

Summary and Conclusion

Study of structure property relationship in segmented polyurethanes has acquired importance due to the broad range of applications of polyurethanes. Their properties can be tailored simply by varying the components such as polyols, polyisocyanates and crosslinkers. Many other factors like NCO:OH equivalent ratio and diol: triol ratio also affect PU properties.

However, the increasing demand for high performance material has promoted the blending of polymers to obtain material with desired properties. Elastomeric polyurethane can be blended with brittle PMMA to obtain reinforced plastics.

Interpenetrating Polymer Networks (IPNs) are blends of crosslinked polymers that are unique in properties among the polymer alloys. However, IPNs synthesized so far exhibit varying degrees of phase separation depending mainly on the miscibility of the polymers. Hence it is necessary to enhance the interaction between the components to develop compatibilized IPNs. We have made use of 2 - HEMA and GMA for the development of compatibilized IPNs of PU / PMMA. Incorporation of GMA into PU / polyacrylate IPNs is reported to enhance miscibility of components. On the other hand, 2 - HEMA has free OH group which can react with the free NCO of polyurethane. This enhances the segmental mixing of the PU and PMMA phases leading to improved thermo-mechanical properties.

The polyurethanes based on two polyols (HTPB and PPG) and diisocyanates (TDI and MDI) were synthesised by varying the NCO:OH and diol:triol ratios. A systematic study of understanding the structure property relationship in PUs was carried out.

The PUs synthesised were observed to swell in many of the organic solvents. Whereas, acrylonitrile-butadiene copolymer (NBR) has good

chemical resistance and is industrially important material. Hence incorporation of NBR into PU will improve its resistance to chemicals. Further, PU / NBR blends have been studied to a limited extent. Hence their thermo-mechanical and morphological properties were investigated. The swelling behaviour in solvents was also studied. The blending was carried out on a two roll mixing mill.

Though PUs and their IPNs have wide spectrum of applications, which has made them technologically and industrially important products, non-biodegradability is restricting their utility in commodity applications. Hence the possibility of converting them into partially biodegradable products is investigated. Very few reports (mostly patents) are available on the use of starch in synthesis of PUs. We have synthesised PUs crosslinked with starch and compared their properties with those of the PUs synthesised from TMP.

From these studies following conclusions are drawn.

1. The studies on mechanical properties of PUs reveal that the HTPB -TDI - TMP system has highest tensile strength and hardness while PPG-MDI-TMP system has highest elongation at break.
2. The tensile strength increases with increasing NCO:OH ratio and decreasing diol / triol ratio, whereas elongation follows opposite trend.
3. Morphology of the films and tensile fractured specimen showed more heterogeneous character of the HTPB-TDI system. The greater phase segregation and leads to superior thermo - mechanical properties.
4. The common feature of all PU systems was the higher tensile strength exhibited by the B1 compositions having higher NCO :OH and diol : triol

ratios. Hence this composition was selected for the development of IPNs with polymethyl methacrylate (PMMA).

5. The trend observed in thermo-mechanical and morphological properties were explained from the results of molecular weight between crosslinks and crosslink density obtained from swelling studies.
6. The studies on HTPB - MDI based PU / PMMA IPNs showed that incorporation of only 2 % GMA or 2 - HEMA leads to an improvement in the thermo-mechanical properties and morphology. On comparison of IPNs containing 2 - HEMA and GMA it was observed that HEMA more effectively improves the molecular mixing of two phases, leading to enhanced thermo-mechanical properties. The bicontinuous morphology observed in SEM and the broadening of the $\tan \delta$ peaks in DM analysis supported this observation. Hence the IPNs based on other PU systems were developed using HEMA.
7. The studies on IPNs derived from HTPB - TDI based PUs and PMMA showed that the PU rich IPNs behave like reinforced elastomers while the PMMA rich IPN behaves as toughened plastic. Incorporation of 2 - HEMA upto 4 % in the PMMA network, improves the thermo mechanical and morphological properties of IPNs. At 4 % of HEMA concentration optimum properties observed indicate optimum interpenetration. SEM showed a single uniform phase, while DMA showed a single broad $\tan \delta$ peak. At 6 % of 2 - HEMA concentration, PHEMA formed started showing phase separation.
8. The IPNs based on P/T PU system showed excellent vibration and sound damping abilities. The DM analysis showed a broad $\tan \delta$ peak extending over a wide range of temperature while SEM showed homogeneous

morphology. With increasing crosslink density of the PMMA network, a shift to higher temperature was observed.

9. IPNs based on PPG – MDI PU system could not be synthesized. Probably this highly flexible PU system is unable to behave compatibly with the PMMA network and shows adverse effect. Hence the system was not further investigated.

10. As observed in the case of the full IPNs, the P / T PU based semi IPNs showed a single phase morphology and a single broad $\tan \delta$ peak indicating a homogeneous phase mixing. These semi IPNs also exhibited enhanced mechanical and thermal properties. The P / M PU based semi IPNs were mechanically weak and exhibited a narrow $\tan \delta$ peak revealing poor morphology. Thus the overall trend observed in full and semi IPNs was similar. Nevertheless, full IPNs exhibit superior mechanical properties and damping abilities compared to the semi IPNs.

11. The present study on IPNs revealed that the compatibilised blends of PU and thermoplastic material like PMMA behave like reinforced elastomers. The properties of IPNs depend not only on the PU composition but also on the miscibility of the components. The IPNs showed improved properties with incorporation of 2 - HEMA irrespective of the PU composition.

12. The studies on PU / NBR blends showed that the two polymers show synergistic effect on their properties. The incorporation of NBR increases the elongation and incorporation of PU increases the tensile strength. The blends exhibited better mechanical properties than the individual polymer.

13. NBR also improved the thermal stability and solvent resistance of the PU network. The Tgs of the two components also shifted inwards indicating increasing miscibility.
14. Incorporation of the carbon black filler led to an increase in the tensile strength and hardness due to its reinforcing effect. The morphology of the 80 / 80, NBR / PU blend containing 15 % carbon black showed bicontinuous morphology with very small domain size.
15. The starch based PUs were found to show better mechanical properties than TMP based PUs. Not only the tensile strength but the elongation also was observed to increase with increasing concentration of starch. However, these properties were also found to depend on the NCO:OH equivalent ratio. With increasing R value, the stress-strain properties were observed to be increased. The DSC thermograms of TMP based PUs showed the presence of only one glass transition whereas those of starch based PUs showed two Tgs indicating phase segregation.
16. Starch based polyurethanes were observed to be better in the thermo-mechanical properties as well as showed potential for biodegradability.