



## **Property modification by full IPN formation with PVC and PBA**

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**Abstract :** Poly(vinyl chloride) (PVC) and (polybutyl acrylate) (PBA) polymers are blended to form a full interpenetrating network (IPN) using diallyl phthalate (DAP) and ethylene glycol dimethacrylate (EGDM) as the crosslinkers of the polymers respectively. Four distinct sets of full IPNs were prepared by varying the composition ratios. PVC, mixed with plasticizer dioctyl phthalate (DOP) and heat stabilizer tribasic lead sulphate (TBLS), alongwith monomer butyl acrylate and initiator benzoyl peroxide ( $Bz_2O_2$ ). DAP and EGDM were added to the polymers PVC and PBA which acted as their crosslinkers respectively. The powdery mix was compression moulded under heat and pressure to allow simultaneous polymerization and cross linking. The samples formed were characterized with respect to their physico-mechanical, thermal and morphological properties with respect to the unmodified base reference PVC compound. The rubbery nature of the modifying resin PBA had an influential effect in modifying the properties of PVC. There was an initial fall up to 10% PBA incorporation in tensile strength followed by a rise nearly up to the original strength of PVC. There was also a significant rise in percentage elongation at break and toughness over unmodified PVC followed by a rise in thermal stability of the samples as shown in the thermomechanical and differential scanning calorimetric studies. Morphologically, the scanning electron micrographs corroborates with the trend in mechanical changes as observed.

**Keywords :** Poly(vinyl chloride), poly(butyl acrylate), mechanical properties, thermal properties, morphology.

### **Introduction**

An important way of diversifying the physical and chemical properties of polymers is by crosslinking. Generally, mechanical or thermal properties of the crosslinked polymers are enhanced at the cost of its processibility. In the case of PVC resin, crosslinking technology is investigated as a major tool to enhance its effectiveness and applicability [1]. IPNs generally consist of two different polymers in which one forms the major matrix and the other gets dispersed within it forming the minor one. When the major matrix is cross linked, semi 1 is formed while if the minor matrix is cross linked, semi 2 IPN is generated. If both the matrices are cross linked, full IPN results. The degree of network interlocking has a profound effect on the physico-mechanical properties of the polymers [2]. Because of their interlocking configuration, the extent of phase separation is restricted such that the properties are not influenced by subsequent ageing. The properties are influenced by the two phase morphology that develops during IPN formation [3].

PVC is commonly used as a general commodity plastic because of its excellent electrical and corrosion resistance, self extinguishing characteristics, low cost and recoverability. Its inherent problem of processing is also quite well known and is overcome by the use of certain plasticisers [4]. But due to the use of common

plasticisers, there is every possibility of compromising on the mechanical properties of rigid PVC. PVC products are restricted to environments not exceeding 80°C and to non structural applications because of low strength [5]. 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 [6].

The present study deals on the improvement of properties of PVC by incorporating polybutyl acrylate (PBA) and forming a full IPN with it. The formation of the full IPNs with PVC and PBA contributes further to retain the physico-mechanical properties of PVC. Here, PVC acts as the major matrix while PBA is the minor one. Paul and Barlow have suggested that the  $\alpha$  hydrogen of PVC can interact with the ester carboxylate group (H bond acceptor of the acrylic polymer) to form hydrogen bond and is also a key factor in achieving miscibility [7]. Also, there is a probability of interaction between the C-Cl dipole of PVC and the hydrogen of the acrylate ester [8]. These two phenomena can be accounted for increased strength of the IPNs and thus interpenetrating networks of PVC and PBA can be expected to display improved modulus as well as toughness behavior [9].

## 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 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 crosslinker for PVC. Benzoyl peroxide from LobaChemie (India) was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company Inc. was used as the crosslinker for PBA. Butyl acrylate was taken from Berger Paints Ltd., India.

### Methods

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. 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/cm<sup>2</sup> 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.

### Characterization

#### Mechanical properties

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like modulus and toughness. In the process of measurement, ASTM D638 method was followed.

#### Thermal properties

The thermomechanical analysis of the various samples of PVC (containing plasticisers and stabilisers in proportion to which they are present in the samples) were carried out in a TMA apparatus from Shimadzu (model TMA 50) in the presence of oxygen. The thermooxidative characteristics were studied under a constant load of 0.008 kg throughout the experiment by using a compressive mode of probe upto a temperature limit of 180°C following a temperature program in which a heating rate of 10°C/min was maintained right from the ambient temperature.

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.

### Morphology

An optical microscope from Krüss (optromic) (Germany) was used to study the surface morphology of the undeformed samples having thickness < 0.5 mm to get a relative idea of the mode of distribution of domains, sizes of the domains, physical state of the domains and mode of their growth as dictated by the method of synthesis, compatibility, etc. The scale of magnification used was 200 X.

## Results and discussion

### Mechanical properties

The mechanical properties of PVC-poly(butyl acrylate) full IPNs as depicted in fig. 1 reveals decreasing order of tensile modulus values with increasing concentration of PBA upto a level of 10% PBA incorporation beyond which there is a slow and steady rise in modulus under study. The initial sharp fall in modulus as observed may be attributed to the breakdown in molecular alignment of crosslinked PVC chain structure by the incorporation of crosslinked, somewhat rubbery PBA molecules within it. At the later stages, after about 10% PBA incorporation, the formation of *in situ* rubbery PBA phases followed by its simultaneous cross linking and more and more extent of interwinding with the crosslinked PVC matrix as dictated by the mode of synthesis results in increased modulus along with increasing percentage of PBA in composition.

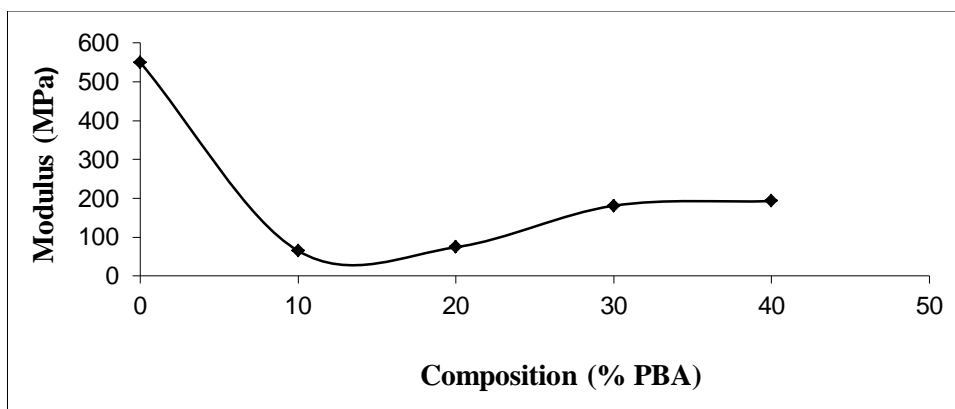
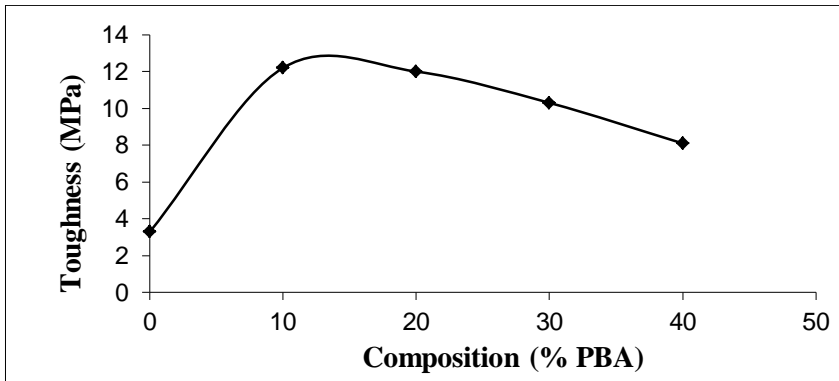


Fig. 1: Variation of modulus with change in PBA concentration

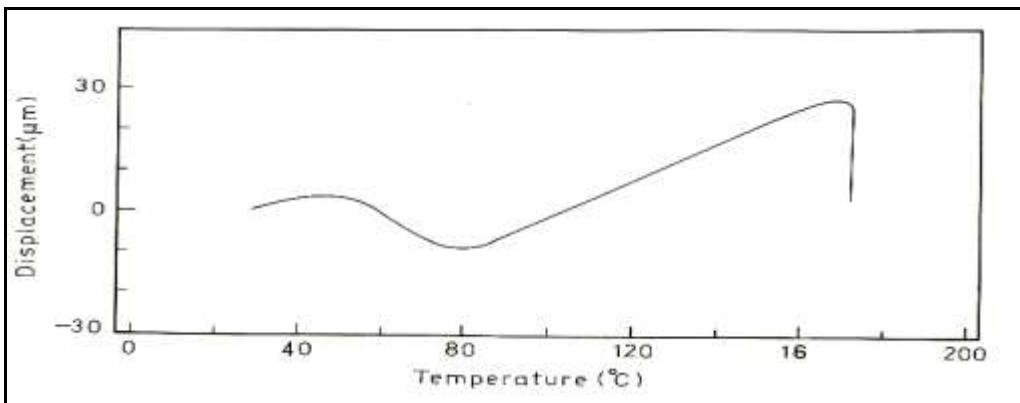
The toughness of the system under consideration as in fig. 2 show somewhat increasing trend initially followed by a steady fall as expected alongwith increasing percentages of the poly(butyl acrylate) into the system. With the introduction of crosslinked PBA moieties within the crosslinked network of PVC, the molecular alignment gets disrupted and crosslinked PBA gets interpenetrated. Although these dispersed PBA moieties acts as stress concentrators, they also help in absorbing the crack propagation energy and thus raises the toughness upto a level of around 10% of PBA incorporation. Beyond this, the IPN compositions having more and more PBA loses ductility owing to the presence of higher compact and crosslinked PBA, thus allowing the PVC chains to come closer and widen the possibility of intermolecular crosslinking. However, it is worth notifying that though the toughness decreases with increase in PBA content, it always remains above that of unmodified cross linked PVC and hence an IPN with improved toughness develops [10].



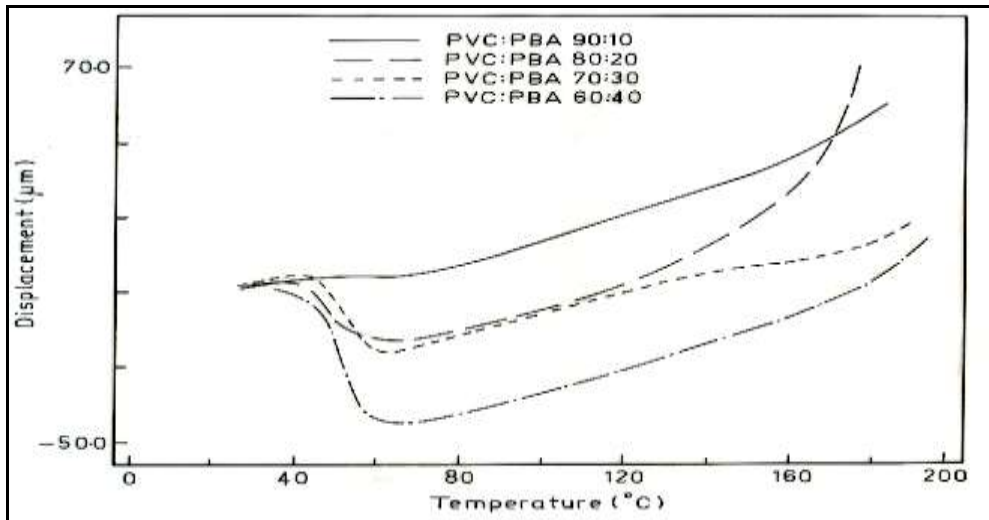
**Fig. 2: Variation of toughness with change in PBA concentration**

### Thermal properties

The thermomechanical curves of the base reference compound PVC and the PVC-PBAfull IPNs under study (figs. 3a and 3b) indicate that in all cases, the probe is slightly pushed up by the expansion of the samples up to a temperature around 50°C. Once the sample starts softening, the loaded probe penetrates the sample at a rate inversely related to the moduli of the various samples. At the initial stages, the lowering of rigidity due to breakdown in regularity of chain structure leads to softness whereas at later stages, the slow and gradual association of the crosslinked PBA moieties probably accounts for the decreased penetration within the range of PBA incorporation studied. After the initial softening, the samples undergo expansion till the upper test temperature is reached. While at this stage, unmodified PVC shows breakdown and sharp fall, the full IPNs remain stable and exhibit stabilization over PVC. However, owing to the significant rubberiness of the polybutylacrylate moieties incorporated into the system, the depth of penetration or the softness increases in a continuous manner as the crosslinked PVC network is gradually replaced by the relatively softer PBA (crosslinked) molecules [11].

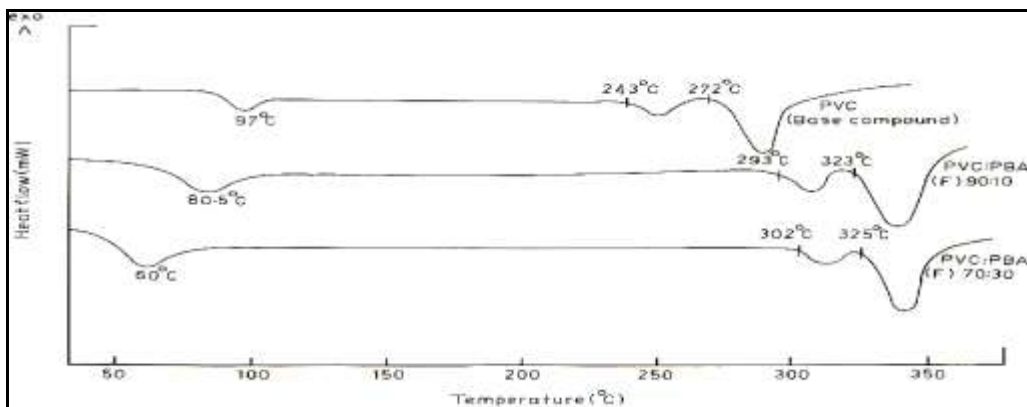


**Fig.3a: Thermomechanical curve of unmodified PVC**



**Fig. 3b: Thermomechanical curves of PVC-PBA full IPNs**

The DSC tracings as depicted in fig. 4 denotes increasing trend of plasticisation with increasing concentration of the modifying crosslinked 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 crosslinked) exhibit delayed onset of degradation temperature compared to unmodified PVC. The two stage of degradation are manifested and in both cases we can find an increase in degradation temperature with increasing proportion of crosslinked PBA.



**Fig. 4: DSC tracings of PVC-PBA full IPNs**

### Morphology

The morphology as envisaged by optical microscopy (fig. 5) displays phase miscibility at the initial stages of PBA incorporation followed by macrophase separated entities of the dispersed rubbery phase distributed within the crosslinked matrix resin of PVC. The agglomerated crosslinked phases dispersed within the continuous crosslinked PVC network possibly produce some reinforcing action which counterbalances the plasticising action of the rubbery polyacrylate moieties and generates enhanced molecular interaction and hence increased mechanical strength [12].

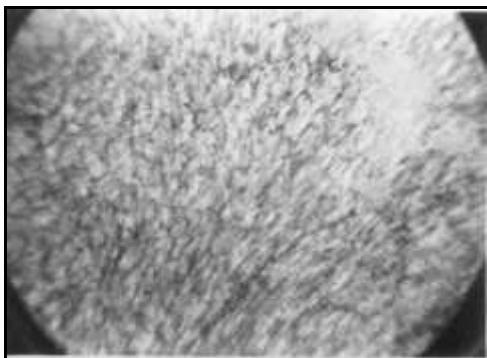


Fig. 5a: PVC:PBA 80:20

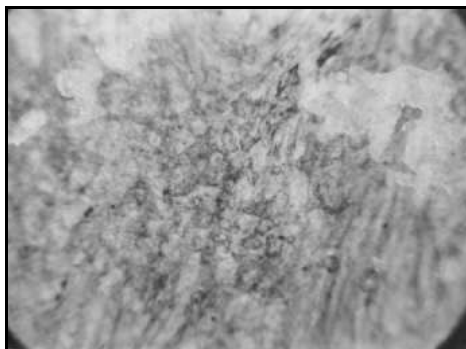


Fig. 5b: PVC:PBA 60:40

## 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 modulus and toughness 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 combination of the two polymers also creates a directing influence one over the other which is explicit from the micrographs. Thus interpenetrating networks with increased modulus and acceptable toughness have been simultaneously achieved. The toughness values though exhibiting a gradual fall along with composition, they however always lie above that of unmodified PVC. The thermomechanical properties have also been modified which produces an overall increasing stability. The morphology supports the observed mechanicals which is explicit from the optical micrographs.

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