

Modification of PVC by IPN Formation with Methacrylate in Relation to their Morphologies

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ABSTRACT

Polyvinyl chloride (PVC) has been modified by way of interpenetrating polymer network formation with polyethyl methacrylate and their resulting morphologies have been related to the various mechanical properties obtained. Semi 1 and semi 2 IPNs of PVC and in situ formed polyethyl methacrylate have been synthesized using diallyl phthalate and ethylene glycol dimethacrylate as cross linkers of PVC and polyethyl methacrylate respectively. The cross linkers aid in cross linking the two polymers resulting in the generation of interpenetrating polymer networks. PVC was taken as the major component in the polymeric mixture and its modification was to be investigated with increasing proportion of the methacrylate. The mechanical properties with respect to hardness, modulus and ultimate tensile strength reveal improvement over unmodified PVC both in cases of semi 1 and semi 2 IPNs. These have also been reflected in their elongation and toughness and cross link density values. The entire mechanical studies have been correlated with their morphological aspects through scanning electron microscopy and optical microscopic studies. Significant modification in thermal behavior has also been observed in thermo mechanical analysis and differential scanning calorimetric results. The softening characteristics as detected by the thermal phenomena are in well conformity with the mechanicals.

Keywords: *Polyvinyl chloride, Mechanical properties, Morphology*

1. INTRODUCTION

Interpenetrating polymer networks (IPNs) comprises of two cross lined polymer networks which are physically interpenetrated with each other and at least one of which is cross linked in the immediate presence of the other. IPNs generally consist of two different polymers in which one forms the major matrix and the other gets dispersed within it forming the minor matrix. When the major matrix is cross linked, semi 1 is formed while if the minor matrix is cross linked, semi 2 IPN is generated. However, if both the matrices are cross linked, full IPN is the result. Cross linking in such a way provides an important method of diversifying the physical and the chemical properties of the polymers. Generally, the mechanical and thermal properties of the cross linked polymer are

enhanced at the cost of processibility. The degree of network interlocking has a profound effect on the properties like ultimate tensile strength, modulus, hardness which in turn depends upon the components cross linked [1].

The present study focuses on the improvement of the properties of PVC by incorporating polyethyl methacrylate (PEMA) and forming a semi IPN with it. Generally, PVC is a commonly used plastic because of its excellent corrosion resistance, electrical properties, self extinguishing properties, low cost and recoverability [2]. But its sensitivity to notched impact, high temperature and poor processibility limits its applications. PVC products are restricted to environments not exceeding 80°C and to non structural applications because of low strength. Hence the polymer is often mixed with other polymers to improve its properties. In such an attempt, the processibility and toughening characteristics of PVC are expected to improve but not at the cost of reduced mechanicals [3]. In this case, the formation of the semi IPNs with PVC and PEMA contributes further to retain the physico-mechanical properties of PVC. Here, PVC acts as the major matrix while PEMA is considered to be the minor one. Several compositions based on these two polymers were prepared and investigated for their changes in properties over increasing concentration of PEMA. The degree of network interlocking changes the entire morphology of the combined systems and has a measurable influence on the harness, tensile properties and even thermal properties. Increased network interlocking is expected to improve the compatibility [4].

2. EXPERIMENTAL:

Materials: PVC (Reon) grade K 67 was procured from M/s Reliance Industries Ltd. (India) and was used as the matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulfate (TBLS) from M/s Kalpana Industries Ltd. (Daman, India) were used as suitable plasticizers and stabilizers respectively. Diallyl phthalate (DAP) from M/s Burgoyne was used as a cross linker for PVC. Benzoyl peroxide from Loba Chemie (India) was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company Inc. was used as the cross linker for PEMA which was also procured from M/s Burgoyne (India).

Synthesis of semi 1 and semi 2 IPNs: A weighed amount of purified monomer was taken in a test tube and thoroughly mixed with 2% by weight (based on monomer taken) of recrystallised Bz_2O_2 . The resin was taken in an airtight dry blender and mixed with 30 parts of DOP and 2 parts of TBLS with respect to the amount of PVC resin taken. 5 parts by weight of DAP w.r.t. PVC was then added in the mix for producing semi 1 IPNs. The monomer containing initiator was then added to the premix of PVC. EGDM to the extent of 2% by weight of the monomer taken was initially added to the monomer mix for generating semi 2 IPNs. Dry mixing was further continued unless a thoroughly mixed powder was obtained.

Moulding: The powdery mix obtained as above was compression moulded into sheets by subjecting a three piece mould under pressure and heat in two stages. Initially, the mould (0.95 m x 0.65 m x 0.001 m) was compressed under a pressure of 15 tons/cm² at a temperature of 80°C to initiate and propagate acrylic polymerization. This was allowed to continue for 30 min. Subsequently, the temperature was raised to 160°C while the pressure was maintained at the same level. The mould was then allowed to cool down to the room temperature and the moulded sheet ejected.

3. MEASUREMENTS:

Tensile properties: An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like ultimate tensile strength, modulus, elongation at break and toughness. ASTM D 638 method was followed.

Thermal properties: The differential scanning calorimetry (Mettler 822e) of the samples were carried out up to a limit of 350°C at a heating rate of 10°C/min. Thermo mechanical analysis of the samples were carried out on a TMA-50 Shimadzu model in presence of oxygen at a heating rate of 10°C/min.

Morphology: Scanning electron microscopic analysis was carried out on the fractured surface of a tensile fractured specimen using Hitachi model S415A.

4. RESULTS AND DISCUSSION:

Mechanical properties:

The various mechanical properties of semi 1 and semi 2 IPN systems of PVC-poly(ethyl methacrylate) are compared as a function of IPN composition (Figures 1&2). The mode of changes in modulus and UTS in case of semi 1 IPNs indicates the influence of plasticization exerted by the plastomeric PEMA embedded within the cross-linked PVC matrix. The initial sharp drop in the modulus value (w.r.t. the cross linked PVC compound) in this case may be ascribed to the presence of linear PEMA domains which not only break down the regular alignment of the PVC chain structure but also prevents formation of completely cross linked matrix of PVC as they already occupy the interspaces between the matrix chains and do not allow the PVC chains to form the cross links. With increasing proportions of PEMA (beyond 10%), the slow decrease in modulus arises due to the entrapment of PEMA moieties within the long cross linked chains of PVC. The semi 2 IPNs of the PVC-PEMA systems however display reverse characteristics. An increase in the proportion of cross linked PEMA within the linear PVC matrix shows an increase in the modulus and ultimate tensile strength values when compared to linear base compound which may be attributed to the chain stiffness and rigidity imparted by the dispersed cross linked PEMA [5].

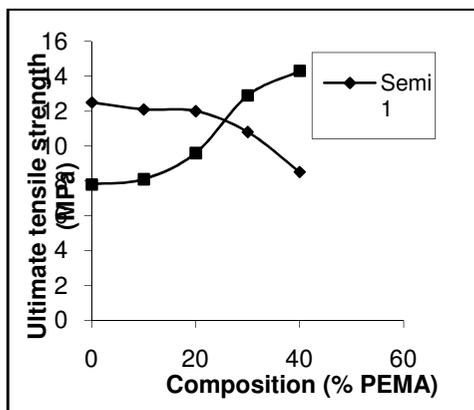


Figure 1: Modulus vs PEMA concentration

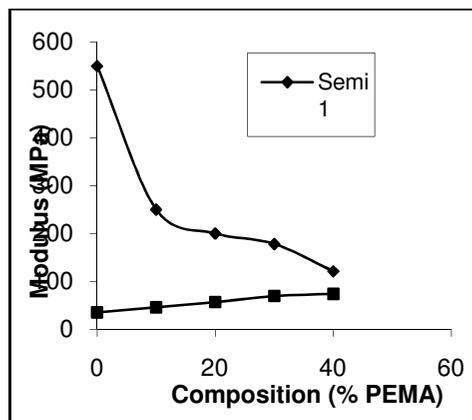
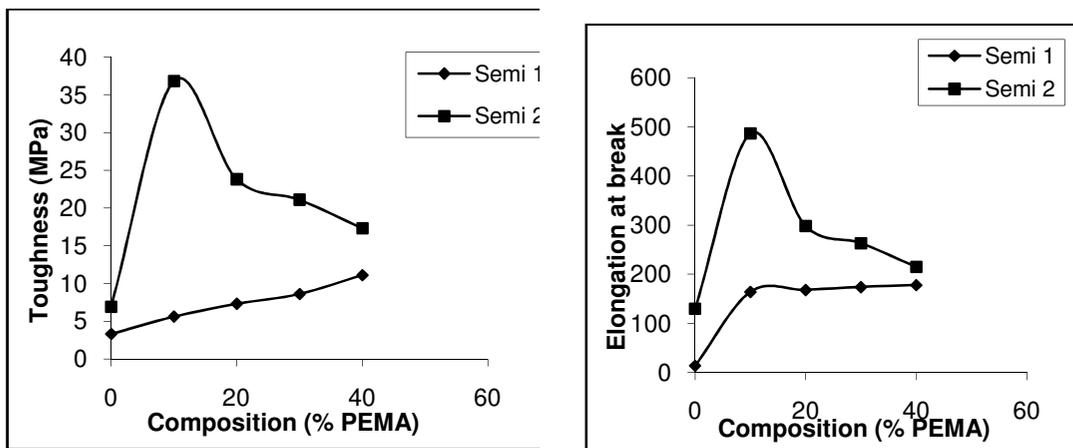


Figure 2: UTS vs PEMA concentration

The percent elongation at break and toughness of the different semi 1 and semi 2 IPNs of the PVC-PEMA system as shown in figures 3 and 4 conform to the observation as expected. In the semi 1 system, the continuous rise in the elongation at break and toughness along with increase in PEMA concentration exhibits the plasticizing effect imparted by the PEMA domains along with an increase in path length at the interfaces between the two phases and thus providing a greater area for absorption of the fracture propagating energy which leads to an overall increase in toughness. The regular chain structure of PVC is also disrupted by the introduction of more and more modifying resin into the system which in turn contributes to the increasing elongation characteristics of the system. The semi-1 IPNs by virtue of having major PVC matrix cross linked, have their % EB and toughness always lower than the semi2 IPNs. In contrast to the observation with the semi 1 IPN system, the semi 2 IPNs exhibit an initial increase in elongation at break and toughness followed by a gradual and steady decrease. The influence of cross links of the major matrix being absent in this case, the effect of the cross linked minor matrix only comes into play. The somewhat rigidity and stiffness conferred by the cross linked PEMA domains possibly accounts for the decreasing tendency of elongation at break and toughness. The initial sharp rise in % EB and toughness are probably due to the presence of linear uncross linked PVC matrix, the dipole-dipole interaction of which has further been weakened by the plasticizing influence of minor cross linked PEMA phase. However, the elongation at break and toughness of the semi 2 IPNs always lie above the values exhibited by the unmodified PVC matrix [6].

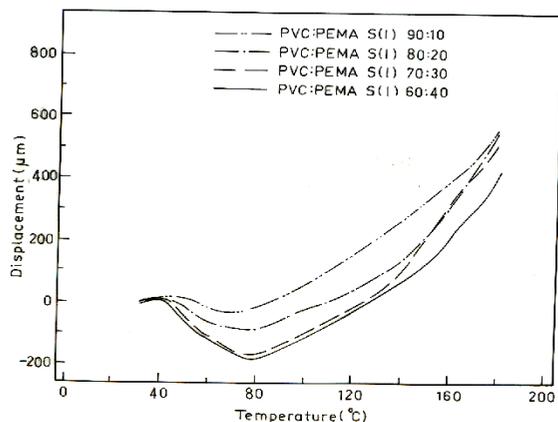
The thermo mechanical curves of the semi 1 and semi 2 IPNs (Figures 5a and 5b) display penetration of the probe into the samples inversely related to their respective modulus. The depth of penetration (a measure of softness) increases with increasing PEMA content in case



Thermal properties:

Figure 3: Elongation vs PEMA concentration **Figure 4: Toughness vs PEMA concentration**

of semi 1 IPNs. The softening range also increases although the temp of incipience or onset of softening advances towards left as the PEMA content increases progressively. The PEMA molecules produce a plasticizing action which reduces the resistance to the penetration. In case of semi 2 IPNs, the crosslinks formed within the dispersed PEMA moieties offers the resistance to deformation which is again enhanced at the later stages of PEMA incorporation. The IPNs exhibit thermal stabilization under a specified load over unmodified PVC at the upper experimental temperature under study.



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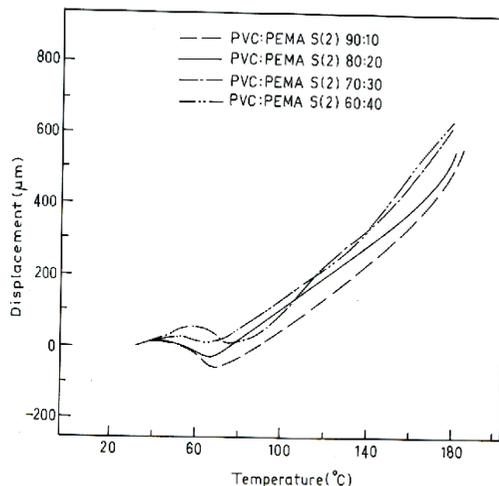


Figure 5a: TMA of Semi 1 IPN

Figure 5b: TMA of Semi 2 IPN

The DSC tracings of the representative samples PVC-PEMA semi 1 and semi 2 IPNs as shown in figure 6 display the similar nature of increasing order of plasticization with the incorporation of more and more polymethacrylate which is indicated by the shift of the glass transition temperature from that of pure PVC, base compound under study. The presence of crosslinks in the major or minor phase appears to affect the T_g 's observed, to a limited extent. The stabilisation effect at the higher temperature ranges is quite evident from the delayed onset compared to that of pure reference compound PVC [7].

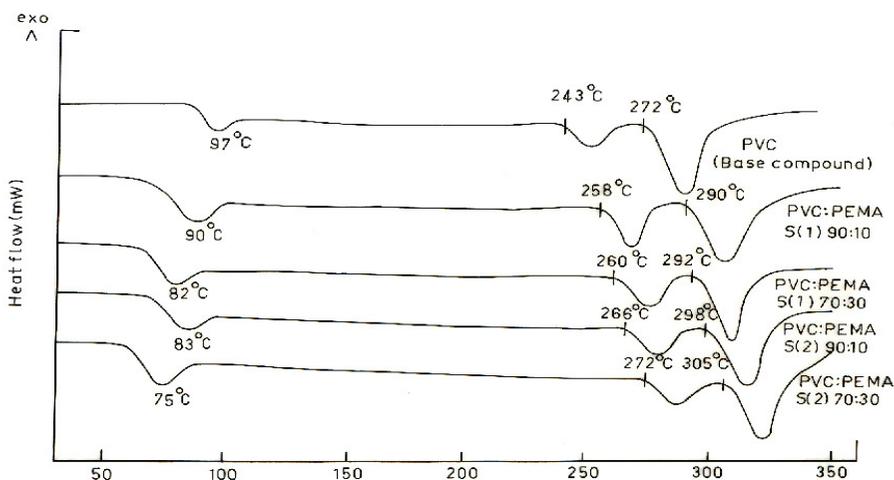
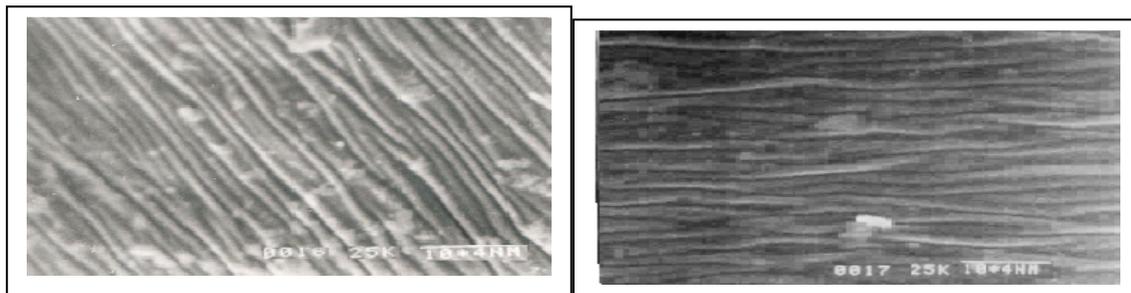


Figure 6: DSC tracings of Semi 1 and Semi 2 IPNs

Morphology:

The scanning electron micrographs as depicted in figure 7a and 7b represent opposite characteristics in either cases of the IPNs. In case of the semi 1 IPNs, somewhat phase miscibility is observed in the earlier stages of PEMA incorporation followed by distinct phase



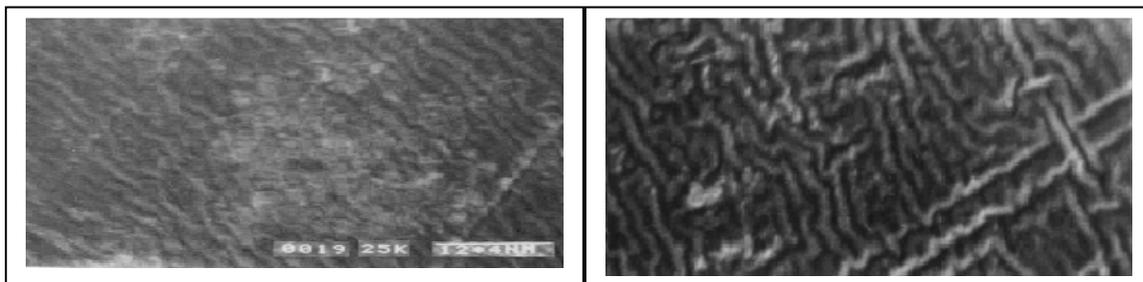


Figure 7a: SEM of 20% and 40% PEMA incorporated Semi 1 IPN **Figure 7b: SEM of 20% and 40% PEMA incorporated Semi 2 IPN**

immiscibility at the later stages. In case of the semi 2 IPNs, the reverse phenomena takes place, i.e. phase heterogeneity followed by phase miscibility. The observation of the micrographs can lead to a conclusion of the mechanical properties (modulus and ultimate tensile strength) in both the types of IPNs. The gradual decrease of modulus and UTS in case of the semi 1 IPNs can be explained morphologically by the increasing tendency of the microfibrils to form distinct entities [8]. It may further be noted that the dispersed microfibrils appear to be somewhat discontinuous and form short fibrils possibly because of the presence of PVC crosslinks particularly the lower ranges of PEMA incorporation. At the higher ranges of PEMA concentration under study, the fibrils assume somewhat kinked morphology and appear to come out of phase. In case of the semi 2 IPNs, the phase homogeneity as observed within the microfibrils with increasing concentration of PEMA leads to greater molecular interaction, thus raising the mechanical parameters (modulus and UTS) and consequently also directing the thermal behaviour of the IPNs. The directing influence of one polymer over the other is evident from the micrographs which is thus the determining factor in controlling the mechanical, thermal and morphological history of the interpenetrating networks formed [9].

5. CONCLUSION

The systems under study revealed the impact of IPN formation of PVC with poly(ethyl methacrylate) ester. The introduction of PEMA moieties within the matrix of PVC produced a rise in the mechanical and thermal stability compared to the base compound PVC. The combination of the two polymers also created a directing influence one over the other which was explicit from the micrographs. Thus interpenetrating networks with increased strength and acceptable toughness have been simultaneously achieved. The toughness values though exhibiting a gradual fall along with composition in case of semi-2 IPNs, always lie above that of unmodified PVC. The thermomechanical properties have also been modified which produces an overall increasing

stability. The rise in the onset temperature of degradation as explicit from the DSC results indicates the influence of the dispersed PEA moieties in producing thermal stability.

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