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Investigation of miscibility and mechanical properties of PMMA/PVC blends

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The present study deals with some results on phase behavior, miscibility, morphology and mechanical properties for Polymethyl methacrylate and Polyvinyl chloride polymer blends prepared by solution casting method at different concentration between 0 to 100 wt %. Dynamic storage modulus (*E*') and Tan δ were measured in a temperature range from 30 ^{0}C to 150 ^{0}C using DMA. The value of the storage modulus was found to increase initially but then decreased with further addition of the PVC in the matrix. Transition temperature (T_g) of pure PMMA and pure PVC is found to be at 90 ^{0}C and 52 ^{0}C, respectively. The result shows that the two polymers are miscible upto about 50wt % of PMMA. Distribution of the phases in the blends was studied through scanning electron microscopy. Also the mechanical properties like elongation at break and fracture energy of the PMMA/ PVC blends increase with the increasing concentration of PVC in PMMA indicating a high level of compatibility between the two polymers. This partial miscibility and compatibility is due to specific interaction between carbonyl groups (C= O) of PMMA and hydrogen from (CHCl) groups of PVC.

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1. Introduction

Blending of two or more thermoplastics may generate new materials with a combination of properties not found in the pure polymers. Blending is often a faster and more cost effective way of achieving the required properties than synthesizing new polymers. Polymers are often used in applications that involve stresses. 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) and mechanical properties their strength, rigidity and ductility of polymers are of vital importance.

The glass transition temperature (T_g) is one of the most important properties exhibited by a polymer, determining its physical state and influencing other properties such as mechanical stiffness and toughness [1]. T_g of a polymer is correlated with the segmental motion of the polymer chains. A blend of two components is classified [2] 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 [3] in between the T_gs 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. Partial solubility results in heterogeneous, two phase structure, in which the size of dispersed phase depends on several factors, among others on the interaction of component and on the condition of mixing. 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. Such blends are often termed compatible.

It is well known that miscibility of polymers is dependent of sample preparation and molecular weight as well as of the tacticity of the polymers. Additionally, due to the kinetic character of the glass transition, the reported glass transition temperatures depend on the mode of definition of T_g for a given method of measurement (DSC, dynamic mechanical methods or P-V-T) as well as the operating conditions during the measurement (heating/cooling rates, frequency and pressure), respectively.

Poly methyl methacrylate (PMMA) is one of the well known brittle materials. In order to enhance the physical and mechanical properties of PMMA, numerical studies on the improvement methods have been extensively carried out 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) [4-6]. A large number of studies indicate that the tacticity of PMMA affects strongly the miscibility of PVC/PMMA blends.

The aim of this work to investigate the effect of intermolecular interactions on the miscibility and mechanical properties of PMMA/PVC blends. It is also aimed to study the compatibility of these blends.

2. Experimental details

2.1 Materials

Poly methyl methacrylate (PMMA, Alfa Essar) and Poly vinyl chloride (PVC, Goodfellow) in powder form were used as received. Tetra hydrofurane (THF) was used as solvent.

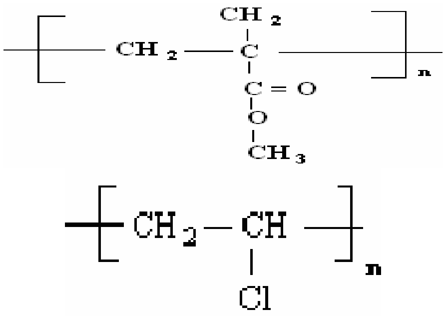


Fig. 1. Repeating units of poly methyl metacrylate and polyvinyl chloride.

2.2 Preparation of blends

Films of Poly methyl methacrylate (PMMA) and Poly vinyl chloride (PVC) blends were prepared by solution casting technique. The blend of PMMA/PVC had compositions of 100/0, 75/25, 50/50, 25/75, and 0/100 by weight. Solutions of PVC and PMMA in (THF) were first prepared at various polymer compositions. The polymer solutions were then mixed with continuous stirring until complete miscibility, and subsequently cast onto glass petrie dishes to form transparent films with a thickness of ~ 0.1 mm. The cast films were dried under ambient conditions for 24 h and then placed in a vacuum oven to remove residual solvent for 24 h at 50 ^{o}C [7].

2.3 Measurements

The glass transition temperature (T_g) was measured by Dynamic mechanical analyser (DMA). In this instrument, a force is applied to a sample and the amplitude and phase of the resultant displacement are measured. The sinusoidal stress that is applied to the sample generates a sinusoidal strain or displacement. By measuring both the amplitude of the deformation at the peak of sine wave and the lag between the stress and strain sine waves, quantities like the modulus, viscosity and the damping can be calculated [8]. When the response of the material to the applied wave is perfectly elastic, the input response is in-phase with that of output i.e. phase lag (δ) = 0^0, while a viscous response gives an out of phase, i.e. $\delta = 90^0$. Viscoelastic materials fall in between these two extremes i.e. $0^0 < \delta < 90^0$. This technique separates the dynamic response of materials in to two distinct parts: an elastic part (E′) and a viscous component (E″).

$$E^* = E' + iE'' \tag{1}$$

where, Complex Modulus E* is defined as the sum of the in-phase or elastic response E′ (which is proportional to the recoverable or, stored energy) and viscous response E″ (which is proportional to the irrecoverable or, dissipated energy). Mechanical loss factor (Tan δ) is another useful parameter, which can be very useful in order to compare viscoelastic responses of different materials, and is given by

$$\text{Tan}\ \delta = E'' / E' \tag{2}$$

where Tan δ (damping factor) is the ratio of energy dissipated/ energy stored. The glass transition temperature (T_g) is measured in terms of maximum damping temperature. T_g represents a major transition for polymers, as the materials move from hard glassy state to rubbery state [9]. Glass transition measurement was performed from 30 to 150 ^{0}C temperatures at a heating rate/ramp rate of 2 ^{0}C/min and all the stress-strain measurement was performed at 30^0C temperature with constant load (10 N) in tension mode. Frequency of oscillation was fixed at 1 Hz and strain amplitude 0.01 mm within the linear viscoelastic region.

2.4 Morphological characterization

The surface morphology of the polymeric blends were analysed using Scanning Electron Microscopy (SEM). The films were fractured in liquid nitrogen and coated with gold. These blended films were examined at 10 kV using a SEM instrument model Quanta Fe-200.

3. Results and discussion

3.1 Glass transitions and blend miscibility

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 [10]. 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_gs using Dynamic mechanical analysis (DMA).

Fig. 2 shows plots of tan δ (Tan δ is defined as the ratio of loss modulus and storage modulus) vs. temperature for pure PMMA, PVC, and selected blends.

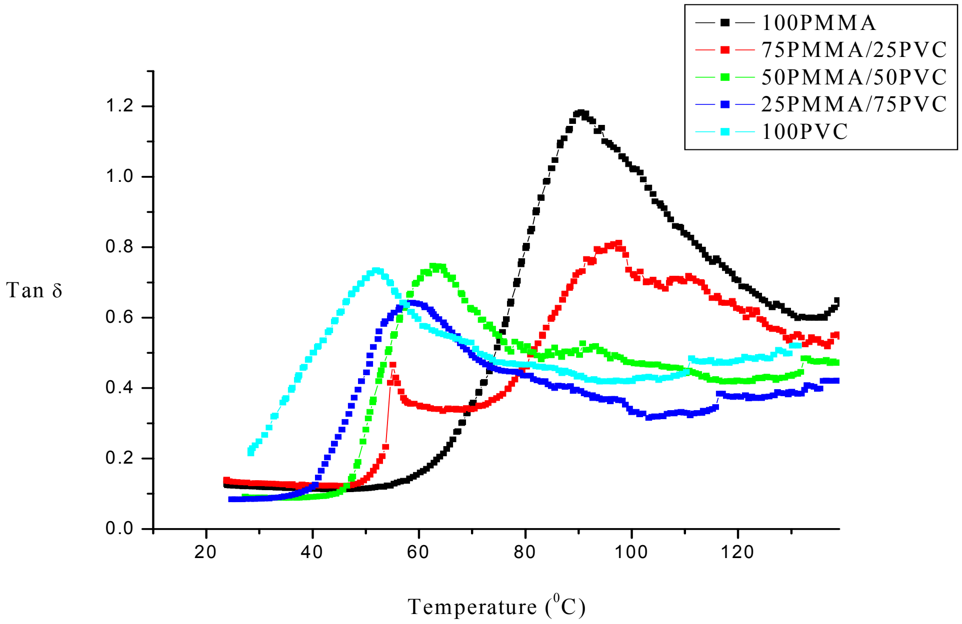


Fig. 2. Variation of Tan δ of PMMA, PVC and PMMA/PVC blends with temperature.

The intensity of the Tan δ peak of PMMA as seen in Fig. 2 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 δ peak depicts an elastic polymeric behaviour whereas the high value shows a viscous behaviour [11]. 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 measurement of T_g as a function of the composition gives an idea about miscibility of the system. However, when a polymer-polymer system demonstrates a single T_g, it does not definitely mean that mixing has occurred on a molecular scale. The materials showing one T_g may also be considered where the two separate phases have been distributed uniformly at the micro-level. The pure PMMA sample shows a T_g at 90°C whereas the pure PVC shows the transition at 52°C. These values depend on molecular weight and agree with literature values for similar polymers [12]. The blend shows two glass transition temperatures for 25 wt% of PVC content in PMMA. 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 ^{0}C and 58.75 ^{0}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 [13].

3.2 Storage modulus

The variation of storage modulus vs. temperature for pure PMMA, PVC, and selected blends are shown in Fig. 3.

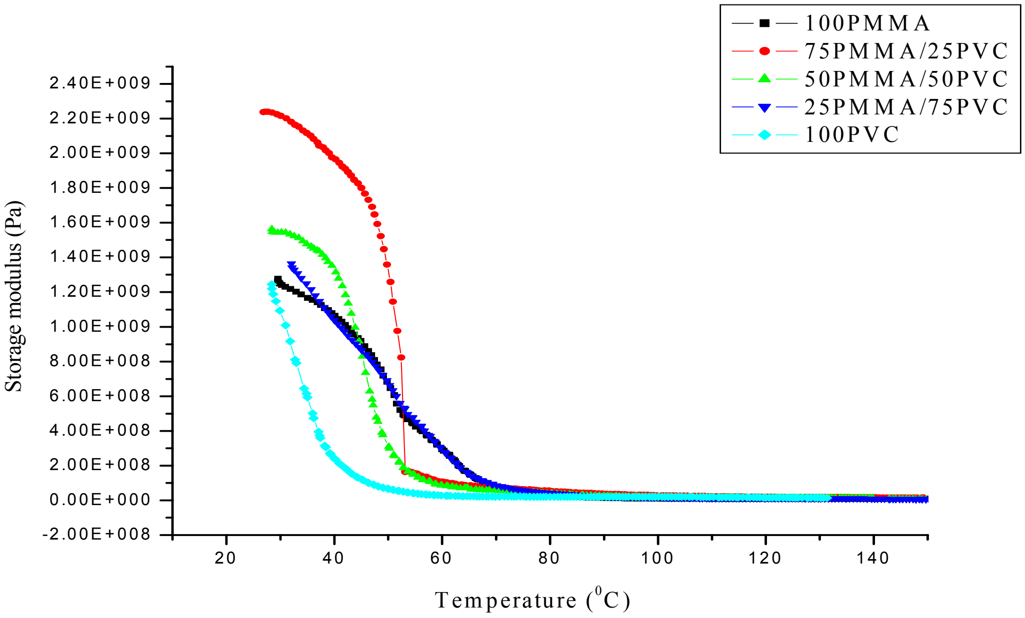


Fig.3. Variation of storage modulus of PMMA, PVC and PMMA/PVC blends with temperature.

All the plots of storage modulus show a small decrement initially with temperature in all samples. As the temperature increases further, modulus shows a sharp decrement and then attains a constant value at higher temperatures. This is due to the fact that the molecules may be considered as a collection of mobile segments that have degree of free movement. At lower temperature, the molecules of the solid material have lower kinetic energies and due to the fact that their oscillations about mean position are small the material is tightly compressed. In this state, therefore, the lack of free volume restricts the possibility of motion in various directions and hence they are unable to respond to the application of load/ stress to which the sample is subjected [14]. This gives a high value of modulus (more stiffness). However, at elevated temperature, free volume of the chain segments increases resulting in an increment of mobility of molecular segments. The motion of these chains produce more strain in the sample with the load applied hence modulus of the sample decreases as temperature increase from room temperature to 150 ^{0}C for all the samples.

The pure polymers PMMA and PVC have the values of storage modulus 1.278 GPa and 1.245 GPa at 30^{0}C, respectively. These values show an increase when PVC is added in PMMA and the storage modulus increases to a maximum value of 2.238 GPa for 25 wt% of PVC in PMMA (Fig. 3). Then there is a decrease in the storage modulus value for the blends greater than 25 wt% PVC contents.

The variation of storage modulus with composition of the PMMA/PVC blends at room temperature is shown in Fig.4. It can be seen from this figure that the modulus of blends exhibits a maximum at some intermediate blend composition. This shows a synergistic behaviour of the blend films.

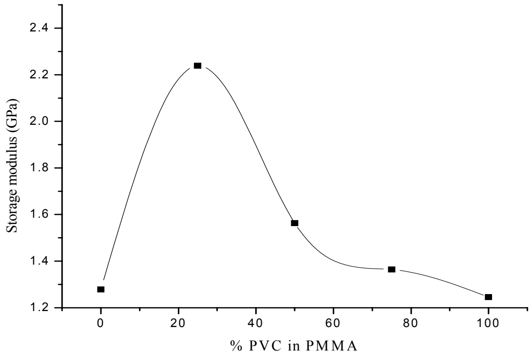
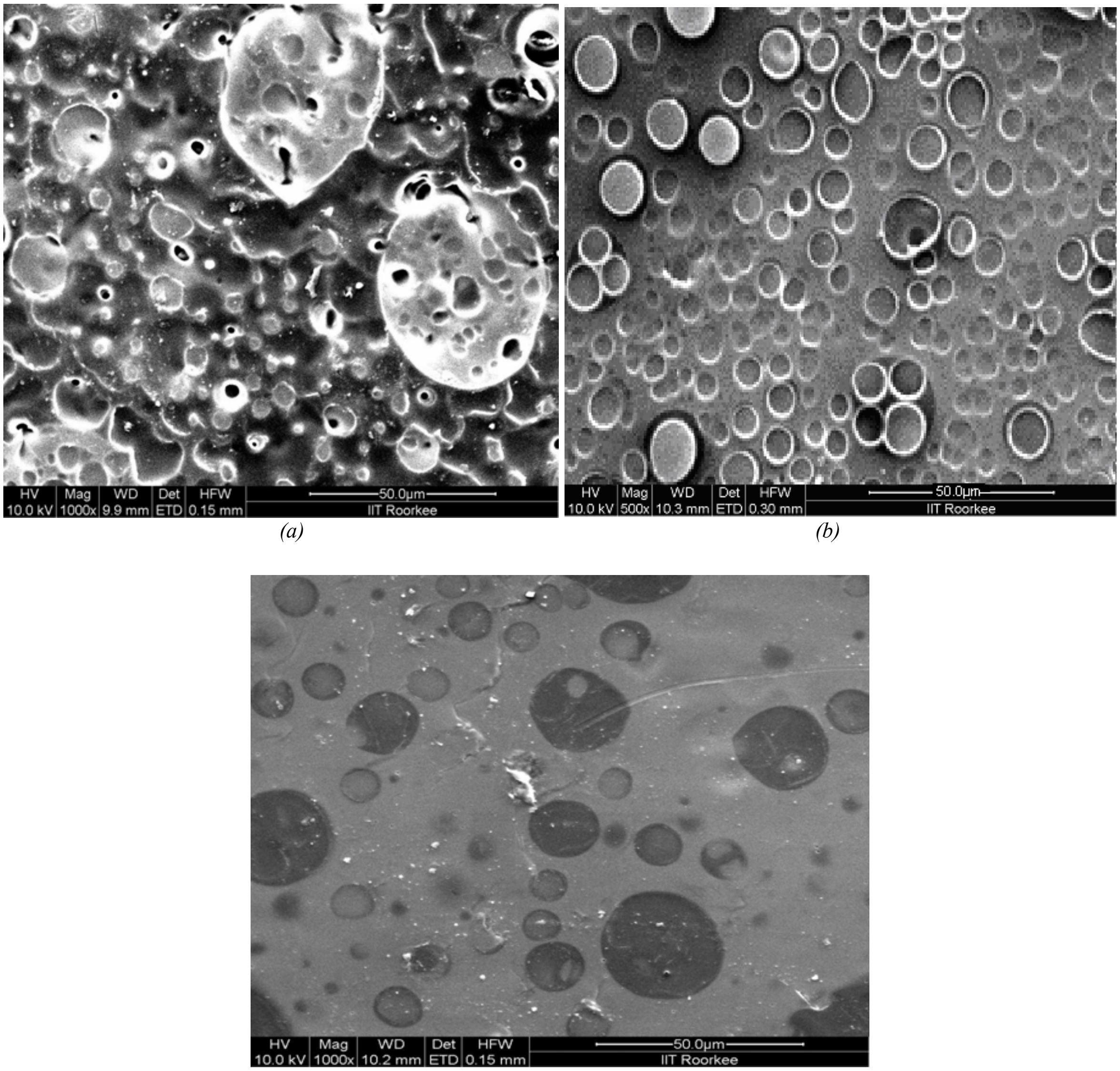


Fig. 4.Variation of storage modulus with PVC content in PMMA.

3.3 Scanning electron microscopy

The SEM micrographs of brittle fractured surface of blends with various amount of PVC in PMMA are shown in Fig. 5.



(a) *(b)*

(c)

Fig.5. SEM micrographs of (a) 75PMMA/25 PVC; (b) 50PMMA/50 PVC; (c) 25PMMA/75 PVC.

These micrographs show almost discrete phases. The observed small spherical particles with smooth surface are of PVC in the matrix. For 25 wt% of PVC the morphology of the blends show a phase separated regions (Fig. 5 (a)). The PVC domains are visualized as the holes from which the material was pulled out. As the amount of PVC increases greater than 25 wt%, the morphology of blends shows a uniform dispersion of PVC particles in the blends (Fig. 5 (b) and (c)). Hence at low concentration of PVC two glass transitions show the phase separation leading ultimately to immiscibility of the blend. Whereas, at higher concentration there is uniform distribution of phase separated regions, the DMA results show one value of T_g (Fig.2).

3.4 Tensile properties of PVC/PMMA

Representative tensile stress–strain curves of PVC/PMMA blends are depicted in Fig. 6. 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 [9]. 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 [15].

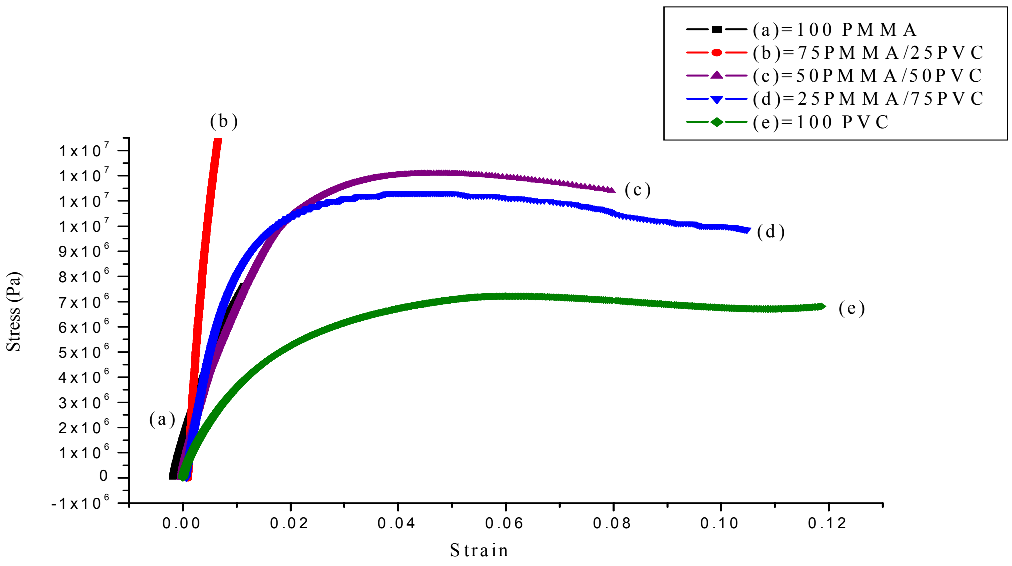


Fig. 6. Stress-strain curve of PMMA, PVC and PMMA/PVC blends.

Curve (a) in Fig. 6 is for pure PMMA, a linear elastic polymer. In PMMA, there is no yield point and fracture is mainly caused by crazing. For curve (a) and (b), the stress increases linearly with strain (or very nearly linearly) until ultimate mechanical failure is obtained. Upon extension neat PVC behaves as a ductile polymer undergoing yielding. Yielding behaviour shows deviations from linearity.This behavior is also noticed in the various blends (Fig. 6, Table 1).

The values of young's modulus, ultimate tensile strength, fracture energy and elongation at break are summarized in Table 1.

Table 1. Mechanical properties of PMMA, PVC and their blends.

Sample	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Fracture energy (Jx10^{-3})	Elongation at break (%)
100 PMMA	0.57	7.62	0.78	1.13
75PMMA/25PVC	2.29	14.41	0.46	0.72
50PMMA/50PVC	0.69	11.35	4.94	7.93
25PMMA/75PVC	0.56	9.87	6.04	10.54
100 PVC	0.27	6.81	4.56	11.8

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. 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.

The elongation at break of a polymer is usually defined as the maximum strain reached during the stress-strain curve, or the strain when the sample breaks. Tensile strain of PMMA/PVC blend is obviously improved by the addition of PVC and it is about ten times higher than that of the neat PMMA. The total area under the stress-strain curve, which represents the fracture energy, also increases with the PVC content. This fracture energy is related to the toughness of polymer. High fracture energy is for tough or ductile polymer and low fracture energy is for brittle polymer. From the table 1 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 [16,17]. 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 (δ=9.27 cal/mL$^{1/2}$) very close to that of PVC (δ=9.47 cal/mL$^{1/2}$), might be expected to have very good compatibility with PVC [18] and hence, enhances the properties.

4. Conclusions

The study of the T_g composition behaviour of PMMA/PVC blends shows that the specific interaction between PMMA and PVC is almost as strong as hydrogen bonding. The DMA and SEM analysis confirmed the miscibility of this pair of polymers upto about 50wt% of PMMA. The result shows that the modulus of PMMA/PVC blends is dramatically influenced by composition and follows a synergic behaviour and it can be concluded that the increase in the PVC content enhances the toughness of PMMA/PVC blend.

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