Enhancement in Thermal Property of Poly(vinyl Chloride) (PVC) by Blending it with Acrylonitrile Butadiene Styrene (ABS) Polymers via Solution Casting Method

Ebbisa Megersa Fayie

A Thesis submitted to

Department of Materials Science and Engineering

School of Mechanical, Chemical and Materials Engineering

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Science and Engineering

Office of Graduate Studies

Adama Science and Technology University

Adama, Ethiopia

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LIST OF SYMBOLS AND ABBREVIATIONS

ABS- acrylonitrile butadiene styrene

AN- acrylonitrile

ASA- acrylonitrile styrene acrylate

DSC- dynamic scanning calorimeter

FTIR- Fourier transform infrared spectroscopy

HDT- heat distortion temperature

KBr- Potassium bromide

LCST- lower critical solution temperature

NMP- N-Methyl-2-Pyrrolidone

PC- poly carbonate

PEI- polyeterinimide

PS- polystyren

PVC- poly(vinyl chloride)

SEM- scanning electron microscope

TGA- Thermogravimetric Analysis

Tg - Glass transition temperature

UCST- upper critical solution temperature

UTM- universal tensile machine

VC- vinyl chloride

Wt.%- weight percent

XRD- X-ray Diffraction

Ψ psi

Φ Ef

ρ rho

δ delta

α alpha

μm micrometer

ABSTRACT

This report presents a new approach which is to synthesize and characterize PVC/ABS blended polymers. Polymer blends are capable of providing materials, which enhance the useful properties beyond the range that can be obtained from individual single polymer equivalents. Blends of Polyvinyl Chloride (PVC) and Acrylonitrile Butadiene Styrene (ABS) were prepared in different ratios (0 to 30 ABS weight %) by solvent cast blending technique using N-Methyl-2-Pyrrolidone (NMP) as solvent. A high impact ABS at different weight ratios was incorporated into the blends to study the effects of blend ratio on the properties of the blend. The blends were characterized by various thermal, morphological, and spectrochemical methods of analysis. Two distinct glass transitions were recorded by differential scanning calorimetry. This suggested the need for a compatibilizer. However, blends with 80/20 and 70/30 weight ratio of PVC/ABS exhibited a single Tg and that was taken as the best result. Thermal decomposition behavior of blends was analyzed by thermogravimetric analysis. Incorporation of ABS had marginal effect on rate, chemistry, and overall pattern of decomposition of poly(vinyl chloride). The interaction of polar functional groups in the two blend components was monitored by Fourier Transform Infrared Spectroscopy technique. Scanning electron micrographs indicated uniform dispersion of acrylonitrile styrene (SAN) particles in the matrix, but poor interfacial adhesion between the two phases was noticed. The impact strength and elongation at break improves significantly with increasing ABS content in PVC/ABS blend and appears maximum value while the tensile strength and modulus almost decrease monotonously with increasing ABS content in PVC/ABS blends up to 20 wt.%. Beyond this point, it starts to increase and reaches maximum value at around 30 wt.% and then there is a gradual decrease.

KEY WORDS

glass transition temperature, heat distortion temperature, stabilizers, lubricants, composite, blending, and morphology, PVC, ABS.

CHAPTER 1

INTRODUCTION

1.1 General Overview

Poly(vinyl chloride) (**IUPAC name** - poly(chloroethanediyl)), better known by its abbreviation PVC, is one of the most versatile plastics**.** It is the second largest manufactured resin by volume worldwide [1]. It is a thermoplastic polymer of major consumption due to its low production and processing costs. It is used intensively in rigid form especially for hydraulic pipes; however, in case of hot water applications its use is restricted since PVC is highly susceptible to thermal degradation during which it produces sequences of double bonds (polyenes) and releases HCl [1]. Poly(vinyl chloride) (PVC) as a thermoplastic polymer which has been used in various applications such as flexible or rigid molded plastics, cables, house siding, pipes, fibers, laminates and films due to its easy modification, special efficiency and low production cost [2, 3]. One of the main problems of PVC has been its low thermal stability compared to other useful polymers such as polyethylene, polypropylene and polystyrene [4].

PVC is one of the general-purpose plastics that may allow for the free and wide adjustment of the required physical and mechanical properties like elasticity, and impact resistance, by adding plasticizers, and modifiers. PVC has been extensively used in transportation, construction and some other areas due to its versatility and competitive price, combined with good physical and chemical properties [5].

Poly(vinyl chloride) (PVC) materials are often chosen for many outdoor applications because of their excellent performance. However, the PVC resin by itself is not a weatherable material. It must be compounded and processed properly to achieve good long-term properties. The main factors influencing degradation of PVC materials include oxygen, humidity, mechanical stress, aggressive media and ionizing radiation, all being accelerated by increasing temperature [6]. Rigid cross-linked PVC foam is an ideal core material for sandwich structure composites because of its excellent features, such as outstanding stiffness and strength to weight ratios, self-extinguishing nature, good chemical resistance, sound and thermal insulation properties and low cost. Therefore, it is widely used in wind energy, marine, road and rail, aerospace, recreation and industrial applications [7].

The low thermal stability of PVC can be related to the presence of unstable structural segments such as adjacent C-Cl and C-H bonds or flaws in the polymer chains [8]. Due to the presence of high chlorine content and low thermal stability, PVC has transformed to conjugated polyene bonds with de-hydrochlorin processes [9]. Therefore, PVC is unstable when used in high temperatures during molding and application and exhibits low toughness [10].

Addition of plasticizer allows hardness and flexibility to be tuned over a wide range of temperature. Rigid PVC contains no plasticizer and is used in a wide range of applications including pipes, gutters and window profiles. Polymers are readily attacked by UV light and must be stabilized in order to allow them to be used in outdoor applications. Even when property-stabilized, most polymers still suffer from color change and a loss of properties, in particular gloss, strength and elongation to break. The durability of PVC has ensured it an important position in the building and construction industry, for example, where it accounts for half of all plastic material used [11].

The first patent for a polymerization process to manufacture PVC was granted to German inventor Friedrich Klatte in 1913 and PVC has been in commercial production since 1933. The material now accounts for about 20% of all plastic manufactured worldwide, second only to polyethylene. Before PVC can be made into products, it has to be combined with a range of special additives. These additives can influence or determine a number of the products properties, namely; its mechanical properties, weather fastness, its color and clarity and indeed, whether it is to be used in a flexible application. This process is called compounding. PVC's compatibility with many different kinds of additives is one of the materials many strengths and is what makes it such a highly versatile polymer. PVC can be plasticized to make it flexible for use in flooring and medical products. Rigid PVC, also known as PVC-U (The U stands for "unplasticised") is used extensively in building applications such as window frames [11]. The functional additives used in all PVC materials include heat stabilizers, lubricants, and in the case of flexible PVC, plasticizers. Optional additives include a range of substances from processing aids, impact modifiers, thermal modifiers, UV stabilizers, flame-retardants, mineral fillers, pigments, to biocides, and blowing agents for specific applications. The actual PVC polymer content in some flooring applications can be as low as 25% by mass, the remainder accounted for by additives [12].

Heat stabilizers are necessary in all PVC formulations to prevent the decomposition of the PVC by heat and shear during processing. They can also enhance the PVC's resistance to daylight, and to weathering and heat ageing [13]. In addition, heat stabilizers have an important influence on the physical properties of the PVC and the cost of the formulation. The choice of heat stabilizer depends on a number of factors including the technical requirements of the PVC product, regulatory approval requirements and cost [14].

Polyvinyl chloride is largely blended with number of polymers and rubbers. In most cases, to improve properties of PVC and rarely to improve properties of other materials. The most inferior properties of PVC are low operating temperature and low impact strength. To overcome this problem, it is blended with many rubbery materials. It has been shown that impact strength of PVC increases by blending with rubbery material such as NBR, SBR etc. However, it follows the decrease in tensile strength, rigidity and in most cases thermal stability.

Hence to achieve high impact strength, better thermal properties along with rigidity, PVC is blended with ABS. The blend of PVC and ABS posses their advantage of impact strength, rigidity, chemical resistance, electrical properties and overall low cost.

In ABS, generally the rubbery phase is made of emulsion polymerized polybutadiene, which constitutes the main polymer chain. The glassy phase is made of styrene and acrylonitrile grafted on Polybutadiene. Thus, it combines the impact strength of rubber and tensile strength, heat stability of styrene Acrylonitrile (SAN) Matrix. Thus, properties of styrene acrylonitrile (SAN) and polybutadiene are imparted in PVC/ABS blend.

While preparing blend, it is necessary to consider compatibility of components of blend with each other, which are used to prepare blends. In case of PVC/ABS blend, PVC and ABS are used as blend components. ABS is made by emulsion polymerization of SAN grafted by Polybutadiene. Polystyrene and Polybutadiene, have solubility parameter close to PVC. Although, solubility parameter of PS and Polybutadiene are close to PVC, they do not have good compatibility because of their being non-polar nature.

The aim of the present work was to investigate the blend developed from commercial grades of PVC and ABS using differential scanning calorimetry (DSC) and Fourier transform infrared

spectroscopy (FTIR). In addition, thermogravimertic analysis (TGA) has been carried out with the aim to study thermal stability and degradation behavior of the blend. Morphology of blended specimens was also observed using scanning electron microscopy (SEM) and optical microscopy.

1.2 Statement of the Problem

Although a wide range of products are manufactured from poly(vinyl chloride) (PVC), alternatives are available for virtually all of them. The biggest user of PVC is the construction industry which commonly installs PVC pipes and ducts, electric cables and wire insulation, windows, flooring, wall coverings, cladding and building membranes. During these applications, they can exposed to high temperature which results in the decomposition of the material in several possible ways. This research is to find solution for this problem without losing the nice properties that PVC exhibits.

1.3 Objective of the Work

1.3.1 General Objective

The objective of this study is to improve the heat resistance ability of PVC products by blending it with two different kinds of acrylonitrile butadiene styrene copolymers. The glass transition study of the given polymers and the formed blends is the core point of this study.

1.3.2 Specific Objectives

The specific objectives of this study are:

- By studying physical and mechanical properties of PVC and ABS polymers, proposing and investigating effective ways to blend the two polymers to enhance its properties.
- Investigating and studying the influence of adding ABS on the glass transition temperature, Tg of the PVC specimen for various composition ratios. This will indicate the thermal property enhancement or its decline.
- In addition to the effect of these additives on glass transition temperature Tg of PVC, its effect on other properties like mechanical properties, morphology, crystallinity, impact strength and others was studied.

1.4 Scope of the Study

The scope of this thesis work is to focus only the experimental findings and the related works available so far. The glass transition temperature, Tg of the blended material is the point of focus throughout the work. The glass transition temperature Tg and softening point of a polymer is strongly related. The synthesis and characterization of the sample take place at ambient condition (room temperature and standard pressure). Since PVC and ABS have similar melting and glass transition temperature Tg of ABS is higher than that of PVC, it is possible to get a blend that have a moderate Tg. This can be obtained from DSC result.

1.5 Significance of the Study

The significance of this study is expected to be:

- Its contribution for PVC producing companies to improve the property of their products.
- For individuals who want to conduct similar research to more improve the temperature resistance property of PVC materials.
- To solve problems related to the temperature while using PVC products at higher temperature, for instance to supply water for areas in which environmental temperature is beyond the temperature resisting limit of the conventional PVC pipe.
- Easily processing of PVC materials for construction purpose that can operate at higher temperature will be possible if the outcome of this research show the expected result.

CHAPTER 2

LITERATURE SURVEY

2.1 Polymer Bending Technology

The emerging area of polymer blends and composites allows choosing a suitable combination of polymers and tailoring them for a desired performance. Although polymer blends and composites are relatively independent, history has shown that the interplay of new methods and ideas results in advancements in the development of new materials via properties and multifunctional approaches. According to Meireles, Dawson, Olabisi, and Weber et al. the study of mixtures of polymer materials has been the subject of a great deal of intense research in the last few decades [15, 16, 17, 18].

Polymer blending is a convenient and attractive route for obtaining new polymeric materials. The polymer blending offers the possibility of adjusting the cost-performance balance and tailoring the technology to make products for specific end user applications, enhancing resins' performance, improving specific properties, viz. impact strength, solvent resistance… etc. and provide means for industrial and consumer plastics waste recycling. However, this approach is complicated by the fact that polymers are generally thermodynamically immiscible. Thus, achieving compatibilization in immiscible polymer blends has been a long-standing academic and technological challenge [19].

When any two materials are mixed together, or blended, the properties of the resulting mixture depend on the level at which intimate mixing takes place and on whether any chemical reactions between the components of the mixture take place [20].

Two or more existing polymers may be blended for various reasons. One reason is to achieve a material that has a combination of the properties of the constituents, e.g. a blend of two polymers, one of which is chemically resistant and the other is tough. Another reason is to save costs by blending a high-performance polymer with a cheaper material. A very important use of

blending is the combination of an elastomer with a rigid polymer in order to reduce the brittleness of the rigid polymer [20].

By blending polymers, new material can be developed that combine physical and mechanical properties of their components, depending on the composition and level of compatibility. Polymer blends are currently receiving great attention because they offer low-cost alternatives to the development of entirely new materials with improved properties [21, 22].

A miscible polymer blend is one for which the miscibility and homogeneity extend down to the molecular level, so that there is no phase separation. An immiscible blend is one for which phase separation occurs [23].

Polymer blend (PB) is a mixture of at least two polymers or copolymers. It is a physical mixture of two or more polymers with/without any chemical bonding between them [20]. Basically, there are three different types of blends depending on miscibility [24, 25]:

1. Completely miscible blends have ($\Delta G < 0$) due to specific interaction.

   Homogeneity is observed at least on a nanometer scale, if not on the molecular level. This type of blend exhibits only one glass transition temperature (Tg), which is in between the glass transition temperatures of the blend components in a close relation to the blend composition.

2. In partially miscible blends, a small part of one of the blend components is dissolved in the other part. This type of blend, which exhibits a fine phase morphology and satisfactory properties, is referred to as compatible. Both blend phases are homogeneous and have their own Tg. Both Tg's are shifted from the values for the pure blend components towards the Tg of the blend component.
3. Fully immiscible blends have a coarse morphology, sharp interface and poor adhesion between the blend phases. So, these blends are of no use without compatibilization.

   Polymer blends are designed to generate materials with optimized chemical, structural, mechanical, morphological and biological properties. Improvement of the performance of polymeric materials for many important industrial applications is achieved with complementary properties. Polymer blend yields average properties of its individual

components. For the two-polymer system, there is a possibility of mutual influence of the filler on the matrix and vice versa [26].

Technological and service properties of polymer blends are determined by mutual distribution of the components, and the type, size distribution, and shape of structures formed by one polymer in the other [27]. Polymer blends:

- Fill the economical and performance gaps;
- Improve processing ability;
- Have interesting engineering applications;
- Have importance in the preparation of materials with new desirable properties;
- Are an economically viable and versatile way for tailoring new specific materials [28];
- Are the most efficient way to satisfy new requirements for material properties that demand advanced materials from a scientific as well as commercial point of view;
- Are a relatively simple solution to the complex problem of providing desired properties which are more economical than traditionally developed new polymers;
- Enable properties of importance to be maximized based on engineering into one material with certain combinations of desired properties exhibited individually by the component polymers.

From the development of polymer materials, polymer blends have reached the status of being considered an important technology. Increased industrial application of polymer blend to commercial utility has grown significantly. Due to its utility and simplicity, blending is used for improving polymer properties [29].

2.1.1 Type of Blends

Polymers blends with thermoplastics are attractive not only for their low cost, but also for their technical performance. Processing, transformation and simplicity in recycling has been directed towards polymer-polymer blending to develop the desired final properties Mixture of polymer with chemicals or other polymer(s) is called blend. The basis of polymer blends is to exploit certain unique properties of individual polymers for multicomponent systems for the benefit of the overall properties. Polymer blends are gaining greater importance due to their unique properties different

from the basic polymers. Blending of one polymer with another polymer is a very common practice [30]. Polymer blends range from completely compatible mixtures to phase-separated systems.

- Lower molecular weight fractions of one of the polymers are more miscible with the other constituent than the higher molecular weight fractions.
- In polymer exhibiting partial miscibility, both equilibrium phases consist of high molecular weight fractions of the major constituent and lower molecular weight fractions of the minor constituent.

2.1.2 Blend Properties

Polymer blends are physical mixtures of structurally different polymers which adhere together through secondary bond forces and have no covalent bond between them [31]. Functional group interactions (hydrogen bonding or dipolar interaction) between the monomer units in the constituent polymers help in part to overcome entropic effects in the polymer blends [32].

2.1.2.1 Interaction Parameters

Polymer blends are generally multiphase systems characterized by high interfacial tension and weak phase adhesion, leading to coarsely phase-separated structures and inferior ultimate mechanical properties [33]. Interaction parameter changes other than temperature are chemically achieved by using a copolymer as one of the components of the interface. The role played by the interaction parameter provides the weld strength of incompatible polymer interfaces [34]. There are three types of interaction forces, namely dispersive, polar, and hydrogen bonding.

- Dispersion forces are the result of a fluctuating atomic dipole formed from a positive nucleus and a negative electron cloud. They occur in all molecules and usually contribute a dominating portion of intermolecular interaction.
- Polar forces can be divided into two types, permanent and induced dipoles. Two molecules, each containing permanent dipoles, can form Keesom interactions. These interactions are the result of symmetrical dipole-dipole orientation. Two molecules, one of which contains

a permanent dipole, can form an induced interaction by polarization of the no dipole molecule.

- Hydrogen bonding forces are reactive molecular interactions. They are explained in many ways: electron pair acceptor-electron pair donor, proton donor-proton acceptor, and Lewis acid-Lewis base. The interaction between hydrogen bonding forces is also unsymmetrical, that is, donor-type and acceptor-type molecules are required to initiate hydrogen bonding.

2.1.2.2 Colloidal Properties

In two-phase polymer blends, colloidal properties should be considered [35]. Blends can be considered to be a special kind of heterogeneous colloidal system. The blends differ from the classical colloidal systems in transient layer between its components. The volume ratio of dispersed phase to polymer matrix, chemical nature of the additive and the polymer, size and shape of the dispersed particles, interfacial interactions between the matrix and the dispersed phase is necessary in order to blend [36].

2.1.2.3 Morphology

The great majority of useful blends are immiscible, and their outstanding performance stems from their multiphase morphologies. Hence, the control and the prediction of morphologies are of great importance for the optimization of desired properties. There needs to be proper interfacial tension leading to a phase size small enough to allow the material to be considered as macroscopically homogeneous; and an interfacial adhesion strong enough to assimilate stresses and strains without disruption of the established morphology. Blends of heterogeneous phase retain their own properties, which are summed up in a final product.

The morphology depends on whether the arrangement of the phases is continuous or discontinuous and if it is based on crystalline or amorphous phase. Morphology of multiphase polymeric systems has a primary effect on blend properties [37]. Blending behavior of commercial polymer blends and their effects on subsequent processing behavior are concerned with changes in the morphology of the polymer blend. The morphology and blend properties also depend on parameters such as composition, viscosity ratio, and processing conditions during mixing [38].

Polymer blend morphology depends on whether the arrangement of the phases is continuous or discontinuous and the degree of order in the crystalline or amorphous phases. Single glass transition temperature (Tg) blends have interphase connections but are still not compatible. Polymer blends may be divided into three categories as follows:

1. With crystalline interactions between two polymers.
2. With polymer interaction in the amorphous phase only.
3. Lack both crystalline and amorphous interactions but still have good mechanical properties.

2.1.2.4 Phase Separation

Phase separation is due primarily to differences in molecular geometry, molecular weight, and functional group incompatibility. It results upon blending in significant proportions. Therefore, direct blending delivers formation and coalescence of sizable dispersed phase domains, low adhesion between phases, and poor final properties [39]. The improved adhesion between the phases of the blend that occur at the boundary has been utilized [40]. To overcome the drawback of phase separation in blends, generally the following are considered:

- Interactive polymers;
- Preparation using opportune additives;
- Graft or block copolymers acting as compatibilizers;
- Reactive mixing (the compatibilizer is formed ***in situ***) [41].

One of the important factors controlling the phase separation process and the morphologies generated is the location of the composition of the initial blend with respect to the critical composition.

2.1.2.5 Crystallinity

The degree of crystallinity is one of the major factors determining the final properties of the blend by the size and distribution of segregated phases within the mixture. The main controlling factors include chemical composition, crystal structure and morphology, molecular weight (MW), and processing. Semi crystalline polymer blends are particularly difficult; the components may

form structures consisting of alternating regions of crystalline and amorphous materials in addition to phase separating into domains [42].

Polymer blends in which both polymers are crystallizable can form mixed or separate crystals embedded in a compatible or incompatible amorphous phase. The crystals can be homogeneously dispersed or form various levels of superstructure. The structure of the blend will strongly affect its properties. Polymer blends of crystalline nature occupy only a small part due to the molecular incompatibility of the polymeric constituent with separate individual phases. Co-crystallization and co-crosslinking result in more stable morphologies that resist coalescence [43].

2.1.2.6 Dispersion

It is challenging to obtain good dispensability in polymer blends, which dissolve within each other with difficulty if they are only mechanically blended. However, it may be possible to obtain good solubility in the blend of these undissolved polymers by introducing a certain suitable interpolymer that has good solubility with each polymer to be blended. Two polymers can be brought into a state of fine mutual dispersion, stable only because of kinetic barriers to phase separation. In immiscible polymer-polymer dispersions, controlling the morphology (phase structure) and the interfacial adhesion between the phases is required in order to obtain an optimized product. Interfacial tension, the shear rate of mixing, and the viscosity ratio of the blend components are key parameters governing the degree of dispersion.

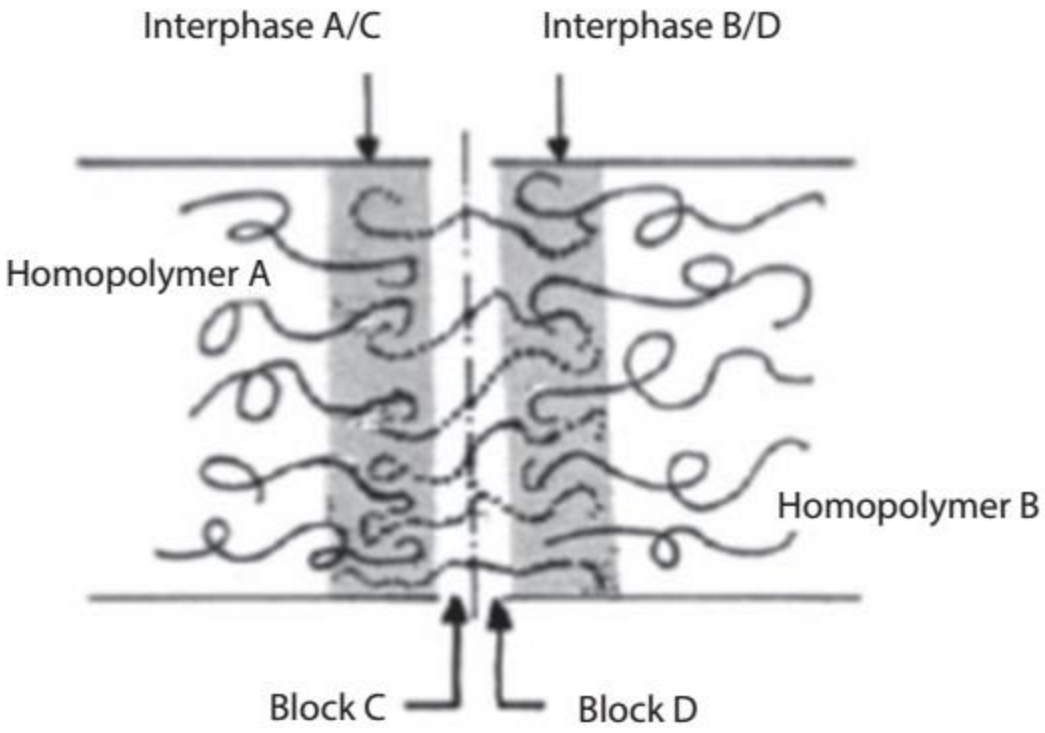


Figure 2-1 Schematic diagram of the formation of an interphase between two immiscible homopolymers, A and B, in the presence of block copolymer, C-block-D [44]).

The schematic in Figure 2.1 shows the formation and dispersion of interphase between two immiscible homopolymers, A and B, in the presence of block copolymer, C-block-D.

2.1.2.7 Physicochemical Properties

Physicochemical properties [45] of polymer blends depend on several factors based on the polymer matrix present:

- Adhesion in polymer;
- Concentration and distribution;
- Relaxation characteristics;
- Composition of the blend and composite;
- Temperature at which blending or composite operation is conducted.

2.2 Compatibilization

Immiscible polymers exhibit inferior mechanical properties [46]. The mechanical properties or thermal stability of immiscible polymers can be improved by physical or chemical compatibilization to create materials with better performance [47]. Mechanical compatibilization of polymer blends is an attractive route with unique property combinations and polymer compatibilizer can be used for recycling mixed polymer scrap. Blends of polyethylene terephthalate (PET) and any polyolefin (PO) would be grossly incompatible and a very effective compatibilizer would be needed to give the blend adequate mechanical properties for any subsequent application [48].

2.2.1 Reactive Compatibilizers

Reactive compatibilizers appear to be more stable than the addition of a previously synthesized copolymer [49]. In reactive compatibilization, the copolymers that are formed lie at the interface and contribute to reduce the interfacial tension to fix the morphology [50]. Important applications and processes require economical reactive compatibilization of polymers.

2.3 Classification of Polymer Blends

Polymer blends are mixed systems of two or more finished polymers, which can be modified through mixing two or more macromolecular compounds. Polymer blends are classified as:

- Miscible blends;
- Immiscible blends.

2.3.1 Miscible Blends

A variety of miscible polymer blends with strong specific interactions show an unusual compositional variation of their Tg [51].

- Symmetric interfaces form miscible blends;
- Polymers interpenetrate into each other;

- Produce blends with good mechanical properties and good cohesion between phases.

Degree of miscibility of polymer blends depends on interpenetration and is generally neither easy to determine experimentally nor easy to predict theoretically. Polymer miscibility results in a mixture with two different chains/segments that are in proximity within a domain small enough. It may be several or tens of repeat units regardless of the types of interactions. A proton-donating polymer is likely to be miscible with a proton-accepting polymer [52].

2.3.2 Immiscible Blends

Most of the polymer blends are immiscible with poor physical properties in comparison with their individual polymers. Tis is due to the lack of favorable interaction between phase blends. It leads to large interfacial tension in the melt blend, which makes it difficult to deform the dispersed phase during mixing. In immiscible blends, a decrease in stress concentration at the interface is responsible for the increase of tensile strength [53]. Immiscible polymer blends exhibit different types of morphologies, which depend on composition, viscosity ratio and elasticity ratio between the components, interfacial tension, process conditions, etc. [54]. Immiscible blends offer attractive developing materials with a useful combination of properties.

Asymmetric interfaces form immiscible blends. Blend systems can be strongly limited by the incompatibility between the polymers. Blends have a multiple glass transition temperature with immiscibility. Generally, there is immiscibility among the high molecular weight polymer pairs as well as mechanical incompatibility [55]. The types of immiscible polymer blends are:

- Blend having dispersed domain structure in matrix phase;
- Blends having co-continuous structure.

Asymmetric blend compositions with the minor component form the dispersed phase in the continuous phase of the major component [56]. The control of microstructure is very important for determining the physical properties of multicomponent blends in immiscible polymer blends [57]. Polymers are normally not miscible because of the large size of their molecules. Polymer-polymer interfaces are sufficiently narrow. There is little entanglement between the different polymers [58].

Mechanical properties of immiscible blends should be very sensitive to the phase morphology generated during processing and should also be widely varied in chemical type. The chemical type of immiscible blends could be significantly improved by addition of certain block copolymers. Most polymer blends of high molecular weight polymers are intrinsically immiscible, and therefore phase separate under appropriate conditions. Heterogeneous structures would result in the blend. In ternary blends containing block copolymers, formation of interlocking or interpenetrating network phases is the ideal morphology for an immiscible blend. It allows for equal sharing of imposed stresses by the component [59].

2.3.3 Immiscible and Miscible Blends

Immiscible and miscible blends require either the addition of an extra component or the synthesis by chemical modification of one or more of its constituent polymers. Blend miscibility is improved by [60]:

- Simply replacing one of the linear components with a cyclic version of the same polymer;
- Addition of copolymer additives;
- In-situ generation of interfacially active polymers by (a) using reactive components with complementary functional groups or (b) solid-state shear pulverization.

Copolymers, such as block, graft, etc., bear segments that are compatible with each component. These copolymers are extensively used to promote blend compatibility. Copolymers may be added separately or formed in situ by blending functionalized polymers.

2.4 Homopolymer and Copolymer Blends

Homopolymer and block copolymer blends are certain ways to control the morphologies. Homopolymer effectively changes the volume occupied by each block chain and hence modifies the interface, which leads to the morphology change. In case of high molecular weight homopolymer, the polymer tends to locate in the middle of the block copolymer. Therefore, block copolymer is hardly affected by homopolymers and the local structure of the domains is kept with the generation of vesicle structures [61].

2.5 Thermoset-Thermoplastic Blends

Thermoset-thermoplastic blends are materials resulting from the mixing of thermoplastic with thermoset precursor such as diepoxy-diamine system. Due to the molar mass increase of the thermoplastic precursor there is a subsequent reaction with the initial mixture of homogeneity, and a liquid-liquid phase separation occurs at a given conversion [62].

Polyetherimide (PEI) and polystyrene (PS) are two non-functionalized thermoplastics. They are composed of a thermoset precursor diglycidyl ether of bisphenol A (DGEBA) and an aromatic diamine as curing agent, 4,4 -methylenebis(3-chloro-2,6-diethylaniline) (MCDEA). Before any reaction, both blends exhibit an upper critical solution temperature (UCST). PS is less soluble than PEI in the thermoset precursor. At curing temperature, both types of thermoplastic are soluble. The liquid-liquid phase separation will arrive for PS than for PEI during isothermal cure [63].

2.6 Reactive Copolymer Blends

The reactive copolymer styrene-maleic anhydride (SMA) is miscible with PS, PPO, PMMA, and SAN at certain concentrations of MA functionality. The immiscible binary blends of all these polymers with PA6 can be compatibilized through addition of SMA as a third component. In all these ternary blends (PA6/X/SMA), the amino end groups of PA6 will react with the anhydride groups of SMA during melt mixing, giving rise to the formation of a graft copolymer and resulting in a compatibilizing effect. The addition of SMA to polyamide leads to an increase in the melt viscosity [64].

PVC is now one of the world's major polymers and a large amount of PVC is produced worldwide for its superior mechanical and physical properties. Fluid plasticity and thermal stability of PVC are, however, inferior to those of other commodity plastics such as polyethylene and polystyrene [65]. PVC is mainly produced by radical polymerization. The radical polymerization of VC, however, results in the formation of molecules with a number of isomeric forms and structural defects. These factors are of vital importance to the users of PVC, because they cause a color problem, thermal stability of the polymer, its crystallinity, processing behavior, and the mechanical properties of the finished article. Studies of defects also give an insight into the nature of the side reactions occurring during polymerization [66].

One of the most severe practical limitations of poly(vinyl chloride) (PVC) lies in its low service temperature. Commercially available rigid PVCs show distortion temperatures around 75–80℃, giving rise to inappropriate modulus and creep compliance values above these temperatures. Many industrial accessories, like electrical and electronic appliances, require suitable mechanical properties at relatively high temperatures. Some of these pieces, such as electrical distribution boards, are submitted to quality tests in a stove for 1h at 100℃ to analyze their deformation. Although other polymers, like polypropylene, pass the test, conventional PVC fails. Furthermore, new control norms are currently required for tubes and pipes, making evident the limitations of PVC at high temperatures [67].

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials. Polymer blends often exhibit properties that are superior to any one of the component polymers alone. However, the manifestation of superior properties depends upon the miscibility of homopolymers on the molecular scale [68].

Polymer blends can combine attractive properties of several polymers into one, or can improve deficient characteristics of a particular polymer. However, immiscible blends often have poor mechanical properties compared to their components. It is well known that the introduction of a small amount of compatibilizer can lead to major changes in mechanical properties. It has been reported that a homopolymer as well as block or graft copolymer can be used effectively as a compatibilizer [69, 70].

For use in making piping or structural panels that require high resistance to impact, polyvinyl chloride often is blended with small proportions of rubbery synthetic polymers. The modification of rigid poly (vinyl chloride) (PVC) having relatively low toughness carried out by incorporation of a rubbery phase [71]. Resins more easily plasticized than polyvinyl chloride can be prepared by adding various properties of vinyl acetate to vinyl chloride before polymerization the mixture; stiffer resins result from treatment of polyvinyl chloride with chlorine. In commercial PVC formulations, proportions of plasticizer range from 15-50% by weight [72].

The thermal degradation of PVC has already been the subject of numerous investigations. Some attention has also been paid to the thermal degradation of PET and PC but the behavior of PVC–PET mixtures and especially the interaction of PVC with PC have been less studied. The dehydrochlorination of PVC starts at temperatures of about 100°C lower than for PET and, if the

polymers are degraded separately, PVC is almost completely degraded before the temperature is reached at which PET starts to degrade [73].

2.7 Polyvinylchloride Blends

Polyvinylchloride (PVC) is one of the most important polymers and is very often blended with other polymers, which results in heterogeneous blends [74]. PVC is a weak proton donor and improved miscibility is expected with acceptor type polymers. It is thermally unstable and is quite frequently blended and compounded with other materials acting as stabilizers or plasticizers which make polymer blending a natural extension. When large amounts of rubbery polymers are added, they can act as macromolecular plasticizers.

Blends affect the thermal stability of PVC. However, PVC blends are made for two reasons:

- PVC is produced in large quantity and has many applications;
- PVC is a homopolymer.

Polymer blend with PVC offers three advantages:

- Improves impact strength of PVC;
- Improves processing ability;
- Has higher heat distortion temperature than a system using liquid plasticizer.

For industrial purposes, the discoloration of PVC is very often used to determine the thermal stability. Polymers such as polybutadiene (PB) and polyacrylonitrile (PAN) show a discoloration under the conditions of degradation. Degradation of pure PVC is compared with its behavior in blends with PS, SAN, HIPS, and ABS. These components can show the effect of a nitrile group or a C–C double bond on the thermal stability of PVC.

Plasticized blends of poly(vinyl chloride)/nitrile rubber combine the low-temperature flexibility and ease of processing of nitrile rubber and the high-temperature permanence and flame-retardent properties of poly(vinyl chloride). Another example is blends of poly (phenylene oxide) with styrene copolymers. These blends have the excellent dimensional stability at high temperatures and good electrical properties of poly(pheny1ene oxide) combined with the lower melt viscosity, shear sensitivity, and cost of polystyrene [75]. Therpolymers of methyl

methacrylate, butadiene, and styrene (MBS) are similar to ABS, having a rubber domain and a polymer matrix [76].

Due to the structure and solubility parameters of polybutadiene (PB), incompatible PVC-PB blends are greatly different from those of PVC. Mechano-chemical interactions between PVC and PB molecular chains lead to the formation of a few graft and block copolymers that enhanced adhesion and mixing at the interphase. Alteration of processing temperature or composition ratios destroys the network structure of PB, leading to phase inversion. When PB forms a network structure enveloping the primary PVC particles, the PVC-PB blend has the optimum impact strength [77]. Some partially miscible systems that show large glass transition temperature (Tg) changes, which are indicative of high interactions and as a consequence high solubility, show mechanical properties below the additivity rule (PVC-PS system) [78]. PVC has relatively low heat distortion temperature. Several α-methylstyrene/acrylonitrile co-and terpolymers improve heat distortion temperature in compounding with PVC.

Table 2-1 Physical and mechanical properties of polyvinyl chloride [78]

Physical and mechanical properties of polyvinyl chloride	
Young's modulus	3.2 MPa
Shear modulus	1.2 MPa
Bulk modulus	1.8 GPa
Poisson's ratio	0.49
Yield strength (elastic limit)	10 MPa
Tensile strength	10 MPa
Compressive strength	20 MPa
Flexural strength (modulus of rupture)	11 MPa
Hardness—Shore D	12
Heat deflection temperature at 455 KPa	-30∘C

2.8 Acrylonitrile-Butadiene-Styrene (ABS) Blends

Acrylonitrile-butadiene-styrene (ABS) consists of two incompatible phases, the polybutadiene rubber phase and the SAN rigid phase. The rubber phase is finely dispersed and embedded in the rigid SAN phase as matrix. When PVC and ABS were mixed, the PVC interacted more easily with the SAN phase than with the rubber phase because of the polarity of the phases. Whether PVC and SAN were compatible in a blend or not depended primarily upon the level of acrylonitrile (AN) content in the SAN. The PVC-ABS blends could be considered a two-phase system composed of a soft polybutadiene (rubber) phase and a rigid PVC/SAN copolymer phase of mutually miscible components.

Acrylonitrile-butadiene-styrene (ABS) blends are miscible [79] with PVC and improve the flame resistance, toughness and processability of ABS in injection molding, extrusion and thermoforming applications while compounding. In specific applications of the commercial blends, the acrylonitrile content of ABS is probably critical relative to miscibility and the phase behavior [80]. The blends of PVC with copolymers of acrylonitrile (AN) and 1,3-butadiene are among the few early examples of miscible polymer blends. It has been pointed out that acrylonitrile-butadiene rubber (NBR) will be miscible with PVC.

The blend has significant commercial applications because a minor portion of PVC improves the ozone resistance of NBR and a minor portion of NBR in PVC decreases the need for volatile plasticizer and improves the flexural properties. PVC-NBR blends bridge the gap between PVC compounds employing phthalate-type plasticizers and polymeric-type plasticizers [81].

The high heat resistance of ABS is based on the blending of α-methylstyrene (α-mS)/acrylonitrile (AN) and styrene (S)/acrylonitrile (AN) copolymers, both at their azeotropic compositions of 69:31 and 76:24 of (α-mS):AN and S:AN respectively [82]. These blends improve the 10-20 °C higher heat distortion temperatures required for ABS. Blends of elastomers and ABS-type blends are devoted to melt flow of blends of crystalline polymers. Application of these blends includes short-term boiling water exposure, parts requiring high temperature due to finishing operations, and appliances.

Because of their good balance of properties, ABS materials are used from the appliance to the car industries. These materials represent a valuable compromise in mechanical, aesthetic and processing properties. ABS is formed by a matrix of random SAN copolymer in which approximately spherical rubbery particles of polybutadiene are dispersed. The adhesion between the matrix and the second phase is provided by some graft SAN-PB copolymer at the interfaces. The presence of rubbery particles is the reason for the improved toughness of ABS. In fact, SAN is a quite brittle material [83].

The ABS terpolymers of commercial interest contain 15 to 35 wt% acrylonitrile and 10–40 wt% butadiene [84]. ABS polymers are based on three monomers: acrylonitrile, butadiene and styrene. High impact resistance, good dimensional stability, and good processability have made ABS terpolymers the material of choice in many engineering thermoplastic applications, particularly in the automotive industry and in electric household appliances. Specific processability properties are often required. Rheological properties of the viscoelastic behavior of ABS in the molten state are related to the fundamental principles, which govern processability [85]. Because of its good balance of properties, toughness/strength/ temperature resistance coupled with its ease of molding and high quality surface finish, ABS has a very wide range of applications. These include electrical and electronic equipment (EEE), as well as widespread applications in communication instruments and other commodities.

Acrylonitrile-butadiene-styrene has excellent low temperature impact strength and is very easy to process. The major disadvantage of ABS is its extremely poor solvent resistance, which tends to prohibit its application in areas involving contact with organic solvents. ABS is used for producing products that exhibit excellent toughness, good dimensional stability, and good chemical resistance.

Owing to its good mechanical and processing properties shown in Table 2.3, ABS copolymer is an engineering polymer that is widely used in industry. ABS is usually filled with rigid inorganic fillers, such as calcium carbonate ($CaCO_3$), talcum powder, kaolin and glass beads, in order to enhance its strength and stiffness and reduce the production cost. On the other hand, the rheological property is an important characteristic of material processability [86].

Table 2-2 Properties of acrylonitrile-styrene-butadiene (ABS) [87]

Properties	**Value**	**Unit**
Density	1.04–1.07	g/cm^3
Heat deflection temperature	70–110	℃
Vicat softening temperature	85–125	℃
Rockwell hardness	80–115	HR
Melt temperature	218–268	℃
Elastic modulus	1.6–2.2	GPa
Critical strain energy rate (G_c)	47	KJ/m^2

2.9 Advantage of Polymer Blends

There are advantages to using polymer blends to replace engineering polymers in the automotive industry [88]. The advantages of polymer blends and composites can be used to:

- Achieve an economic or property advantage;
- Exploit the unique properties of individual polymers for multicomponent systems;
- Improve the impact strength, resistance to environmental stress cracking, optical properties, crystallization rate, low temperature impact strength, rheological properties and overall mechanical behavior.

2.10 Acrylonitrile–Butadiene–Styrene (ABS) As an Engineering Material

The term styrenics (or styrenic polymers) is used to describe a family of major plastic products that use styrene as the key building block. Due to their amorphous structure, styrene polymers can be easily processed over a wide temperature range well above their softening point, the so-called ‘glass transition temperature’ (Tg). Other than partly crystalline polymers such as polyethylene (PE) or polypropylene (PP), polyamides (PA), polyesters, styrenic polymers (except syndio- and iso-tactic polystyrene) do not show a distinct melting point and, hence, no thermal energy for melting of polymeric crystals (melt enthalpy) is required during processing. That means faster processing under the same conditions, but also high dimensional stability and largely

constant mechanical properties up to the Tg. Styrenics show a comparably slow change of melt viscosity with temperature. This benign rheological behavior is beneficial for processing as well.

Acrylonitrile-butadiene-styrene copolymer (ABS) is an opaque, ductile and stiff thermoplastic polymer with a broad processing window, which is strong and durable even at low temperatures, with good resistance to heat and chemicals [89].

Acrylonitrile–butadiene–styrene (ABS) is an important engineering thermoplastic with many useful properties, such as good mechanical properties, toughness, high temperature resistance, chemical resistance, and excellent electric properties. Furthermore, ABS is an easy processing material with good dimensional stability and glossy surface. As an important engineering plastic with good properties, ABS is used in a wide variety of applications including aerospace, automobile, electronic appliances, textile industry, construction industry, etc. However, poor aging resistance, such as ultraviolet aging and thermal oxidative aging, is the critical drawback of ABS because the incorporation of butadiene as the impact modifier causing the existence of double bonds in the main chain of ABS. The double bonds undergo physical or chemical aging caused by UV radiation and oxygen condition when used in outdoors, resulting in the continuous decline in mechanical properties and color changes. As a result, poor aging resistance of ABS deters its application in some areas [90].

ABS polymers have a high toughness (even in the cold), satisfactory rigidity and **good resistance to heat**, chemicals, and environmental stress cracking. Molded articles with high dimensional stability and good surface quality can be produced by simple processing techniques. Although each of these properties can be bettered by other thermoplastics, no other system displays such a good combination of technically important [91].

Styrene–acrylonitrile (SAN) copolymer, compared with ABS, shows better aging resistance but worse impact resistance. Thus, the application of SAN is limited when high impact strength is required. Acrylonitrile–styrene– acrylic (ASA) is developed to improve the aging resistance of ABS and the poor impact strength of SAN. As the impact modifier butadiene was replaced by acrylic polymer in ASA, the aging of butadiene rubber is resolved [92].

Because of its flame retardancy, chemical resistance and low cost, poly(vinyl chloride) (PVC) is extensively utilized in sheets, pipes, profiles and cables. However, rigid PVC has deficient characteristics that deter its use in some areas. The limitations of low heat distortion temperature (HDT) and weak notched impact strength of rigid PVC must be overcome to obtain better end-use properties and to broaden the applications. To overcome the limitations of rigid PVC, blending PVC with another polymer is effective, since blending makes it possible to improve the properties of the final products, depending on the blend ratios, the compatibility and other factors. To enhance the HDT of PVC, polymers with higher glass transition temperature than PVC have been extensively blended with it, including α-methylstyrene/styrene/acrylonitrile copolymer, α-methylstyrene/acrylonitrile copolymer (α-MSAN), chlorinated PVC, imide polymers, and styrene/maleic anhydride copolymer. Unfortunately, the improvement in HDT sacrifices some toughness [93].

There are several methods to improve the heat resistance of a PVC resin, such as copolymerization, crosslinking, halogenation and blending modifications. Crosslinking occupies an important position in numerous modification methods, and plays an active role in overcoming the defects of PVC, such as low softening point and poor dimensional stability at elevated temperatures. Chemical crosslinking methods of PVC mainly include peroxide crosslinking, silane crosslinking and triazine compound crosslinking, *etc*. Most studies are focused on the crosslinking of flexible PVC foam, and seldom does research pay attention to rigid PVC foam crosslinking because of the difficulties involved [94].

The macromolecular chains of PVC are cross-linked by crosslinking agent under the action of initiator, and thus a foam plastic with an interpenetrating polymer network structure is formed by winding with the cross-linked network generated by the action of isocyanate, anhydride and water. The third cross-linked PVC foam plastic is prepared by the following method: copolymerization of maleic anhydride (MAH) and acrylonitrile (AN) is followed by grafting with PVC macromolecular chains, and then reacted with isocyanate and water. The three foam plastics obtained have good heat resistance, and are very compatible with higher processing or service temperatures, so they should have extensive applications and a bright development future [95].

Another important criterion of PVC quality is the morphology of the PVC particles. The particles should be porous and irregular; the surface area should be as large as possible. Given

these properties, a good absorption and dispersion of stabilizer one-packs and other additives is guaranteed. A too-even surface area of the PVC particles cannot properly absorb the additives, resulting in local decomposition of the PVC, thereby causing surface defects (pit marks, pitting, and specks) [96].

2.11 Hansen Solubility Parameters

A widely used solubility parameter approach to predicting polymer solubility is that proposed by the author. The basis of these so-called Hansen solubility parameters (HSP) is that the total energy of vaporization of a liquid consists of several individual parts [97]. These arise from (atomic) dispersion forces, (molecular) permanent dipole–permanent dipole forces, and (molecular) hydrogen bonding (electron exchange). Needless to say, without the work of Hildebrand and Scott and others not specifically referenced here such as Scatchard, this postulate could never have been made [98]. The total cohesive energy, E, can be measured by evaporating the liquid, i.e., breaking all the cohesive bonds. It should also be noted that these cohesive energies arise from interactions of a given solvent molecule with another of its own kind. The basis of the approach is, therefore, very simple, and it is surprising that so many different applications have been possible since 1967 when the idea was first published. Others are found in Barton [99]. A lucid discussion by Barton enumerates typical situations where problems occur when using solubility parameters [100]. These occur most often where the environment causes the solvent molecules to interact with or within themselves differently than when they make up their own environment, i.e., as pure liquids.

Materials having similar HSP have high affinity for each other. The extent of the similarity in a given situation determines the extent of the interaction. The same cannot be said of the total or Hildebrand solubility parameter [97]. Ethanol and nitromethane, for example, have similar total solubility parameters (26.1 vs. 25.1 $MPa^{½}$, respectively), but their affinities are quite different. Ethanol is water soluble, while nitromethane is not. Indeed, mixtures of nitroparaffins and alcohols were demonstrated in many cases to provide synergistic mixtures of two non-solvents, which dissolved polymers [101]. This could never have been predicted by Hildebrand parameters, whereas the HSP concept readily confirms the reason for this effect.

There are three major types of interaction in common organic materials. The most general are the “non-polar” interactions. These derive from atomic forces. These have also been called dispersion interactions in the literature. Since molecules are built up from atoms, all molecules will contain this type of attractive force. For the saturated aliphatic hydrocarbons, for example, these are essentially the only cohesive interactions, and the energy of vaporization is assumed to be the same as the dispersion cohesive energy, E_D.

The permanent dipole–permanent dipole interactions cause a second type of cohesion energy, the polar cohesive energy, EP. These are inherently molecular interactions and are found in most molecules to one extent or another. The dipole moment is the primary parameter used to calculate these interactions. A molecule can be mainly polar in character without being water soluble, so there is misuse of the term “polar” in the general literature [101].

The third major cohesive energy source is hydrogen bonding, E_H. This can be called more generally an electron exchange parameter. Hydrogen bonding is a molecular interaction and resembles the polar interactions in this respect. The basis of this type of cohesive energy is attraction among molecules because of the hydrogen bonds. In this perhaps oversimplified approach, the hydrogen bonding parameter has been used to more or less collect the energies from interactions not included in the other two parameters. Alcohols, glycols, carboxylic acids, and other hydrophilic materials have high hydrogen bonding parameters.

Solubility and swelling have been used to confirm the solubility parameter assignments of many of the liquids. These have then been used to derive group contribution methods and suitable equations based on molecular properties to arrive at estimates of the three parameters for additional liquids. The goal of a prediction is to determine the similarity or difference of the cohesion energy parameters. The strength of a particular type of hydrogen bond or other bond, for example, is important only to the extent that it influences the cohesive energy density [102].

HSP do have direct application in other scientific disciplines such as surface science, where they have been used to characterize the wettability of various surfaces, the adsorption properties of pigment surfaces, and have even led to systematic surface treatment of inorganic fibers so they could be readily incorporated into polymers of low solubility parameters such as polypropylene [103]. Many other applications of widely different character have been discussed by Barton and Gardon. Surface characterizations have not been given the attention deserved in terms of a unified

similarity-of-energy approach [104, 105]. The basic equation, which governs the assignment of Hansen parameters is that the total cohesion energy, E, must be the sum of the individual energies, which make it up.

$E = E_D + E_P + E_H$……..2.3

Dividing this by the molar volume gives the square of the total (or Hildebrand) solubility parameter as the sum of the squares of the Hansen D, P, and H components.

$E/V = E_D/V + E_P/V + E_H/V$……...2.4

$\delta_{SP}^{\ 2} = \delta_D^{\ 2} + \delta_P^{\ 2} + \delta_H^{\ 2}$ ……..……2.5

2.12 Compatibility of the Blends

It should be noted that PVC and ABS are compatible and this can be shown based on the solubility parameter theory. In this theory, two polymers (substances) are said to be miscible if the difference between their solubility parameters (δsp) is less than 1.02 $MPa^{0.5}$. The components of solubility parameters of PVC and ABS are shown in table 2.3 in which δ_D, δ_H and δ_P are dispersion cohesion (solubility) parameter, hydrogen bonding (solubility) parameter and polar cohesion (solubility) parameter, respectively. Having these components on the hand, solubility parameter is calculated using the following equation:

Table 2-3 Solubility parameters of PVC and ABS

Polymer	δd (MPa^{-1})	δp (MPa^{-1})	δh (MPa^{-1})	δsp (MPa^{-1})
PVC	17.6	7.8	3.4	19.54
ABS	10.46	15.1	7.9	20

$$\delta_{SP}^{\ 2} = \delta_D^{\ 2} + \delta_H^{\ 2} + \delta_P^{\ 2}$$

According to Table above, it can be seen that $\left|\delta_{SPP}^{PVC} - \delta_{SP}^{ABS}\right| = 0.46$, indicating that PVC and ABS are miscible because in the solubility theory when $\left|\delta_{SP}^{\ i} + \delta_{SP}^{\ j}\right| < 1.02\text{MP}^{0.5}$ then two polymers are compatible [106].

$\left|\delta_{SPP}^{PVC} - \delta_{SP}^{ABS}\right| = 0.46$, nearly completely miscible.

- When $\left|\delta_{SP1} - \delta_{SP2}\right| < 0.5$, the polymer blends are completely miscible.
- When $0.5 < \left|\delta_{SP1} - \delta_{SP2}\right| < 1.7–2.0$, the blends are partly compatible.

2.13 Glass Transition Temperature (T_g)

The glass transition temperature is an important characterizing parameter for amorphous polymers. It is a kinetic rather than a thermodynamic transition and depends on cooling rates. During cooling, the temperature at transition point where the material forms glass from its equilibrium liquid state, molecular mobility decreases with decreasing temperature, which is known as the glass transition temperature [107, 108]. In thermoplastic polymers below glass transition temperature (Tg) the inter chain bonds limit chain motion and above Tg the bonds of the polymer chains move freely and are of viscoelastic nature. Both polymers of thermosets and thermoplastics operating below Tg release stress, causing the molecular chain to spring back to its original position.

The Tg is affected depending on the extent of branching. With a low number of branches, Tg is reduced due to increased free volume. Higher branching density, as with side groups, restricts mobility and therefore results in higher Tg. Crosslinking tends to reduce the specific volume of the polymer. The free volume is reduced and the molecular motion becomes more difficult when Tg is raised in the case of reduction of specific volume. Some polymers are either crystalline or partially amorphous, giving them both a melting point and one or more glass transition temperatures (Tg is the temperature above which the extent of localized molecular flexibility is substantially increased).

The relationship between the chemical structure and Tg of polymers is an important aid in the search for materials with specific physical properties in a given temperature range. The insertion of new chemical units into a polymer chain leads to a change in the Tg. As the temperature is lowered, the expansivity of all polymers, even in the absence of crystallinity, decreases from a value of about that of a normal liquid to a value near that of a normal crystalline solid. The structure as a function of the polymerization temperature has shown that the degree of stereospecifcity and crystallinity increase as the polymerization temperature is lowered [109]. The Tg is determined by measuring the stiffness modulus versus temperature and mechanical loss versus temperature curves. The Tg of a polymer to a large extent determines its processability, hardness, heat distortion temperature and other mechanical properties. Polymer structural

variations, such as molecular weight, symmetry, polarity, pendant groups, hydrogen bonding, stereoregularity, etc., affect the Tg.

Table 2-4 Tg and Tm of the Blend Components [109]

No	Plastics	Tg °C	Tm(°C)
1	PVC	82	100 °C (212 °F) to 260 °C (500 °F) No true Tm, not perfect crystal (amorphous)
2	ABS	105	Commonly 230°C (no true melting point, amorphous)

2.14 Solvent Selection

2.14.1 N-Methyl-2-Pyrrolidone (NMP)

1-Methyl-2-pyrrolidone is a liquid, also called by several other names, such as 1-methyl-2- pyrrolidinone, 1-methyl-5-pyrrolidinone, 1- methylazacyclopentan-2-one, 1 methylpyrrolidinone, 1-methylpyrrolidone, methylpyrrolidone, N-methyl-2-pyrrolidinone and N-methyl-2-pyrrolidone (NMP). It is a solvent with high power for solubilizing chemicals and pharmaceutical agents. It is a product of the petroleum industry and can be recycled by distillation and extraction with water [110]. NMP is a biodegradable solvent therefore, environmental contamination considerations are fewer in its applications [111]. It is used in different fields and is considered a safe solvent [112].

N-Methyl-2-Pyrrolidone (NMP) is a high boiling, polar aprotic, low viscosity liquid. NMP has a good solvency for a wide range of organic and inorganic compounds and it is miscible with water at all temperatures and has a high chemical and thermal stability. It is used as a solvent for engineering polymers and coating resins. Its chemical structure is as shown below in fig 2.6.

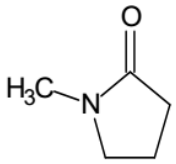


Figure 2-2 Chemical structure of N-methyl-2-pyrrolidone (NMP)

NMP dissolves polyamides, polyimides, polyesters, polystyrenes, polyacrylonitriles, polyvinyl chlorides, polyvinyl acetates, polyurethanes, polycarbonates, polysulfones, polymethylmethacrylate, and many copolymers. Assemblies containing these materials should be

tested before using NMP. NMP will dissolve or swell Buna-N rubber, natural rubber, neoprene, and Viton. Assemblies containing these materials should be tested before using NMP.

NMP is typically used as a reaction medium, an extraction/purification solvent, a carrier solvent, and a stripping solvent in the production of basic organic chemicals, along with specialty/fine chemical and pharmaceutical compounds, and polymeric materials. NMP use is widespread due to its strong solvating power, which allows it to dissolve materials that will not dissolve in many other solvents. NMP is also important in applications that require a dipolar aprotic solvent [113].

The use of NMP in polymer manufacturing presents issues because NMP is not consumed by synthesis and processing steps and exits the process as waste. NMP is used in polymer manufacturing because it is a thermally and chemically stable polar compound, with powerful solvent abilities. NMP is used as a solvent in the synthesis and processing of polymers for membranes, coatings, resins, plastics, and rubbers, for example, the synthesis of thermoresistant polymers such as polyamides, polyimides, polyether sulfones, and polyacrylene ethers, and for the synthesis of polyurethanes [114]. An analysis of green alternatives for resin precursor manufacture showed that NMP recovery from aqueous waste could be environmentally and economically beneficial. NMP can be recovered at the end of the process and can be reused. This property made it a material of choice compared to other dipolar aprotic solvents like THF, DMSO, acetonitrile, dimethylformamide (DMF), dimethylacetamide (DMAc). Acetonitrile was not considered as a potential substitute for NMP because it is not a strong base, like is needed for the resin precursor synthesis [115].

Based on the so far discussed literatures, it was aimed to blend PVC with ABS polymers by the solution casting technique, the technique that uses less energy, less cost and easily applicable when compared with the melt blending counterpart. The solution casting blending method can be apply for a lot of polymers without necessarily require hot mixing equipment like Bunbury extruder, roll mill, compression and extrusion molding, etc. PVC starts to decompose when the temperature reaches 140 °C (284 °F), with melting temperature starting around 160 °C (320 °F). Up to this date, it was possible to increase the HDT of PVC by around 8℃ with the help of styrenic polymers. This research work tries to improve the glass transition temperature, Tg at least by 12-15℃ using two kinds of acrylonitrile butadiene styrene polymers.

CHAPTER 3

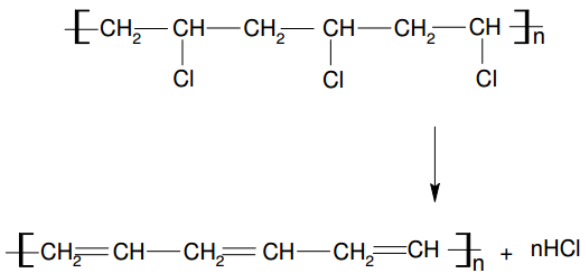
MATERIALS AND METHODOLOGY

3.1 Design Ideology

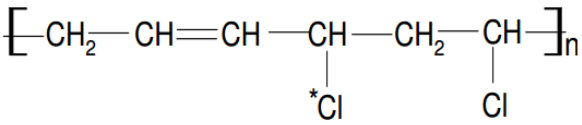
Material selection is one of the important factors to be considered while preparing blend because it plays an important role in mixing, processing and morphology of blend. This entails the materials needed, steps, process and methods of the manufacture of polyvinyl chlorides (PVC) blends. Polyvinyl chlorides (PVC) and Acrylonitrile butadiene styrene (ABS), the polymers of our interest, are only soluble in aprotic solvents like N-methyl pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), and dimethylformamide (DMF). Among these different solvents, NMP was chosen because of its relatively environmentally benign nature.

The other components that were added during fabrication of the blends like stearic acid, titanium oxide, zinc sulfate were also easily dissolvable in NMP.

Many excellent reference texts cover the instability of PVC at elevated temperature. It is known that PVC degrades at elevated temperatures, giving off hydrochloric acid (HCl) that in turn accelerates the degradation process. Thermal degradation is a process whereby the action of heat or elevated temperature on a material, product or assembly causes a loss of physical, mechanical or electrical properties. Thermal degradation of PVC (Scheme 1) occurs by an autocatalytic dehydrochlorination reaction (zipper elimination) with the subsequent formation of conjugated double bonds. After the loss of the first HCl molecule, the subsequent unsaturated structure formed in a PVC chain is an allylic chlorine structure.



Scheme 1. Thermal degradation of PVC



Scheme 2. (*) Allylic chlorine atom

The process starts at the glass transition temperature by elimination of HCl, which is the main volatile product up to about 330°C.

So based on this, ideology, any mechanism that can improve the glass transition temperature of PVC can also decrease the thermal degradation of PVC. Theoretically, ABS polymers have glass transition temperature higher than that of PVC and can be blended by both melt blending and solution casting method. The focus point in this project is also to get a blend that experiences modified **glass transition temperature, Tg** by blending PVC with ABS.

3.2 Lab Equipment

Magnetic stirrer Mixer, Isostatic Press for compression molding, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) to determine the glass transition temperature (Tg) of the prepared blends with the desired composition. FTIR (Fourier Transform Infrared Spectroscopy), universal tensile testing machine (UTM). The impact-fractured surfaces of PVC blends were detected by an SEM.

3.3 Raw Materials for Sample Preparation

The materials needed for sample preparation for the experiment are: suspension of 100 phr (parts per hundred resin) PVC with K value 65, ABS, two types of **Acrylonitrile butadiene styrene (**8540T grade and BK902051), N-Methyl-2-Pyrrolidone (**NMP**), stearic acid (4 phr), Titanium dioxide (TiO_2 3 phr) (stabilizer) . N-Methyl-2-pyrrolidinone (NMP, >99.5%, Loba Chemie) was used as the solvent for preparation of the casting solutions. Commercial grades of resins, with their manufacturer companies listed in table 3.1 were used as received.

Table 3-1 Chemicals Used in this Study

No.	**Chemicals**	**Sources**
1	PVC resin SG5 with K value 65-67	CHINA NEW CHEMICALS CO., LTD
2	Acrylonitrile Butadiene Styrene with acrylonitrile (AN) content 35 wt. % (SAN 35) (**ABS1**)	GLS POLYMERS PVT. LTD (India)
3	Acrylonitrile Butadiene Styrene with acrylonitrile (AN) content 25 wt. % (SAN 25) (**ABS2**)	TAITA CHEMICAL CO. LTD., (Taiwan)
4	N-Methyl-2-Pyrrolidone (**NMP**)	Loba Chemie Pvt. Ltd., (India)
5	Stearic acid ($CH_3(CH_2)_{16}COOH$) (lubricant)	LG CHEMICALS CO. LTD (Korea)
6	Titanium dioxide (TiO_2) (stabilizer)	KOJUNDO CHEMICAL LABORATORY CO., LTD (Japan)

Table 3-2 Weight ratio of PVC and ABS blends

No.	Sample Designation	PVC (phr)	ABS1(phr)	ABS2 (phr)
1	P00	100	0	0
2	PA01	85	15	0
3	PAA1	85	10	5
4	PAA2	85	5	10
5	P0A1	85	0	15
6	PA02	80	20	0
7	PAA3	80	15	5
8	PAA4	80	10	10
9	PAA5	80	5	15
10	P0A2	80	0	20
11	PA03	70	30	0
12	PAA6	70	25	5
13	PAA7	70	20	10
14	PAA8	70	15	15
15	PAA9	70	10	20
16	PAA10	70	5	25
17	P0A3	70	0	30
18	0AA	0	50	50

Table 3-3 PVC/ABS blend compositions

PVC (wt. %)	**ABS (wt. %)**
100	0
85	15
80	20
70	30
0	100

3.4 Preparation of the Polymer Blends

After all necessary materials were collected; samples of the following ratio were prepared separately. For each test, five specimens were tested, and the average value was obtained. In each case, the ABS contents varied from 0% to 30% of the PVC.

Different weight ratios of PVC/ABS blends were dissolved separately in NMP and these solutions were then mixed together and stirred for 24 hours at room temperature to obtain a homogenous mixture. The solution was then poured into silica crucibles and allowed to evaporate at room temperature for one day. Then the samples were placed inside a vacuum oven at 80℃ for 2 hours to remove any traces of solvent. After evaporation in a vacuum oven for 2 hours, the as-cast substrates with the silica plate were immersed into a deionized (DI) water coagulation bath at the ambient temperature to initiate the phase inversion. Afterwards, the obtained substrates were transferred into a flowing DI water bath for 8h to remove residual solvent before further use. This procedure yields mechanically stable and free standing specimen of average thickness of the order of mm.

3.4.1 General Steps Followed During Blend Preparation

1. Before the casting process, refractory materials with cavity in centimeters dimensions were prepared as molds with dimensions (3*4.5*0.5) cm^3.

2. PVC powder was weighed with analytical balance to be dissolved in the prepared solvent by magnetic stirrer at 25 ± 2 ℃ and a speed of 100 rpm.
3. After dissolving (PVC) powder in its solvent (NMP), ABS resin separately dissolved was mixed with PVC at different percentages to prepare the binary polymer blend casts.
4. Five specimens of (PVC/ABS) blend with different weight ratios (0%, 15%, 20%, 25%, and 30%) of ABS were prepared, respectively.
5. These sheets were left at room temperature for (24 / hours) and then removed from the molds after completing the solidification process; the casts were put into a vacuum oven at (80^oC) for (2 hours) to complete the curing process.
6. The homogeneity case of these blends was tested by using scanning electron microscope (SEM).
7. It was found that the best ratio of mixing between the two polymers is (80/20) % which exhibits the compatibility case between them.
8. The rule of mixture (equation 3.1) was applied for calculating the volume fraction of fibers (Ψ) for the composites.

$$\Phi = \frac{1}{1+(\frac{1-\Psi}{\Psi})x(\frac{\rho_f}{\rho_m})} \quad \text{.....3.1}$$

Where (Φ, Ψ) are the volume and weight fractions of the fibers, respectively, $(\boldsymbol{\rho_f},\ \boldsymbol{\rho_m})$ are the density of fibers and the density of matrix, respectively.

The density of the prepared blends was determined from the following equation:

$$\rho_m = X_1\rho_1 + X_2\rho_2 \quad \text{.....3.2}$$

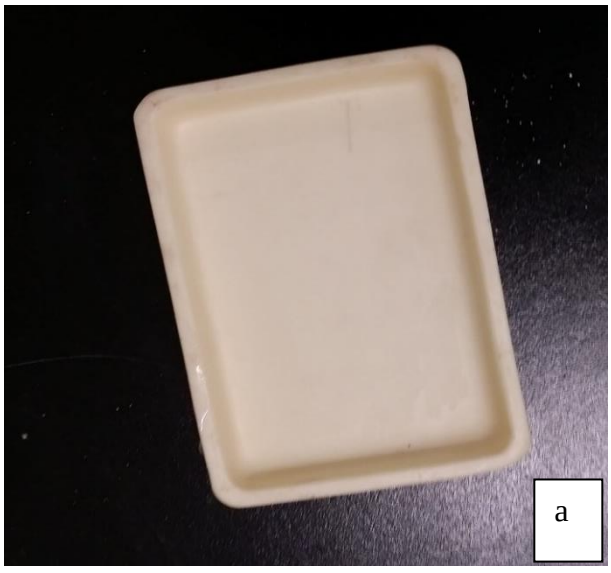
Where ρ_m: the density of the matrix (polymer blends), ρ_1, ρ_2: the density of the first polymer and the second polymer, respectively and X_1, X_2: the percentage of the first polymer that of and the second polymer, respectively.

9. The previous step was repeated with the two different types of reinforcement under study.

Table 3-4 Determination of the amount of each components in the solution that is required for the blend preparation

Preparation of the Solution				
Components of the solution	**Amount**			
	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**
PVC/ABS1/ABS2	20g	20g	20g	20g
NMP	30ml	35ml	40ml	45ml
Stearic Acid	0.75	0.75	0.75	0.75
Titanium Dioxide	0.55	0.55	0.55	0.55
Remark	Not dissolved	Slightly dissolved	Fully dissolved	Fully dissolved with difficulty in evaporating

The information provided in table 3.4 indicates that the amount of NMP solvent needed for the preparation the solution is twice as the amount of polymer in the solution. The prepared specimens are shown in figure below.



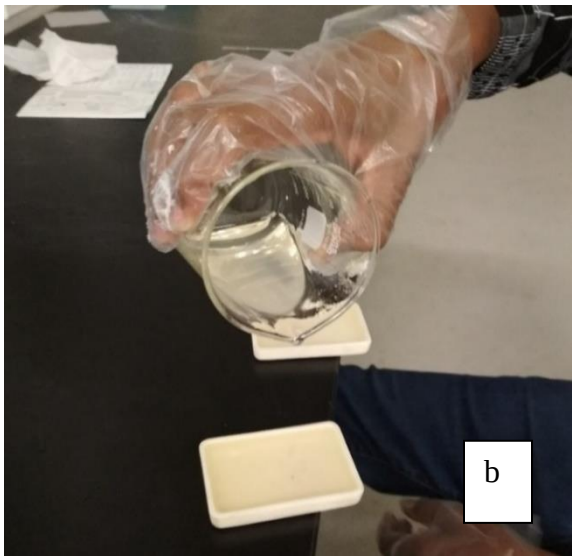


Figure 3-1 (a) Refractory mold in which the solution is casted (b) a photograph showing while casting the solution in the given mold (c) specimens of the blend prepared by the steps explained earlier

Samples for tensile testing were molded in dumb-bell shape (dog bone) according to the size specified in ASTM-D638 (1990). The samples were eventually subjected to the following tests:

1. Stress/strain testing
2. SEM characterization
3. DSC characterization
4. DTG characterization
5. FTIR characterization
6. XRD characterization and others.

3.5 Sample Details

The samples of PVC blends were made from PVC resin SG5 K = 65-67 for general-purpose suspension grade, carbide based. It has good performance in thermoplasticity, insolubilization in

water, gasoline or ethanol, swelling or dissolving. PVC resin SG5 is widely used in the production of PVC boards, PVC pipes, PVC profiles, PVC doors and windows structural section, PVC rigid transparent sheet, PVC monofilament and on. It is also used as electric insulation made of technical data sheet.

3.6 Characterizations

Physicochemical characterization of PVC/ABS blend systems was carried out using various thermal and spectrochemical techniques. Morphology of the blends was studied using a JEOL–44 scanning electron microscope with an accelerating voltage of 15 kV. Thermal behavior was analyzed by using a differential scanning calorimeter, DSC–60 plus Shimadzu, coupled with a TA–2000 data processor. Thermograms were recorded by heating the samples from 30 to 300℃ at the rate of 10℃/min. Glass transition temperature, Tg, and change in specific heat, ΔC_p data, obtained from first heat scans were compared. Degradation characteristics were studied using a Shimadzu DTG 60H instrument. The blends were heated at 10℃ /min from 30 to 300℃ under an inert atmosphere. Nitrogen gas flow rate was maintained at 50 ml/min. FTIR spectroscopy was carried out on a Spectrum 65 FTIR (Perkin Elmer instrument).

3.6.1 XRD Characterization

Different methods are available for investigating the structure of multiphase polymeric materials. X-ray scattering is a very powerful technique for the morphological characterization of semi-crystalline polymers, microphase separated block copolymers, or polymer blends.

Radiation can interact with matter without any energy loss and only the momentum of the radiation will be changed. In this case, the radiation is diffracted or scattered. Although the first terminus is correct, often the second terminus is used in the literature. This so-called static scattering can be used to investigate the structure of a material by measuring the scattered intensity as a function of the angle.

X-rays interact with all the electrons of atoms, independent of their binding energy to the nucleus, because the energy of X-rays is usually much higher than the energy of electrons in an atom. The interaction between X-rays and electrons is rather weak and thus only a weak function

of wavelength (if no absorption processes take place). The probability of interactions between radiation and matter depends on the density of these properties within the matter.

In a good scattering experiment most of the incident photons passing through the sample are transmitted, i.e. pass through the sample without any interactions. This can be achieved by using sufficiently thin samples. Otherwise, a photon may interact more than one time with the sample, leading to multiple scattering. Multiple scattering is not useful for gaining structural information of the sample, since no unambiguous relation between the direction of the finally scattered (and detected) photon and the incident direction of the beam can be determined.

In this project, X-ray diffraction study of the prepared blends was conducted by using a diffractometer (XRD – 7000S SHIMADZU) equipped with monochromatic Cu-Kα radiation (λ=0.154 nm). All samples were analyzed in continuous scan mode with the 2θ ranging from 10° to 80°.

3.6.2 Fourier Transform Infrared Spectrophotometer (FTIR)

Infrared spectroscopy historically has been a method of choice for characterizing a broad range of materials such as plastics, catalysts, ceramics, coatings, and chemicals. Fourier transform infrared (FTIR) spectrometers are found in many material science groups as well as quality control departments and testing laboratories. Acquiring an infrared spectrum is frequently the first step in identifying or characterizing a sample of unknown material, as well as analyzing for contaminants or chemical differences in a sample of a rejected product. The infrared spectrum of a material can be considered a molecular fingerprint, which can be used to identify the specific chemical components. Large databases of infrared spectra from many chemicals and materials make it possible to rapidly compare the fingerprint from a sample to thousands of reference spectra and determine the most similar compounds. Reference spectra are available for solids, liquids, and gases in items such as polymers, additives, coatings, ceramics, minerals, and many other commercial materials. Sophisticated computer algorithms were developed to perform complex matches for multiple components in seconds, providing valuable information about the chemical composition of unknown materials, degradation, contaminants, or treatments.

In this project, Spectrum 65 FTIR (Perkin Elmer, Addis Ababa University) was used to determine the spectra of each hydrocarbon composition found in the prepared specimens running in the range of 400-4000 wavelength cm^{-1} using KBr pellets.

3.6.3 Mechanical Testing (Tensile Strength)

Tensile data (tensile strength, modulus of elasticity and elongation at break) for the virgin PVC and blended PVC samples were obtained at 25±2℃ using a Santam, universal tensometer (5T). Tests were conducted on at least three specimens, at a cross-head rate of 50 mm min^{-1}.

Table 3-5 ISO 527 and JIS K 7161 Specimen Dimensions

Size	Dimensions in (mm)
Full length, l_3	150
Mid length, l_2	80
Parallel length, l_1	60
Gauge length, L_0	50
Parallel section width, b_1	10
Thickness, h	4
Grip section width, b_2	20
Grip face length, L	115

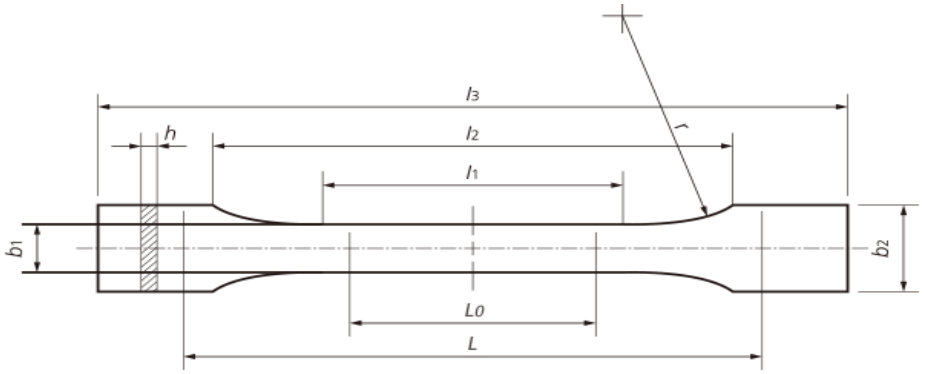


Figure 3-2 ISO 527 PVC specimen dimension for tensile test

The stress-strain behavior of a material determines the material contribution to part strength (or stiffness), the relationship between load and deflection in a plastic part. Other factors that affect part strength include part geometry, loading, constraint conditions on the part, and the residual stresses and orientations that result from the molding process. There are various types of strength,

such as tensile, compressive, torsional, flexural, and shear, depending on the load and restraint conditions the part is subjected to. These types also correspond to the primary load state present in the part. The stress-strain behavior of the material in the same mode as the primary load state in the part is most relevant in determining part strength.

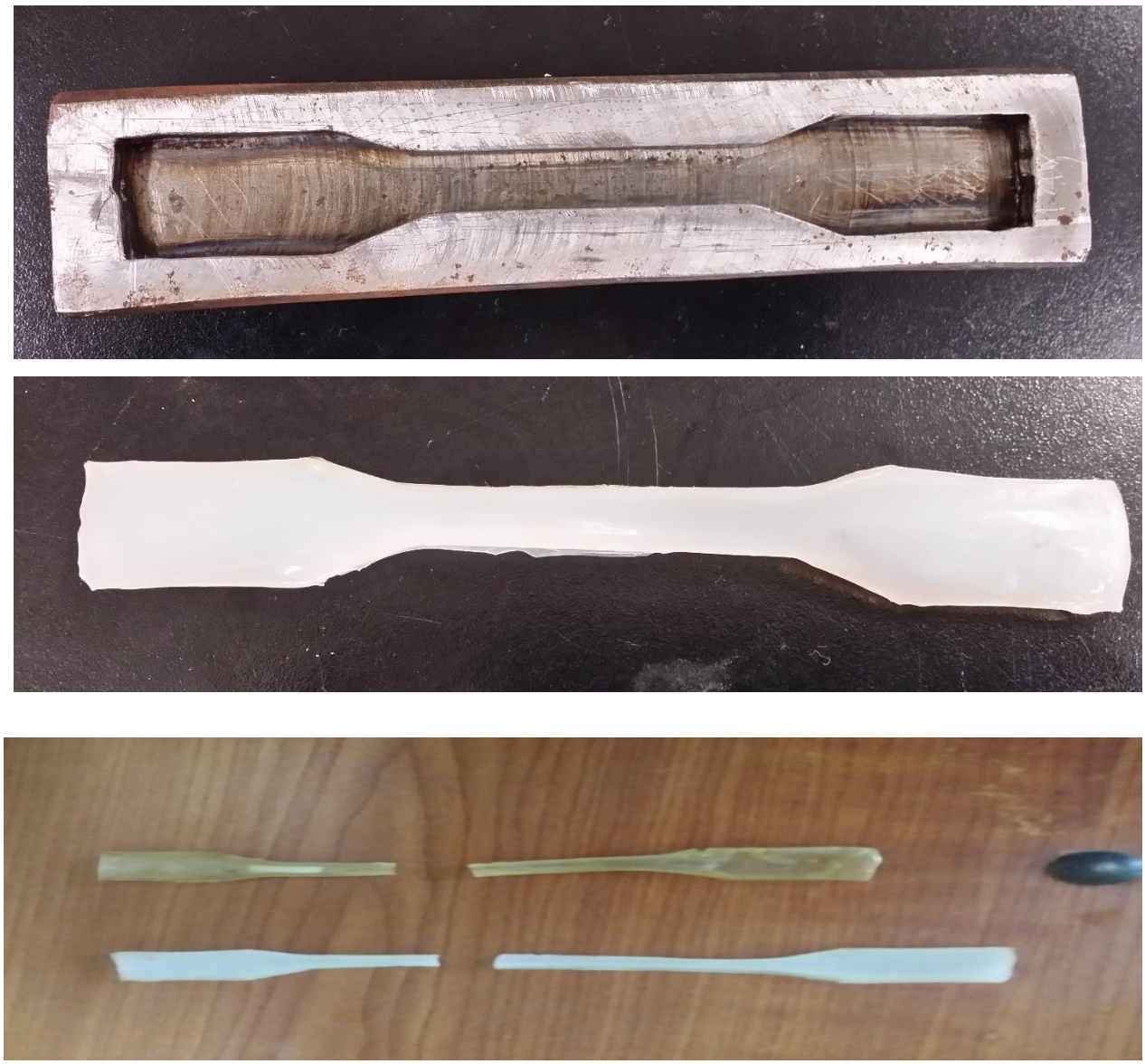


Figure 3-3 Mild steel mold prepared according to the dimensions specified in ISO 527 for making the specimen that undergo tensile test

3.6.4 Thermal analysis technique

Thermal analysis instrumentation has found wide acceptance in plastic industry for quality control and basic material characterization. Thermal analysis consist of two technique that may be used individually or in combination.

3.6.4.1 DSC Characterization

Differential Scanning Calorimetry, or DSC, is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time.

Very thin flat samples are necessary for this work, because the DSC is measuring heat-flow differences in response to sample shape changes caused by the various relaxations, seen up to 180 °C. Samples were therefore cut from the sections of PVC extrusion in the area shown for all four samples. The cuts were made using a low-speed diamond saw which does not produce any stresses in the sample during preparation, and produces very smooth samples, which allow good thermal contact with the DSC sample pan.

Using a knife to cut samples produces distortions in the material (curling) during cutting, resulting in poor thermal contact with the sample pan at the start of the test. When such a sample is heated subsequently, these stresses are released and produce distortion of the baseline as the glass transition is passed, causing changes in thermal contact and leading to errors in the determination of Tg.

Cutting using the diamond saw produced thin sheets sample material about 0.5 mm to 0.7 mm thick and these were cut to size to suit the DSC sample pan using a circular “punch”. The flattest side following the “punching” process was laid downwards in the open aluminum sample pan used for the test to ensure the best possible thermal contact. Sample masses of around 6.6 mg were used for this testing.

The method used in the DSC was to heat from ambient to 180 °C at 10 °C/min under a nitrogen atmosphere flowing at 50 mL/min. The sample pans used were Perkin Elmer standard aluminum sample pans (0219-0041), which are about 6 mm diameter. The sample pan is crimped to prevent the sample freedom to move and distort in the pan during heating.

3.6.4.2 Thermogravimetric Analysis (TGA)

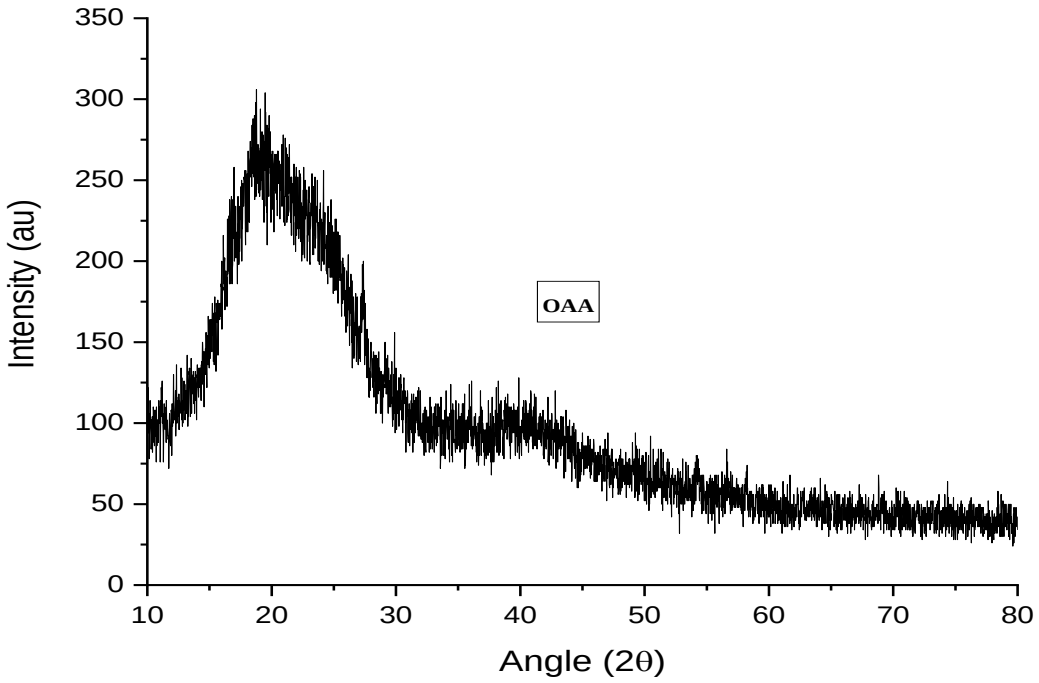
TGA has been quite useful in determining the thermal stability of PVC/ABS blend. Thermo gravimetric analysis is test procedure in which change in weight of specimen is recorded as the specimen is progressively heated. The sample weight is continuously monitored as temperature is increased at constant rate and component of a polymer that volatilize or decomposed at different temperature are quantitatively measured. TGA for polymer is carried out on granules while for various blends composition by using pellets. It was carried out on SHIMDZU DTG 60H thermo gravimetric analysis equipment. Plot of % weight Vs temperature as obtained from the TGA testing are as shown in graphs on subsequent pages. Primary thermo gram of PVC, ABS and PVC/ABS blends (for 15 %, 20 % and 30 %) were shown in graph. For PVC two-step decomposition was observed. Major volatilization started at around 250℃ and above 350℃. Complete dehydochlorination of PVC took place and HCl is predominant product of degradation. In case of ABS, volatilization started at around 300℃ with sharp loss of weight.

CHAPTER 4

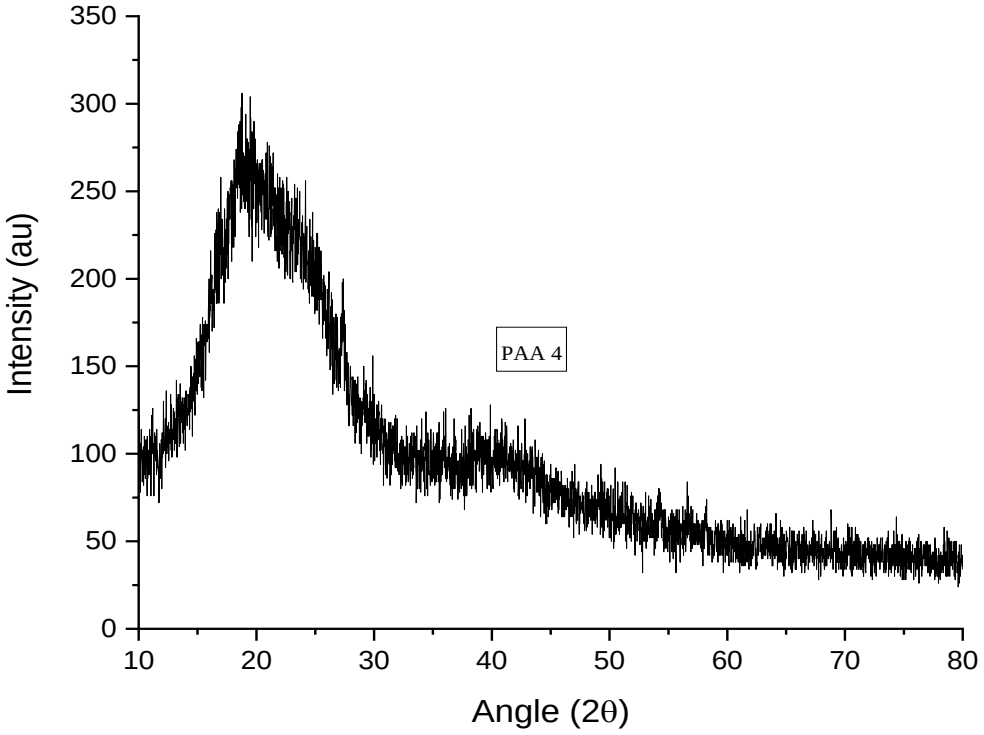
RESULTS AND DISCUSSION

4.1 XRD Results Analyzation

The X-ray diffraction pattern shows the amorphous nature of the commercial PVC and the studied polymer blends as in (Figure 4.1 below). The X-ray diffraction pattern for PVC is shown in Fig. 4.1 d. PVC generally exhibits an amorphous phase. The incorporation of ABS into the PVC matrix causes a shift in the Bragg peaks from 20.6º to 22º and from 28.4º to 40.3º as observed in Fig. 4.1 b to c.



a)



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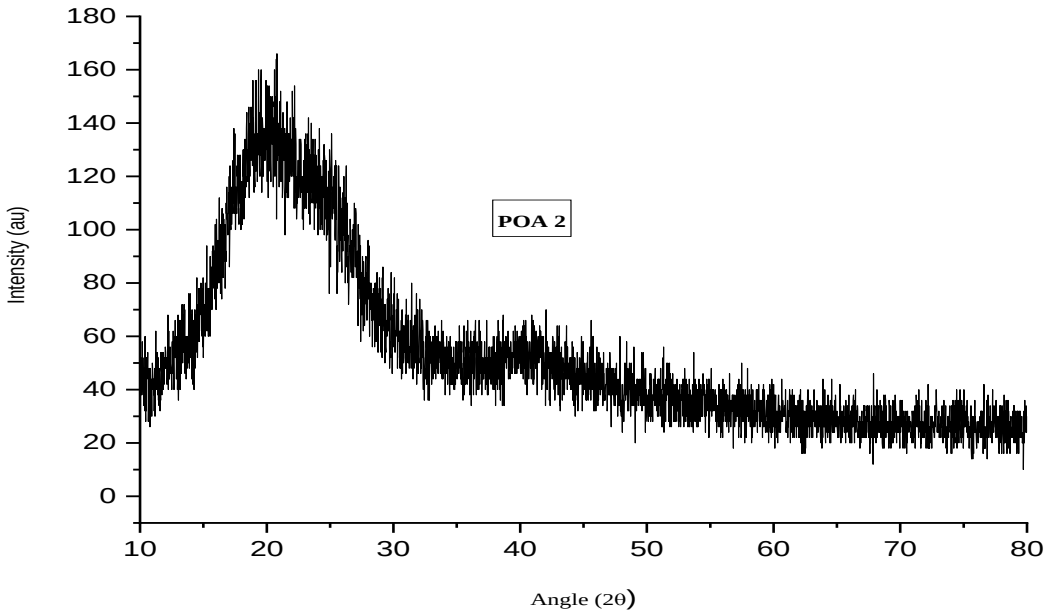

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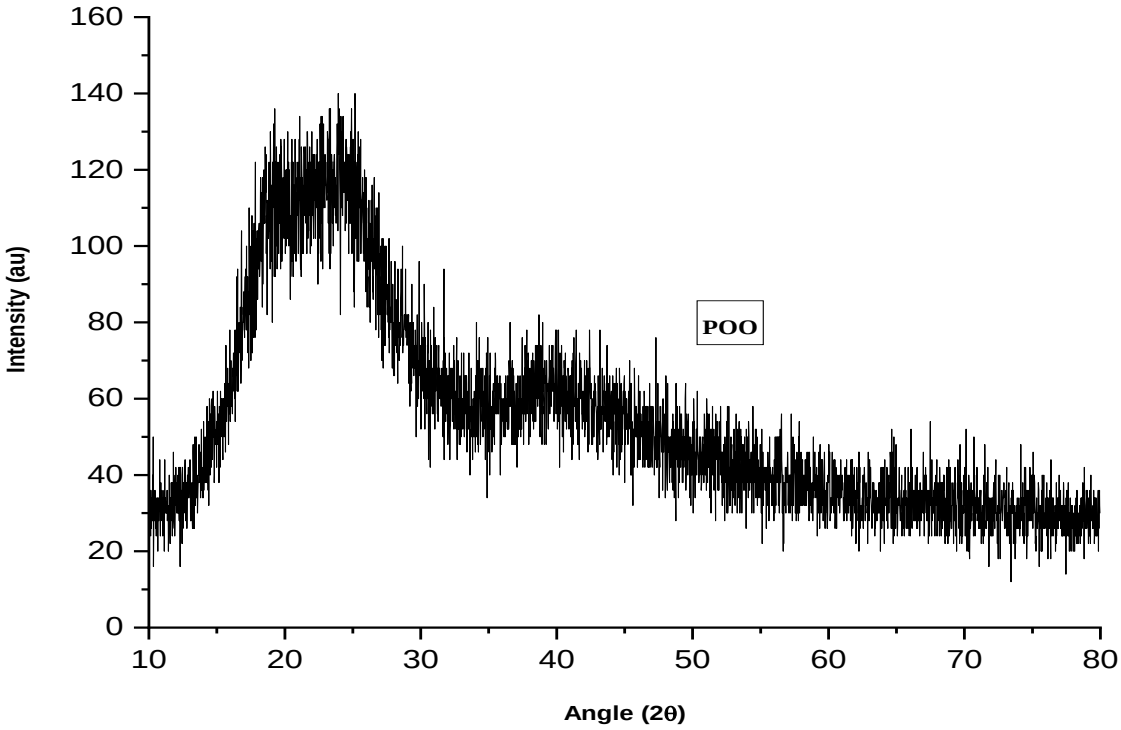
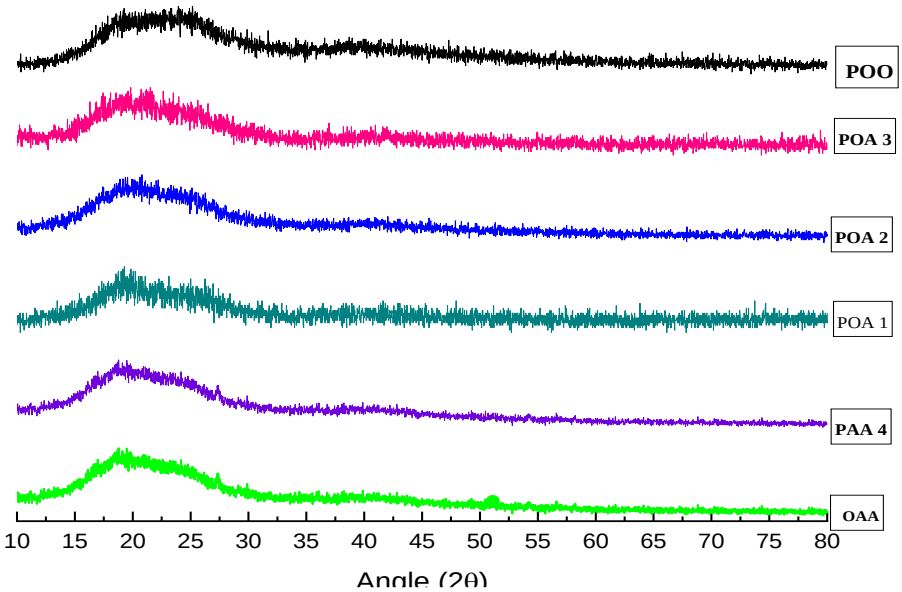


d)



e)

Figure 4-1 XRD Diffraction patterns of the prepared PVC/ABS blends (a) POA 2 (70/30) (b) POO (pure PVC) (c) stacked graph of all samples

The compatibility of PVC and ABS was also confirmed by XRD analysis as shown in Fig. 4.1. In XRD diffraction pattern of neat PVC specimen, there is a broad peak in the 2θ range of about 15–30° which indicates the amorphous nature of PVC [116]. In addition, the small peak observed at 2θ of 38° represents the semi crystallinity of PVC [117]. On the other hand, a broad peak in the 2θ range of about 13–25° was observed in XRD pattern of neat ABS membrane indicating that ABS is also amorphous. It can be seen that all blends prepared have almost the same XRD diffraction patterns and as the content of ABS increased in the blends, the broadness of the peak decreased slightly and the maxima shifted toward smaller 2θ. These results confirm the compatibility of PVC and ABS blends. There is no additional peaks observed in the blends in all ratios treated, which confirmed the absence of the effect of solvent used in the synthesis method.

4.2 Fourier Transform Infrared Spectrophotometer (FTIR)

Infrared spectroscopy is an important tool for the identification of polymeric chemical structures. The IR spectra vary according to material chemical composition and can indicate the complexation and interaction between its constituents. The analysis of the FTIR spectra showed that all of the blends are quite identical by their chemical structure. IR analysis has been quite extensively used in the determination of terpolymer ABS in PVC blends [118]. In the present study, solutions of the PVC/ABS blend samples were made in methylethylketone (MEK) cast as films and subjected to IR analysis. Figure 4.2 represents IR spectra of PVC/ABS blends and the individual components. The band at 2237cm^{-1} is associated with the nitrile (C≡N) functional group, characteristic of acrylonitrile in ABS. There is absence of a peak in this region in the IR spectrum for PVC. In case of an interaction of the C≡N group with the C-H group of PVC, a shift in peak position is expected. However, in the present case, only the intensity of the peak at 2237cm^{-1} has changed.

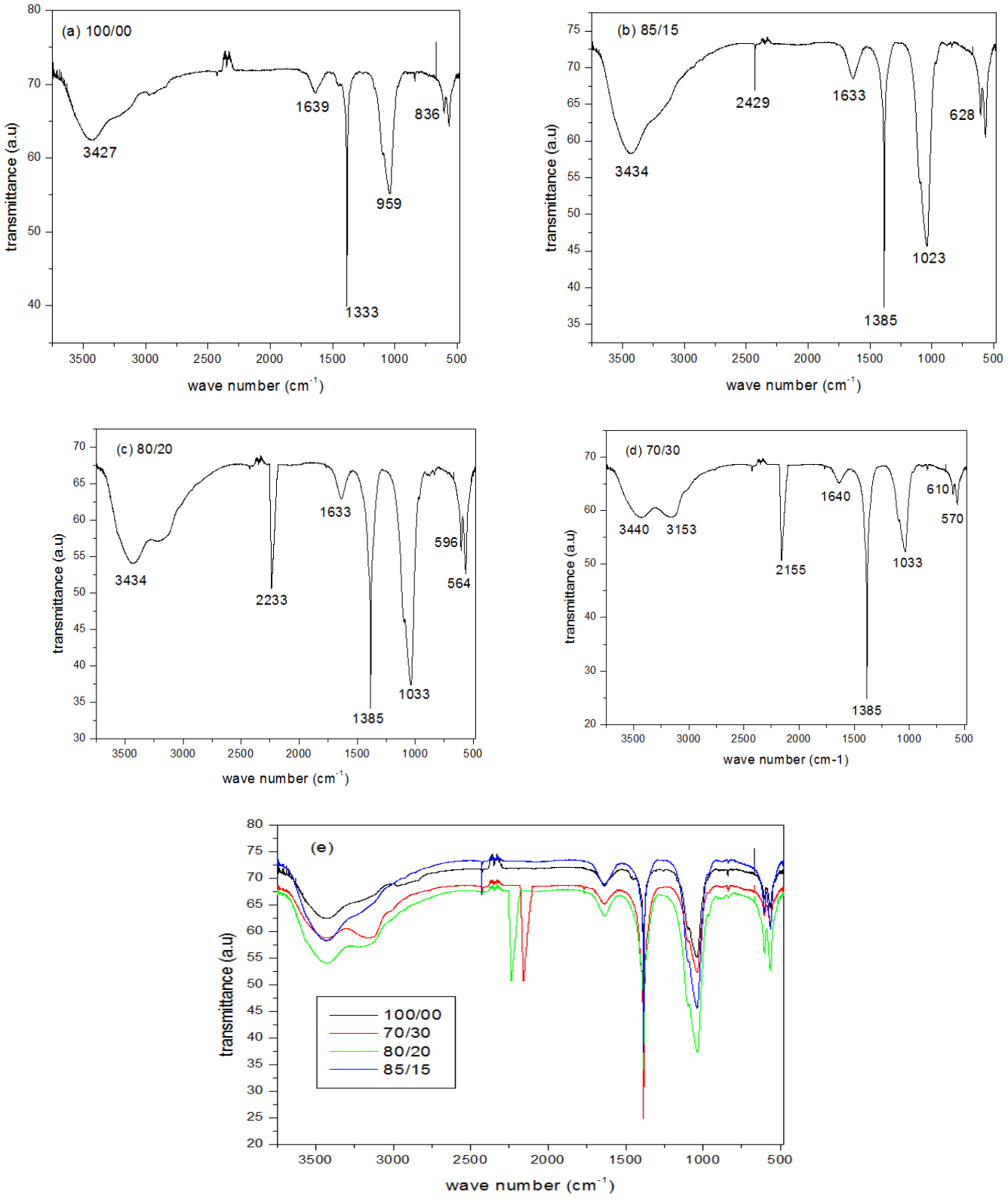
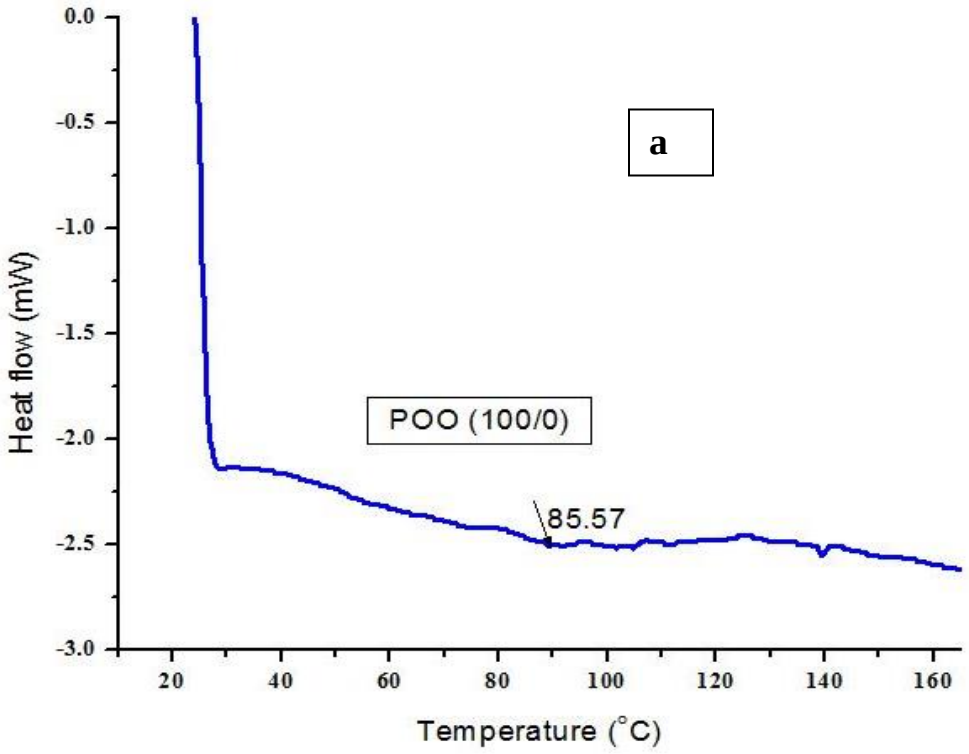


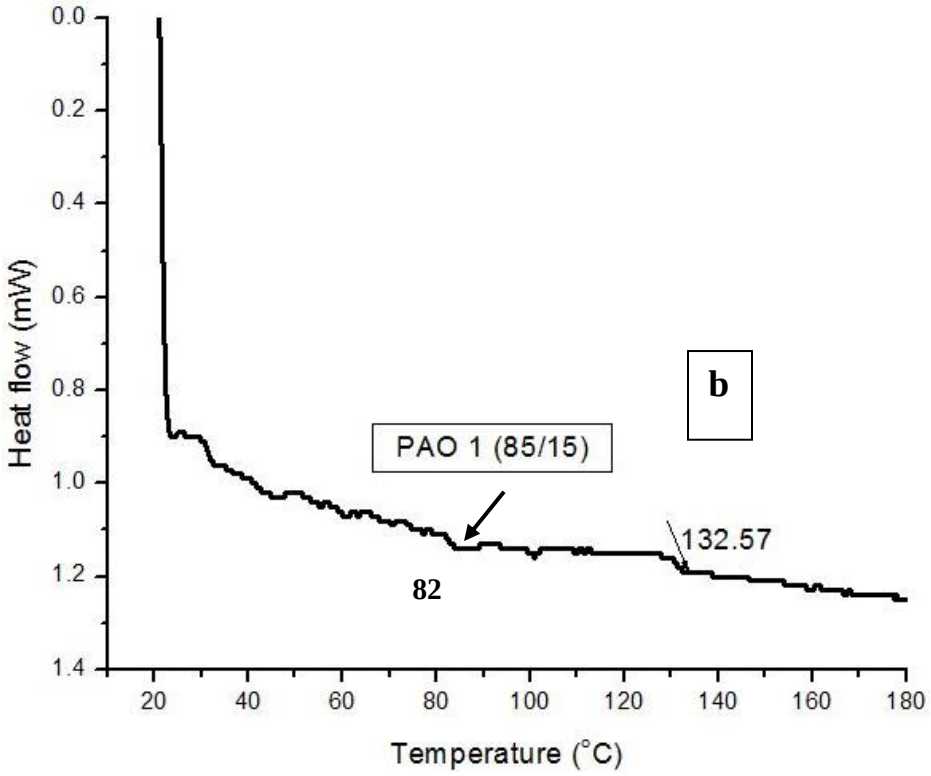
Figure 4-2 FTIR spectrum of (a) pure PVC (b) PVC/ABS (PVC/ABS 85/15 blend) (c) PAA 4 (PVC/ABS 80/20 blend) (d) PAA 6 (PVC/ABS; 70/30 blend) (e) stacked graph of all compositions

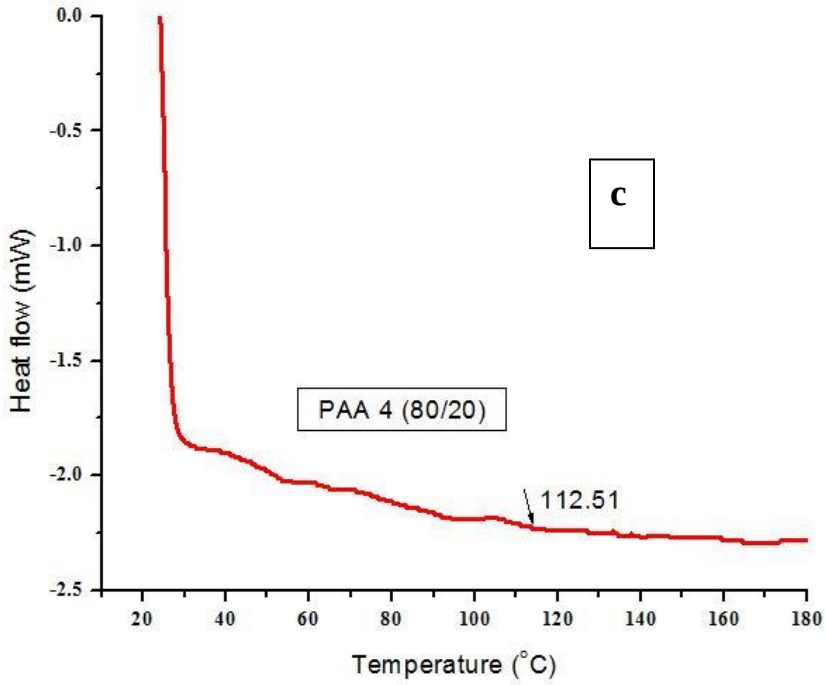
The FTIR spectrum for pure PVC specimen showed characteristic peaks of this polymer (Fig.4-2). C–H bond stretching is observed at 2411 cm^{-1}, CH_2 groups deformation at 1333 cm^{-1}, out of plane angular deformation (ρCH) at 1254 cm^{-1}, out of plane trans deformation (ωCH) at 959 cm^{-1} and C–Cl bond stretching at 836 cm^{-1}. These bands are in accordance with data found in literature for PVC.

4.3 DSC Results Analyzation

Because there is a change in heat capacity, but there is no latent heat involved with the glass transition, we call the glass transition a *second order transition*. Transitions like melting and crystallization, which do have latent heats, are called *first order transitions*.




b
PAO 1 (85/15)
132.57
82
Heat flow (mW)
Temperature (°C)


c
PAA 4 (80/20)
112.51
Heat flow (mW)
Temperature (°C)

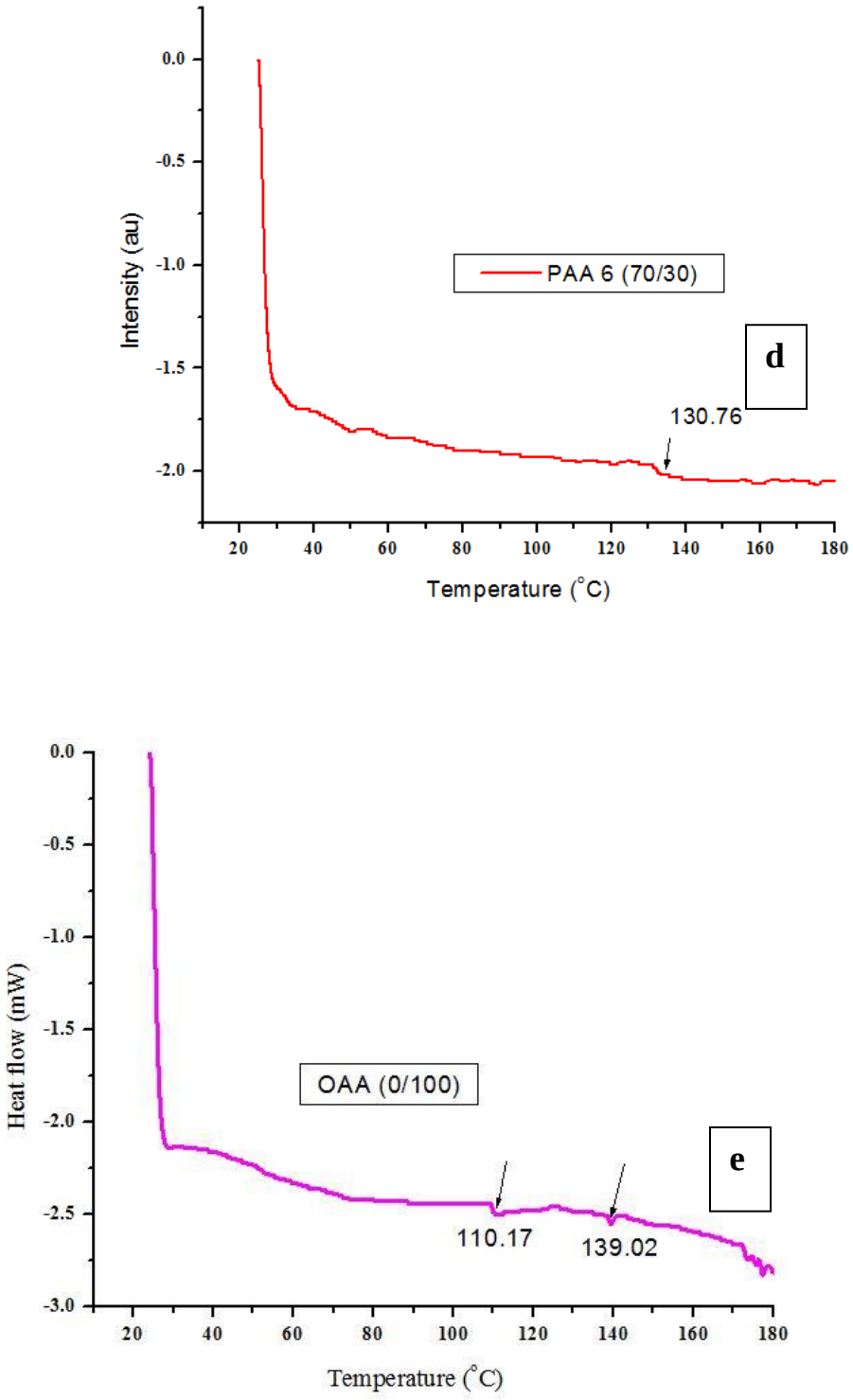


Figure 4-3 DSC curves for the prepared PVC/ABS blends

The DSC first heat scans for formulated PVC, the blend samples, and virgin ABS are shown in Fig. 4.3 the sample of 50/50 wt.% ABS1/ABS2 showed two glass transition temperature (Tg) values above room temperature, one at 110℃ which can be ascribed to polystyrene and the other at higher temperature, at 139℃, to polyacrylonitrile. This may be on account of the fact that the ABS used in the present study was a block co-polymer, whereas for graft co-polymer, two Tg's one at –108℃ due to polybutadiene and the other at 114℃ due to rigid poly(styrene-co-acrylonitrile) are reported [119]. The sub ambient Tg corresponding to polybutadiene could not be observed in this case since the analysis was carried out above room temperature. The formulated PVC pellets showed (Fig. 4.3 e) a Tg near 110℃ with corresponding change in specific heat of about 2.6 J (gm K)$^{-1}$. It can be noted from Table 4.1 that the blend samples also show two glass transitions one at 110.17℃, and the other at 139.02℃. The variation of corresponding ΔC_p(I) value with % ABS is shown in Fig.4.3. It can be marked from the DSC curves that there is a total disappearance of a higher temperature Tg at 139℃, originally observed in virgin ABS. Thus, all the blend samples, which their DSC graphs not appear here, were characterized by the presence of two distinct glass transition temperatures. This suggested incompatibility of the PVC/ABS blend. In practice, complete miscibility of such rubber modifiers as ABS in PVC is not always desirable to achieve useful mechanical properties [120].

Table 4-1 DSC results of PVC/ABS blends

		Tg (℃)		
PVC %	**ABS %**	**I**	**II**	**III**
100	0	85.57	--	--
85	15	102.57		
80	20	112.51		
70	30	130.76		
0	100	110.17	139.02	--

For each of the composition of the specimen composition listed 1-18 in table 3-2 above, glass transition temperature obtained from DSC result is tabulated in the following table 4-2.

Table 4-2 Glass transition temperature of each sample obtained from test DSC results

No.	Sample Designation	PVC (phr)	ABS1(phr)	ABS2 (phr)	Tg1	Tg2	Tg3
1	P00	100	0	0	85.57	--	--
2	PA01	85	15	0	82.14	132.57	--
3	PAA1	85	10	5	83.51	109.11	--
4	PAA2	85	5	10	81.45	101.12	--
5	P0A1	85	0	15	102.57	--	
6	PA02	80	20	0	50.6	104.7	132.96
7	PAA3	80	15	5	103.71	--	123.56
8	PAA4	80	10	10	112.51	--	--
9	PAA5	80	5	15	101.35	119.19	134.8
10	P0A2	80	0	20	112.51	123.23	--
11	PA03	70	30	0	87.04	111.6	--
12	PAA6	70	25	5	130.76	--	--
13	PAA7	70	20	10	123.12	129.21	--
14	PAA8	70	15	15	103.63	127.43	--
15	PAA9	70	10	20	104.5	117.45	131.76
16	PAA10	70	5	25	79.56	97.02	123.35
17	P0A3	70	0	30	84.74	132.82	--
18	0AA	0	50	50	110.17	139.02	--

As it can be seen from values in the table 4-2 above, a large number of samples exhibited two or three glass transition temperature, which means there is a failure to complete miscibility. The possible reason is supposed to be preparation procedure. According to literatures, results based on glass transition temperature measurements and on LCST behavior, have indicated that for SAN copolymers having an acrylonitrile (AN) content ranging from about 11 to 26 wt. %, miscibility with PVC is observed in the continuous phase when prepared in melt blending method. The other point is that it should be pointed out that the polybutadiene in ABS is not miscible with PVC, because of the difference in their polarity. Thus, the PVC/AMS-ABS blends are likely to exhibit a dual-phase structure: one phase is composed of PVC and the other phase is polybutadiene. This heterogeneous structure is also supported by the SEM micrographs, which are shown in the next section.

In case of ABS with 35 wt. %, SAN, the number of polybutadiene content is less and hence there is a great chance compatibility between polybutadiene and polyvinyl chloride. Samples of PVC/ABS blends that showed enhanced properties were that of ABS with 35 wt. % SAN. In the subsequent pages, all characterizations and tests focus on the blends that exhibited enhanced properties, which are blends of PVC and ABS with higher SAN content.

4.4 Thermogravimetric Analysis

Thermograms of pure components as well as blend specimens recorded by TG analysis are shown in Figure 4.3. The temperature of onset of degradation (T_{onset}), and temperature at which half the decomposition was completed (T_{50}), as calculated from the degradation curves, are presented in Table 4.3. PVC showed a two-stage decomposition pattern in agreement with the literature [118]. The temperature of onset of the first stage decomposition was found to be around 250℃. 57.646% weight loss during a temperature interval of 100℃ was predominantly due to the dehydrochlorination leading to formation of unsaturated hydrocarbons. After the first stage decomposition, a stable temperature zone was recorded for about 80℃. In the second graph, decomposition reaction started around 260℃. The major decomposition products in the second stage were reported to be benzene and toluene. This resulted into 38.089% weight loss up to a temperature of 280℃. ABS followed a single-step rapid degradation with the onset at 400℃. Nearly 100% decomposition was completed within the narrow temperature interval of 558℃.

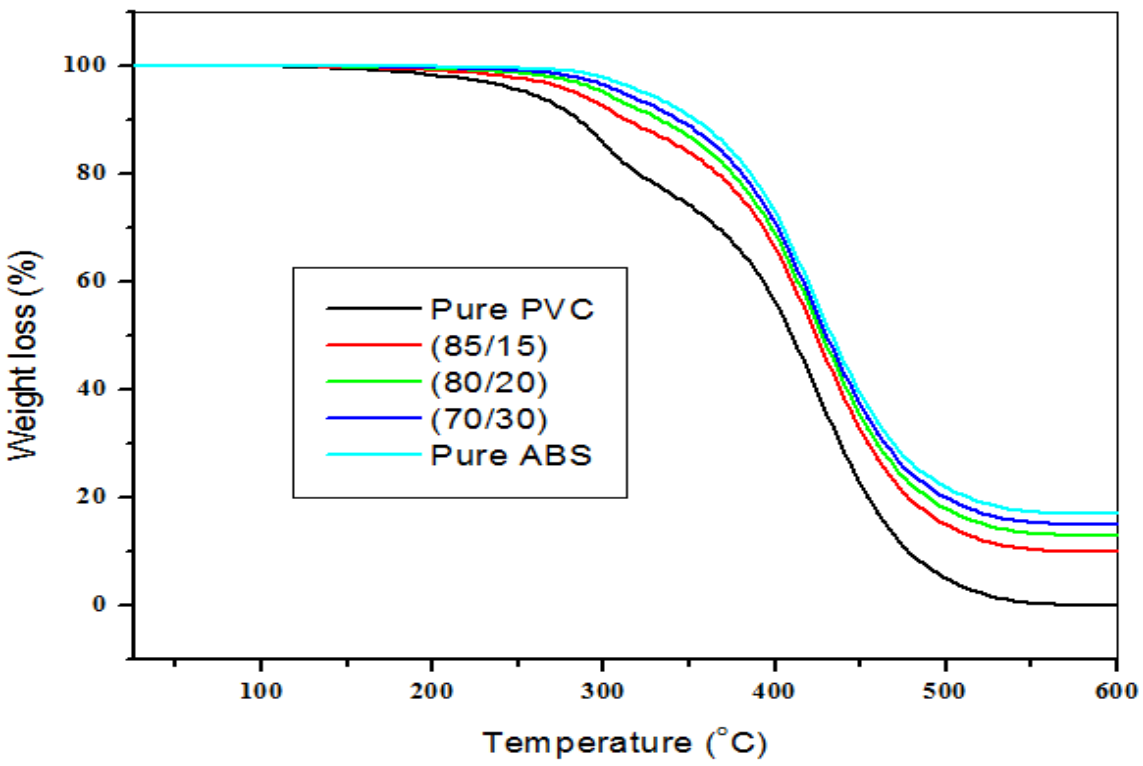


Figure 4-4 TGA graph of the formulated blends

Table 4-3 TGA results of PVC/ABS blends

PVC %	***ABS %***	T_{onset} ℃	T_{50} ℃	***Weight loss %***
100	0	250	350	57.646
85	15	255	360	47.852
80	20	255	380	38.059
70	30	260	410	32.143
0	100	360	430	26.228

A marginal increase in heat stability of the blend with increase in percent composition of ABS was indicated by a slight increase in the temperature of onset of degradation. A two-stage decomposition pattern, characteristic of virgin PVC, was reflected in the blend as well. The relative size of the two stages varied in relation to the percentage concentration of the two components. Decomposition data obtained from the DTG curves corresponding to both the stages was tabulated in Table 4.4. First-stage decomposition due to evolution of HCl was quantitatively suppressed with progressive addition of ABS. 54% weight loss in the first stage and 26% in the second stage was recorded in the sample of pure PVC. The rate of decomposition was affected by the presence of ABS. This was indicated in the changed slope of the TGA curves. This was confirmed by plotting the same against % ABS as shown in Fig. 4.5. This figure shows that the rate of decomposition of actual blends is less than that expected from the rule of mixtures indicated by the straight line in the graph. Subsequently, higher temperature and time was required for the weight, to decrease to 50% of its initial valve. Incorporation of ABS thus affected the decomposition pattern, rate, and overall chemistry.

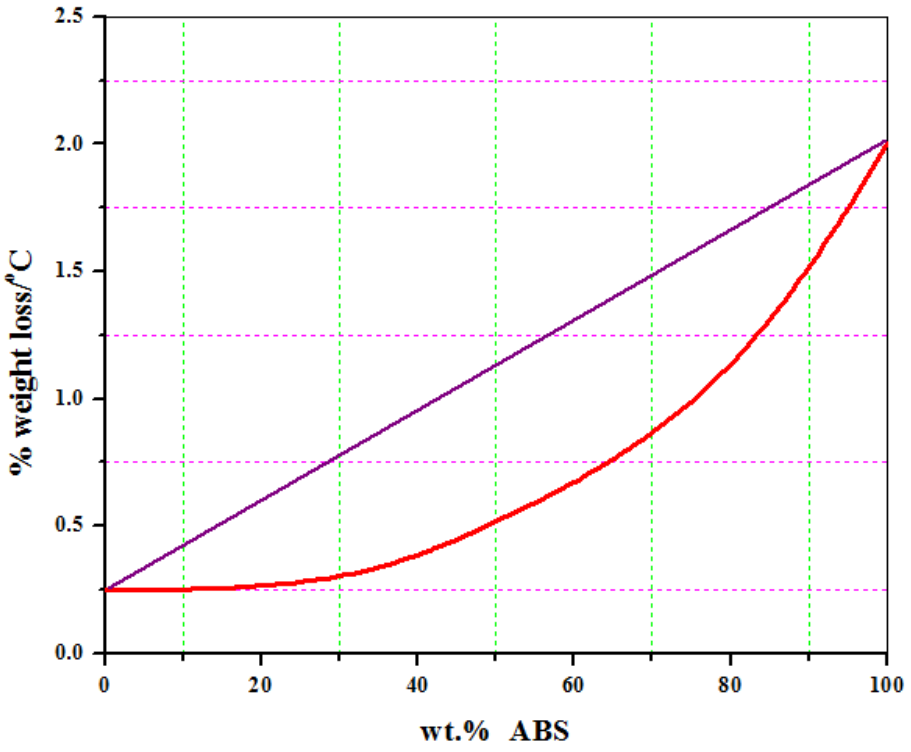


Figure 4-5 Variation of rate of weight loss versus % ABS in the blends

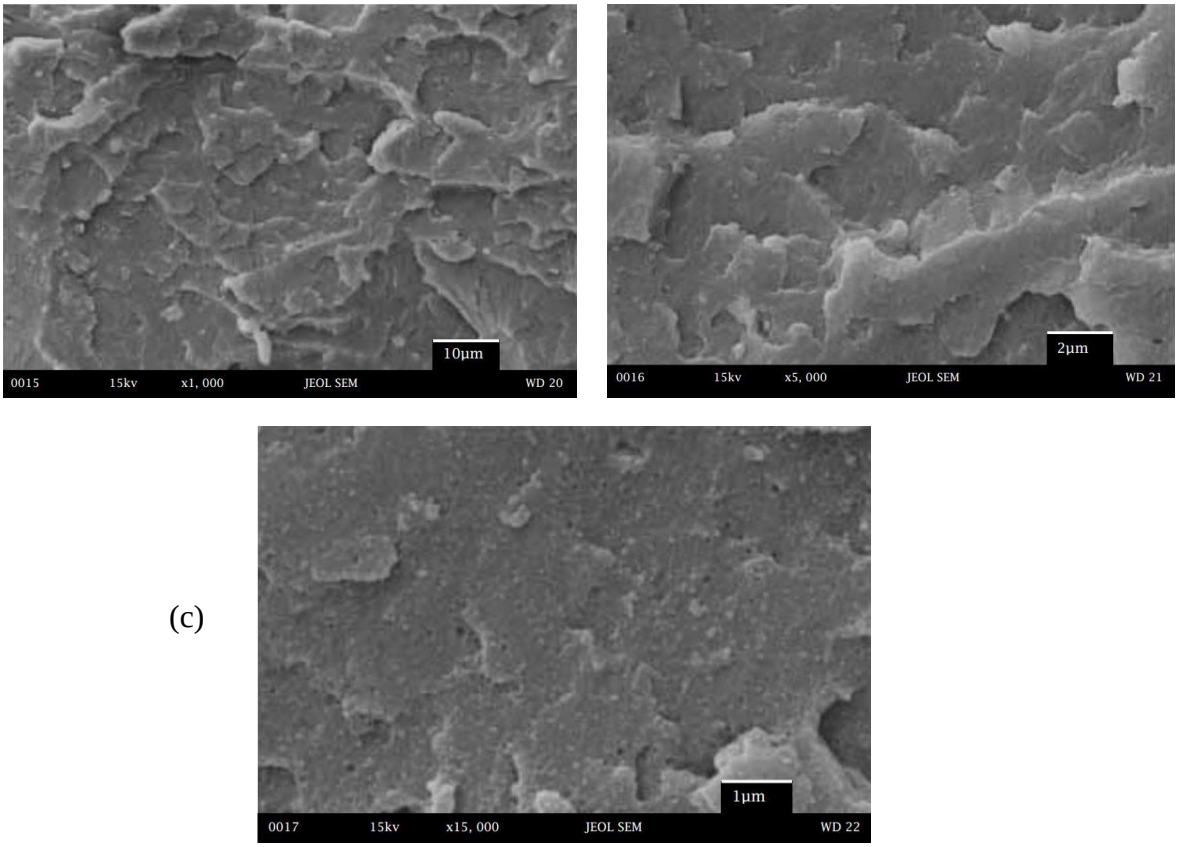
Table 4-4 First and second stage degradation (%) of PVC/ABS blends

PVC%	**ABS %**	**First stage degradation %**	**Second stage degradation %**
100	0	57.64	26
85	15	41	22.51
80	20	38	16.56
70	30	77	43
0	100	26.13	11.56

4.5 Scanning Electron Microscopy Studies of the Morphology

Scanning electron micrographs of the blends surfaces of the PVC/ABS specimens were observed under different magnifications. The examination of micrographs of PVC/ABS blend under 15000X magnification, shown in Fig 4.6 (a) – (c), reveals a good uniform dispersion of fine elastomeric particles in the PVC matrix. It was also observed from the cavities present in Fig. 4-6 (c) that the elastomeric component falls out. This indicates poor interfacial adhesion between the matrix and the dispersed phase, which further complements the findings of Kulsherashtha et al. [121].

(a) (b)



(c)

Figure 4-6 SEM micrographs of PVC/ABS; 80/20 blend, magnification 1000X, (b) SEM micrographs of PVC/ABS; 80/20 blend, magnification 5000X, (c) SEM micrographs of PVC/ABS; 80/20 blend, magnification 15000X.

The morphology of the fractured surfaces of PVC/ABS blend under 1000X magnification is shown in Figure 4.7 (a) – (c). The surfaces were mainly composed of separate tiny platelets and were shaped like clouds. The asperity of the surface increased with increasing amounts of ABS,

and the platelets began to overlap each other, so more energy was dissipated in the fracture. This agrees with the observations of Zhou et al. [117] and Zhou et al. [119].

(a) (b) (c)

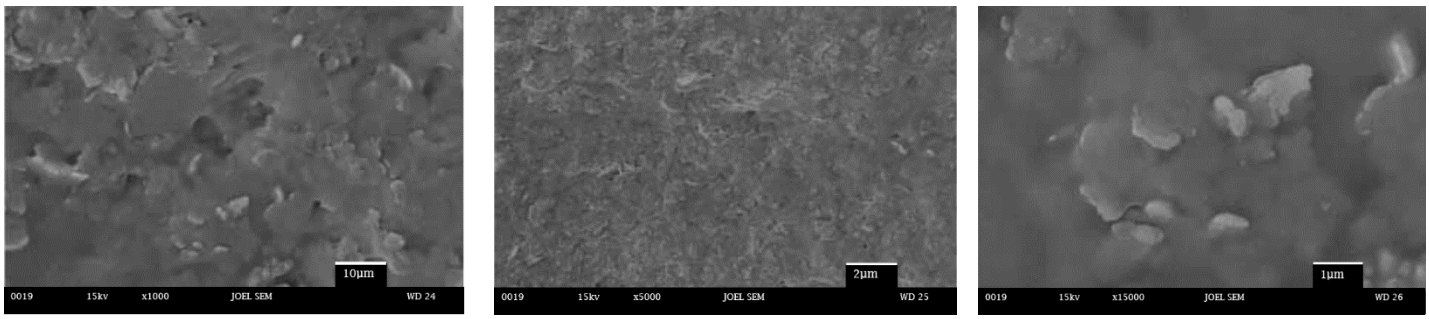


Figure 4-7 (a) SEM micrographs of PVC/ABS; 70/30 blend, magnification 1000X, (b) SEM micrographs of PVC/ABS; 70/30 blend, magnification 5000X, (c) SEM micrographs of PVC/ABS; 70/30 blend, magnification 15000X.

The SEM studies of PVC/ABS blends revealed uniform dispersion of one phase in the other, up to 30% of ABS in the blend. With higher percentage of ABS, agglomeration, in-homogeneity, and poor adhesion at the interface was noted.

4.6 Mechanical Test (Tensile Test) Result Analysis

4.6.1 Analysis of Elongation at Break of PVC/ABS Blends

The elongation at break increases with increasing ABS content when a small amount of ABS is added into PVC as shown in Figure 4.8. When the ABS content increases to 30%, the elongation at break will gain peak value. When ABS content is more than 30%, the elongation at break will decrease and reach the minimum when ABS content is 70%. When ABS content is more than 70%, the elongation at break will increase rapidly as ABS content increase and reach about 29% with 100% of the ABS content.

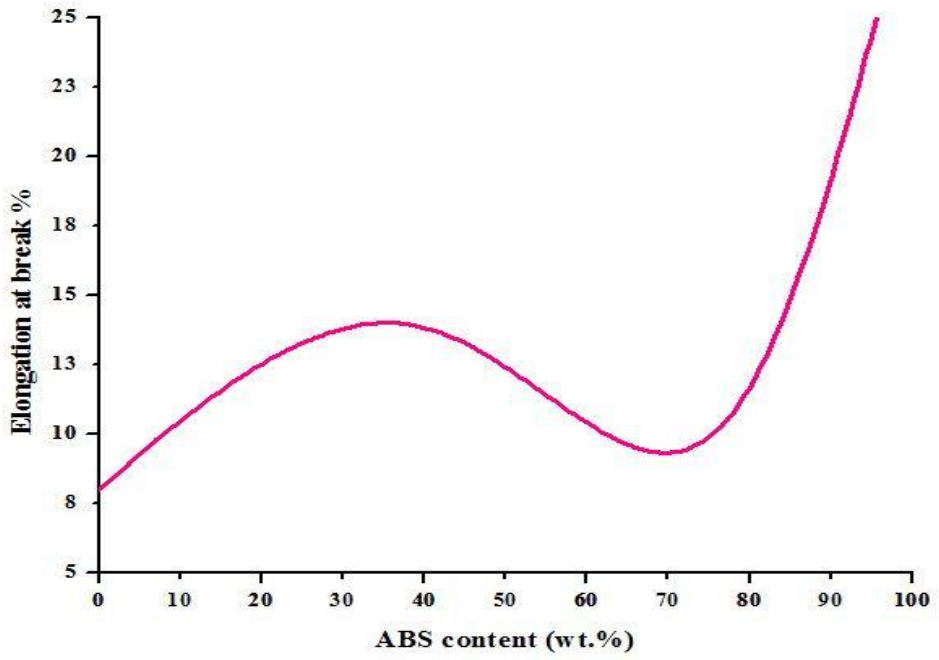


Figure 4-8 Elongation at break as a function of ABS content in the blend

Most of the trials strongly prove that there is no clear crack tracks in PVC/ABS composite materials. When the ABS content increases to 30%, elongation at break reaches its peak value due to the formation of network structures, which enhances interactions between PVC and ABS. The changes of elongation at break with the changes of ABS are closely related to the compatibility of the two components.

4.6.2 Analysis of Impact Strength of PVC/ABS Blends

The addition of ABS into PVC increased impact strength of blend materials as shown in figure 4.9. Rubber phase has dramatically toughening effect on the composites with all different proportions. The impact strength curve can be divided into three sections: brittle fracture zone, brittle-ductile transition zone and ductile fracture zone according to difference of toughening effect and fracture properties.

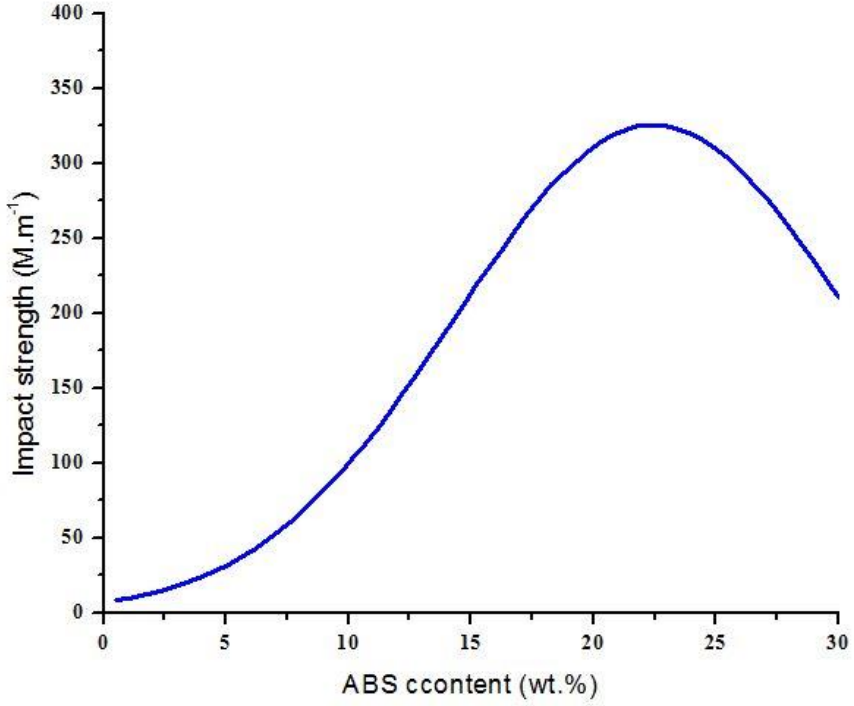


Figure 4-9 Impact strength of the formulated blend

Figure 4.11 also shows that in the brittle fracture zones (ABS content was 0~15), the impact strength of composites increased relatively slowly when ABS content increases. In the brittle-ductile transition zone (ABS content was 15~ 20), the impact strength increased very fast (from 4.8 $J.m^{-2}$ to 17.5$J.m^{-2}$) with ABS content increasing. In the ductile fracture zone (ABS content was 20 ~ 30 or probably beyond this value), the composite material presented a high toughness and reached the maximum value when the ABS content increased to 30 (the ratio between PVC and ABS is 70:30), then the impact strength decreased to a single value with the increase of ABS content. Clearly, the impact strength of PVC/ABS composite is closely related to the ABS content.

The dynamic mechanical properties of PVC/ABS composite materials reveal that PVC/ABS composites have chain micro-compatibility. Combination of PVC and ABS can form multiphase system with combining ability and an interfacial layer with certain thickness. The binding force of two-phase interface layer dramatically improves toughness of composite materials.

The rubber phase (Polybutadiene phase, SAN) is the major factor that affects the changes of PVC/ABS impact strength following ABS content. SAN in PVC or ABS has similar molecular

structures, polarities and solubility parameters, thus it has very good compatibility between them. After adding ABS into PVC, ABS and PVC can be fully dispersed, prompt penetration and diffusion of macromolecular chains and enhance the interfacial adhesion, finally form macro-uniformity and micro-phase multiphase system, thereby enhancing impact strength of the PVC/ ABS composites.

In the PVC/ABS composite material system, when the ABS content is less, ABS rubber particles have less effects on the impact strength of composite materials. With the increase of ABS content, the compatibility of PVC and ABS will gradually increase and the impact strength of composites will continuously increase. When ABS content increased to 20, the multiple factors of composite materials' toughness achieved the best balance or gained the maximal value with the right combination between multiple cracks and the shear deformation. When the ABS content is more than 20, further increasing the density of rubber particles will break the balance, so the impact strength will decrease with increasing ABS content and finally approach a single value.

4.6.3 Analysis of Tensile Properties of PVC/ABS Blends (Stress-Strain)

At beginning, the tensile strength of PVC/ABS composite almost monotonically decreases as adding ABS into PVC as shown in Figure 4.10. The tensile strength starts to increase when ABS content is 15% and gains peak value when the ABS content reaches 25%. The tensile strength decreases with the increase of ABS content when ABS content is more than 25%. ABS might play a major role in toughening when a small amount of ABS is added into the PVC.

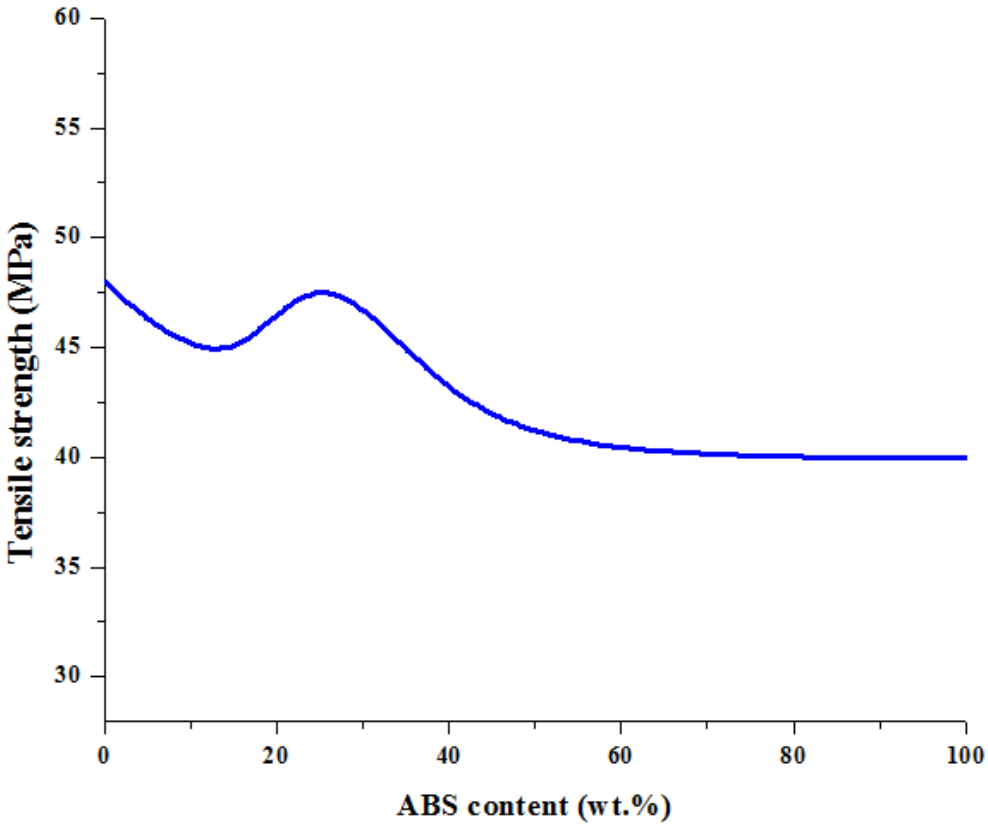


Figure 4-10 Tensile strength as a function of ABS content in the blend

As the strain rate or cross-head speed is increased, the tensile modulus of the polymer blend being tested also increases. However, the elongation rate is inversely proportional to the strain rate. The rubber phase (Polybutadiene phase, SAN) is the major factor that affects the stress strain curve of the blends. The blends with higher composition of ABS (35 wt. % SAN) showed the best tensile strength property. As can be seen from the following figure 4-12, sample codded PAA 6 which is composed of 80 wt.% PVC and 20 wt.% ABS (with 35 wt. % SAN) exhibited the best property among others.

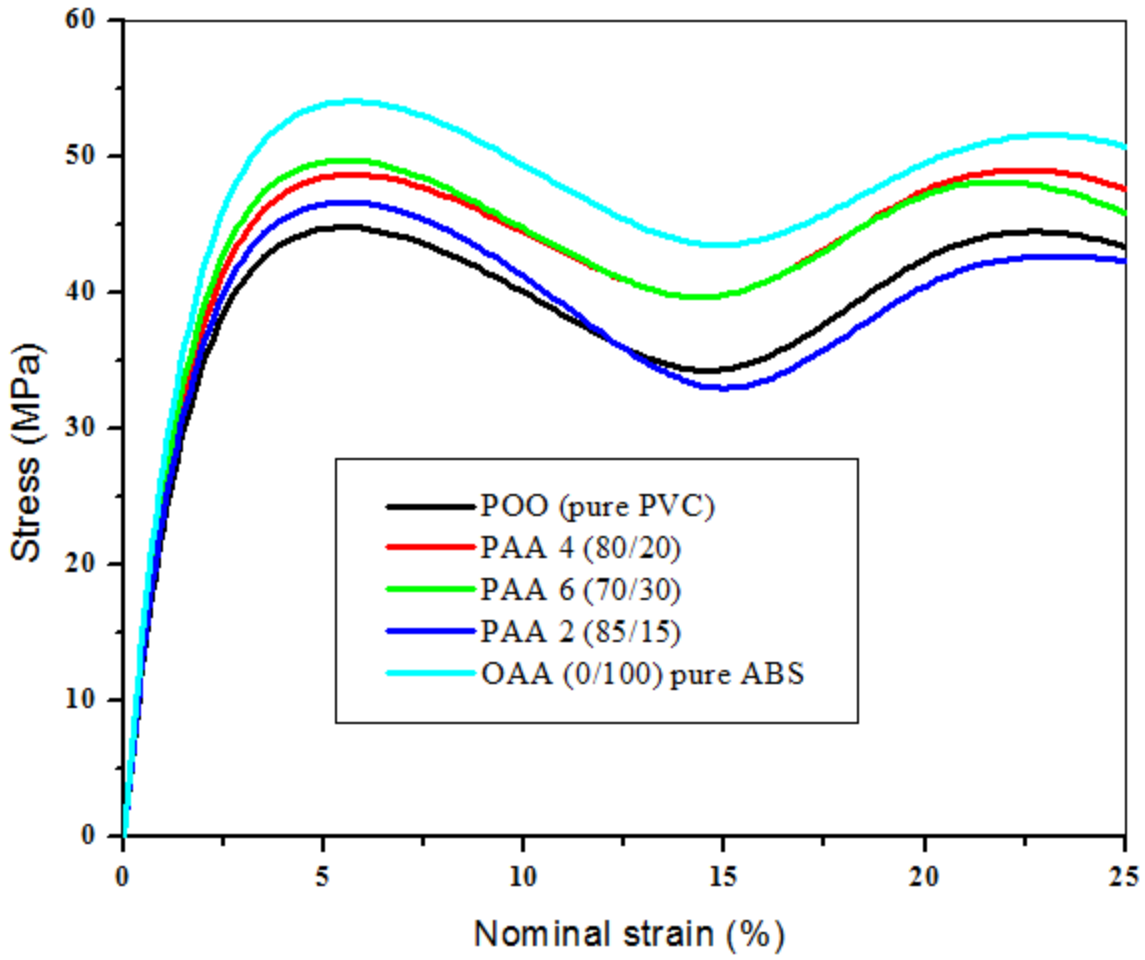


Figure 4-11 Stress-strain curve of the blends

When ABS reaches a certain amount, SAN content in the ABS will also increase. SAN, a high strength rigid glass material, will contribute to the tensile strength due to the similar solubility parameters and a certain degree of compatibility between SAN and PVC. The synergistic effect between the SAN and PVC results in the peak value of the tensile strength when ABS content is 25%. When the ABS content is in a range (20% ~ 30%), SAN and PVC intersperse with each other to form a network structure, resulting in improved tensile strength. The fact that SAN in ABS improves the tensile strength at certain ABS content suggests the effect of gel content on the tensile strength is significant. The fact that the best particles of PVC resin can be used to explain the observed synergistic effect of tensile strength also indicates that critical fracture of PVC/ABS only depends on component ratio of composites.

Heat distortion temperature (HDT):- For amorphous polymers such as PVC, the main mechanism for improvement in HDT is increasing the Tg. The addition of filers to amorphous polymer gives HDT value, which is close to its Tg, whereas filers in semi-crystalline polymers will give the HDT value which is close to its Tm [122]. In the present work, the glass transition temperature, Tg of the formed blend was modified as indicated by DSC results. As indicated in table 4-1 and 4-2, the glass transition temperature, Tg of pure PVC was about 85℃ and that of modified PVC with ABS copolymers was around 112℃. From the results obtained, it can be concluded that the HDT of the blends also increased along with Tg increased.

The HDT can be considered as a measure of the temperature at which certain creep compliance is reached after the polymer has been subjected to a standard temperature program. To function as structural material, plastic is expected to maintain its shape under load, and hence heat distortion temperature (HDT) represents an upper limiting point at which a plastic may be used.

The results from the glass transition temperature, Tg studies also revealed that different grades of ABS have different HDT values. The results obtained are similar to data presented by Toray, where a virgin high rigidity ABS has the highest HDT value followed by medium impact and super high impact ABS. The reason is due to the higher content of acrylonitrile (AN) at high rigidity ABS results in higher HDT value.

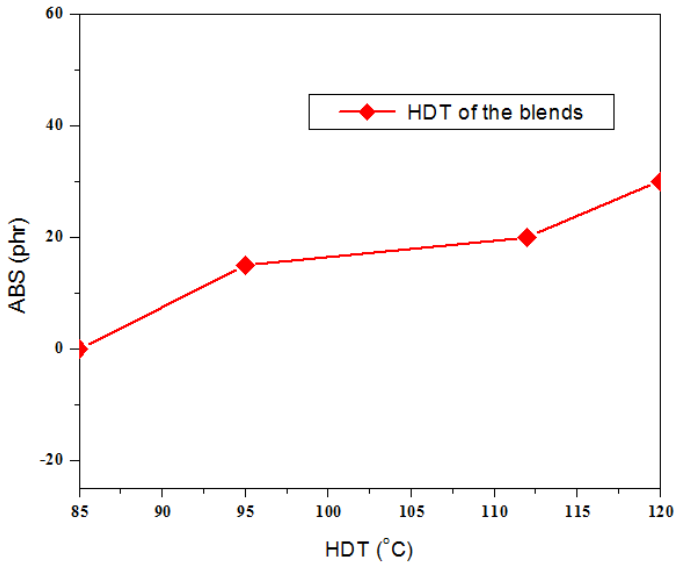


Figure 4-12 Heat distortion temperature, HDT of the blends as a function of ABS content

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Polymer blends are capable of providing materials, which extend the useful properties beyond the range that can be obtained from single polymer equivalents. Blends of Polyvinyl Chloride (PVC) and Acrylonitrile Butadiene Styrene (ABS) were prepared in different ratios by solvent cast blending technique using N-Methyl-2-Pyrrolidone (NMP) as solvent. A high impact ABS at different weight ratios was incorporated into the blends to study the effects of blend ratio on the properties of the blend. Blends were characterized by various thermal, morphological, and spectrochemical methods of analysis. Two distinct glass transitions were recorded by differential scanning calorimetry. This suggested the need for a compatibilizer. However, blends with 80/20 and 70/30 weight ratio of PVC/ABS exhibited a single Tg and that was taken as the best result. Thermal decomposition behavior of blends was analyzed by thermogravimetric analysis.

The blend of PVC and ABS reduces free volume of the system or makes the compact structure, thus increases their interactions and improves the compatibility of PVC/ABS composite materials, resulting in enhancement of the impact strength. The network system in PVC/ABS composite material not only helps improve the impact properties, but also conducive to the improvement of tensile properties. Therefore, the system region with network presence resulted in higher mechanical properties.

IR analysis indicated an absence of functional group interaction between the two blend components. Thermal decomposition behavior was marginally different in the blend samples. Thermogravimetric studies showed that the presence of ABS affected the rate of decomposition. Incorporation of the ABS into PVC result in decrease in hardness and increase in impact strength, which may give ductility to blend. TGA analysis shows that incorporation of ABS into PVC improves its thermal stability to greater extent.

Since blend possess excellent mechanical and thermal properties, it is useful in electrical applications such as electrical switches, plug and knobs. Also useful for automotive application such as automobile panels and clutches and other parts, where thermal stability along with weather resistance is desired. Preparation of polymer blends by using this method is cost effective and environmental friendly.

The NMP solvent used in this technique is reusable after one step is fully completed. This can save cost that expended for solvent purchasing if this technique is used at industry level for mass production. The energy needed for polymer preparation is very low when compared with melt bled method counterpart. The applications of the blended materials could be in areas like constructions, window profile, making bottles, pipes and many others.

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