

# Influence of crosslinked PMMA on crosslinked PVC for modification of its properties

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**Abstract**— Interpenetrating polymer networks (IPNs) of polyvinyl chloride (PVC) and polymethyl methacrylate (PMMA) were produced using diallyl phthalate (DAP) and ethylene glycol dimethacrylate (EGDMA) as the cross linkers of PVC and PMMA respectively. Methyl methacrylate, 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 PMMA on PVC matrix. The properties revealed significant effect of the cross linked PMMA polymer on cross linked PVC. The tensile modulus showed a decrease but the elongation displayed significant improvement over unmodified PVC. The thermal behavior was also modified in the full IPNs as evidenced from the thermo mechanical results. The morphological properties as observed by scanning electron microscopy were in corroboration with the changes in mechanical properties observed.

**Keywords**- Mechanical properties, morphology, polymethyl methacrylate, polyvinyl chloride, thermal properties.

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## I. INTRODUCTION

Cross linking polymeric chains provide an important way of diversifying the physical and chemical properties of polymers. Interpenetrating networks constitute a special category of blends where two cross linked polymers are physically interpenetrated and at least one of the polymers are cross linked in the immediate presence of the other. In any case, if both the matrices are cross linked, a full IPN is the result. The degree of interlocking between the components has a measureable effect on the various mechanical properties like the modulus, ultimate tensile strength and hardness. Increased network interlocking is expected to improve the compatibility. Because of their interlocking configuration, the extent of phase separation is frozen in such that the properties are not influenced by subsequent ageing. The properties are influenced by the two phase morphology that develops during IPN formation [1,2].

The present study deals with the cross linking technology which is investigated as a major tool in case of PVC to enhance its applicability. PVC is commonly used as a general commodity plastic because of its excellent electrical and corrosion resistance, self extinguishing characteristics, low cost and recoverability. But its low impact strength and poor thermal stability poses a limitation on 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 which often occurs with common plasticisers [3,4,5].

In this study, PVC is blended with in-situ generated poly(methyl methacrylate) having high chain stiffness and rigidity and both the polymers are cross linked with the help of their respective cross linkers to generate full IPNs of PVC and

PMMA [6,7]. Here, PVC is considered to be the major matrix and PMMA, the minor and both the polymers are taken in varying composition ratios to study the dynamics of mechanical and thermal properties over a concentration sweep of incorporated PMMA. The obtained results are also analyzed with the obtained morphological features [8,9].

## II. 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 crosslinker 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 PMMA.

## III. EXPERIMENTAL METHODS

### A. Synthesis of full IPNs

PVC resin was taken in an airtight dry blender and thoroughly mixed with 30 parts by weight of DOP and 2 parts by weight of TBLS in proportionate amount of PVC taken. 5 parts by weight of DAP was added to the mix as the cross linker of PVC. The purified monomer methyl methacrylate (MMA) was taken in a separate test tube along with 2% by weight of recrystallized benzoyl peroxide as the initiator. These constituents were mixed thoroughly and subsequently added to the PVC premix. EGDM to the extent of 2% by

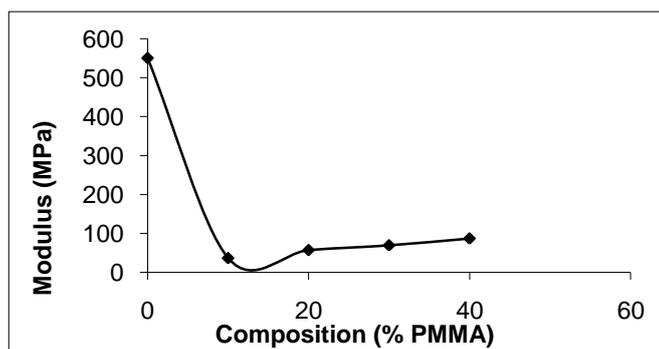


Fig.1 Variation of Young's modulus of PVC-PMMA full IPNs with variation of PVC-PMMA blend ratio (w/w)

weight of monomer was added as the cross linker to produce cross linked PMMA. The constituents were thoroughly mixed unless a free flowing powdery mass is obtained.

#### B. Conditions of moulding

The mixture of the constituents as obtained by the above process was compression moulded into sheets under heat and pressure in two stages. The mix was placed in the mould and was compressed under a pressure of 15 tons/cm<sup>2</sup> at a temperature of 80°C to initiate and propagate acrylic polymerization. This was continued for 30 min after which the temperature was raised to 160°C maintaining the same pressure. After 5 min, the mould was allowed to cool down to room temperature and the moulded sheet was ejected.

#### C. Characterization

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like tensile modulus and elongation at break. For this measurement, ASTM D638 method was followed.

The thermo mechanical analysis of the various full IPN samples of PVC and PMMA were carried out in a TMA apparatus from Shimadzu (model TMA 50) in the presence of oxygen. The thermo oxidative characteristics were studied maintaining a constant load of 0.008 kg throughout the experiment. The heating temperature limit was 180°C and a temperature sweep of 10°C was maintained.

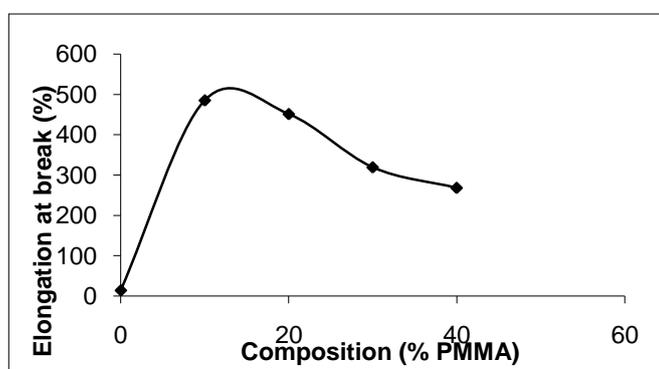


Fig. 2 Variation of percent elongation at break of PVC-PMMA full IPNs with variation of PVC-PMMA blend ratio (w/w)

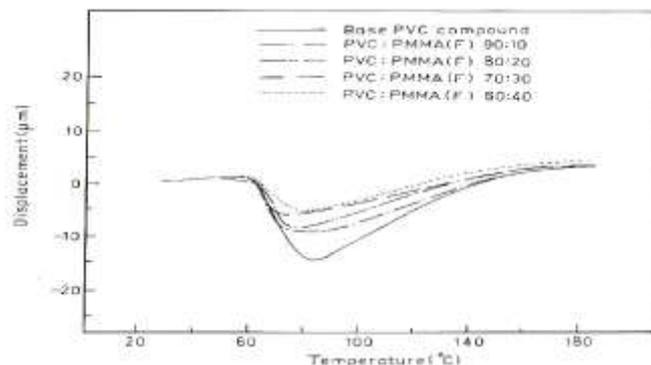


Fig. 3 Thermo mechanical curves of PVC-PMMA full IPNs

Scanning electron microscopic studies were carried out in a scanning electron microscope (Hitachi model S415A) after suitable gold coating on the samples. A tensile fracture specimen was inspected for testing the morphology. The scale of magnification was 500X.

The surface morphology of the samples were inspected by optical microscopy 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. The scale of magnification used was 200 X.

### IV. RESULTS AND DISCUSSIONS

#### A. Mechanical properties:

The tensile modulus of PVC-PMMA full IPNs as exhibited in Fig. 1 display a steady, sharp and abrupt reduction initially with respect to completely cross linked base compound as the cross linked PMMA content increases up to a level of 10%. Both the components, PVC and PMMA being cross linked in this case, the major matrix of cross linked PVC may be considered plasticized by the cross linked PMMA moieties and produces the effects as observed [10].

At the initial stages of PMMA incorporation, the dispersed cross linked PMMA phase by occupying the interstitial spaces within the cross linked PVC chains might exert some plasticizing influence by

- i) not allowing the complete formation of cross links. Hence the tight network in the PVC chains might be expected to inhibit the close approach of the reactive sites of the PVC chains,
- ii) inhibiting the usual dipole-dipole interaction primarily operating within the PVC chains
- iii) increasing the apparent free volume.

At the later stages, the influence of cross linked dispersed PMMA phase is somewhat evidenced once the tight network of PVC is shattered and furthermore, the association of their hard and rigid segments (as explicit from their optical micrographs) also plays a dominant role in enhancing the mechanical parameter. Thus after an abrupt sharp fall in mechanicals, there is a slow and steady development of new morphology which results in such improvement [11].

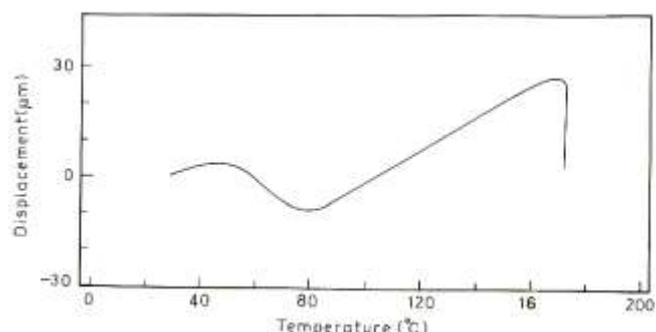


Fig. 4 Thermo mechanical curve of unmodified base reference compound PVC

The changes in percent elongation at break are in conformity with the changes in modulus as shown in Fig. 2. The EB% exhibit a steady decrease with increasing concentration of PMMA (cross linked) into the system after an initial rise up to about 10% PMMA incorporation. The initial rise observed might possibly be explained by the dominating plasticizing effect exerted by almost co continuous fibrils of the dispersed PMMA phase as a result of which the matrix gets very little opportunity either to form cross links within itself or to create any dipole-dipole interaction. This has been exemplified in the scanning electron micrographs.

At the later stages, i.e. when the proportion of cross linked PMMA increases, the continuity is lost somewhat with the formation of agglomerates. A tendency to phase separate becomes prominent due to close association of hard PMMA system and hence this phenomenon can be accounted for the decrease in %EB and toughness at an appreciable rate at the later stages. It is worth notifying that though the toughness and %EB decreases with increase in PMMA content, it always remains above that of pure cross linked PVC and hence an IPN with improved toughness develops.

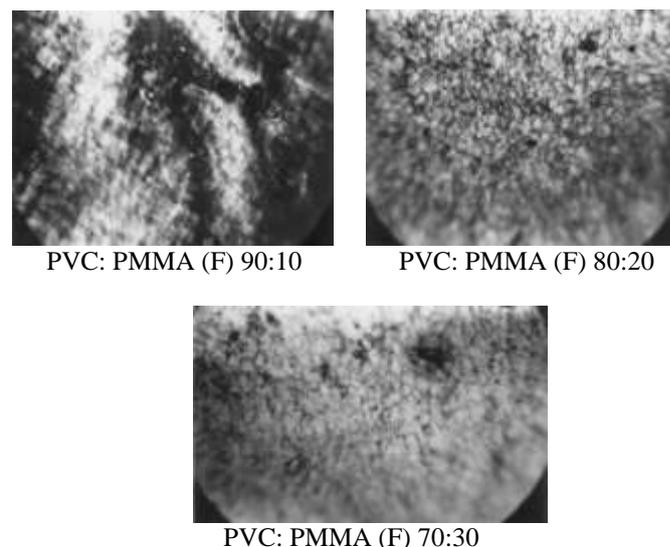


Fig. 6 Optical micrographs of PVC-PMMA full IPNs with magnification 200X.

*B. Thermal properties:*

The thermo mechanical curves of PVC-PMMA full IPN systems are displayed in Fig. 3 and 4. As shown in Fig. 3, in all cases, the probe is slightly pushed up by the expansion of the samples at a temperature around 50°C followed by penetration of the probe at a rate inversely related to the moduli of each. At the initial stages of PMMA incorporation, the somewhat labile cross links within the PVC matrices coupled with the lowering of rigidity due to breakdown in chain structure leads to softness but at the later stages, the combined effect of the crosslinked PVC and PMMA phases and the association of the rigid PMMA molecules as its concentration increases within the matrix plays the dominant role. At the upper test temperature, PVC shows breakdown and a sharp fall as in Figure 4 while the samples of full IPNs remain stable and exhibit stabilization over unmodified PVC [12].

*C. Morphology:*

The white fibrils of polymethacrylates appear to be well dispersed in the dark PVC matrix as exhibited in Fig. 5. In all the cases of different composition, both the phases seem to be continuous. However, the interfacial regions which are more or less distinct at the earlier stages of methacrylate incorporation become more and more diffusing in nature as the proportion of cross linked PMMA increases. The density of the fibrils and their interwinding either among themselves or with the cross linked PVC matrix increases with increasing proportion of cross linked PMMA and this is estimated to be the reason for the observed increase in mechanicals [13].

The optical micrographs as in Fig. 6, display the typical structure of a phase separated polymer blend in which the PMMA moieties gets distributed more or less evenly in the PVC matrix along with its percentage increase in composition. The PMMA phase appears to develop a regularity in structure (spherical in nature) which can possibly be attributed to its cross linking which helps it to attain a more defined shape. This effect of phase miscibility (as also reflected in the

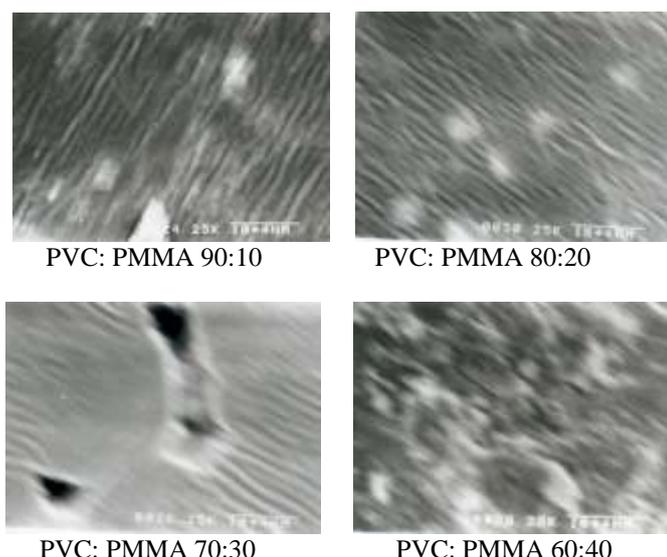


Fig. 5 Scanning electron micrographs of PVC-PMMA full IPNs with magnification 500X

scanning electron micrographs) causes better molecular interaction, leading to better strength properties as already referred to. The distribution of the crosslinked PMMA particles become more and more uniform and dense indicating solubility of the modifying PMMA resin into the crosslinked major PVC phase. However, the rigid PMMA groups undergo coalescence and agglomeration producing sites of increased hardness and this effect rises with rise in its proportion in composition. The tendency of the dispersed PMMA phase to undergo conglomeration at the initial stages of PMMA incorporation is gradually reduced and they exhibit a trend to form micro domains as the PMMA content increases [14]. This micro domain formation leads to better dispersion and hence improved mechanicals.

## V. CONCLUSION

The present study deals with the modification of PVC with PMMA 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 PMMA incorporated and there is an improvement in mechanical properties in terms of tensile modulus and elongation than unmodified PVC. There has also been a notable modification in thermal behaviour as per thermo mechanical study where thermal stability is exhibited in the full IPNs depending on the dose of PMMA incorporation. The morphological properties are in conformity to the mechanical behavior and well explain the rise and fall in tensile behavior with increasing proportion of crosslinked PMMA moieties within the crosslinked network of PVC.

## REFERENCES

- [1] S. P. Han, K. J. Park and K.J. Lee, "Crosslinked PVC polymerization: Study on process dependencies", *J. Appl. Polym. Sci.*, vol. 83, pp. 1947-1954, 2002.
- [2] R. Chakrabarti and D. Chakraborty, "Studies on Engineering properties of PVC-PMMA semi interpenetrating polymer networks", *J. Appl. Polym. Sci.*, vol. 97, pp. 1725-1735, 2004.
- [3] A. Sluszný, M. S. Silverstien, S. Kalaby, A. Schmidt and M. Narkis, "Novel semi-IPN through vinyl silane polymerization and cross linking within PVC films", *J. Polym. Sci., Part A: Part Polym. Chem.*, vol. 39, pp. 8, 2001.
- [4] H. Kaczmarek, M. Nowicki, I. V. Kwiatkowska and S. Nowakowska, "Crosslinked blends of poly(lactic acid) and polyacrylates:AFM, DSC and XRD studies", *J. Polym. Res.* vol. 20, pp. 91, 2013.
- [5] R. Chakrabarti and D. Chakraborty, "Engineering properties of PVC-PBMA semi1 and semi2 interpenetrating polymer networks", *J. Appl. Polym. Sci.*, vol. 107, pp. 966-975, 2008.
- [6] H. Kaczmarek and I. V. Kwiatkowska, "Preparation and characterization of interpenetrating networks based on polyacrylates and poly(lactic acid)", *Exp. Polym. Lett.* vol.6, pp. 78-94, 2012.
- [7] A. Mathew and B. C. Deb, "Studies on semi interpenetrating polymer networks from poly(vinyl chloride-*CO*-vinyl acetate) and poly(butyl acrylate)", *J. Appl. Polym. Sci.*, vol 45, pp. 2145-2151, 1992.
- [8] S. Goswami, D. Bandyopadhyay, P. K. Mandal and D. Chakraborty, *J. Appl. Polym. Sci.*, vol. , pp. 412, 2003.
- [9] R. Bhattacharyya, N. Roy and D. Chakraborty, "Mechanical, thermomechanical and related morphological characterization of PVC-polybutylmethacrylate blends and full IPNs", *J. Appl. Polym. Sci.*, vol. 99, pp. 2033-2038, 2006.
- [10] R. Chakrabarti, M. Das and D. Chakraborty, "Physical , mechanical and thermal properties of PVC-PMMA blends in relation to their morphologies", *J. Appl. Polym. Sci.*, vol. 93, pp. 2721-2730, 2004.
- [11] R. Chakrabarti and D. Chakraborty, "Modification of Poly(vinyl chloride) by IPN formation with Poly(ethyl acrylate)", *J. Appl. Polym. Sci.*, vol. 113, pp. 3450-3459, 2009.
- [12] K. Pielichowski and B. Janouski, *J. Therm. Anal. Calorimet.*, vol. 80, pp. 147, 2005.
- [13] C. Xiong, S. Lu, T. Wang, Y. Hong, T. Chen and Z. Zhou, "Study on morphology of compatibilized poly (vinyl chloride)/ultrafine polyamide-6 blends by styrene-maleic anhydride", *J. Appl. Polym. Sci.*, vol. 97, pp. 850, 2005.
- [14] Y. Yang, H. Fujiwara, T. Chiba and T. Inoue, "Morphology development in a thermoset/thermoplastic blend: DAP/PPE system via apparent two-step spinodal decomposition", *Polymer*, vol. 39, pp. 2745-2750, 1998.