

MISCIBILITY STUDIES, CHARACTERIZATION AND PROPERTIES EVALUATION OF PVC/PMMA BLENDS.

Chandramohan, B.Rajam, V.V.Basava Rao

Abstract: Poly Vinyl Chloride (PVC) and Poly methyl methacrylate (PMMA) blends are prepared by injection moulding method over an entire composition range of 0/100, 25/75, 50/50, 75/25 and 100/0 by weight. The miscibility of the blends was characterized by dynamic mechanical thermal analysis. The effect of polymer-polymer interactions on the miscibility of PVC/PMMA blends were studied using the method. The effect of blending poly (methyl methacrylate) in various proportions with suitably stabilized and plasticized poly (vinyl chloride) was studied with reference to their physical, mechanical, and thermal properties. Distribution of the phases in the blends will be studied through scanning electron microscopy. These properties of PVC/PMMA blends are correlated with spectroscopic investigation.

Keywords: Poly Vinyl Chloride, Poly Methyl Methacrylate, dynamic mechanical analysis, Morphology studies, Injection moulding



1.0 Introduction:

Poly vinyl chloride (PVC) is a normal impact, high corrosion resistant thermoplastic. Due to the exceptional corrosion resistance of the material, it is used where maximum chemical resistance is necessary. The low cost is also one favourable factor in choosing the compound for various applications in industries and in domestic usage. Approximately 75% of the world's PVC is produced by the suspension polymerization (S-PVC) process in which the polymerization is carried out inside vinyl chloride monomer (VCM) droplets dispersed in water. The product is in the form of porous 100-150 μ m-diameter grains. PVC is used as an insulator for cables and in the manufacture of 'artificial' leather (e.g. car upholstery), household goods such as curtains and table clothes, of records (records generally) and floor coverings others include the use of PVC as garden hoses, 'vinyl plastics' films water pipes, phonograph records etc.

Poly Methyl methacrylate (PMMA), an ethylene derivative, is a synthetic polymer made by the chain growth method of polymerization. It is a tough, rubbery and moderately hard polymer. Due to high resistant and non tracking characteristic of the compound, it is used in high voltage applications. Its excellent weather resistance has promoted the use of PPMMA for outdoor applications. In order to enhance the physical and mechanical properties of PMMA, many studies are carried in the past decades. The most common method for promoting the toughness of PMMA is blending with the PVC. Conflicting data have been

presented in literature concerning the compatibility of poly vinyl chloride (PVC) and poly methyl methacrylate (PMMA). A large number of studies indicate that the tacticity of PMMA affects strongly the miscibility of PVC/PMMA blends.

Blending is an effective method for designing polymer materials with various properties. It is a faster and cost effective way of achieving the required properties than synthesizing new polymers. The advantage of blending is that properties of commercially available polymers may be adjusted without the development of new macro molecules. The polymer blends often exhibit properties that are superior to those of each individual component polymer. Blending of two or more thermoplastics may generate new materials with a combination of properties those not found in pure polymers. Before using polymers in load-bearing applications, it is essential to study the effect of stresses on them. Therefore for ascertaining the fabrication and possible practical application, the glass transition temperature (T_g), mechanical properties, strength, rigidity and ductility of polymers are of vital importance.

The glass transition temperature (T_g) is one of the important properties exhibited by a polymer, determining its physical state and influencing other properties such as mechanical stiffness and toughness. A blend of two components is classified miscible, thermodynamically, if the Gibbs free energy of mixing is less than zero and the second derivative of the Gibbs free energy of mixing is zero or positive. Experimental evidence of miscibility is often found when a single and a sharp glass transition temperature, T_g , is observed in between the T_g s of the individual components. In the case of moderate or weak interactions, the miscibility of polymer pairs is limited; it depends on temperature and composition. Although most polymers pairs are immiscible or only partially miscible, several combinations have good mechanical, thermal or other properties which are useful in certain applications.

2.0 Literature Survey:

Hee-jin Rhoo et. al[1], Prepared polymer gel electrolyte in solution casting technique by taking the blend of PVC-PMMA as the host polymer, mixture of EC-PC as plasticizer and LiCF_3SO_3 as salt. They studied the effect of the PMMA-PVC blend ratio and the plasticizer content on the ionic conductions of the system. The mechanical property was improved by the incorporation of PVC into the electrolyte system. But the ionic

conductivity decreased with increasing the PVC/PMMA ratio and increased with increasing the plasticizer content.

Rupa Chakrabarti et al [2] have studied The effect of blending poly (methyl methacrylate) (PMMA) in various proportions with suitably stabilized and plasticized poly (vinyl chloride) (PVC) was studied with reference to their physical, mechanical, and thermal properties. The resulting morphologies of the various blends were also studied to find a suitable explanation of these properties. The physical and mechanical properties of such polyblends revealed a substantial increase in toughness accompanied with unusual increase in modulus and ultimate tensile strength after an initial drop at the initial stages of PMMA incorporation compared to pure reference compound PVC. The toughening effect, however, undergoes a reduction with increasing proportion of PMMA but it never goes below that of pure PVC (reference compound) within the ranges of PMMA incorporation under study.

M. Ramesh Prabhu et al [3] studied Hybrid, solid polymer electrolyte films consisting of poly(vinyl chloride)/poly(methyl methacrylate)-based polymer blend electrolytes comprising propylene carbonate as a plasticizer and a lithium salt LiX (X = BF₄⁻, ClO₄⁻, CF₃ SO₃⁻) are prepared by a solvent casting technique. X-ray diffraction, Fourier transform infrared spectroscopy and Differential scanning calorimeter analysis have been made to investigate the structural, complexation and variation in film morphology of the polymer electrolyte. The temperature dependence of ionic conductivity of the polymer films is explained on the basis of a free volume model.

X. Helan Flora et.al [4] prepared polymer blend electrolytes using solution casting technique. They studied for various concentration of LiClO₄ salt with the constant ratio of PVC and PMMA. The maximum ionic conductivity was found for the polymer electrolyte containing PVC (75 wt %) – PMMA (25 wt %) – LiClO₄ (8 wt %) to be 0.56 x 10⁻⁵ at 303 K.

Mohammad Saleem Khan [5] et al studied the effect of polymer-polymer interactions on the miscibility of PVC/PMMA and PS/PMMA blends were studied in a broad composition range using viscosity and FTIR techniques. From the viscometric data, the presence of attractive forces among different polymers was evaluated according to Sun et al. (1990), by the determination of χ parameter. Based on sign convention involved in the

criterion, PS/PMMA system was found as immiscible while miscibility was observed in PVC/PMMA blend. FTIR analysis also supports the viscometric data.

Gautam kumar sah et al [6] studied The density and Coefficient of Viscosity for Polyvinyl chloride/poly(methyl methacrylate) (PVC/PMMA) blends in THF at 303.15 K and 313.15 K were measured. These measured parameters were then used to estimate few other related physical quantities like Huggin's constants and the interaction parameters μ and α proposed by Chee and Sun et al. to identify the molecular interaction arising in the mentioned polymer blend solutions. The peculiar deviation confirms the structural changes in the solution of blends.

Y. H. Liao et al. [7] Prepared a self-supported P (MMA-VC) based gel polymer electrolyte containing LiPF_6 as salt. It is found that, the above gel electrolytes have high thermal stability of 310 °C, good mechanical strength, electrochemically stability up to 5.6 V and conductivity of 3.48×10^{-3} at ambient temperature.

Zahoor Ahmad et al [8] studied the PVC is a common and important commodity plastic which ranks third in consumption of the world after polyethylene and polypropylene. Despite its advantageous properties the PVC suffers from poor thermal, thermal-oxidative and photo-stability. The evolution of hazardous chemicals like HCl and other chlorinated hydrocarbons in structural applications of PVC can be very dangerous during fire accidents which may hinder its use in building construction fields. The HCl is both sensory and pulmonary irritant and appears to be the major toxicant responsible for deaths that occur following acute inhalation exposure to PVC decomposition products. In the present work we have stabilized PVC using a small amount of poly(methyl methacrylate) PMMA. The binary blends of poly(vinyl chloride) (PVC) with (PMMA) of various compositions were prepared and thermogravimetric and pyrolysis studies of these blends were carried out. The volatile products separated and quantitatively analyzed by GC/MS. Harmful pyrolysis products from PVC like HCl and different aromatic hydrocarbons were found to be significantly suppressed in presence of a small amount of PMMA. Mechanism of the stabilization has been explained by the interaction of micro- and macro-radicals resulting from PMMA with PVC, which stabilize the unzipping of polymer chains by a reversible blocking mechanism and increase the amount of cross-linked residue retained above 500°C.

S.Ramesh et al[9] , The miscibility of PVC blends (PVC/PMMA and PVC/PEO) was investigated. Experiments using viscosimetry and differential scanning calorimetry (DSC) were performed. The presence of attractive forces among polymers was evaluated according to the Sun theory by the determination of the α parameter from the viscosimetric data. The melting depression in a binary blend is an indication of miscibility. Viscosimetric and thermal analysis showed that the PVC/PMMA and PVC/PEO blends are miscible. The miscibility of the PVC/PMMA and PVC/PEO blends is explained in terms of donor–acceptor interactions between chlorine atoms (a weak acceptor species) of PVC and oxygen atoms (a donor species) of the PMMA and PEO.

3.0 Experimental Procedure:

For proper stabilization of PVC, 100 parts of compound is to be treated with 5 parts of MgO, 5 parts ZnO and 2 parts of stearic acid. For 10Kg. of PVC 500g of MgO, 500g of ZnO and 200g of stearic acid is added. The mixture is compounded in a Twin Screw Extruder. The PVC obtained is cut into granules and the material is fed to the injection moulding. The tensile properties of PVC which has been stabilized is compared with that of original PVC.

The PVC stabilized with Mgo/ZnO system shows slightly higher tensile strength. This might be due to a slightly higher degree of cross linking in the former sample. This suggests an increase in the crosslink density in the PVC matrix during compounding.

3.1 Preparation of blends:

Poly methyl methacrylate (PMMA) and Poly vinyl chloride (PVC) blends were prepared in the following compositions of 100/0, 75/25, 50/50, 25/75 and 0/100 by weight in batches of 3 kg and mixed thoroughly (as shown in Table.1)

Table.1

S.No.	Sample	PVC%	PMMA%	PVC (Weight)	PMMA (Weight)
1	S1	100%	0%	3kg	0 kg

2	S2	75%	25%	2.25 kg	0.75 kg
3	S3	50%	50%	1.5 kg	1.5 kg
4	S4	25%	75%	0.75 kg	2.25 kg
5	S5	0%	100%	0 kg	3 kg

4.0. Results and Discussion:

4.1. Tan δ Vs Temperature plots

The most commonly used method for establishing miscibility or partial miscibility in polymer blends is through determination of the glass transition (or transitions) in the blend vs. those of the unblended constituents. A miscible polymer blend will exhibit a single composition-dependent glass transition located between those of two pure components. With cases of limited miscibility, two separate transitions between those of the constituents may result, depicting a component 1-rich phase and a component 2-rich phase. The difference between the glass temperature of the partially mixed phase and that of the corresponding pure component gives information concerning the level of partially miscibility. In this paper, the miscibility of PMMA/PVC blends is first discussed in terms of the appearance of either single or double T_g using Dynamic mechanical analysis. Figure.1 shows the ratio of loss modulus and storage modulus with temperature for pure PMMA, PVC and selected blends.

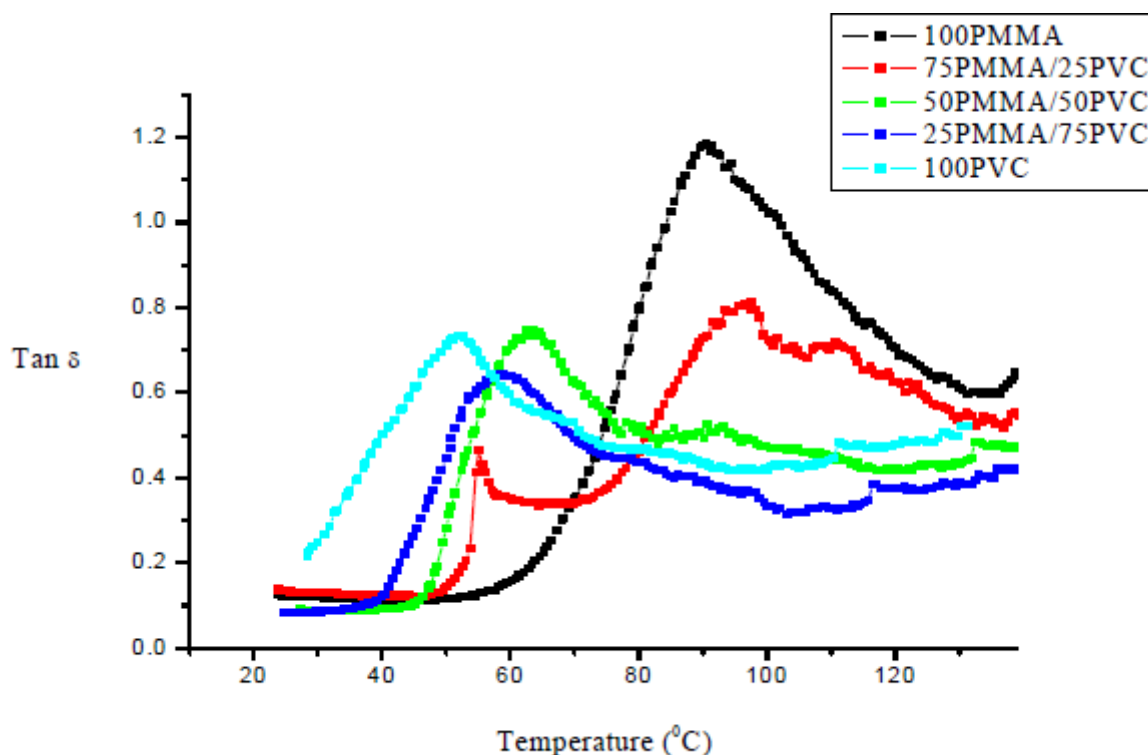


Figure.1:

Ratio of Loss Modulus and Storage modulus ($Tan \delta$) Vs Temperature for Pure PMMA, Pure PVC and the selected blends.

From the Figure.1 it was observed that, the intensity of the $Tan \delta$ peak of PMMA has been reduced gradually with increase in the PVC contents. This implies that the mobility of molecules is drastically reduced after blending i.e. PVC restricts the molecular mobility of PMMA. The low value of $Tan \delta$ peak depicts an elastic polymeric behaviour whereas the high value shows a viscous behaviour. The PVC chains being polar in nature can resist the viscous flow behaviour whereas the PMMA phase shows viscous behaviour. As expected by increasing the PVC content in the blends, a decrease in the PMMA peak height is observed. The blended material is thus transforming from viscous to an elastic behaviour. The pure PMMA sample shows a T_g at $90^\circ C$ whereas the pure PVC shows the transition at $52^\circ C$. These values depend on molecular weight and agree with literature values for similar polymers. The blend shows two glass transition temperatures for 25 wt% of PVC content in PMMA. The lower glass transition is observed at $55^\circ C$, with T_g of pure PVC being $52^\circ C$. This transition can be attributed to the PVC- rich phase. The higher glass transition is observed at $97^\circ C$, with T_g of pure PMMA composition gives an idea about miscibility of the

system.

The lower glass transition is observed at 55°C, with T_g of pure PVC being 52°C. This transition can be attributed to the PVC- rich phase. The higher glass transition is observed at 97°C, with T_g of pure PMMA being 90°C, and can be attributed to transitions occurring in the PMMA-rich phase. This is an indication that PVC, which is incompatible with the matrix, develops the phase separation tendency at this concentration and therefore it is not distributed uniformly in the matrix.

However, the blends show a single T_g at 63.27°C and 58.75°C temperature for 50-75 wt% PVC in the matrix, respectively. These single glass transition temperatures indicate miscibility between two polymers, suggesting that PVC is compatible with PMMA greater than 25 wt% of PVC. The close value of the solubility parameters of PVC and PMMA might be expected to account for this miscibility and compatibility of PMMA/PVC blends.

The location of the transition peaks is composition dependent. Increasing the PVC content greater in the PMMA/ PVC blends results in decreasing the glass transition temperature values. This shift of the transitions indicates that blending of the components results in at least some molecular mixing, thus partial miscibility of PMMA in the PVC phase. Partial miscibility may result through specific interactions is between carbonyl groups (C=O) of PMMA and hydrogen from (CH-Cl) groups of PVC.

4.2. Mechanical and Thermal Properties:

The mechanical properties like Tensile strength, Compressive strength and Flexural strength are estimated by using UTM (Universal Testing Machine). Impact strength is calculated by using Notched IZOD machine. Heat Deflection Temperature (HDT) is calculated by HDT /VST Tester. Hardness is estimated by Shore Durometer (Shore D).

4.3. Tensile properties of PVC/PMMA:

Tensile test was performed according to the ASTM D-638. The speed of cross-head movement for tensile test was 5.0 mm/min. Representative tensile stress–strain curves of PVC/PMMA blends are depicted in Figure 2. In all cases, at low strain, there exists in the materials the so called elastic energy, which is stored in the form of strain energy of the chemical bonds prior to break. For greater strain the stored energy is termed plastic energy and in this region, the specimens exhibit “irreversible” plastic deformations with increasing

strain. In plastic flow, the material is undergoing a rearrangement of its internal molecular or microscopic structure, in which atoms are being moved to new equilibrium positions.

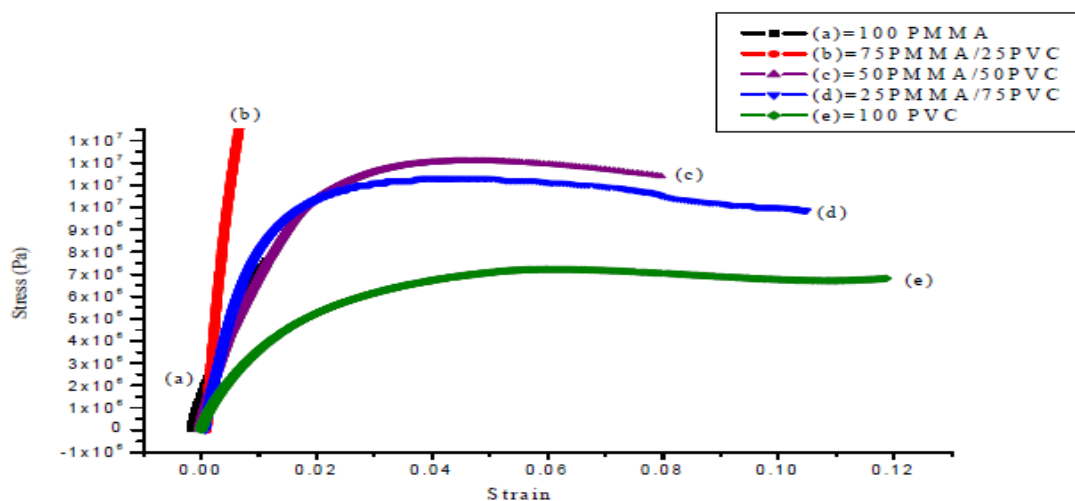


Figure.2 Stress Vs Strain plot for Pure PMMA, Pure PVC and selected blends

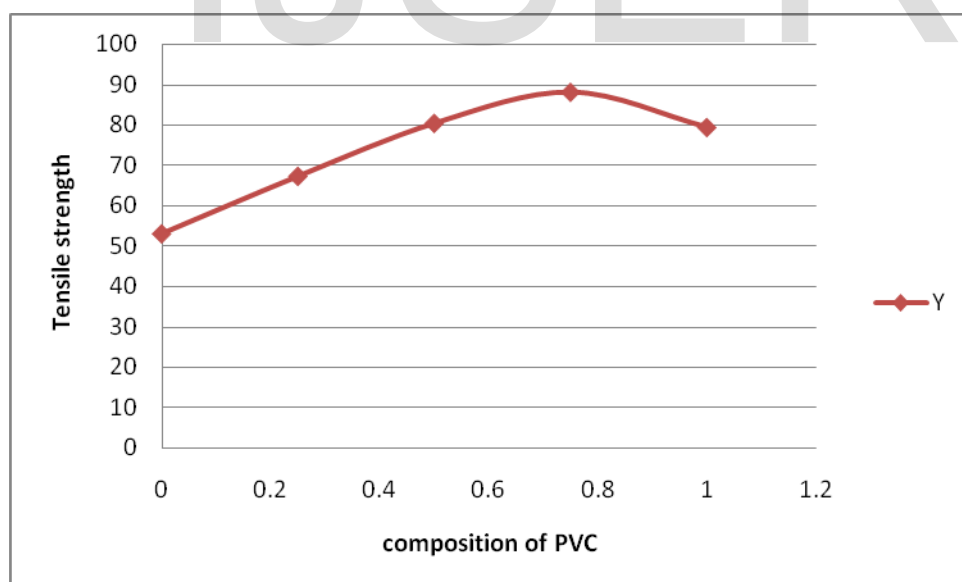


Figure.3: Tensile strength Vs composition plot for all the blends

From the values of Young's modulus and ultimate tensile strength of PMMA/PVC blends

it is observed that there is a marginal reduction in modulus and ultimate tensile strength with an increase in PVC content from 25 to 75% by weight ratio in the blends(as shown in Figure 3). PMMA has a high modulus due to its brittle nature. Addition of PVC in PMMA leads to a decrease in Young's modulus and ultimate tensile strength which further reduces stiffness of blends, making the material useful for engineering purpose.

Table.2: Physic mechanical properties of the blends

S.NO.	Sample	Tensile strength (MPa)	Flexural strength (MPa)	Compressive Strength (MPa)	Impact Strength (KJ/m ²)	HDT (°C)	Hardness (shore D)	Tg (°C)
1	S1	52.94	70.74	126.67	205.81	69.3	72	52
2	S2	67.18	87.37	143.28	173.85	73.6	84	58.75
3	S3	80.29	110.48	123.94	142.92	77.3	107	63.27
4	S4	87.98	124.72	98.74	126.68	84.8	116	55.97
5	S5	79.26	107.53	87.21	94.74	76.71	97	102

From the Table 2 it is revealed that PMMA is a brittle polymer and PVC is ductile in nature. The elongation at breaks and fracture energy of the PVC/PMMA blends are higher than that of neat PVC and PMMA indicating a high level of compatibility between the two polymers. The improved property of such blends may be attributed to specific interactions such as H-bonding and dipole-dipole interactions between molecules of the constituent polymers. It was suggested that the hydrogen of vinyl chloride can interact with the ester carbonyl group (H-bond acceptor of the acrylic polymer) to form a hydrogen bond. PMMA, having a solubility parameter ($\delta=9.27 \text{ cal/mL}^{1/2}$) very close to that of PVC ($\delta=9.47 \text{ cal/mL}^{1/2}$), might be expected to have very good compatibility with PVC and hence, enhances the properties.

4.4 Hardness:

Hardness, a surface phenomenon is measured by Durometer. The specimen is first placed on a hard flat surface. The indenter for the instrument is then pressed into the specimen making

sure that it is parallel to the surface. The hardness is read within one second (or as specified by the customer) of firm contact with the specimen. The test specimens are generally 6.4mm (¼ in) thick. It is possible to pile several specimens to achieve 6.4mm thickness, but one specimen is preferred.

Various blends exhibits somewhat different mode of changes with variation in PMMA content (As shown in Figure 4). The hardness increases almost linearly and progressively with increasing proportion of PMMA. The stiff and rigid domains of the dispersed and somewhat miscible (because of the close values of the soluble parameters) PMMA phase, coupled with the possibility of H-bond formation as described earlier leads to a steady increase in hardness within the ranges of PMMA concentration studied.

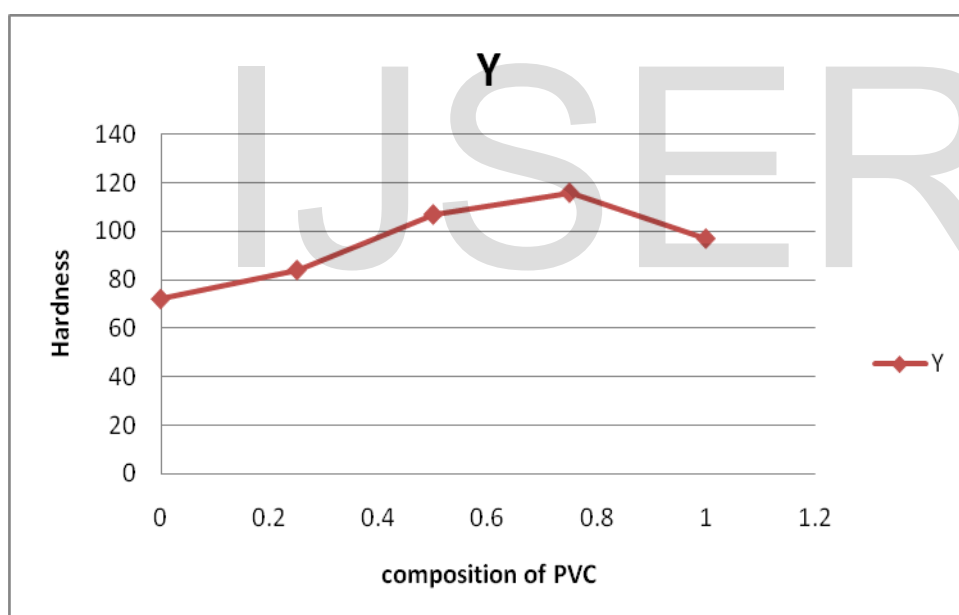


Figure.4: Hardness Vs composition of PVC plot for all the blends

4.5 Flexural Strength:

Flexural strength test was performed according to the ASTM D-790. Both the flexural modulus and the strength of the blends have been measured. For testing, the support span was fixed at 100 mm and the rate of crosshead motion at 3 mm/min. Three specimens of each formulation were tested and the average values were reported which is shown in Figure 5.

From the figure, it is observed that with increase in the percentage composition of PVC, the flexural strength increases.

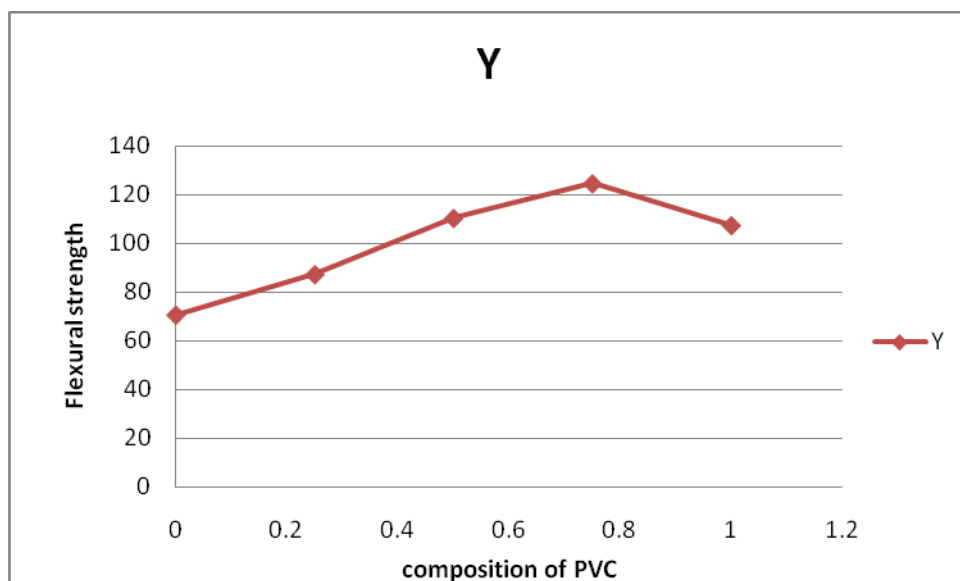


Figure.5: Flexural strength Vs composition of PVC plot for all the blends

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4.6 Impact Strength:

The impact strength of the PVC/PMMA blends was measured by Notched Izod Impact Strength Method according to the ASTM D- 256 specifications. The specimen is clamped vertically as a cantilever beam so that the notched end of the specimen is facing the striking edge of the pendulum. The result can be observed in Figure 6.

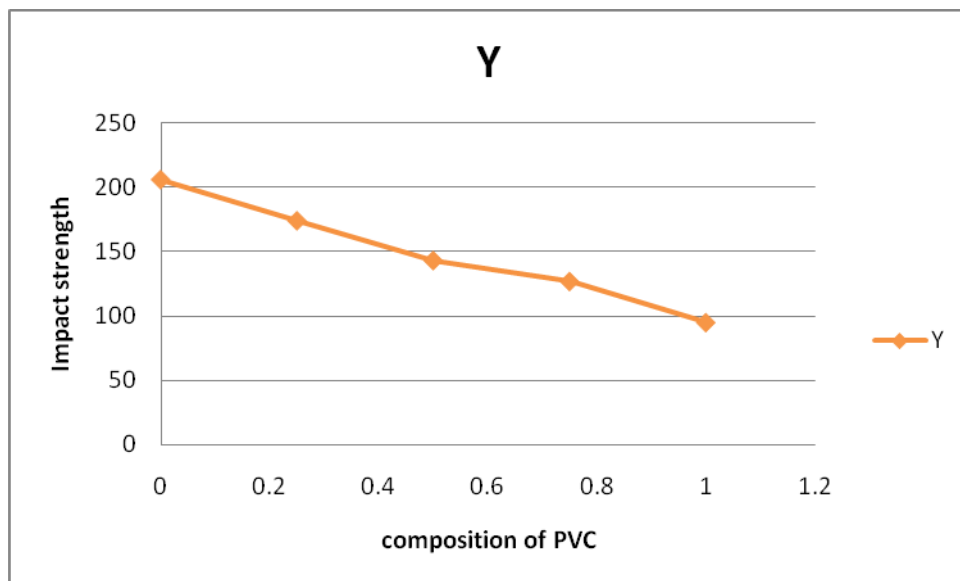


Figure.6: Impact strength Vs composition of PVC plot for all the blends

From the above graph it was observed that the impact strength increases with increase in PMMA content.

4.7 Compressive Strength:

The compressive strength of PVC/PMMA blends was measured by Universal Testing Machine according to the ASTM D-784. Samples are to be placed in the compression fixture and the values are calculated.

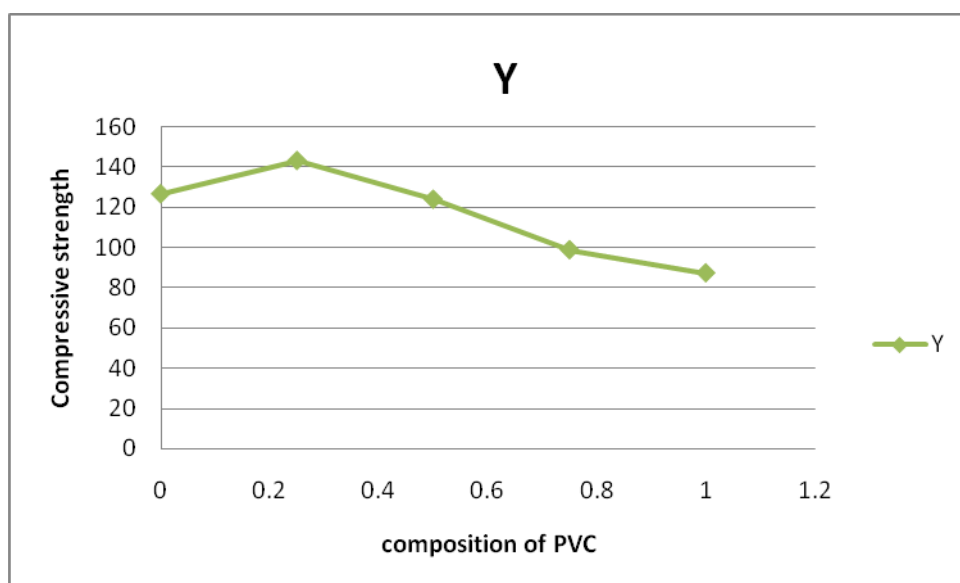


Figure.7: Compressive strength Vs composition of PVC plot for all the blends

From the above Figure 7 it was observed that the compressive strength of blend with 25% of PVC is more than that of both pure PVC and pure PMMA. The compressive strength of the blends shows a decreasing trend by increasing the composition of PVC.

4.8 Heat Deflection Temperature (HDT):

HDT is one of the important factors in estimating the efficiency of engineering plastics. It is the temperature at which a polymer or plastic sample deforms under a specified load. This property is applied in many aspects of product design, engineering, and manufacture of products using thermoplastic components. HDT is determined by the procedure outlined in ASTM D-648. The test specimen is loaded in three-point bending in the edgewise direction. The outer fibre stress used for testing is 4.6 kg/cm^2 or 18.5 kg/cm^2 , and the temperature is increased at $2 \text{ }^\circ\text{C/min}$ until the specimen deflects 0.25 mm . The HDT of various blends are presented in Figure.8.

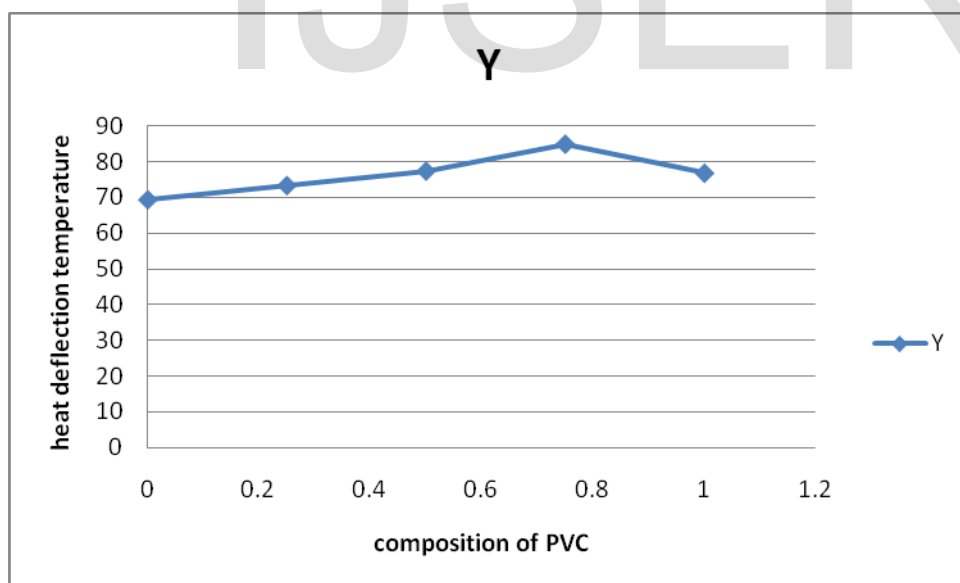
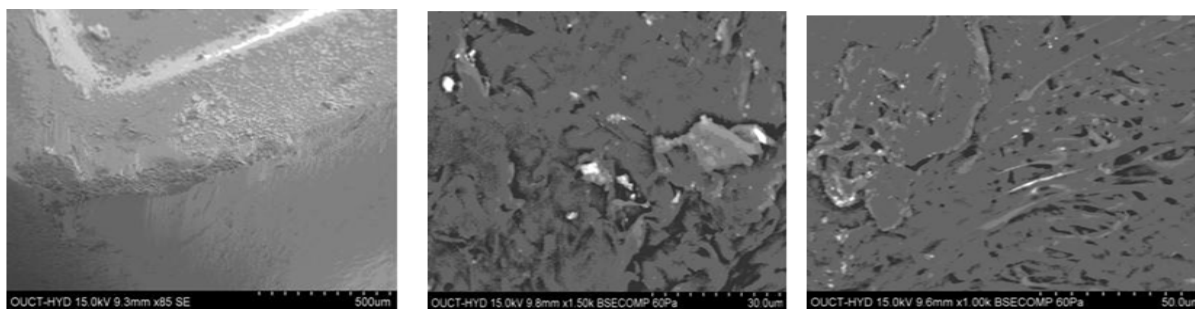


Figure.8: Heat Deflection Temperature Vs composition of PVC plot for all the blends

4.9 Scanning Electron Microscopy:

This is the technique that used to analyse the miscibility of two or more solid phases. For pure compounds of PVC, PMMA and blends the SEM studies are carried and the images

are presented in the following Figures. The images are showing clear picture but addition of PS/PP is not mixed properly. In the experimental observation 75%PMMA - 25% PVC has exhibited high interfacial tension between the components. Also, we can observe layers formed during stretching on the fractured specimen.



PVC-100%
PMMA-0%

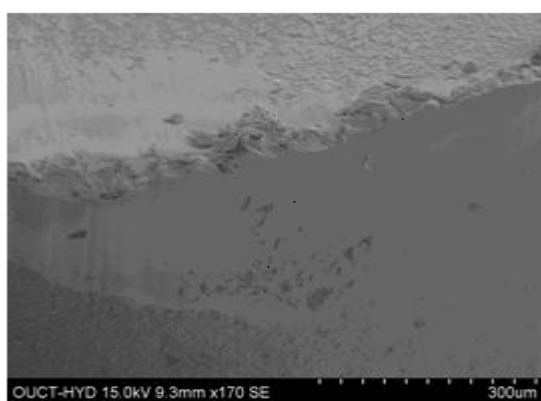
PVC-75%
PMMA-25%

PVC-50%
PMMA-50%

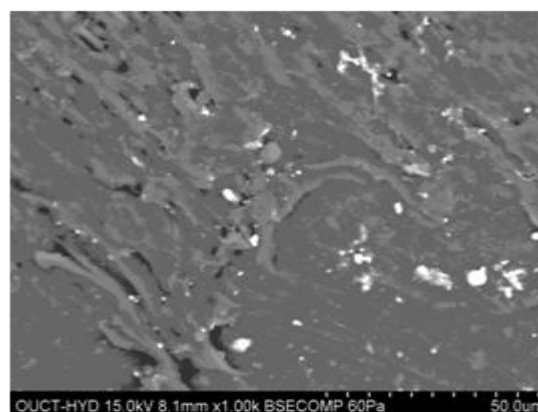
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SEM Images

SEM Images



PVC-25%
PMMA-75%



PVC-0%
PMMA-100%

5.0 CONCLUSIONS:

The following conclusions have drawn from the study

1. There is a clear indication of feasibility of producing better grade polymers from polymer blend studied in this research.
2. By detecting the concentration of maximum interaction between the functional groups of the polymer blend, a cheaper, more flexible, toughened and better commercial grade polymer can be produced.
3. Properties like Tensile Strength, Flexural Strength and Impact Strength are varied with an increase in one components of the blend. This shows improved characteristics of the blend when compared to that of individual polymers, hence reducing production cost for materials which require the use of very expensive material, making toughened polymer more flexible for production and vice versa.
4. From the values of T_g which were calculated by using Dynamic Mechanical Analysis, it is found that at a composition of 0.25 of PVC the blends are not completely miscible as we got two values of T_g and for 0.5% and 0.75% of PVC, we got a single glass transition temperature showing that the blends are miscible.
5. The Tensile Strength, Flexural Strength, Compressive Strength, Hardness and Heat Deflection Temperature of the blends has shown increasing trend with increase in PMMA content whereas the Impact Strength was decreased.
6. The morphological studies of the prepared blends were studied with the help of Scanning Electron Microscopy.

6.0 References:

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