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Recent Developments in Polyurethanes and Poly(acrylates) Interpenetrating Polymer Networks

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ABSTRACT

Owing to the great versatility offered by polyurethanes regarding the ease of synthesis and variable properties of the final product obtained (elastomeric or rigid polymer), polyurethanes become a basic component used in IPN formation. Numerous studies were conducted on IPNs based on polyurethanes and various vinyl monomers. Tensile strength, hardness, swelling, and thermal properties were obtained, and morphology studies have been conducted. This review gives a comprehensive compilation of the recent studies on these properties. The article specifically deals with the systematic coverage of all the research work carried out in the field of interpenetrating polymer networks (IPNs) based on polyurethanes (PUs) and various vinyl monomers.

Key Words: Interpenetrating polymer networks; Polyurethanes; Vinyl polymers.

1. GENERAL INTRODUCTION

1.1. Structures and Definitions

Interpenetrating polymer networks (IPNs) are defined as a combination of two polymers in network form, at least one of which is synthesised and/or crosslinked in the immediate presence of the other.^[1]

Many different kinds of IPNs exist. The following definitions identify some of the more important types:

- **Sequential IPNs.** Monomer I is polymerised together with crosslinker I to produce a network. Then, monomer II along with crosslinker II is swollen in and then polymerised in a sequential mode to make the IPN (Fig. 1).
- **Simultaneous interpenetrating networks (SINs).** The monomers and/or prepolymers plus the crosslinkers and initiators of both networks are mixed, followed by simultaneous polymerisation via noninterfering reactions (Fig. 1). Interference is minimised if one of the polymerisation processes involves chain polymerisation while the other involves step polymerisation kinetics. While both reactions proceed simultaneously, the rates of polymerisation are rarely identical.



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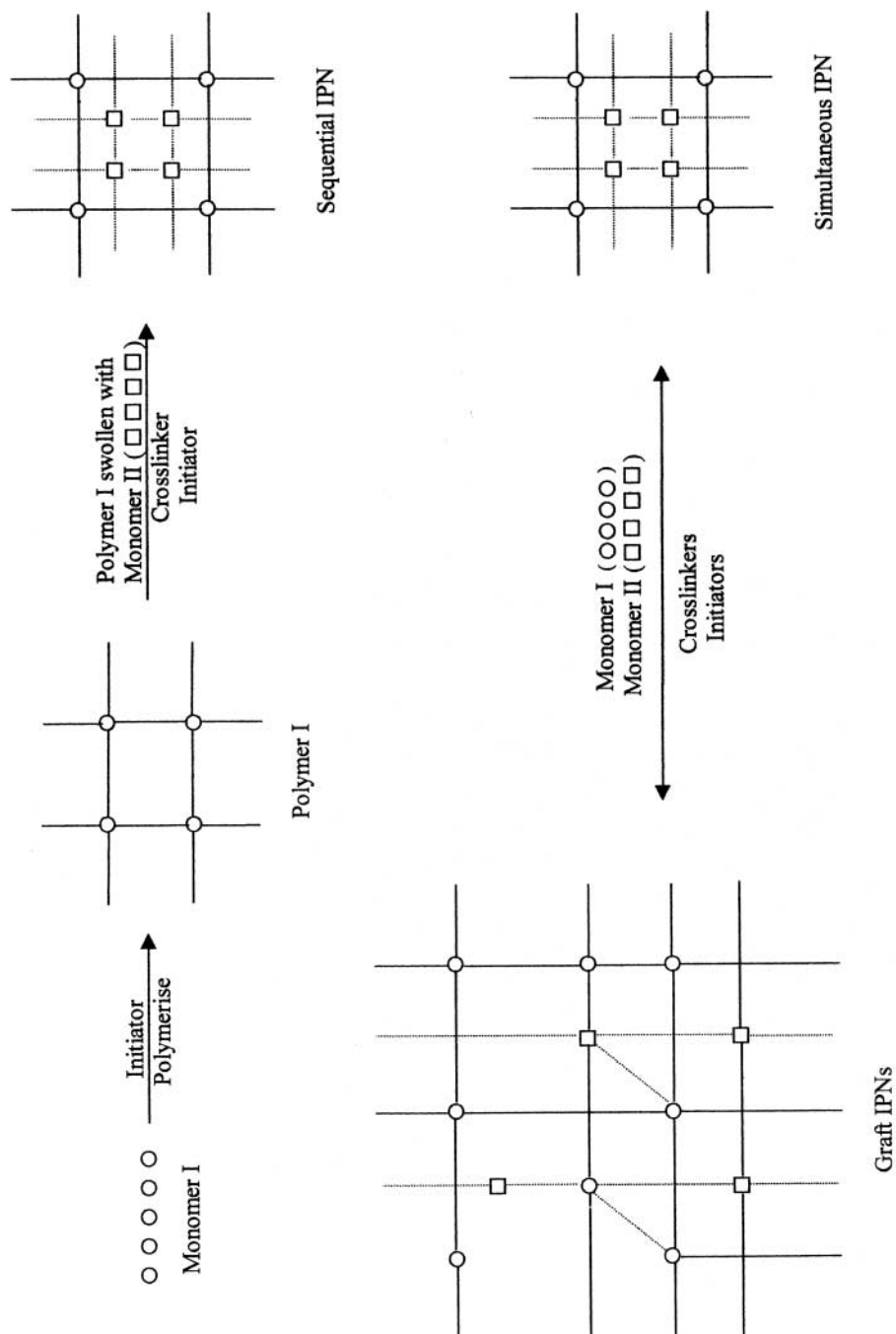


Figure 1. Schematic diagram for the synthesis of sequential, simultaneous and graft types of IPNs.



- **Latex IPNs.** In this case, the polymers are synthesised by emulsion polymerisation of monomer II together with the crosslinker and activator in the original seed latex of crosslinked polymer I.
- **Gradient IPNs.** In this case, a film can be made with polymer network I predominantly on one surface and polymer network II on the other surface, with a composition gradient existing throughout the interior.
- **Thermoplastic IPNs.** These materials contain physical crosslinks rather than chemical crosslinks. As such they are hybrids between polymer blends and IPNs. Such crosslinks may utilise block copolymers, ionomers, and/or semicrystalline polymers. Being thermoplastic, they flow at elevated temperatures.
- **Semi-IPNs.** These are sequential IPNs in which only one of the constituent polymers is crosslinked while the other is linear. If polymer I contains crosslinks, it is called a semi-I IPN, whereas if polymer II contains the crosslinks, it is called a semi-II IPN.

1.1.1. Historical Developments

IPNs of polystyrene/polystyrene (PS/PS) were first prepared by Millar in 1960. Sequential IPNs with different polymer entities based on chain polymerisation reactions have been investigated by Sperling et al.^[2] with various polymer combinations. Latex IPNs (LIPNs) were first reported by Frisch et al.^[3] in 1969 by blending poly(urethaneurea) and polyacrylate latices. A number of different polymer combinations were also studied by Frisch et al., who were the first to prevent chain transfer between the networks. Simultaneous IPNs (SINs) were first reported and studied by Frisch et al. by mixing a urethane prepolymer with a low-molecular-weight epoxy resin. Further SINs were also studied by Touhsaent et al.^[4]

1.1.2. Objective

The ever-increasing demand for new engineering materials has led to a flourishing interest in IPNs of various types from both scientific and technological viewpoints.^[2-4] The interest in the field of IPNs is manifested in the increasing number of research articles and reviews based on these polymers in recent years.

This article summarises the research work carried out in the field of IPNs based on polyurethanes (PUs) and various vinyl polymers. Some facets of the materials compiled here have been treated differently by different authors. From the beginning of the IPN era, polyurethanes were one of the most widely used polymeric components in the synthesis of IPNs. This is due to the ease of their synthesis and the versatility offered in the properties obtained (elastomeric to rigid polymers). A plethora of research article.^[1-7] on IPNs involving polyurethanes as one of the constituent polymers are available. However, in recent years no literature is available



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which compiles all the developments in the field of polyurethanes (PUs) and the various vinyl polymers.

Hence, we undertook a systematic compilation of all the research work carried out in the field of IPNs based on PUs and various vinyl polymers under convenient headings such as (i) syntheses, (ii) characterizations which encompass morphology, glass transition temperatures, physical properties, thermal properties, and swelling behavior, and (iii) applications.

Among these, syntheses and characterizations sections are further subdivided as sequential and simultaneous, and other types of IPNs (i.e., graft and joint IPNs).

1.2. Review Profile

Suthar and coworkers synthesized a host of castor oil urethane network-based IPNs with various acrylic monomers. A review by Suthar^[5] on castor oil-based crosslinked polyester and polyurethane IPNs discusses their synthesis and physico-mechanical properties. The review deals with three important areas: (i) Prepolyesters were prepared from castor oil and dibasic acids and interpenetrated with acrylamide using benzoyl peroxide (BPO) initiator and ethylene glycol dimethacrylate (EGDMA) crosslinker. (ii) Prepolyurethanes were prepared from castor oil and diisocyanates, respectively, and were subsequently interpenetrated with vinyl monomers and crosslinker. (iii) Glass-reinforced IPNs were prepared from castor oil. All of these IPNs were characterised for their thermal behaviour, mechanical properties, and resistance to chemical reagents. Dielectric properties, which included conductivity (σ), dissipation factor i.e., loss tangent ($\tan \delta$) ($\tan \delta$ = power loss/total power output) were studied at different temperatures.

A review dealing with synthesis and characterisation of gradient IPNs from polyurethane and butylmethacrylate-triethyleneglycol dimethacrylate copolymer was written by Lipatov.^[6] Polymer alloys with wide temperature ranges of vibration damping behaviour have been developed. A brief review of these IPNs was given by Shuren.^[7]

1.3. Syntheses

1.3.1. Sequential IPNs

PU/PS-based semi- and full-IPNs were sequentially synthesised.^[8–13] The PU prepolymers were made using different diisocyanates, i.e., diphenyl methane diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), and various polyols (having different molecular weights), followed by polymerisation of styrene by the photolytic method at different temperatures and were studied for their gas transport behaviour.

In another study, polymerization of styrene and acrylonitrile was carried out by using the free radicals initiated by ^{60}Co - γ radiation and subsequently swelling them in the PU prepolymer.^[11] Semi- and full-IPNs based on PU and various acrylates were prepared by thermally initiated polymerization.^[14–20] PU-poly(methyl



methacrylate) (PMMA) IPNs of fixed composition (50/50) were prepared at 20 MPa pressure.^[14] The high-impact-strength, high-transparency cast sheets of PU/PMMA were obtained using the IPN technique, in which the PU content was kept <10 weight %.^[18]

The renewable resource-based IPNs include PUs based on castor oil and other natural oils^[21–32] along with various vinyl polymers. Two component IPNs of castor oil based on PU and PS were prepared by the sequential technique. The liquid PUs were prepared by reacting the hydroxyl groups of castor oil with methylene diisocyanate (MDI). These PUs were swollen in styrene monomer and subsequently polymerised by free radical polymerisation initiated with benzoyl peroxide in the presence of the crosslinking agent divinyl benzene. In recent years, a considerable amount of work has been carried out on IPNs based on renewable resources which are synthesized by the sequential technique. Athawale prepared IPNs based on both modified castor oil PU-PMMA/PBMA^[23–27] and soybean oil uralkyd-vinyl polymers.^[28–31] Castor oil was modified with glycerol by transesterification, and the resultant polyol was utilised in the PU synthesis, which was subsequently interpenetrated with the MMA monomer.^[24] In another study, soybean oil-based uralkyd resin (UA) was synthesised and treated with excess hexamethylene diisocyanate to form –NCO-terminated UA, which was then swollen in to poly(ethyl methacrylate) (PEMA)/, poly(butyl methacrylate) PBMA, or PMMA along with a BPO initiator and an ethylene glycol dimethacrylate (EGDMA) crosslinker at 80°C.^[29,30]

1.3.2. Simultaneous IPNs

IPNs were synthesised by the simultaneous technique via photopolymerisation.^[33] and thermal methods.^[34–38] It was observed that radiation-initiated polymerisation was effective in obtaining networks with a high degree of interpenetration.^[33] The study shows that the synthesis of PU/PMMA IPNs under radiation can yield homogeneous dispersions of two incompatible polymers. The extent of component mixing and size scale of heterogeneities can be reduced by including radiation exposure during synthesis. PUs from different diisocyanates and polyols with varied NCO/OH ratios and diol-to-triol ratios were prepared, and the resultant prepolymer was swollen in styrene to form IPNs. The results showed that increasing crosslinking density and interpenetration had introduced “forced compatibility” by accelerating the curing rate and decreasing phase separation.^[34] IPNs composed of hydrophilic PU and hydrophobic PS were synthesised^[36,37] in which the PU network was prepared using isocyanate-terminated PU prepolymer based on polyethylene glycol (PEG), a highly hydrophobic oligomer, and HDI.

IPNs comprised of PU and various acrylates and methacrylates were synthesised simultaneously.^[39–43] Two component IPNs of PU and PMMA were synthesised in which two different PUs were prepared, based on (i) hydroxyl-terminated polybutadiene and (ii) polyol (synthesised at Indian Space Research Organisation) interpenetrated with two different vinyl polymers. These IPNs were used as a binder for solid propellants. It was observed that both mechanical strength and combustion rate of ammonium perchlorate-based solid propellant can be suitably



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modified by simply changing the nature and/or the ratio of the IPN components.^[39] Simultaneous IPNs based on PU and poly(glycidyl methacrylate) (PGMA) were prepared in which the PU was synthesised by using different catalysts such as dibutyl tin dilaurate (DBTL), stannous octoate, etc., and the gelation time of PU in the IPN formation^[42] was studied.

Simultaneous IPNs based on castor oil PUs with different acrylates and methacrylates have been synthesized.^[44–50] Simultaneous elastomeric networks of castor oil and poly(butyl acrylate) were prepared by varying the percentage of acrylic crosslinker EGDMA.^[45,46] Semi-IPNs of castor oil PU–PS were prepared by first mixing all the reactants (castor oil, MDI, styrene, and BPO at a concentration of 0.5 weight % by weight of styrene) at room temperature. The PU network was synthesised in the presence of styrene at room temperature for 24 h, using closed molds. In the next step, the styrene monomer was allowed to polymerise at 80°C for another 24 h. In another study, Varghese and Krishnamurthy^[50] synthesised IPNs based on PU and PMMA and/or poly(butyl acrylate) (PBA) by two methods. In the first one, castor oil was chain-extended and bridged by selective combination of butanediol and trimethylol propane using isophorone diisocyanate as curative. In the second method, vinyl monomers such as MMA and butyl acrylate (BA) were interpenetrated with a castor oil urethane network by the simultaneous interpenetration technique, using BPO and butanediol dimethacrylate as a crosslinker.

Graft and joint IPNs based on PU and various vinyl monomers were prepared.^[51–58] PMMA-graft-poly(carbonate urethane) (PCU) and fully gelled mutually crosslinked networks composed of both PMMA and PCU were synthesised by Zhou and Frisch.^[51] Castor oil-based crosslinked polymers (joint IPNs) from urethane and various vinyl polymers were synthesised by Liu.^[52] RIM (reaction injection moulding) PU and vinyl ester resin-based IPNs were prepared by Chen Yonglin.^[54,55] Kuznetsova synthesised semi-IPNs based on crosslinked and thermoplastic PU and examined the effect of crosslinker on the formation process and physicomechanical, thermal, viscosity, and viscoelastic properties of IPNs.^[56] Grafted semi-IPNs were synthesised based on functional prepolymers having –COOH as a functional group, along with methacrylic copolymers and tertiary amine group as a crosslinker, as has been reported.^[58] Structure-property relationships in thermoplastic-apparent interpenetrating polymer networks (t-AIPNs), prepared by mechanical blending in a common solvent of crystallizable polyurethane (CPU) and styrene/acrylic acid random copolymer (S/AA), were studied by wide-angle and small-angle X-ray scattering (WAXS and SAXS), dynamic mechanical analysis (DMA), thermally stimulated depolarization currents (TDSC) techniques, and dielectric relaxation characteristics measurements by Kyritsis.^[59] The synthetic principle and technology of ionic polyurethane/polyacrylate (IPU/PA) latex interpenetrating polymer networks (LIPNs) used in leather coatings were introduced by Chen Liahua.^[60] The core-shell structure of the latex particles was proved by SEM. DSC showed that the compatibility of IPU and PA and the stability of the IPU/PA LIPN emulsion were improved by interpenetrating the polymers. The IPU/PA LIPN film had compromised the properties of the IPU and PA films.



1.4. Morphology and Glass Transition Temperatures

1.4.1. Sequential IPNs

The combination of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM) can effectively provide valuable information regarding the existence as well as the extent of interpenetration in IPNs. SEM and transmission electron microscopy (TEM) reveal information on or about the domain size, domain shape, and its continuity. However, this study gives minimal knowledge relevant to the polymer compositions within the phases. However, using DSC and DMA tools, coupled with the analysis of the shift and broadening of the T_g s of the component polymers involved, quantitative information can be derived regarding the composition of the various phases and the degree of their interpenetration.

Lee studied PU/PS sequential IPN-based membranes.^[8–10] The degree of intermixing between component polymers in the IPN membrane increased with a decrease in temperature of synthesis from +50 to –10°C. Each IPN showed an inward shift in the T_g by up to 12°C as compared to their parent networks.^[8]

The effect of synthesis temperature on the resultant morphology and properties of polyurethane/poly(methyl acrylate) (PU/PMA) IPNs of fixed composition was studied. It was observed that the PU/PMA networks at 50/50 weight % composition under 200 MPa pressure showed improved mixing of the two constituent networks with a decrease in the synthesis temperature.^[14] Another morphological study^[15] of poly(ethyl methacrylate) (PEMA)/PU IPNs, by modulated DSC (M-DSC) and small-angle X-ray scattering (SAXS), revealed that the morphologies of all the IPN samples (90:10 to 10:90 weight % compositions of PU/PEMA) are multiphase structures. It was investigated whether network formation in IPNs was a competitive process with respect to phase separation or formation of crosslinks. A study was conducted to verify the extent of phase separation in both sequential and simultaneous IPNs prepared from elastomeric polyurethane (25 weight %) and crosslinked PMMA.^[19] It is well known that in sequential IPNs, the two networks are formed after each other, and the network formed first is thought to impede gross phase separation in the final material. This is contrary to the simultaneous IPNs, in which formation of both networks, once initiated, proceeds to completion more or less simultaneously. The transmission electron microscopy (TEM) findings revealed that these IPNs, when prepared sequentially, have a higher degree of phase dispersion than those observed by the simultaneous method. The results were confirmed by a solid-state NMR lineshape analysis technique. The morphology of polyurethane (PU)-poly(ethyl methacrylate) (PEMA) IPN was investigated by means of SAXS and M-TDSC techniques by Song.^[61] Based on the analytical method employed by Tan,^[62] the interfacial thickness in the IPNs was calculated from SAXS. It was observed that the interfacial thickness was zero, and there were sharp domain boundaries in the PU-PEMA IPNs. The M-DSC results showed that the PU-PEMA IPNs had a multiphase morphology with a diffuse interphase region. The M-DSC, TEM, and DMTA results contradicted those obtained from analysis of SAXS data; hence it was concluded that the method employed for IPNs by Tan is questionable. Surface segregation of components in semi- and full-interpenetrating



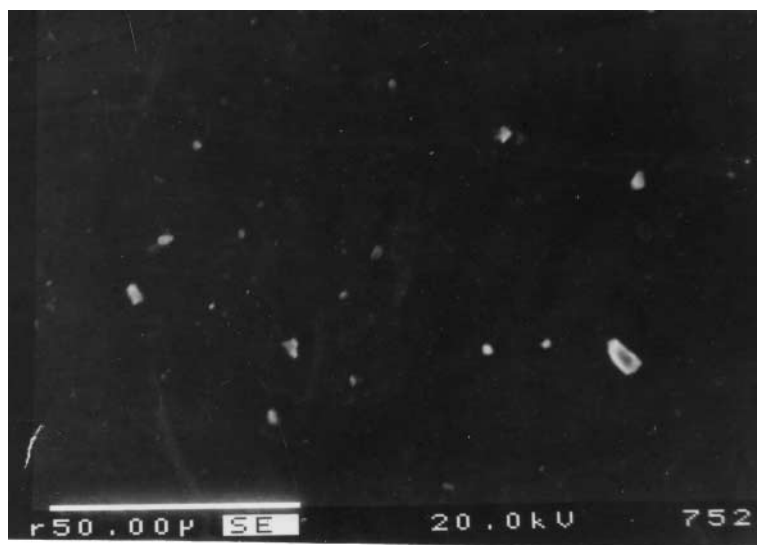
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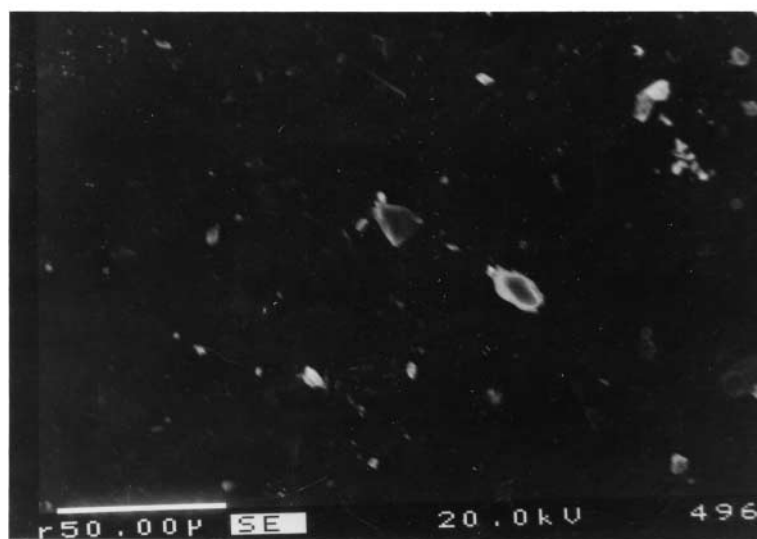
networks based on crosslinked polyurethanes poly(ester acrylate), poly(butyl methacrylate), and poly(vinyl acetate) has been studied at the interfaces with solids of high and low free surface energy by Lipatov.^[63] The method of attenuated total reflectance in IR spectra was used to estimate the composition of the system near the interface. A series of IPNs of PU/polyacrylates were synthesised by Xiaoqiang.^[64] Their morphology was investigated by means of SAXS and TEM. The influence of an active positive charge group ($-\text{N}(\text{CH}_3)_2$) on the phase structure of the aforementioned IPNs was studied. This study indicates that the SAXS technique can provide much valuable information about IPN morphology, such as the short-range correlation distance, the transverse length of domain, the interfacial area, etc. Combining with other methods, such as TEM, the SAXS provides a powerful new method of analysis for investigating the miscibility and the degree of interpenetration of two-component networks in an IPN system. The morphology and the interfacial area of the PU/polyacrylates IPNs varied with composition. The interattraction between the positive-charge group in the dispersed phase (polyacrylate) and the negative-charge group in the continuous phase (PU) was found to improve the miscibility between two components.

Synthesis and morphology of filled two-component semi-IPNs from crosslinked and linear polyurethanes were studied by Brovko.^[66] A comparison has been made of polyblends, and filled and unfilled semi-IPNs by examining their mechanical spectra in an investigation of the influence of active dispersed filler on the semi-IPNs phase structure. Four kinds of PU/polyacrylate IPNs (crosslinked polyacrylate semi-IPNs, crosslinked polyurethane semi-IPNs, all IPNs and all IPNs, with opposite charge groups) were synthesised by a simultaneous polymerisation process by Xiaoqiang Yu.^[67] Their damping properties, mechanical properties, and multiphase morphology were investigated by automatic torsional braid analysis, Instron tester, SAXS, and TEM. The results showed that the attraction between positively charged groups and negatively charged groups improved the miscibility of the two components. When the weight ratio of PU/polyacrylate was 1:2, the resulting IPN materials possessed better damping and mechanical properties, and the specific surface area reached a maximum. Athawale^[23–31] studied the morphology of modified castor oil PU-PMMA and PU/PBMA IPNs. The morphology of the IPNs was revealed by electron micrographs (Fig. 2a,b). In all the micrographs the polyurethane was present as the continuous phase with large globules of polyacrylate dispersed within it, indicating phase separation. The domains of the dispersed phase were clearly irregular, rather than spherical in shape. It was interesting to note that the phase separation between two polymers was more pronounced in the case of I-2 (UA40%/PBMA60%, domain size 3–12 μ) than in I-5 (UA20%/PBMA80%, domain size 1–8 μ), indicating low compatibility of the former over that of the latter. This clearly proves the relatively high degree of crosslink density in UA-P/PBMA IPNs.^[26]

In another study, the glass transition temperature and phase morphology of a soybean oil-based uralkyd (UA)/PEMA system revealed that there was phase separation in the semi-IPNs since two T_g s were obtained. This result is compared to the full-IPNs, which exhibited good interpenetration because of enhanced phase mixing and showed only one T_g .^[29]



(a)



(b)

Figure 2. Scanning electron micrographs of (a) UA-P/PBMA and (b) UA-D/PBMA (20/80 wt % composition) IPNs.



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1.4.2. Simultaneous IPNs

From the morphology studies^[33] of PU/PS IPNs by DSC and SEM, it was observed that the extent of component mixing and heterogeneity of domain sizes of the dispersed component in the IPN matrix can be reduced by including radiation exposure during IPN synthesis. It was revealed that increasing crosslink density and interpenetrating entanglement introduced forced compatibility in PU/PS IPNs, which accelerated the curing rate and decreased the phase separation.^[34] In the poly(oxyethylene oxide) (POE) urethane and PS IPNs, all the IPNs showed phase separation with phase inversion at ~60 weight % PEO and exhibited inwardly shifted T_g s corresponding to the T_g s of the parent networks.^[35] IPNs of PU/PS, in which PU and PS act as a hydrophilic and hydrophobic component, respectively, exhibited microphase separation structures, which have dispersed PS domains in a continuous PU matrix, and showed two T_g s.^[36,37]

The morphology of these types of IPNs has been examined using SEM, DSC, TEM, and DMA techniques by many authors.^[38,42,43,51] TEM micrographs of IPNs based on PU and PS of a 60/40 weight % blend resulted in a very complicated morphology, with phases within phases within phases.^[38] Zhou and Frisch^[51] studied poly(carbonate urethane) (PCU) /PMMA IPNs and concluded that single-phase morphology can be changed to two-phase morphology by changing the kinetics of the network formation. They also observed that two-phase simultaneous IPN (SIPN) of PCU/PMMA has been obtained by employing a nonsimultaneous crosslinking reaction for two different networks, while single-phase SIPN of PCU/PMMA can be made by adjusting the gelation time (formation of crosslink) for both networks. However, from DSC data, it was revealed that the T_g s of the products increased with the increasing degree of conversion. Compatibility behavior of IPNs of various castor oil-based PUs and vinyl polymers was investigated.^[44–47,50] Ma Song^[44,45] studied the effect of content of crosslinking agent in PBA on the morphology of PU/PBA IPNs. SEM studies showed that the level of PBA continuous phase in the network increased with increasing EGDMA content. The full-simultaneous elastomeric network (SEN) had a two-phase morphology and better compatibility than that of the semi-SEN. In another PU/PS IPN system, Hsuing^[46] found that the domain size of the microphase structure (~100Å), established by NMR proton spin diffusion, was two to three orders of magnitude smaller than the domain size (0.1–1.0μ) observed by SEM. Phase inversion was observed at 20–80 weight % PU content. The morphology of IPNs based on PU (NCO/OH = 1.0) and/or highly crosslinked PU (NCO/OH = 1.5) at 90/10 and 60/40 weight % ratios) with PMMA and/or PBA was carried out using the DMA technique by Varghese and Krishnamurthy.^[50] All the IPNs showed a single glass transition temperature. The lower tan δ values compared to the parent network showed enhanced compatibility. The T_g values of the PU network increased from 18°C to 52°C as the NCO/OH ratio increased from 1.0 to 1.5. Incorporation of 10 wt % MMA in the PU network increased the T_g from 52°C to 57°C. The inward shift of T_g to 47°C for PU-PMMA 60/40 weight % ratio was indicative of semi-compatible SIPNs. The appearance of a single broad transition for all the PU-PMMA and PU-PBA SINs was a direct indication of extensive but incomplete mixing of the component polymers. From the SEM study it was observed that the entanglement of vinyl monomer in the PU network is more pronounced in PU-PBA than in PU-PMMA.



The morphologies of the IPNs of PU/vinyl ester resin were studied with the aid of DSC and SEM by Chen.^[54] Three kinds of PU and vinyl ester resin IPNs were synthesised to study their morphologies and mechanical properties for potential application in the reinforced reactive injection molding (RRIM) process. The IPN systems consisting of PU prepared from modified MDI-vinyl esters showed microphase separation between rubber and plastic phases, whereas IPNs from PU based on TDI showed higher compatibility. In the case of polycarbonate urethane (PCU) and poly(methyl methacrylate-co-N,N-disubstituted urea)-based IPNs,^[57] which exhibited nonlinear optical (NLO) properties, it was observed that the full-IPNs had only one T_g as determined by DSC. This was further supported by the SEM studies, suggesting a single-phase morphology. The grafted semi-IPN based on PU-prepolymer and acrylic polymer having terminal carboxylic group and methacrylic copolymers as a second component along with tertiary amine (PU crosslinker) showed a two-phase morphology due to the segmented structure of PU prepolymer. It was stated that the lowering of average molecular weight (M_n) values of the starting component did not improve their compatibility. The compatibility between PU hard segments and poly-methacrylic component led to the conclusion that the preparation of IPNs of finer morphology would be possible by using PU prepolymer with shorter soft segments.^[58] The DMA study of castor oil-based PU and vinyl copolymer graft IPNs indicated two T_g s. The difference between the two T_g s narrowed considerably as the components became more compatible. However, a broad T_g region occurred in the IPN system of PU/poly(acrylonitrile) at the 60/40 weight % composition.^[68]

1.4.3. Physical Properties

1.4.3.1. Sequential IPNs

Studies on mechanical properties such as tensile strength, elongation, hardness, and impact strength of the IPNs have been carried out.^[12–13] IPNs of PU based on hydroxyl-terminated natural rubber with varying NCO/OH ratios and PS were prepared under different experimental conditions. The IPNs exhibited an increasing trend in density, hardness (Shore A), and tensile strength with increasing PS content.^[12] Hsieh^[13] studied linear blends and IPNs of PU ionomer (based on various diols, chain extender diethanolamine, and crosslinker triethanolamine) and the second component poly(styrene-acrylic acid) (PSA) (modified with acrylic acid and divinyl benzene). The linear blend showed a maximum value in tensile strength for the PU/PSA with the 20/80% composition and 30 mol% of acrylic acid (AA) in the PSA. Likewise, when networks were constructed with PU and PSA ionomers, the IPN system showed maxima at 25/75 weight % composition. Depending upon the type of diols used, the tensile and impact strength increased or decreased with increasing molecular weight of the diols.

Studies regarding influence on mechanical properties of semi- and full-IPNs based on PU/poly(methyl acrylate) were carried out as a function of change in synthesis temperature by Hourston and Huson.^[14] Synthesis at higher temperature resulted in deterioration in tensile strength and a decrease in the hardness of the IPNs. High-impact cast sheets of PMMA/PU IPNs showed maximum impact at a critical PU concentration.^[18]

**Table 1.** Mechanical and physical properties of homopolymers and IPNs.

Sample code	Composition PU/PMMA (wt %)	Tensile strength (Mpa)	Elongation at break (%)	Hardness Shore A
Homopolymers				
^a CU	100/0	1.8	207	72
^b HCU	100/0	2.3	228	86
PMMA	0/100	62.0	8	Hard
Full-IPNs				
CU/PMMA	25/75	2.3	20	90
CU/PMMA	50/50	1.7	45	76
CU/PMMA	75/25	1.3	140	71
HCU/PMMA	25/75	3.0	25	100
HCU/PMMA	50/50	2.2	60	96
HCU/PMMA	75/25	1.6	165	92
Semi-IPNs				
CU/PMMA	25/75	3.7	15	90
CU/PMMA	50/50	2.5	33	88
CU/PMMA	75/25	1.9	92	86
HCU/PMMA	25/75	4.2	18	100
HCU/PMMA	50/50	2.8	43	92
HCU/PMMA	75/25	2.1	96	88

^aCU = castor oil urethane.^bHCU = hydrogenated castor oil urethane.

Mechanical properties of IPNs based on castor oil PU and various vinyl polymers such as PMMA, PBMA, and PEMA have been reported by many authors.^[20,23–31,53] Athawale studied the tensile strength, elongation, and hardness of modified castor oil and PMMA IPNs^[24] which are shown in Table 1. In all the cases, a minimum in the tensile strength was observed for the IPNs having 75 weight % polyurethane content, and a maximum at 25 weight % polyurethane. It can be noted from Table 1 that the tensile strength increased, whereas elongation at break decreased with a corresponding decrease in the polyurethane content in the IPNs. Further, it was found that the variation of blend ratio resulted in drastic changes in the elongation, whereas nominal changes were observed in the tensile strength. On comparing the tensile strength and elongation of castor oil urethane (CU) and hydrogenated castor oil urethane (HCU) and their IPNs using poly(methyl methacrylate) (PMMA) as a second component, it was found that HCU/PMMA IPNs showed slightly better mechanical properties over those of CU and CU/PMMA IPNs. Both the CU- and HCU-based IPNs exhibited somewhat inferior mechanical properties as compared to those of the constituent component networks. On further inspection of Table 1, it was found that semi-IPNs exhibited higher tensile strength and lower elongation than the corresponding full-IPNs. This may be due to the difference in PMMA continuous phase contributions, which are easier to obtain in semi-IPN as compared to that in full-IPN. This results in ample scope for threading of polyurethane with PMMA networks in the case of semi-IPNs, where the chains are



linear and have greater mobility. On the other hand, in the case of full-IPNs, the high degree of crosslinking lowers the statistical probability of threading (easy mobility of entangled chains), thereby precluding the reinforcement effect of interpenetration. Interestingly, during tensile strength measurements, all the semi-IPNs were observed to stress whiten, indicating failure arising from crazing mechanism, whereas in the case of full-IPNs, this phenomenon was not observed, because of the improved compatibility of urethane and PMMA. Hardness data (Table 1) revealed that the hardness increased with the corresponding increase in the PMMA concentration in the IPNs. This is because soft and flexible urethane resin was being substituted by hard poly(methyl methacrylate). On further inspection of Table 1 it was found that HCU/PMMA IPNs exhibited higher hardness than those of CU/PMMA IPNs, possibly due to the formation of more crosslinked network by the former. Interestingly, the semi-IPNs showed greater hardness than the full-IPNs, because in the case of semi IPNs due to partial mixing of the hard PMMA phase with soft PU phase, only some part of PMMA gets interpenetrated, whereas the remaining uninterpenetrated PMMA behaves like a filler. Guo^[53] examined the IPNs based on polyol [synthesized from castor oil modified with telechelic (functional oligomer) hydroxyl terminated polybutadiene] and TDI urethane–vinyl polymer. These IPNs were more elastic and behaved like elastomers than the IPNs obtained from neat castor oil polyurethane and vinyl polymers. The elongation of IPNs based on modified castor oil PU–vinyl polymers was >200% and the permanent set was <75%.

1.4.3.2. Simultaneous IPNs

In PU/PS simultaneous IPN system, Zhang^[33] found that by increasing PU content the fracture stress increased, whereas ultimate elongation increased with the increase in the content of crosslinking agent. It was also observed that the ultimate elongation of IPN containing >50 weight % PU was greater than that of the PU-homopolymer. Shin^[37] studied the hydrophilic PU- and hydrophobic PS-based simultaneous IPNs and demonstrated that, the IPN containing 50 weight % of PS showed good mechanical properties.

Chen^[42] developed a method to investigate the mechanical properties of IPNs based on PU-PMMA and found that the tensile strength and elongation can be improved by adding MMA microgel in the IPNs. Stress-strain and density studies of IPNs composed of polyurethanes and different vinyl polymers [i.e., PMMA and PS^[39,42] and PGDMA^[43]] were carried out by Liu and others, and it was found that PU-poly(glycidyl dimethacrylate) (PGDMA) IPNs with different gelation sequences (network formation) showed opposite physical and mechanical properties. The sample in which PU gelled first was transparent and brittle while the sample in which PGDMA gelled first was opaque and highly elastic.^[43]

Ma Song^[44,45] carried out the study on effect of crosslinking agent (EGDMA) in PBA and on the mechanical properties of castor oil-based PU-PBA IPNs. It was found that the tensile strength and Young's modulus of IPNs of *n*-butyl acrylate-EGDMA copolymer and castor oil PU decreased while elongation at break increased with increasing *n*-butyl acrylate-EGDMA copolymer content in the network. In the PU/PS IPN system,^[46] there was a sharp increase in the tensile strength with PS weight fraction, at 20–30% PU content in the IPNs. Maximum elongation

**Table 2.** Effect of NCO/OH ratio on mechanical properties of IPN-II (UA/PMMA 50/50 weight %).

NCO/OH (molar ratio)	Tensile strength (MPa)	Ultimate elongation (%)
2.25	18.8	103
1.92	22.0	142
1.60	19.4	172
1.34	10.2	265
1.08	5.50	236

at 50% PU was observed. Similar types of PU/PS simultaneous IPNs system showed a significant improvement in the mechanical properties, beyond a critical styrene level (25% by weight). However, percent elongation at break showed a maximum at 40 weight % styrene.^[48] Xie^[49] studied the mechanical properties and adhesive strengths of the PU/PAN (polyacrylonitrile), PU/PS, PU/PBA, PU/PEMA, and PU/PEA-based IPNs. It was revealed that the maximum tensile strengths of IPNs containing different vinyl or acrylic polymers decreased in the following order: PU/PAN > PU/PS > PU/PBA > PU/PEMA > PU/PEA. It was observed that acrylonitrile (AN) was a better monomer than styrene and MMA with respect to tensile strength. In the system studied, the polarity also played an important role in deciding the adhesive strengths of the various IPNs. The polarity of PU/AN IPN was much higher than that of PU/PS IPN, though their T_g s were about the same. Most of the IPNs containing AN (IPN II) exhibited ultimate elongation between 100% and 200%. Table 2 indicates that maximum tensile strength was observed at NCO/OH = 1.92. However, with increasing NCO/OH ratio, ultimate elongation decreased.

Anzlovar^[58] investigated the effect of functional groups (such as terminal –COOH group and tertiary amine group in methacrylic copolymers) and M_n (number average molecular weight) of the polymer components as well as their ratio on mechanical properties of semi-IPNs based on PU and various methacrylic copolymers. It was found that the mechanical properties of the semi-IPNs changed with an increase in the concentration of functional groups. Young's modulus was mostly influenced by physical interaction between the functional groups, while M_n of the polymethacrylic acid component influenced the tensile strength of the IPNs.

1.4.4. Thermal Properties

1.4.4.1. Sequential IPNs

Many researchers studied the thermal behavior of IPNs based on the castor oil polyurethane and various vinyl polymers by means of thermogravimetric analyzer (TGA) and DSC,^[17,21–31,51] computed activation energy, and thereby established the thermal stability of the IPNs. More recently, Nayak^[21,22] reported the temperatures and kinetics of high-temperature degradation of IPNs based on castor oil PU and various vinyl polymers. From the TGA study it was observed that the IPNs

**Table 3.** Thermal decomposition of homopolymers and IPNs.

Sample code	Compositions U/PMMA (wt %)	Decomposition stages			
		Stage I (°C)	Activation energy (kJ/mol) E*	Stage II (°C)	Activation energy (kJ/mol) E*
^a CU	100/0	254–391	150.62	391–502	184.10
^b ICL1U	100/0	220–387	133.89	387–502	163.18
^c ICL2U	100/0	185–353	92.05	353–505	142.26
IPN-2	50/50	194–365	121.34	365–562	167.36
IPN-5	50/50	182–378	117.15	378–560	150.62
IPN-8	50/50	182–540	71.13	—	—
PMMA	0/100	154–450	66.94	—	—

^aCU = unmodified castor oil urethane.^bICL1U = modified castor oil (using 20% linseed oil) urethane.^cICL2U = modified castor oil (using 30% linseed oil) urethane.

degraded in three steps, and the activation energy values were considerably higher in the temperature range of 300–400°C than in the range of 410–500°C. Athawale^[23–26] examined the thermal behavior of various renewable resource-based IPNs comprised of modified castor oil PU and PMMA. Thermal behavior of IPNs and homopolymers suggested that the thermal stability of the IPNs falls intermediate between those of urethane and PMMA. However, from the activation energy data (Table 3) it was observed that CU (unmodified castor oil urethane) homopolymer and the corresponding CU/PMMA (50/50 weight %) IPNs were relatively more stable than ICL1U (modified castor oil urethane using 20% linseed oil), ICL2U (modified castor oil urethane using 30% linseed oil) and their corresponding IPNs with PMMA. In all the cases, generally, two-stage decomposition was observed (Fig. 3a–f). Stage I corresponds to the urethane bond breaking in case of urethane, whereas in the IPNs, along with urethane bond breaking, unzipping of PMMA network also occurred, in the temperature range of 330–340°C. Stage II, which is the polyol decomposition, took place at 450–455°C in case of both polyurethane and the IPNs. Finally, polyurethane and IPNs showed complete weight loss at 500°C and 550°C, respectively.^[25] Zhou^[51] carried out studies on PMMA-graft poly(carbonate urethane) (PMMA-g-PCU) and fully crosslinked networks composed of both PMMA and PCU (PMMA-PCU-N) IPNs. In comparison with PMMA-g-PCU IPNs, the PMMA-PCU networks were thermally less stable.

1.4.4.2. Simultaneous IPNs

The thermal stability of PU-PS IPNs was measured using thermogravimetry, and the kinetic parameters were evaluated by using the methods developed by Ozawa, Friedman and Kissinger.^[34,35] Crosslinked PEO and its IPNs decomposed in two stages. The first stage was caused by cleavage of the urethane bond, and the second stage by increased thermal stability of the IPNs with increasing weight fraction of crosslinked PS. The study revealed that activation energies for the

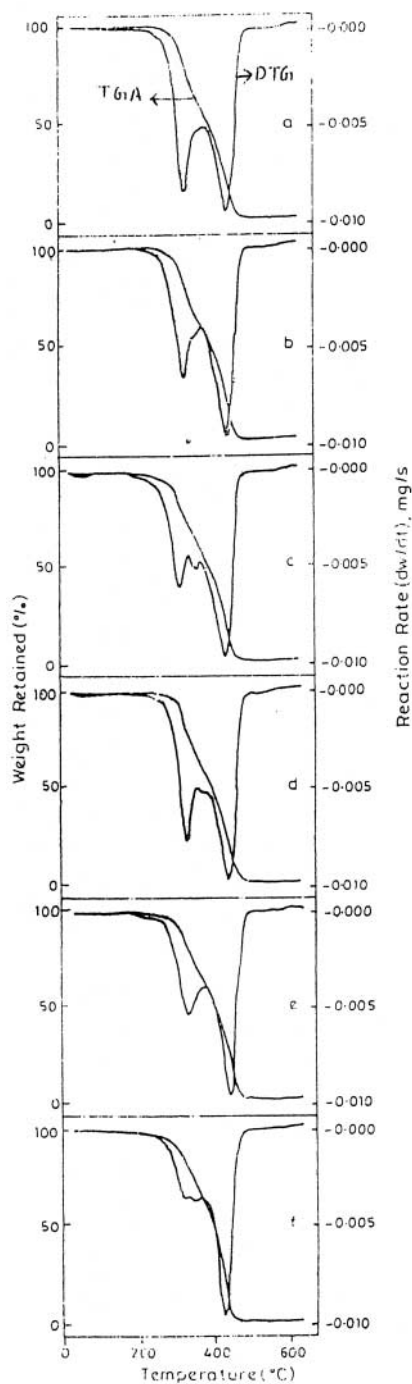


Figure 3. TGA and DTG of castor oil, linseed oil modified polyurethane homopolymers and corresponding IPNs with PMMA (50/50 wt % composition) (a) CU, (b) ICL1U, (c) ICL2U, (d) C-IPN, (e) L1-IPN and (f) L2-IPN.



thermal decomposition of the IPNs were affected by phase behavior of each polymer network.^[35]

Thermal properties of simultaneous IPNs based on castor oil-TDI polyurethane and various vinyl polymers were studied.^[46–50] In the thermal study of PU/PMMA and PU/PnBA simultaneous IPNs (SINs), it was found that SINs are thermally more stable than the PU networks. All the SINs began to decompose at 300°C. Complete decomposition was observed around 500°C, while major decomposition peaks shifted to higher values with the increase in the vinyl content. The interpenetration of PMMA or PnBA up to 40 weight % in the PU network improved the thermal stability of the IPNs as compared to that of 100% PU.^[50]

1.4.5. Swelling Studies

1.4.5.1. Sequential IPNs

Athawale reported swelling behavior of renewable resource IPNs.^[23–31] Swelling was more prominent in toluene and MEK, whereas no swelling was observed in water.^[28] It was evident from Table 4 that the IPNs with triethanolamine (which acted as a chain extender as well as a crosslinker) showed greater swellability than those without triethanolamine. A perusal of Table 4 also revealed that swelling was more prominent in toluene than in MEK. This is attributed to the low polarity of toluene.

1.4.5.2. Simultaneous IPNs

Bai^[48] and coworkers carried out the equilibrium swelling study of castor oil-based IPNs in a polar solvent (ethyl acetate) and a nonpolar solvent (toluene). The results showed that there was slow increase in the percent equilibrium swelling by volume in both solvents with increase in styrene concentration in the IPNs.

Table 4. Swelling of homopolymers and IPNs.

Sample code	Composition UA ^a /PS ^b (wt %)	Swelling (%)		
		Toluene	MEK	Water
UA100T ^c	100/0	60	58	1
UA25/PS75	25/75	200	99	No change
UA50/PS50	50/50	107	81	No change
UA75/PS25	75/25	81	68	No change
PS100	0/100	1030	900	1.09
UA25/PS75T	25/75	229	122	1
UA50/PS50T	50/50	136	102	No change
UA75/PS25T	75/25	93	87	No change

^aUralkyd resin.

^bPolystyrene.

^csample codes containing “T” indicate presence of triethanolamine.



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However, a marked rise in percent swelling occurred between 25–40% styrene, which then decreased with a further increase in the styrene fraction. The extent of swelling in ethyl acetate was much greater.

1.5. Applications

Lee et al.^[8–10] synthesised PU/PS IPN membranes and studied their gas (oxygen and nitrogen) transport characteristics. The effects of synthesis temperature, composition, molecular weight of the polyol used, and aromatic content (of MDI, TDI, HDI) on the gas permeability were analysed. It was observed that the permeability coefficient decreased and the separation factor increased with decreasing synthesis temperature. The permeability coefficient showed a minimum value and the separation factor showed maximum value at 25 weight % PU composition. The permeability decreased and separation factor increased with increasing aromatic content. In another case, they studied the effect of crosslinked state and annealing on PU/PS IPN, semi-IPN, and linear blend membrane. The annealing effect on the permeation characteristics depends on the nature of crosslinking of the membrane (IPN < semi-IPN < linear blend).^[8] In another development Xie^[49] developed castor oil-urethane/acrylic or vinyl IPN for coating rusted iron. A redox reaction was employed for the vinyl or acrylic portion, with rust providing part of the catalyst system. The monomer mix soaks through and on polymerisation provides both significant adhesion to iron as well as protective properties. Huang et al.^[55] studied IPNs using two different types of PU and vinyl esters. They studied the mechanical properties of IPNs for the application in reaction injection molding (RIM). Hua^[69] studied two-component simultaneous IPN based on water blow flexible foam of PU and poly(vinyl esters). The IPN foam exhibited a maximum in tensile strength at 10% by weight of vinyl esters either in the group of equal density (18 kg/m³) foam or in the group of foam with same water level (2 parts by weight). The resilience of all the IPN foams decreased with increasing vinyl ester content. Lee^[70] prepared PU/P(MMA-AA) IPN pervaporation membranes in which alcohol and water could be easily separated. The pervaporation process is highly useful in areas where conventional techniques are difficult to apply, such as fractionation or isomeric mixtures. In this process, alcohol-water mixture can be fed over a PU/P(MMA-AA) IPN membrane. The water diffuses through faster and is removed in the vapor state. After three stages, 94% ethanol can be obtained. Sound and vibration damping.^[71] has been an important area for IPNs because they have broad but controllable temperature ranges of damping. Hitachi Chemical has a new high-temperature sound and vibration damping material, which is based on vinyl-phenolic compositions.^[72] IPNs are also used as biomedical materials. Arkles^[73] made IPNs based on silicone and polyurethane useful as steam-sterilizable medical tubing. Roemer and Tateosian^[74] of Dentsply developed prosthetic teeth made from acrylic sequential-IPN compositions. Suspension-sized particles of crosslinked PMMA were mixed with linear PMMA, MMA monomer, crosslinker, and initiator. After polymerisation, the false teeth had two superior properties. Because a suspension polymerisation route was used, the teeth were ground to a fine powder, useful in the dentist's office when fitting the opposing set of teeth. Second because they were densely crosslinked, they did not swell significantly



in highly edible plasticizers such as salad oils, margarines, or similar materials. A gradient IPN was developed and used for constant rate of medicine delivery.^[75] In this case, a polymer network I is made into suspension sized particles and extra ingredients are dissolved into the network; the drug to be delivered is one of the components of a condensation polymer. Davison and Gergen^[76,77] prepared thermoplastic IPNs based on block copolymers of hydrogenated styrene butadiene-styrene triblock materials, known as styrene-ethylene butylene-styrene (SEBS) triblock copolymers. The crystalline polymers are polyamides^[76] or thermoplastic saturated polyesters.^[77] The thermoplastic IPNs have outstanding resistance to shrinkage and distortion on heat aging, resistance to ozone, and an improved balance of mechanical properties.

PROGNOSIS

Increasing pressures to improve performance yet reduce costs amidst new regulatory guidelines and requirements are just a few of the many challenges the researchers investigating IPNs are faced with in today's ever-changing environment. Synthesis and development of new IPNs, which require a thorough understanding of component materials so as to make informed choices about what will best fit the overall intended use of the polymer produced, have given rise to a rather complex nomenclature system for unambiguously classifying these materials. The system is gradually gaining acceptance among concerned researchers world wide.

New advances in polymer science and development of materials to meet specific application requirements have resulted in a renewed partnership between IPN researchers and the industry. New trends in materials characterization will only continue to strengthen this relationship. IPNs offer an inherent combination of properties unmatched by any other material. IPNs can be readily modified to enhance specific capabilities and hence are promising materials for a variety of industrial applications. Since IPN-based materials cover a broad spectrum of useful properties they are used in diverse fields like coatings, sound and vibration damping, biomedical applications, etc. and can prove to be valuable substitutes for existing materials.

An interesting common feature of most of these materials is the incorporation of polyurethane technology. Among polymers, polyurethanes are easy to synthesis as well as crosslink and provide a range of elastomeric to leathery compositions in IPN form. Constant research in this field will definitely yield ideal polymeric materials that will render themselves extremely useful from an industrial application point of view and for the end user.

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