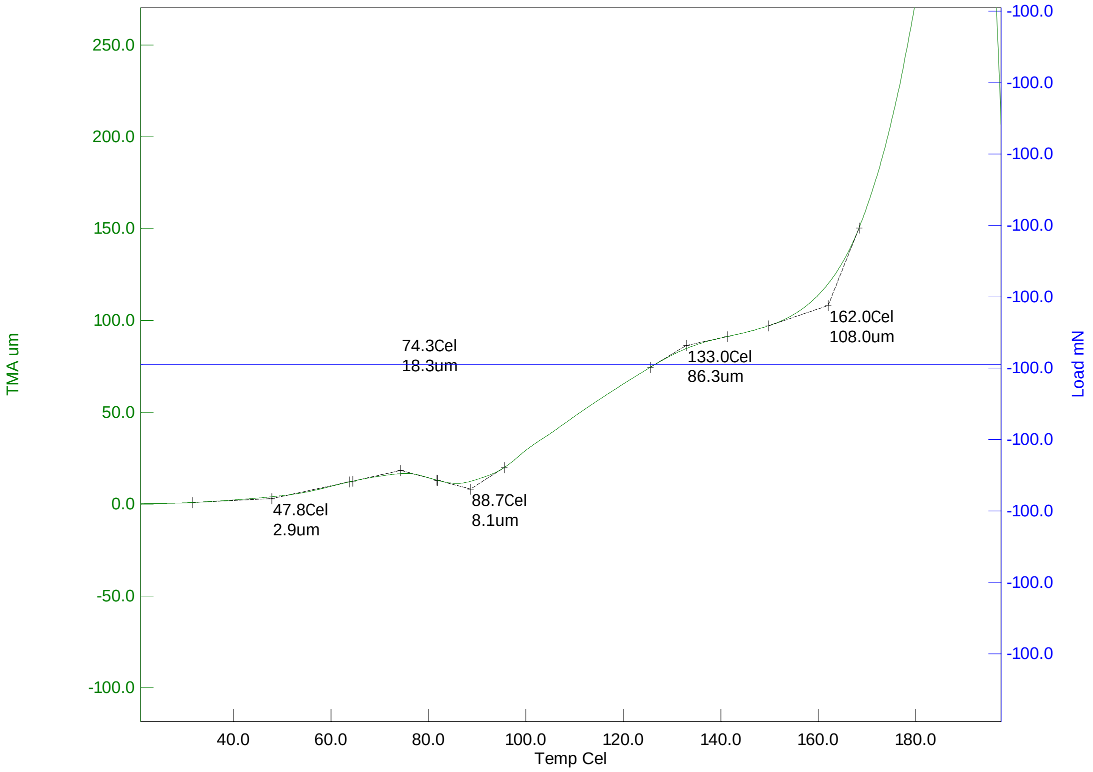


*Fig.12.6 TMA curve of recycled uPVC (50 phr domestic scrap)*

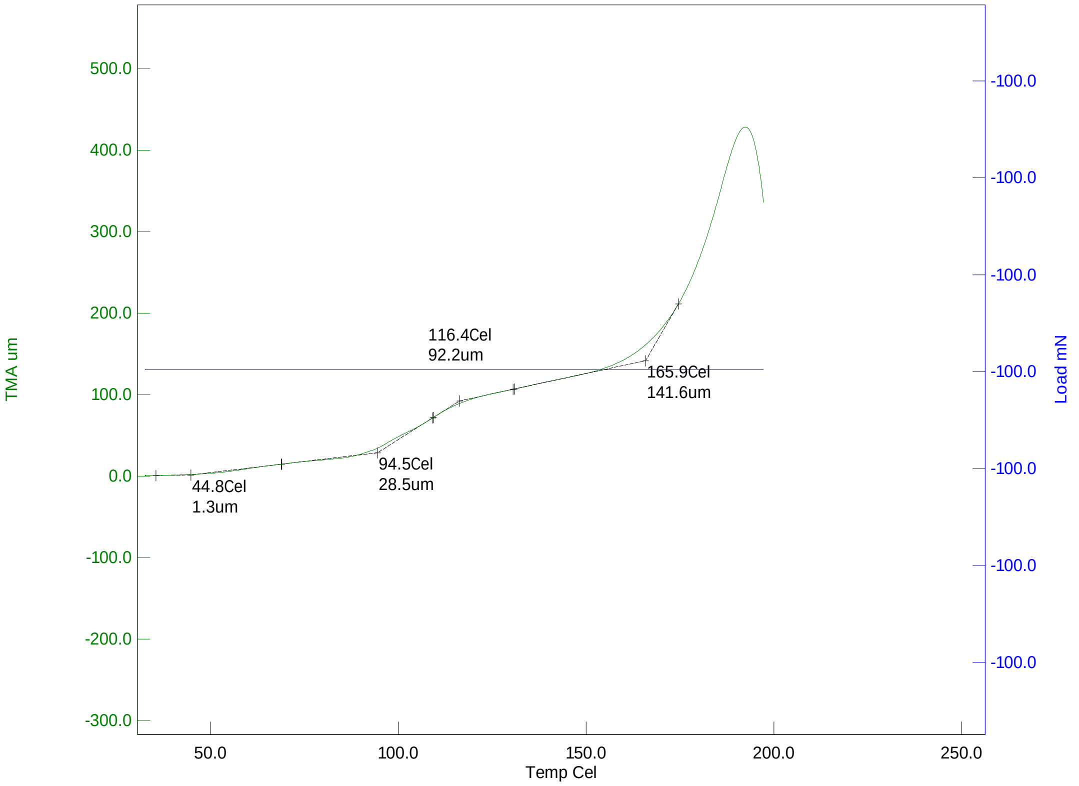


*Fig.12.7 TMA curve of recycled uPVC (100% domestic scrap)*

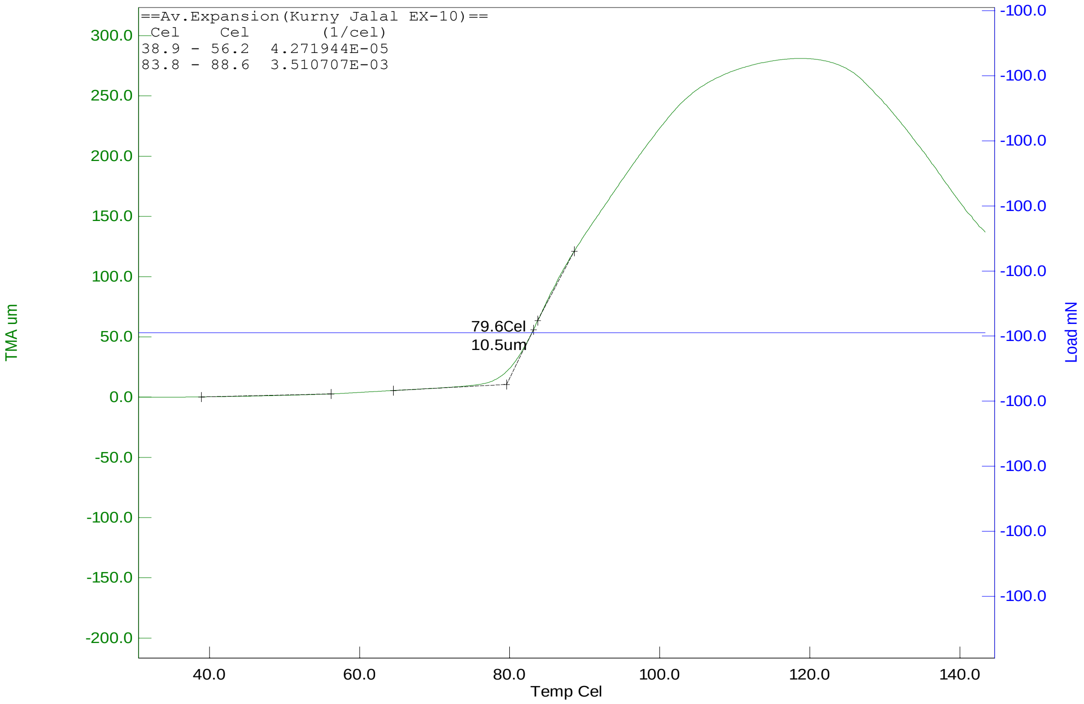


*Fig.12.8 TMA curve of recycled uPVC (10 phr external scrap)*

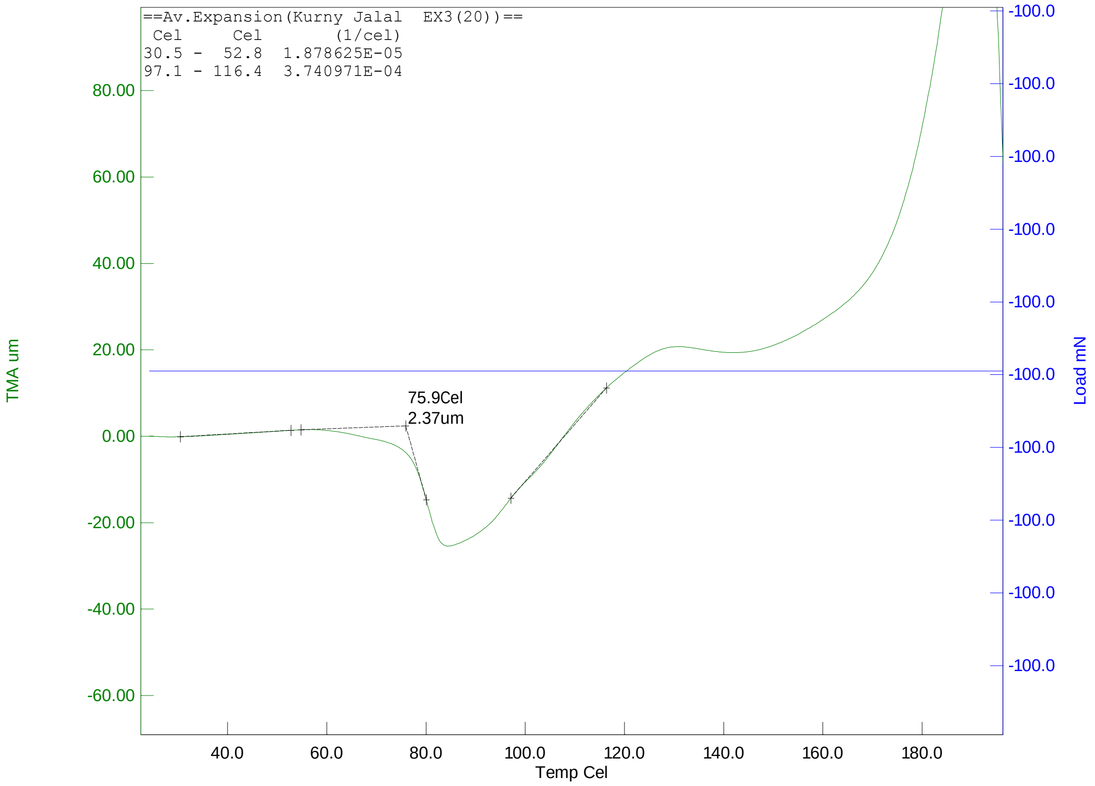


*Fig.12.9 TMA curve of recycled uPVC (20 phr external scrap)*

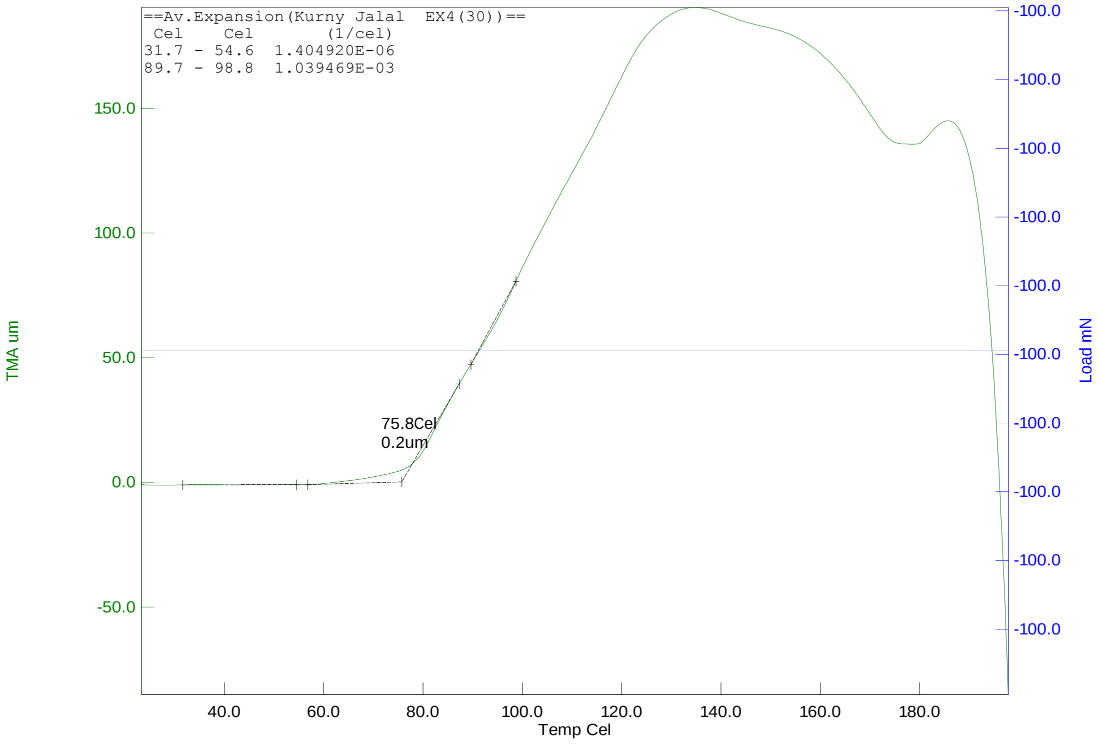


*Fig.12.10 TMA curve of recycled uPVC (30 phr external scrap)*

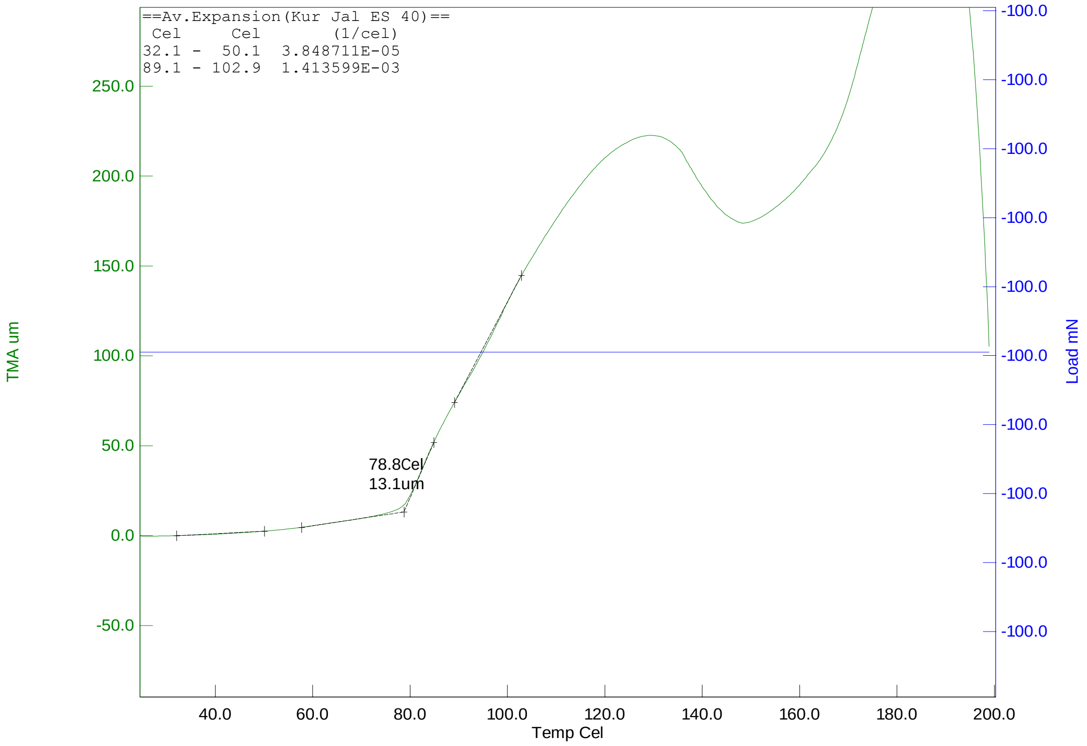


*Fig.12.12 TMA curve of recycled uPVC (40 phr external scrap)*

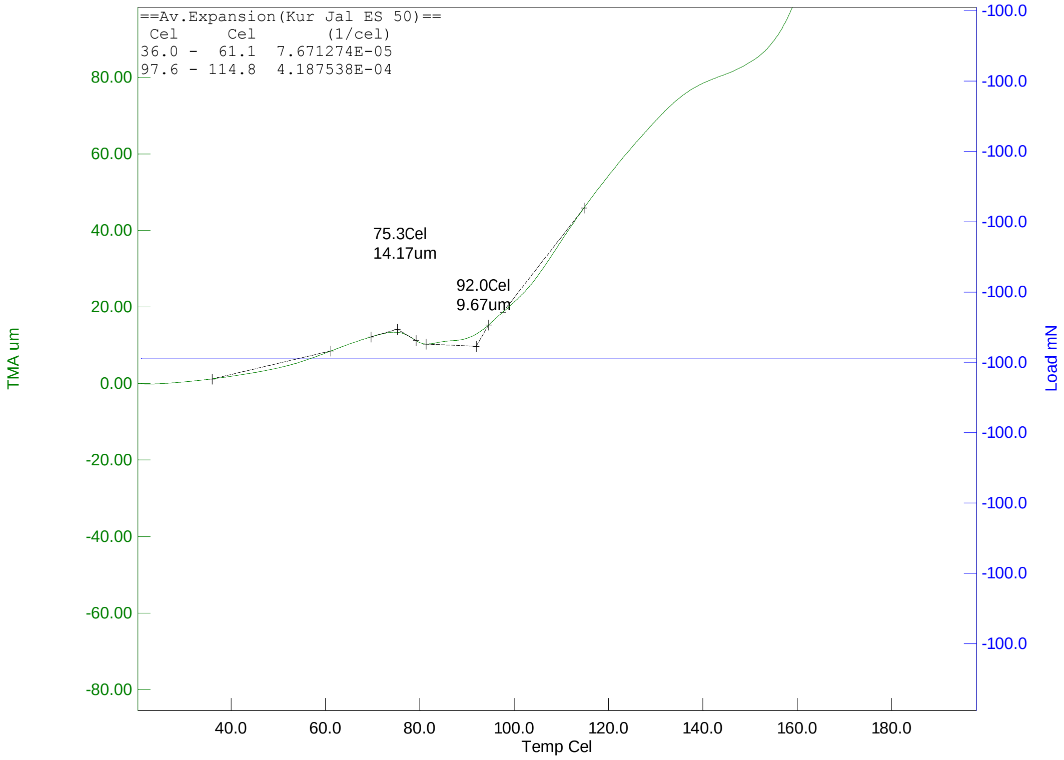


*Fig.12.12 TMA curve of recycled uPVC (50 phr external scrap)*

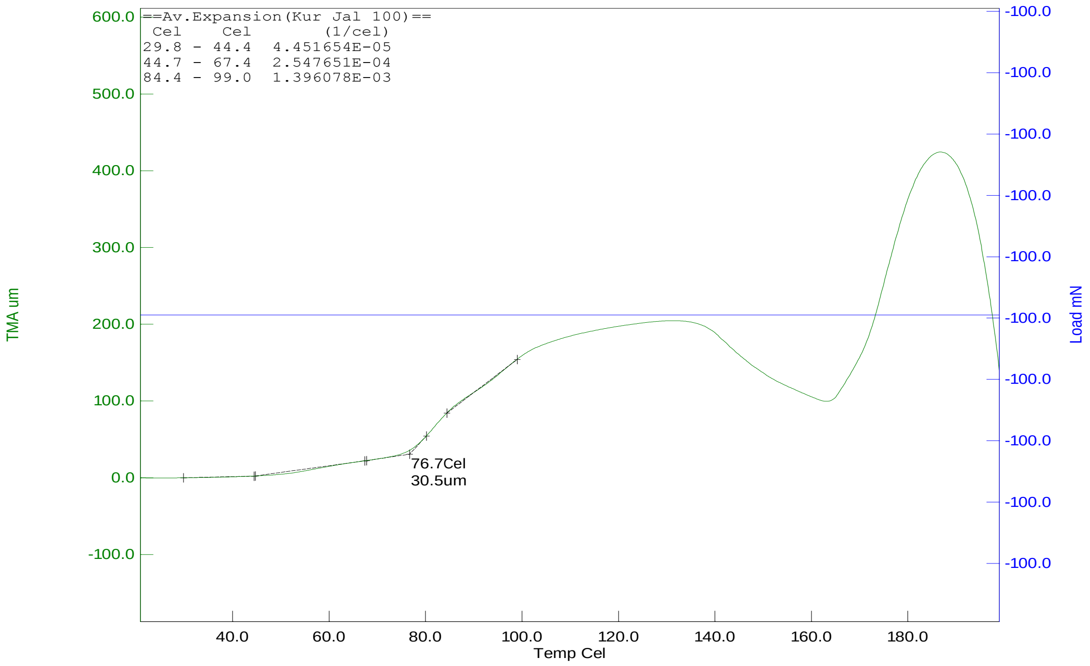


*Fig.12.13 TMA curve of recycled uPVC (100% external scrap)*

## 13. Thermo-gravimetry Analysis (TGA)

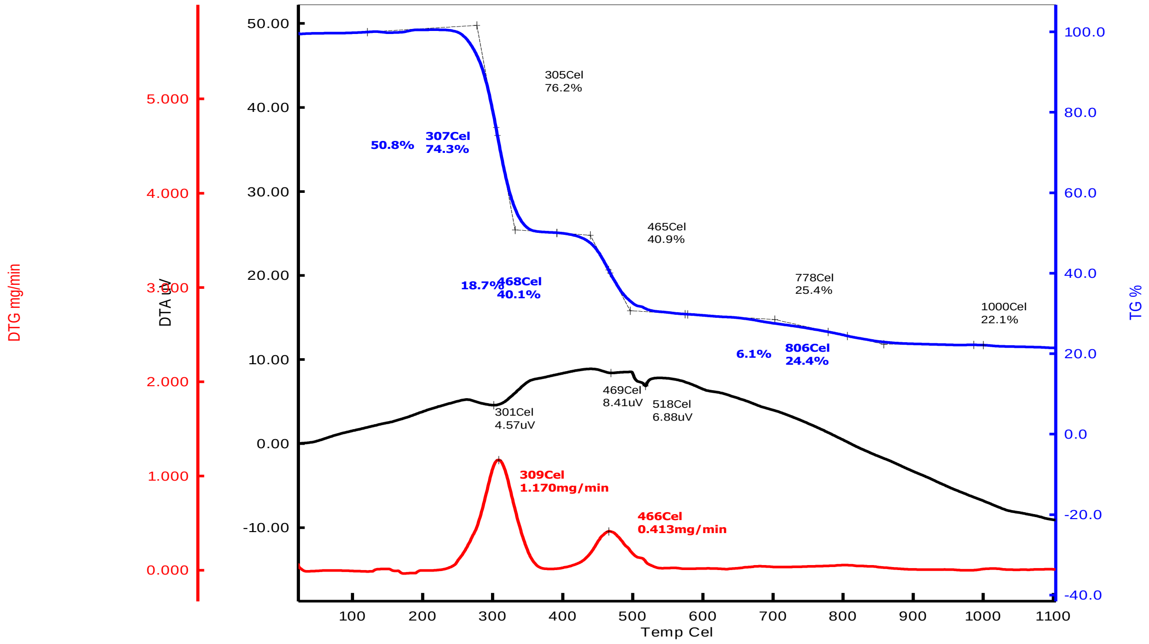


*Fig.13.1 TGA curve for uPVC having 10 phr scrap (domestic) which shows weight changes in each step*

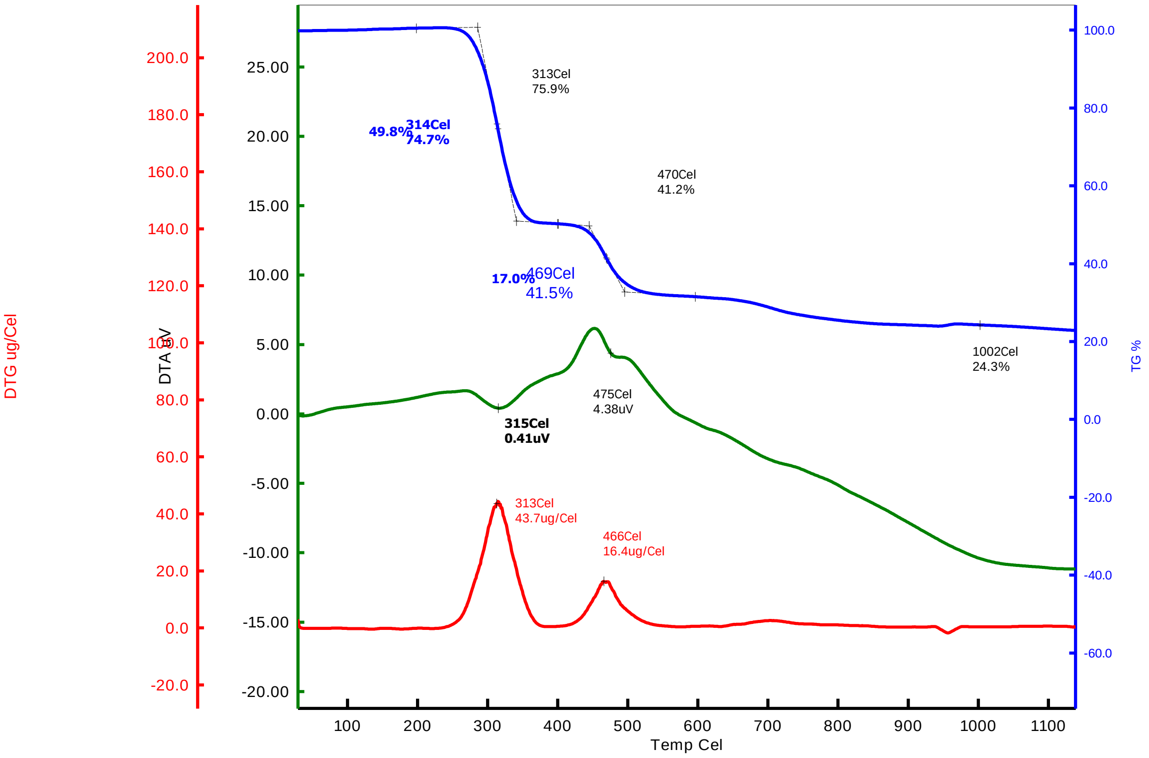


*Fig.13.2 TGA curve for uPVC having 20 phr scrap (domestic) which shows weight changes in each step*

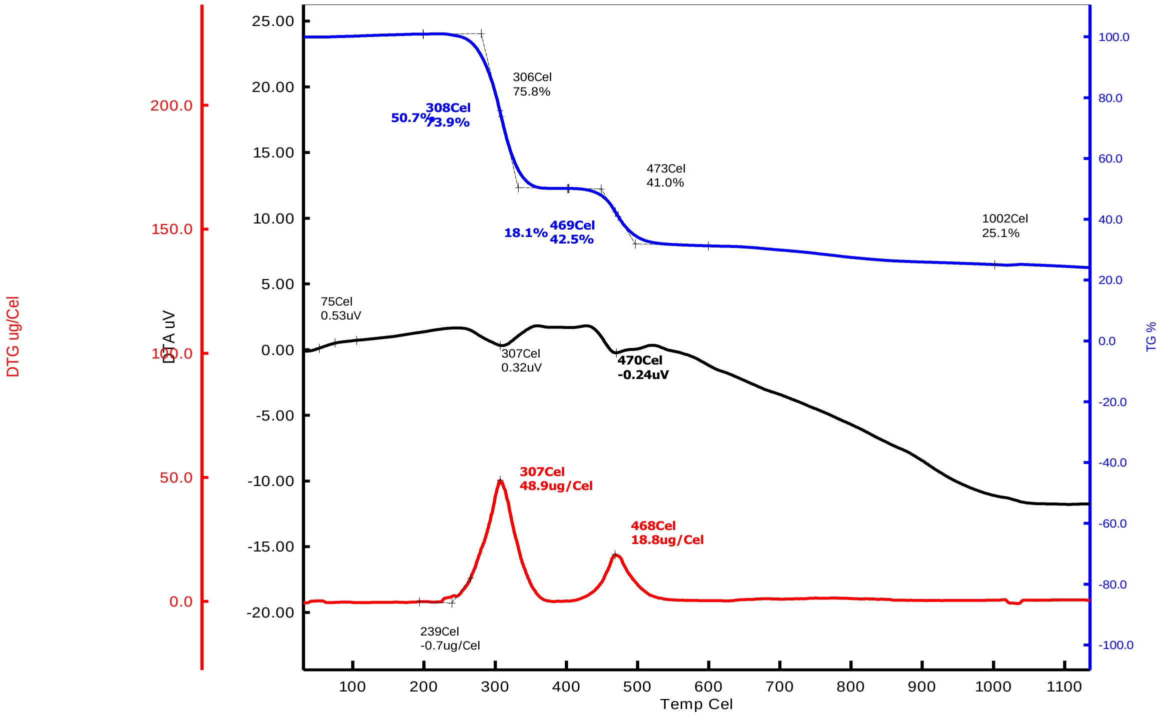


*Fig.13.3 TGA curve for uPVC having 30 phr scrap (domestic) which shows weight changes in each step*

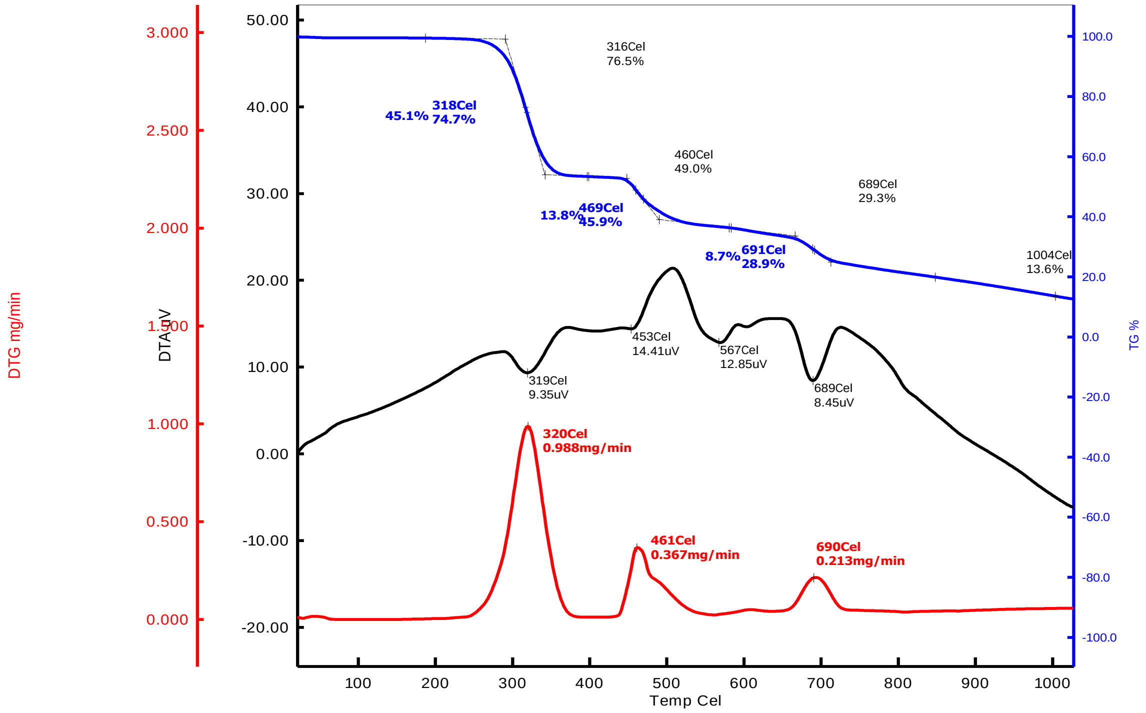


*Fig. 13.4 TGA curve for uPVC having 40 phr scrap (domestic) which shows weight changes in each step*

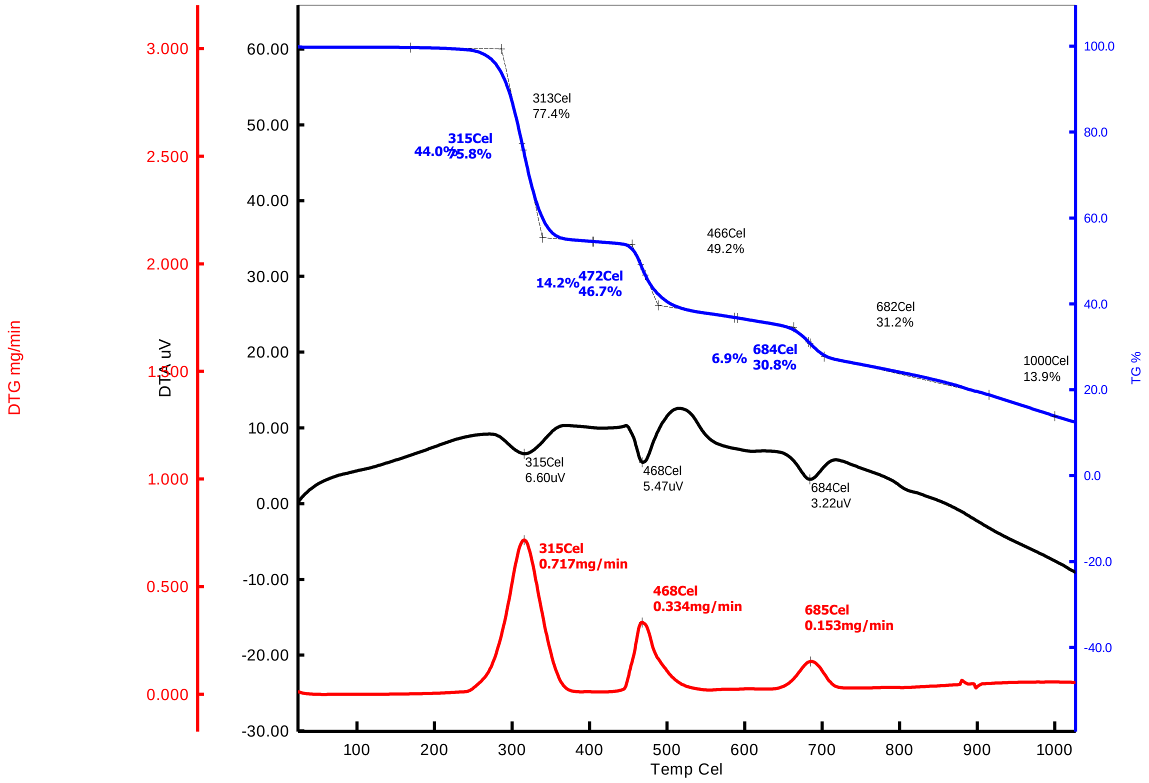


*Fig. 13.5 TGA curve for uPVC having 50 phr scrap (domestic) which shows weight changes in each step*

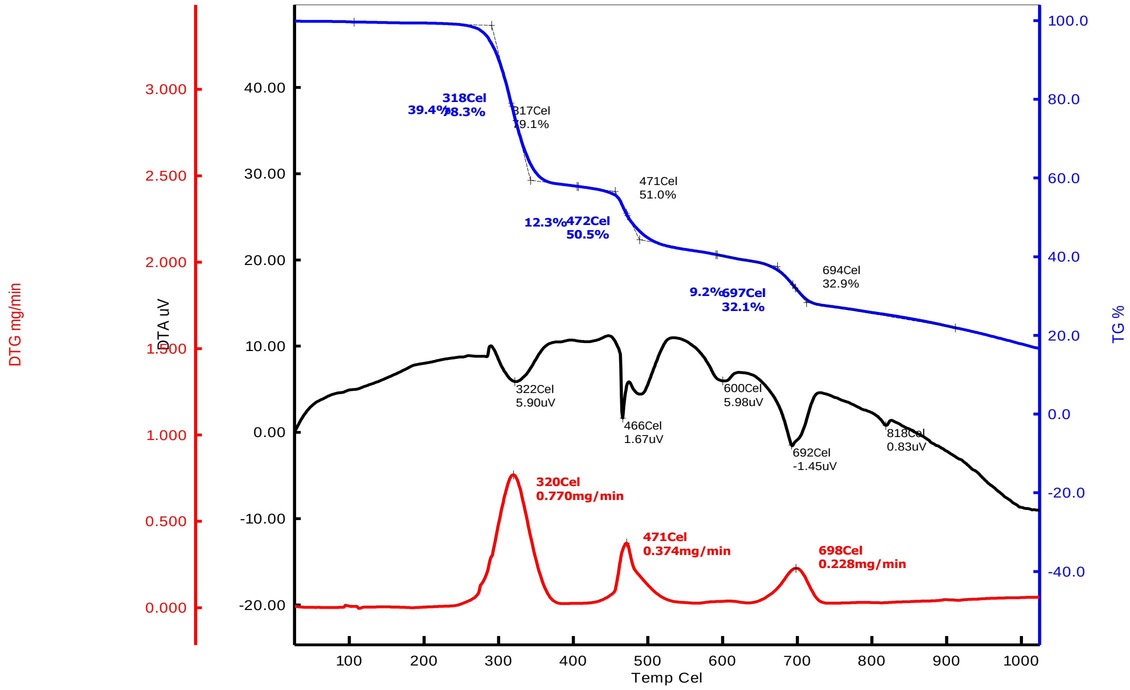


*Fig.13.6 TGA curve for uPVC having 100 phr scrap (domestic) which shows weight changes in each step*

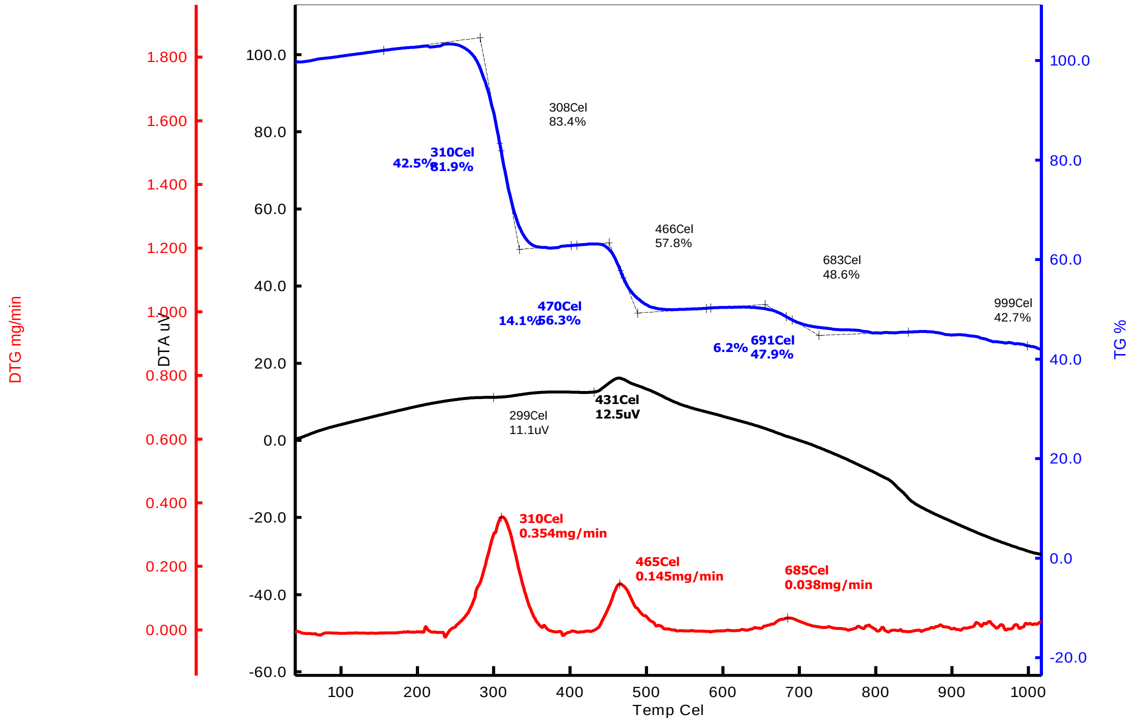


*Fig. 13.7 TGA curve for virgin uPVC (external) having 10 phr scrap which shows weight changes in each step*

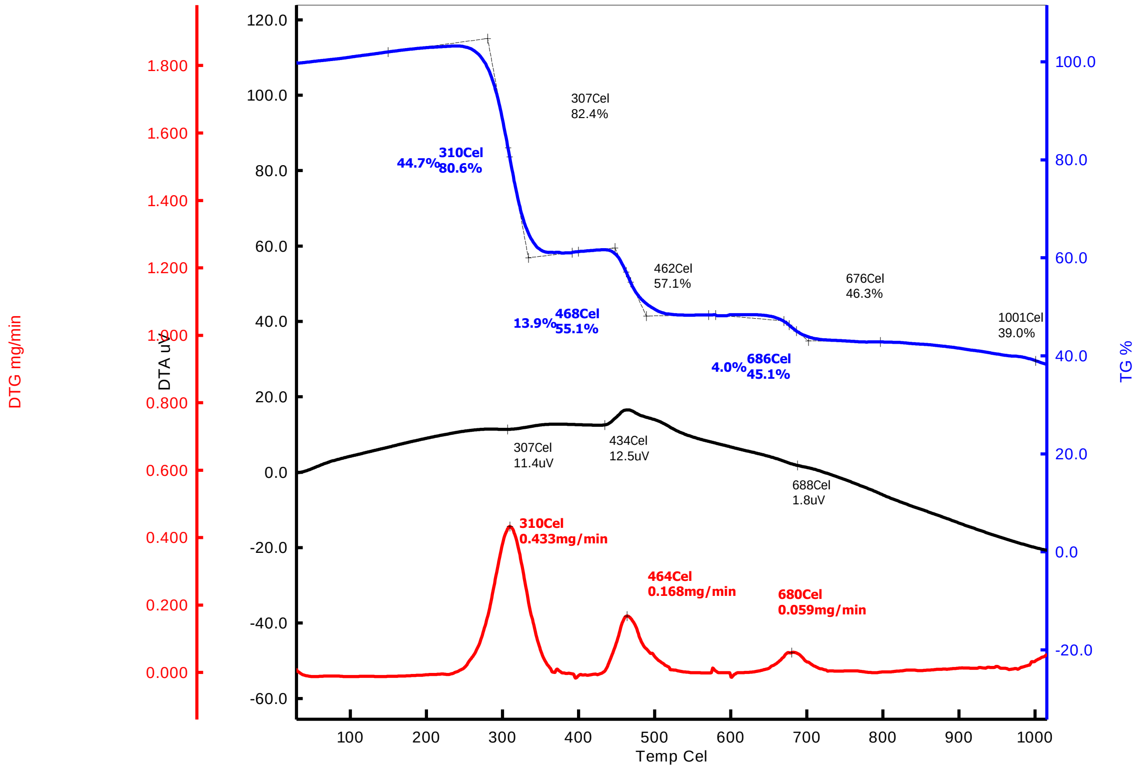


*Fig. 13.8 TGA curve for virgin uPVC (external) having 20phr scrap which shows weight changes in each step*

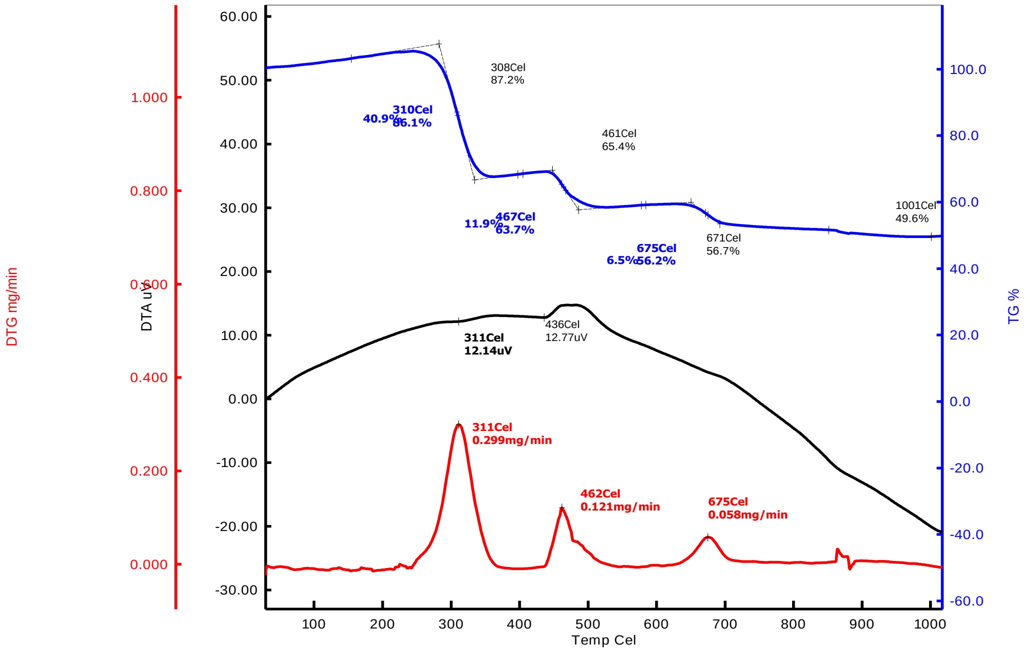


*Fig. 13.9 TGA curve for virgin uPVC (external) having 30 phr scrap which shows weight changes in each step*

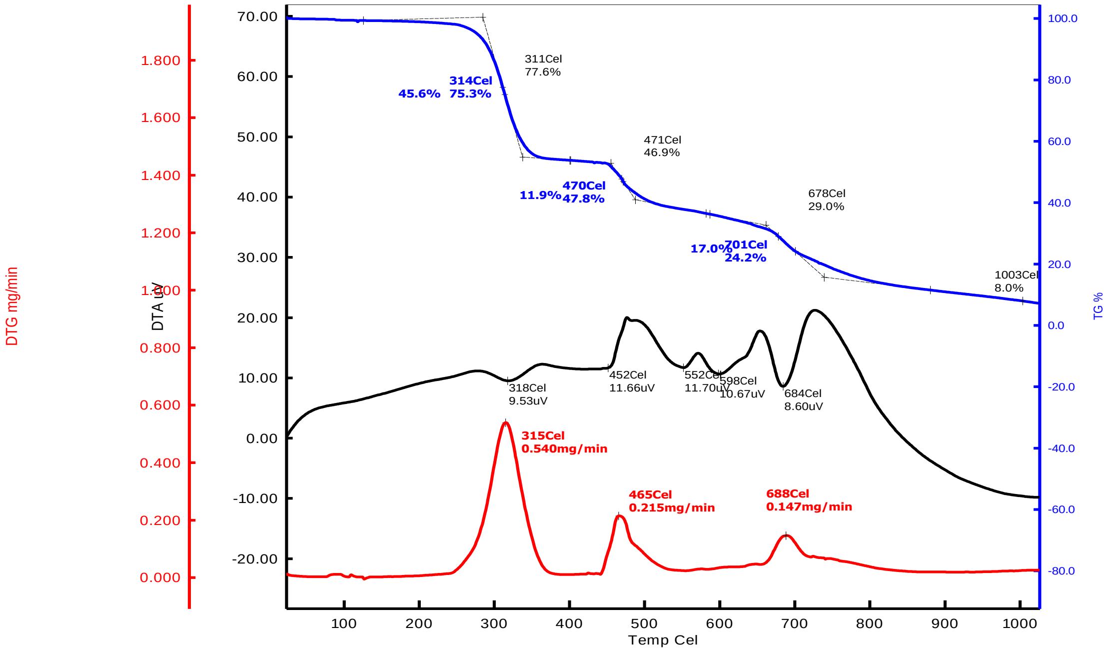


*Fig. 13.10 TGA curve for virgin uPVC (external) having 40 phr scrap which shows weight changes in each step*

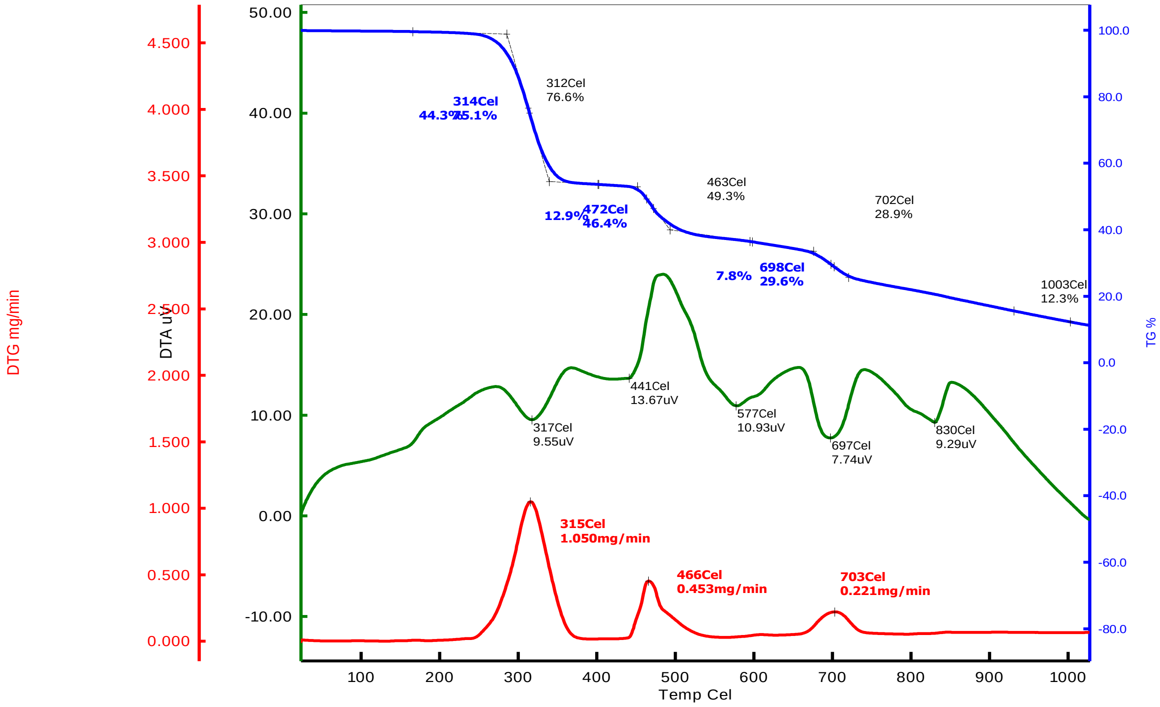


*Fig. 13.12 TGA curve for virgin uPVC (external) having 50 phr scrap which shows weight changes in each step*

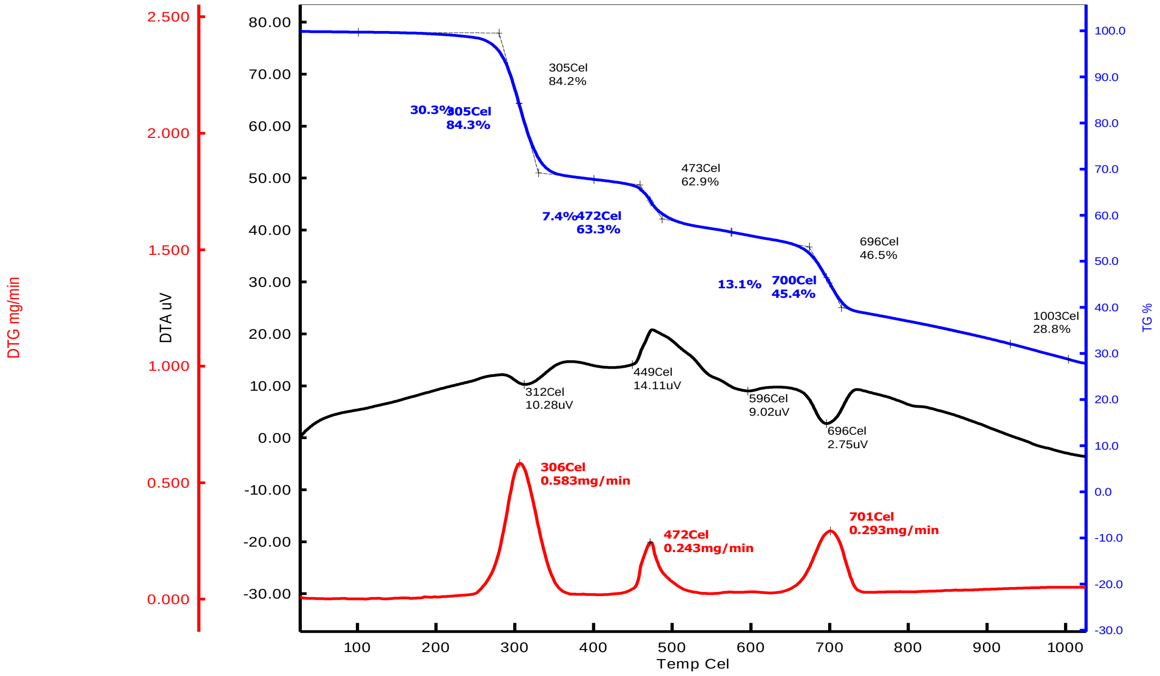


*Fig. 13.12 TGA curve for virgin uPVC (external) having 100% scrap which shows weight changes in each step*