

Modification of the Properties of PVC by full IPN Formation with Polybutyl Acrylate

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ABSTRACT: Interpenetrating polymer networks (IPNs) of polyvinyl chloride (PVC) and polybutyl acrylate (PBA) were produced using diallyl phthalate (DAP) and ethylene glycol dimethacrylate (EGDMA) as the cross linkers of PVC and PBA respectively. Butyl acrylate, the monomer was polymerized in the presence of PVC which was premixed with the heat stabilizer, TBLS (tribasic lead sulphate) and plasticizer (dioctyl phthalate). The two polymers were simultaneously cross linked with their respective cross linkers and full IPNs were generated. Four distinct sets of IPNs were prepared by varying the composition ratio of the constituent polymers. The IPNs were characterized with respect to their physico-mechanical and thermal properties and an endeavour had been made to investigate the influence of PBA on PVC matrix. The properties revealed significant effect of the cross linked rubbery PBA polymer on cross linked PVC. The tensile strength showed a decrease but the elongation displayed significant improvement over unmodified PVC. The thermal behaviour was also modified in the full IPNs as evidenced from the DSC results. The changes in glass transition temperature and degradation temperature indicate stability of the samples over unmodified PVC. The morphological properties as observed by scanning electron microscopy were in corroboration with the changes in mechanical properties observed.

KEYWORDS: Polyvinyl chloride, Polybutyl acrylate, mechanical properties, thermal properties, morphology.

I. INTRODUCTION

Interpenetrating polymer networks constitute the class of polymers where two cross linked polymers are physically interpenetrated and at least one of which is cross linked in the immediate presence of the other. Cross linked polymer chains provide an important way of diversifying the physical and chemical properties of polymers. Generally, the mechanical and thermal properties of the polymer are enhanced but the processibility of the polymer deteriorates [1]. IPNs are characterized by their bi-continuous structure with no chemical linkage within the constituent polymers [2]. IPNs are mostly constituted of two polymer matrices, one being the major matrix which covers a larger proportion of the entire polymer mass and the other forming the minor matrix. When the major component is cross linked, semi 1 IPN results whereas when the minor component is cross linked, semi 2 IPN is generated. However, if both the matrices are cross linked, full IPNs are formed. When both the polymers are cross linked, the morphology is fixed and well defined and the associated properties do not vary much [3]. Increased network interlocking is expected to improve compatibility. The mechanical and thermal properties are influenced by the extent of network interlocking [4]. The present study focuses on the modification of the properties of PVC by forming a full IPN with polybutyl acrylate. Generally, PVC is a commonly used plastic because of its excellent corrosion resistance, electrical properties, self extinguishing properties, low cost and recoverability. But its sensitivity to notched impact, high temperature and poor processibility limits its applications. 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. In this case, polybutyl acrylate used as the polymeric modifier is supposed to modify its processibility, mechanical and thermal properties by way of full IPN formation [5]. The somewhat rubbery PBA moieties is expected to aid in the processibility of the PVC polymer whereas the cross links generated by formation of the IPNs are supposed to aid in improving the physical strength of the PVC polymer. Here, PVC is taken as the major matrix and PBA as the minor one which remain dispersed within the network structure of PVC. The mechanical and thermal properties are scanned through a concentration sweep of PBA and the findings are analyzed with increasing PBA concentration. 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 [6].

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II. LITERATURE SURVEY

Several related works have been reported in literature relating to blends and IPNs of PVC systems. In this study, we have tried to modify PVC with somewhat rubbery PBA in an attempt to produce tougher IPNs keeping the mechanical parameters at par with original PVC or even better. This can be hinted at from a study by Paul and Barlow [7,8] in which it was stated that the a hydrogen of PVC interacts with the ester carboxylate group (H bond acceptor of the acrylic polymer) to form a hydrogen bond and is also the key factor in achieving miscibility. Characterization of semi-interpenetrating polymer networks (IPNs) of polyurethane and PVC was carried out by Pielichowski and Janouski [9]. The cure behavior of silicone epoxies and urethane-modified acrylates in IPNs was studied by Price et al [10]. This was done in an attempt to improve the toughness and flexibility of poly(epoxyurethane-acrylic). In a recent study, it is observed that the mechanical properties display a dynamic behaviour with the quantity of PEA incorporated and there is an improvement in mechanical properties in terms of ultimate tensile strength, elongation at break and toughness than unmodified cross linked PVC. There has been a notable modification in thermal behaviour where thermal stability is exhibited depending on the dose of PEA incorporation [11]. Another related study on PVC-PEMA full IPN systems, a notable modification in the mechanical and thermal properties were observed depending on the dose of PEMA incorporation [12].

III. MATERIALS AND METHODS

A. Chemicals: 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 sulphate (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 crosslinker for PBA. PBA was taken from Berger Paints Ltd., India.

B. Synthesis of full 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. 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. Dry mixing was further continued unless a thoroughly mixed powder was obtained.

C. Conditions of 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 polymerisation. 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.

D. Mechanical properties: An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like ultimate tensile strength and elongation at break. In the process of measurement, ASTM D638 method was followed.

E. Thermal properties: The differential scanning calorimetry (Mettler 822e) of the samples were carried out upto a limit of 350°C at a heating rate of 10°C/min right from the ambient temperature. The transition behaviour above ambient temperature and the temperature ranges of degradation were only studied. The weights of the samples were maintained between 0.005 to 0.008 gm.

F. Morphology: Scanning electron microscopic studies were carried out in a scanning electron microscope (Hitachi model S415A) after suitable gold coating on the samples. Completely dried samples were coated with a thin layer of gold using a high vacuum gold sputterer. The fractured surface of a tensile fracture specimen was inspected for morphology. The scale of magnification was 500X.

IV. RESULTS AND DISCUSSIONS

A. Mechanical properties: The mechanical properties of PVC - polybutyl acrylate full IPNs as depicted in figures 1 and 2 reveals decreasing order of ultimate tensile strength followed by a corresponding increase in elongation at break with increasing concentration of PBA upto 10% PBA incorporation. Beyond 10%, a steady rise in the ultimate tensile strength was observed. There was a fall in the elongation at break values with increasing PBA concentration but the lowest value of this parameter remained significantly higher than that of unmodified PVC.

The initial sharp fall in tensile strength as observed may be attributed to the breakdown in molecular alignment of cross linked PVC chain structure by the incorporation of cross linked, rubbery PBA molecules within it. At the later stages, after about 10% PBA incorporation, the formation of *in situ* rubber phases of PBA followed by its simultaneous cross linking and more and more extent of interwinding with the cross linked PVC matrix results in increased ultimate tensile strength along with increasing percentage of PBA in composition.

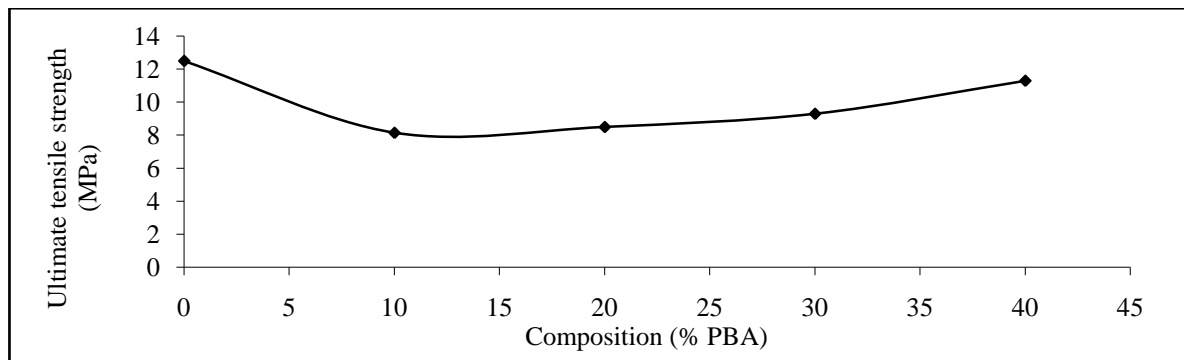


Fig. 1 Variation of UTS of PVC-PBA full IPNs with variation of PVC-PBA blend ratio (w/w)

The sharp rise in elongation upto 10% PBA concentration may be ascribed to the effect of plasticisation imparted by the incorporation of cross linked PBA moieties within the cross linked matrix of PVC. The incorporation of more and more cross linked PBA molecules in the continuous cross linked matrix of PVC disrupts the structural regularities of PVC which breaks down the molecular packing and provides an alternative path length for dissipation of energy before its ultimate rupture resulting in increased elongation at break [13]. Moreover, the incorporation of the more and more rubbery polybutyl acrylate into the system contributes to the enhanced flexibility of the polymer matrix resulting in higher elongation values. So, the changes in the mechanical properties are directly influenced by the effect of full IPNs formed by the networks of PVC and PBA.

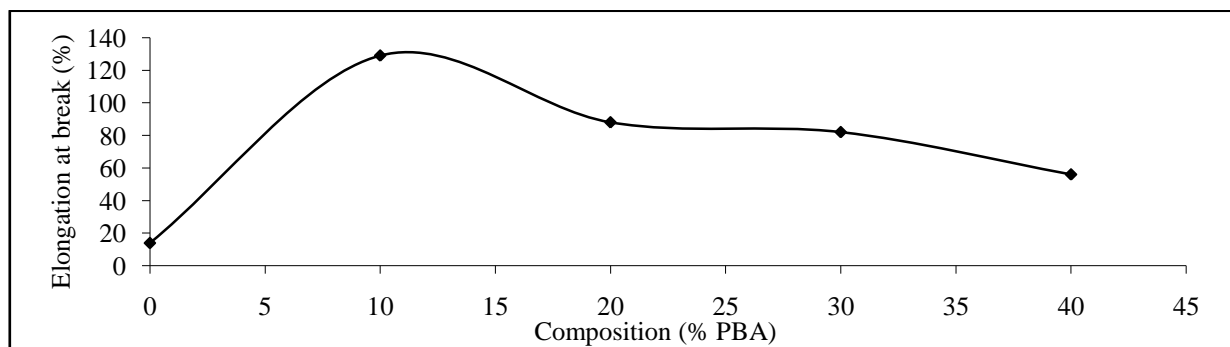


Fig. 2 Variation of percent elongation at break of PVC-PBA full IPNs with variation of PVC-PBA blend ratio (w/w)

B. Thermal properties: The DSC tracings as depicted in figure 3 denotes increasing trend of plasticisation with increasing concentration of the modifying cross linked PBA resin. The generation of cross links within the major and minor phases individually appears to influence the glass transition temperature and the consequent onset of degradation

significantly. The influence of the rubbery segments of the PBA moieties plays the major role in this regard. The PBA incorporated PVC (both phases cross linked) exhibit delayed onset of degradation temperature compared to unmodified PVC [14]. The two stage of degradation are manifested and in both cases we can find an increase in degradation temperature with increasing proportion of cross linked PBA.

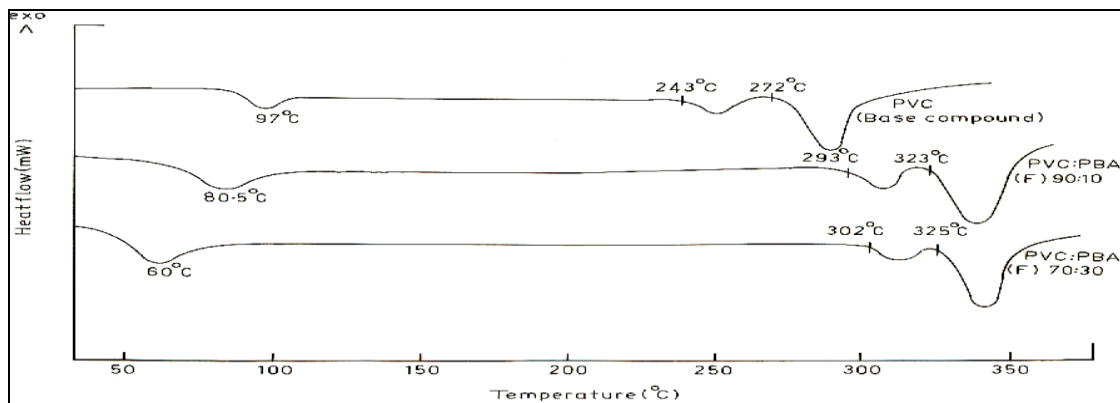


Fig. 3 DSC curves of PVC-PBA full IPNs; (F) refers to full IPNs

C. Morphology: The scanning electron micrographs as in figure 4 of the system under consideration reveal phase heterogeneity in the form of fibrillar structures. They display typical bicontinuous mode of morphology with the two phases existing simultaneously. The dual continuity of the phases, accompanied by an increase in the number of kinked microfibrils possibly accounts for the enhanced properties at the initial stages although at the later stages of PBA incorporation the bicontinuity is blotched by grossly phase separated PBA phase [15]. The intensity of phase separation however increases with rising concentration of the polyacrylate resin as observed in the other cases. The consequent cross linking and interwinding of the two phases exhibit reduced diameter of the microfibrils formed at the later stages due to the dual cross linking of the PVC and PBA phases which makes it more dense and compact giving rise to increased mechanical strength [16].

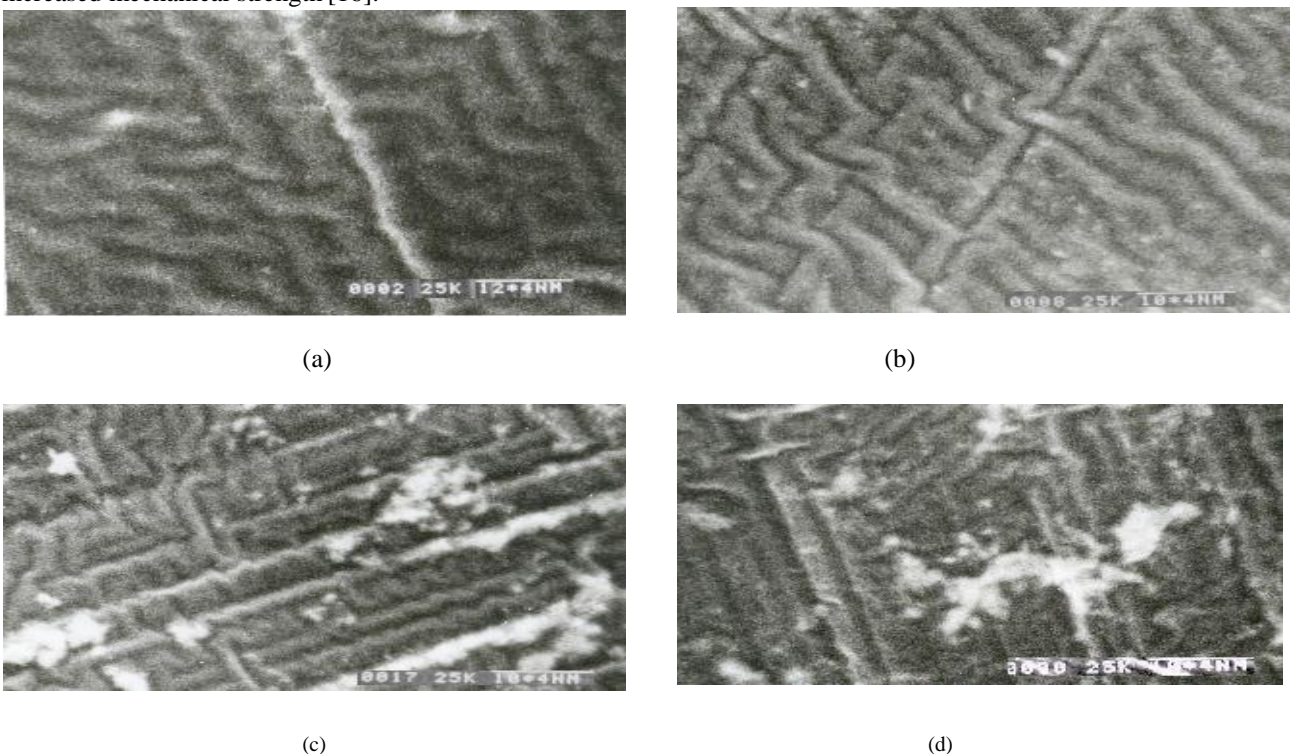


Fig. 4 (a) PVC: PBA (F):: 90:10 (b) PVC: PBA (F):: 80:20 (c) PVC: PBA (F):: 70:30 (d) PVC: PBA (F):: 60:40

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V. CONCLUSION

The present study deals with the modification of PVC with PBA by the formation of full IPNs with both the matrices. It has been observed that the mechanical properties display a dynamic behaviour with the quantity of PBA incorporated and there is an improvement in mechanical properties in terms of ultimate tensile strength and elongation than unmodified cross linked PVC. The introduction of PBA moieties within the matrix of PVC produces a rise in the thermal stability as well. The elongation values though exhibiting a gradual fall along with composition, they however always lie above that of unmodified PVC. The DSC tracings have also been modified which produces an overall increasing stability. The morphology supports the observed mechanicals which is explicit from the scanning electron micrographs.

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