INTERPENETRATING POLYMER NETWORKS FROM RENEWABLE RESOURCE - CASTOR OIL

The summary of the thesis submitted to
The Maharaja Sayajirao University of Baroda
for the degree of
DOCTOR OF PHILOSOPHY IN CHEMISTRY

BY

AJITHKUMAR.S

Departmet of Chemistry, Faculty of Science
M.S.University of Baroda
Baroda, India

SUMMARY

The rate of appearance of new polymeric types have diminished over the years. Therefore, in order to maintain pace with the demands of the fast developing modern science and technology, it has become necessary to develop polymeric materials having combination of various useful properties. This has lead to widespread interest in multiphase polymeric systems.

Depending on the interest and requirements, there are many ways to prepare polymer mixtures. The simplest way involves mechanical blending of two polymers. However, mechanically blended polymers often experience phase stability problems due to lack of permanent chemical bonding between two polymer phases. Moreover mechanical blends, grafts and block copolymers are restricted to thermoplastics only.

Interpenetrating polymer networks(IPNs) are different from those mentioned above. IPNs are defined as a mixture of two or more polymers in which at least one of them is synthesised and/or crosslinked in the immediate presence of the other. The IPNs have advantages over classical blends and grafts due to permanent entanglements of chains and hence improvement in phase stability. They find wide range of applications in day to day life like in sound and vibration damping materials, high impact strength materials, microencapsulation, control release agents etc.

Unsaturated polyester (UPE) is a thermoset having good thermal stability and electrical insulating properties. However, because of its brittleness it causes failure by application of impact blows and stresses. This can be improved by toughening them through the incorporation of judicious quantities of elastomeric materials like polyurethane (PUR) having good elongation and low modulus to produce IPNs with better properties.

The first chapter give a review of the work on the synthesis and characterization of polyurethane based IPNs with various glassy polymers like acrylates, styrene, epoxy, polyester etc. with special emphasis on castor oil based polyurethane and its IPNs.

In the second chapter, the detailed synthesis of unsaturated polyester resins and IPNs have been illustrated in detail. The characteristics of the two castor oil based polyols (R60 & R92) and UPE resins (IPE & OPE) like hydroxyl number, acid value and equivalent weights have been also included. The FTIR spectra of polyols and UPE resins are also included in this chapter.

The third chapter deals with the kinetic aspects of the polymerization reactions of castor oil and two polyols based on it differing in their hydroxyl number with toluene diisocyanate (TDI). The Polymerization kinetics were studied under isothermal conditions using different amount of dibutyltin dilaurate (DBTDL) as the catalyst at various temperatures. The catalyzed reaction have

been described by only a single second order equation, while that of uncatalyzed reaction have been described by two independent second order equations corresponding to the ortho and para isocyanate groups present in TDI molecule. The para isocyanate group showed two to three fold reactivity than that in the ortho position. The activation energies were found to be less in polyols compared to CO, indicating higher reactivity of the former both in catalyzed and uncatalyzed systems. The rate of polyol - TDI reaction was found to increase with increase in catalyst concentration up to $1.7x10^{-3}$M. Further increase in DBTDL concentration showed no profound effect on the reaction rate. The primary hydroxyl groups as well as the amount of OH groups in R60 and R92 are responsible for their higher reactivity compared to CO both in catalyzed and uncatalyzed systems.

The complete characterization of the IPNs have been described in sections 4.1 to 4 7 of the last chapter.

The sorption and diffusion of various organic solvents through IPNs have been discussed in section 4 1 and 4.2. The equilibrium swelling were performed in various solvents in order to determine the solubility parameter of all the IPNs. The kinetics of swelling of the samples were carried out in chlorobenzene, in which IPNs showed maximum swelling. The uptake capacity of IPNs varied with change in composition of components and NCO/OH ratio. Increase in NCO/OH ratio or UPE content had a negative effect on the uptake capacity of all the samples studied. Swelling parameters like diffusion coefficient (D), sorption coefficient (S) and permeability coefficient (P) were also calculated from the swelling data. For a given crosslink density, the sorption decreases with increase in UPE content. Increase in crosslink density also reduced the sorption for a given composition. The diffusion process from the sorption kinetic study was found to be anomalous in nature. The low values of molecular weight between two crosslinks (Mc) showed that, all the IPNs are highly crosslinked and hence low values of D and S compared to common crosslinked networks.

The dynamic mechanical behavior (DMA) of IPNs based on IPE with PUR60 and PUR92 have been discussed in the next section (section 4 3). The variation in dissipation factor (tan δ), storage modulus(E^{I}) and loss modulus(E^{II}) with change in composition of components and crosslink density of IPNs have been explained in detail.

Dissipation factor : Pure PUR showed a single tan δ peak at around 32.6°C and 40°C for PUR60 and PUR92 respectively, where as IPE showed two peaks, one at ~98°C corresponding to the polystyrene domains and a second peak as shoulder at about 198°C, corresponding to the IPE backbone. IPNs showed their characteristics ranging from two tan δ peaks to one broad tan δ peak depending on their composition and crosslink density. With increase in NCO/OH ratio and IPE

content, IPNs showed a broadening in their tan δ behavior indicating more mixing. Evidence of mixing have also been observed from the half peak width(HPW) values, which showed an increase with increase in IPE content in the IPNs.

Dynamic loss modulus : Almost all the IPNs except certain samples showed their loss modulus peak appeared at almost the same temperature as that of pure PUR at low NCO/OH ratio This indicates that the system is composed of a continuous phase of PUR. With increase in NCO/OH ratio and or IPE content, the samples showed a broad loss modulus peak over a wide range of temperatures. It can be inferred from these behavior that, it is possible to develop vibration damping materials of requisite characteristics by optimising the composition of both the components and crosslink density of PUR in an IPN.

Dynamic storage modulus : The results suggest the possibility of impact modification of UPE by adding judicious quantities of rubbery PUR without lowering the modulus seriously. In the case of 20:80 sample based on PUR60(1.2)/IPE, the storage modulus plateau region was exceptionally broad and it surpasses that of pure IPE.

Section 4.5 describes the mechanical properties of IPNs based on PUR60 and PUR92 with IPE as well as OPE. Results indicate that mechanical properties of IPNs vary from rubbery to tough plastics depending on the type of polyol and polyester used, their composition and crosslink density. The improvement in mechanical properties (%e) is significant in case of IPNs based on OPE. It can be inferred from the results that, the environmental stress cracking of polyester networks can be greatly reduced by incorporation of rubbery PUR through interpenetration technique.

The phase behavior of the IPNs based on PUR60 and PUR92 with IPE was also studied by scanning electron microscopy (SEM) and results have been described in section 4.4. The studies revealed that, both NCO/OH ratio and composition of the components play their role in deciding the final morphology of the IPNs. The miscibility was enhanced with increase in crosslink density or IPE content in all the samples studied. At low level of crosslinking, samples showed two distinct phases of PUR and UPE with well resolved domains of either of the two phases depending on the composition. With increase in crosslink density , enhanced mixing took place and samples with a coarse morphology resulted. The same was the case when IPE content was increased in the samples. The effect is more prominent in 20:80 sample at all levels of crosslinking.

Thermogravimetric analyses (section 4.6) of some of the IPNs were carried out in order to have an idea of their thermal stability when two polymers differing in their thermal stability are combined. It can be inferred from the data that, irrespective of the type of polyol, type of polyester and NCO/OH ratio, the 20:80 samples showed a synergistic behavior in the thermal stability. Thermal stability of

IPNs increased with increase in polyester content, while NCO/OH ratio did not make much contribution towards the stability. IPNs based on OPE and PUR92 have been found to be more stable thermally than those based on IPE and PUR60.

Section 4.7 of the last chapter refers to the differential scanning calorimetry (DSC) studies of some of the samples. In the case of PUR60(1.5)/IPE system, the Tg values are shifted to higher temperatures with increase in IPE content. Samples with low IPE content only showed a single transition while those with higher polyester content showed two distinct Tg values corresponding to the individual components. In the case of OPE based IPNs, the Tg values are found to increase for a particular composition when NCO/OH ratio was increased from 1.2 to 1.5. Also it was clear that, IPNs based on PUR92 showed slightly higher Tg compared to that based on PUR60.

Thus the technique of interpenetrating polymer network can be used to synthesize materials with a set of desired properties by proper selection of the composition of constituents and crosslink density.