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Interpenetrating Polymer Networks

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INTRODUCTION

Interpenetration of polymer networks is a unique way of physically combining two crosslinked polymer networks where the chains of one network are permanently entangled with those of the other network with the absence of covalent bond between the networks¹.

The concept of IPN topology was long known and described as early as 1951. The term "IPN" was first used by Millar in 1960 in his styrene-divinyl benzene networks (homo IPN's). In 1969, IPN topology was rediscovered independently by Frisch² and Sperling³ through the concept of catenanes⁴ and polymeric catenanes (Fig. 1).

The concept of IPN is broadened recently to include the thermoplastic IPN's which employ physical crosslink instead of chemical crosslink. Three types of physical crosslinks can be considered, namely, the glassy domains in multi-block copolymers, ionic bonding, and crystallites in semicrystalline polymers⁵.

SYNTHESIS

The various technics of IPN synthesis can be viewed as a statistical method of preparing polymer catenanes where a cyclization (crosslinking) of one component occurs in the presence of the other already cyclized component (crosslinked polymer

network). The probability of obtaining interpenetration is, however, much greater since the mobility of the chains is restricted by their high molecular weight. Two major synthetic procedures are employed in preparing IPN's. The sequential IPN (SIPN) is prepared by forming one crosslinked polymer network first and then swelling the network in liquid monomer plus crosslinking agent of the other network, followed by polymerization and crosslinking of the imbibed monomers.

The simultaneous IPN (SIN) is formed by mixing two or more monomers or low molecular weight prepolymers with crosslinking agents followed by simultaneous polymerization and crosslinking each network via noninteracting reaction⁶. One network is formed by polycondensation reaction (mostly polyurethane networks were employed as an elastomeric component), and the other by free

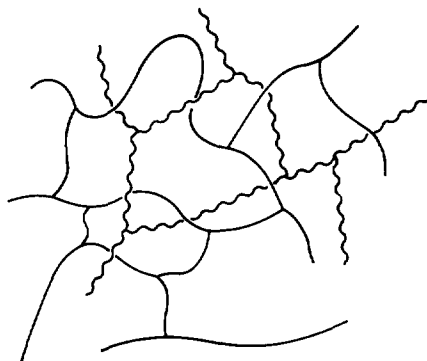


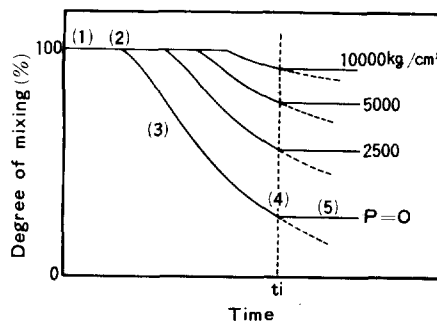
Fig. 1. Schematic diagram of IPN (polymeric catenane)

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POLYURETHANE IPN'S SYNTHESIZED UNDER HIGH PRESSURE

During the simultaneous polymerization process, the following changes are expected to occur in both PU and PS (or PMMA) components. The PU oligomer is formed first and the molecular weight is increased gradually until the PU component forms a three dimensional network structure. The styrene (or MMA) monomer, which acts as a solvent for both components, starts to polymerize and turns into microgels of PS swollen in styrene monomer, until the PS component also forms a three dimensional network structure. The morphology of the IPN is determined at this time of interlocking.

The pressure affects both the compatibility and the mobility. Compatibility increases under high pressure when the system shows negative volume change of mixing like PU-PMMA and PU-PS. Mobility is reduced at high pressure with reduced free volume which causes slow rate of phase separation. The effect of pressure during polymerization on the degree of intermixing of the component polymers is schematically shown in Fig. 2. At high



pressure, the onset time of the phase separation is shifted towards later stage of polymerization due to the increased compatibility. The rate of phase separation is also shown to be reduced at high pressure. Phase separation is stopped at the time of physical interlocking (t_i) when both components form three dimensional network.

The T_g behavior shown in Fig. 3 (tan δ behavior measured by DMA) reveals the different level of intermixing in PU-PS IPN's synthesized at pressure ranges of 0-10,000 Kg/cm². The IPN's formed under 10,000 Kg/cm² are optically transparent and show a single T_g intermediate of the two component T_g 's. The physical interlocking of the two component polymers prohibit the further phase separation to occur when the IPN is heated above the T_g of the PS component. The small angle X-ray scattering from the synchrotrone radiation reveals that the scattering maxima stays constant when the PU-PS SIN synthesized at 10,000 Kg/cm² is heated from

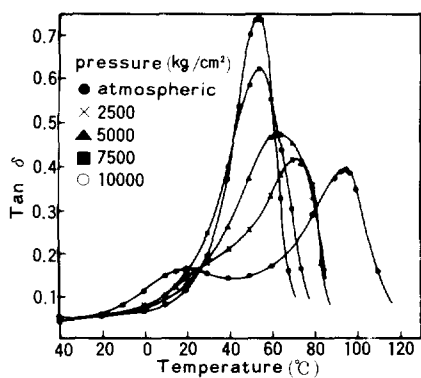


Fig. 3. Dissipation factor vs. temperature of PU-PS IPN (50% PU, $\bar{M}_c = 2,000$) synthesized at varying pressure.

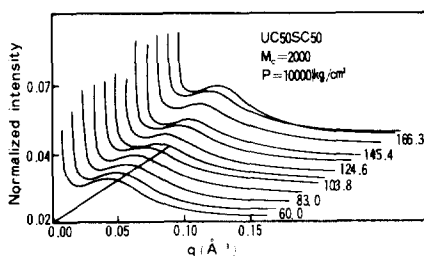


Fig. 4. Synchrotron SAXS spectrum of PU-PS IPN synthesized under 10,000 kg/cm². (heated from 60°C to 180°C).

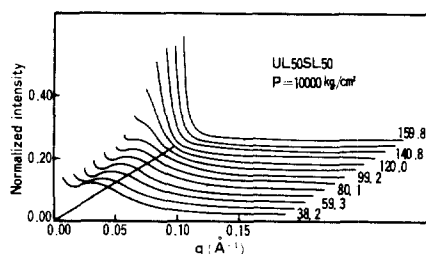


Fig. 5. Synchrotron SAXS spectrum of PU-PS linear blend synthesized under 10,000 Kg/cm². (heated from 38.2°C to 159.8°C).

60°C to 180°C, which proves the existence of physical entanglement between the component polymers (Fig. 4). The linear blends (without crosslinking agent) synthesized under high pressure, however, reveals phase separation occurring at about 120°C (above the T_g of PS) and shows disappearance of the scattering maxima (Fig. 5).

Hydrophobic-hydrophilic IPN membranes were

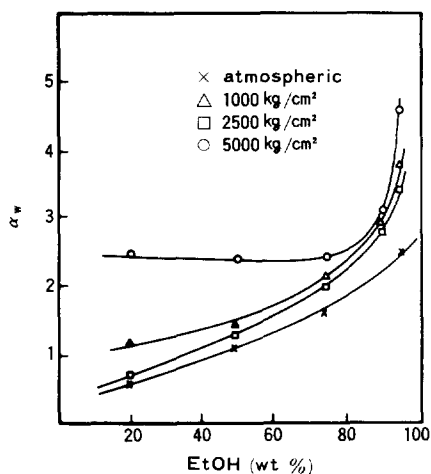


Fig. 6. Effect of synthesized pressure on separation factor (α_w) of water in water-ethanol pervaporation for the IPN membranes of hydrophilic PU and hydrophobic PS (membrane: UC50SC50, feed conc.: EtOH 95.6 wt%).

prepared utilizing the permanent physical interlocking of the networks to reduce the phase separation of the component polymers. IPN membranes of hydrophilic polyurethane from polyethylene glycol and hexamethylene diisocyanate and hydrophobic polystyrene were prepared under high pressure^{12,13}. It was observed that the increased synthesis pressure reduced the phase separation in the membrane and the selectivity of water was increased when the membrane was used in water-ethanol pervaporation process (Fig. 6).

INDUSTRIAL APPLICATION

Increasing number of commercial products are developed utilizing the concept of IPN. These products range from high impact plastics, adhesives, vibration damping materials, high temperature alloys, etc. Polyurethane-silicone, Nylon-silicone IPN's are commercialized by Petrarch Systems and the SEBS-Ionomer thermoplastic IPN's are commercialized by Shell.

Reaction injection molding (RIM) materials of PU IPN's are also under development, utilizing the second component to increase the thermal stability

of polyurethane. Epoxy-polyurethane¹⁴ and polyurethane-unsaturated polyester¹⁵ systems were reported.

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