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SYNTHETIC RUBBER-BASED IPNs

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3.1 INTRODUCTION

Synthetic rubber is any type of artificial elastomer that can undergo much more elastic deformation under stress than most materials and still return to its previous size without permanent deformation. Among the synthetic polymers in use today, synthetic rubber is unique in that it was developed not as an interesting new material but to fill a dire need of the modern world. The reason for this unique position of synthetic rubber is its unique property: the only substance that exhibits long-range elasticity [1]. Therefore, it can fill a special need in modern technology. It is widely used in industry, agriculture, defense, transportation, and daily life, serving as a substitute for natural rubber in many cases, especially when improved material properties are required.

Synthetic rubber can be made from the polymerization of a variety of monomers. The common synthetic rubbers are listed in Table 3.1. Synthetic rubber is usually divided into two categories: general-purpose rubbers and specialty rubbers. General-purpose rubbers mainly include styrene-butadiene rubber (SBR), polybutadiene rubber (BR), polyisoprene rubber (IR), ethylene

TABLE 3.1 List of Part Common Synthetic Rubbers

ISO 1629 Code ^a	Technical Name	Common Names
BR	Polybutadiene	Buna CB
CR	Polychloroprene	Chloroprene, neoprene
EP	Ethylene propylene	
EPDM	Ethylene propylene diene monomer	EPDM
FKM	Fluorinated hydrocarbon	Fluororubber
IR	Polyisoprene	(Synthetic) natural rubber
IIR	Isobutylene isoprene butyl	Butyl rubber
NBR	Acrylonitrile butadiene	NBR, nitrile rubber, Perbunan, Buna-N
PU	Polyurethane	PU, polyurethane
SBR	Styrene butadiene	SBR, Buna S, GRS, Buna VSL, Buna SE
SI	Polysiloxane	Silicone rubber
VMQ	Vinyl methyl silicone	Silicone rubber

^aISO 1629:1995—Rubber Test Standard.

propylene diene monomer (EPDM) rubber, chloroprene rubber (CR), and so on. Specialty rubbers mainly include nitrile rubber (NBR), butyl rubber (IIR), silicone rubber, fluororubber (FKM), PU rubber, and so on.

Interpenetrating polymer networks (IPNs) are polymer alloys consisting of two polymers in a network form, held together by permanent entanglements with only occasional covalent bonds between the chains of the two different types of polymers [2]. In the IPNs, at least one of them was polymerized and/or crosslinked in the immediate presence of the other. In most cases, phase separation occurs, resulting in a two-phase polymer system. The IPNs can be prepared by sequential polymerization, simultaneous polymerization, or a latex blending technique [3, 4].

The IPNs show excellent thermal stability and mechanical properties because of a synergistic effect induced by the forced compatibility of individual components. The IPN technology can conquer the disadvantages of sole polymer to obtain integrated high-performance polymer composites, and the properties of the IPNs can be designed ranging from a filler-reinforced elastomeric material, to a rubber-reinforced plastic material via used original polymers with different properties. Therefore, attention has been given to IPNs in recent years.

The crosslinking density of the IPN system strongly influences the phase morphology of the IPNs, and thus the physical and mechanical properties of a given IPN can be modified by varying the crosslinking density [3]. The crosslinking density is directly related to the composition of the IPNs. For the IPNs, of particular interest are systems based on brittle plastics and elastomers, which may give rise

to tough IPNs. There is much information regarding the influence of composition and method of synthesis on mechanical and damping properties [5, 6].

Synthetic rubbers (including general-purpose rubbers and specialty rubbers) are artificial elastomers that have many types and uses: they can not only serve as substitute of natural rubber but also fill a special need in modern technology. Therefore, synthetic rubbers are often selected as rubber phases and the synthetic rubber-based IPNs are interested by many researchers and have had many important advances in recent years.

3.2 SYNTHETIC RUBBER-BASED IPNs

3.2.1 The Synthesis Methods of Synthetic Rubber-Based IPNs

As previously mentioned, the basic synthesis methods for the IPNs are sequential polymerization, simultaneous polymerization (shown in Figure 3.1) [4], or a latex blending technique:

1. *Sequential IPN (SIPN)*: Polymer A is swollen in polymer B, as well as its crosslinking agent, and initiator, polymerizing B *in situ*.
2. *Simultaneous IPN (SIN)*: Monomers A and B, and their respective crosslinking agents and initiators, are polymerized simultaneously by way of noninterfering modes.
3. *Latex IPN*: The polymers are made in the form of latexes. Thus, each particle constitutes a micro-IPN. Frequently, a core-shell structure develops. And after film formation, further crosslinking between the particles may take place.

For synthetic rubber-based IPNs, sequential polymerization method is the most frequently used. The forming of crosslinking rubbers needs relatively high temperature, a certain pressure, and special apparatus (curometer). Thus, the basic synthesis process of synthetic rubber-based IPNs is as follows [7–9]: synthesis of synthetic rubber network, swelling of the synthetic rubber network in monomer solution of polymer B, polymer B polymerization, and then the synthetic rubber-polymer B IPN formation.

3.2.2 General-Purpose Rubber-Based IPNs

3.2.2.1 SBR-Based IPNs SBR is the largest general-purpose synthetic rubber varieties that consist of styrene and butadiene. It has good abrasion resistance, good aging stability when protected by additives, and is widely used in car tires. Polystyrene (PS), a relatively low-cost thermoplastic material,

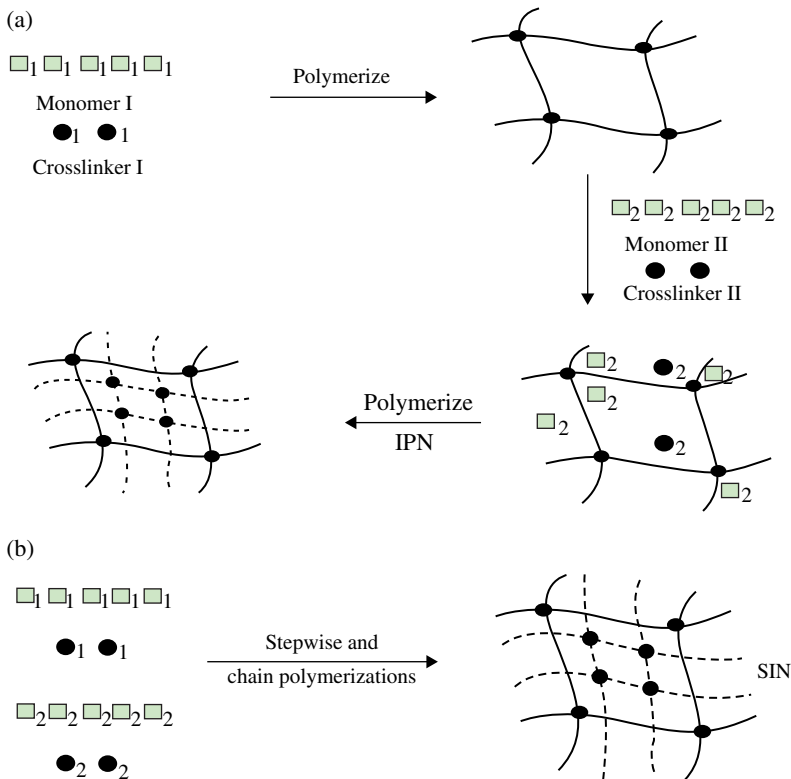


FIGURE 3.1 The basic synthesis methods for IPNs: (a) Sequential IPN and (b) simultaneous interpenetrating network. Source: Sperling and Mishra [4]. Reproduced with permission of John Wiley & Sons

having some excellent properties, has a prominent limitation in its brittleness. Therefore, combination with synthetic rubbers can improve the impact property of PS and thus complement the properties of each other.

Donatelli and coworkers [10, 11] prepared IPNs and semi-IPNs based on SBR as polymer A and PS as polymer B. The IPNs and semi-IPNs were synthesized by thermal polymerization techniques. The rubber phase for the IPN was prepared by dissolving the SBR in benzene, adding the appropriate amount of dicumyl peroxide (DiCup) for crosslinking, and then evaporating the solvent. The SBR was then cured in a compression molding operation. Then the obtained crosslinked SBR was swollen in the monomer of styrene before the styrene was polymerized thermally. The studies showed that the polymer synthesized first tends to control morphology and forms the more continuous phase when the polymerizing system is not stirred. The size of the cellular structure is a function of the degree of crosslinking of the polymer A component, with an increase in crosslinking, producing

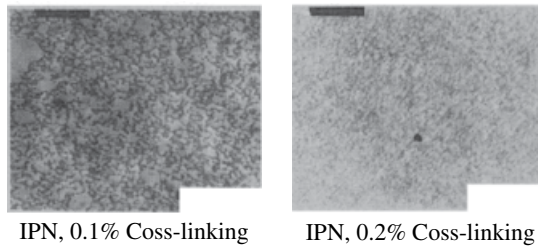


FIGURE 3.2 Phase morphologies of SBR/PS IPN (20% SBR and 80% PS: the elastomer is stained dark with osmium tetroxide). Source: Donatelli, Sperling, and Thomas [10]. Reproduced with permission of American Chemical Society

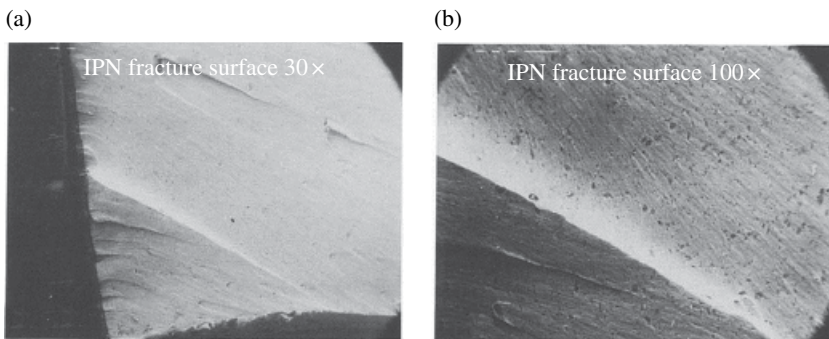


FIGURE 3.3 IPN (70% PS and 30% SBR) fracture surface (stained with OsO_4): (a) $\times 9.9$ and (b) $\times 132$. Source: Burford *et al.* [5]. Reproduced with permission of Springer

a finer structure (Figure 3.2). Dynamic mechanical behavior as a function of temperature shows two distinct transitions, which indicated that the SBR/PS system is incompatible. Yield strength and modulus decrease with increasing SBR content but increase with the degree of crosslinking of the rubber phase. Impact strength tends to increase with SBR content. The results presented the relation between crosslinking, composition, chemical compatibility, morphology, and their properties that directed the research about SBR/PS IPNs.

Burford and coworkers [5] described their work to determine the fracture toughness, K_{Ic} , of the IPNs based on PS and SBR. At high plastic levels, the material behaves in a similar manner to conventional rubber-toughened plastics, and the impact strength is superior to that of the unmodified plastic (Figure 3.3). Therefore, the determination of K_{Ic} is helpful to understand the mechanics of fracture of the elastomeric network.

Besides the previously discussed SBR/PS IPN systems, the synthesis and characterization of sequential IPN based on SBR-polyalkyl methacrylates [7] were performed by Patri *et al.* The IPNs based on SBR and polyalkyl (methyl,

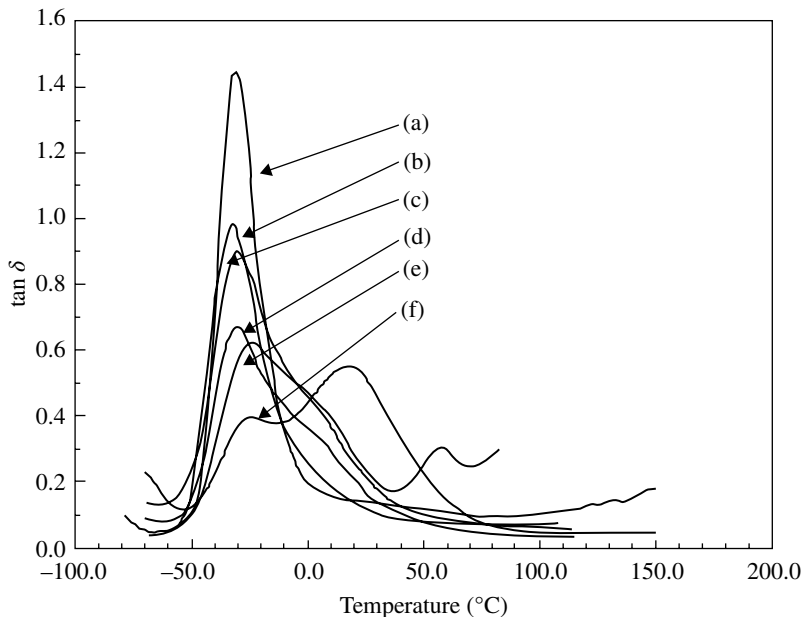


FIGURE 3.4 Damping plot of SBR/PBuMA IPNs: (a) SBR, (b) SBR/PBuMA (87/13), (c) SBR/PBuMA (80/20), (d) SBR/PBuMA (73/27), (e) SBR/PBuMA (72/28), and (f) SBR/PBuMA (57/42). Source: Patri *et al.* [7]. Reproduced with permission of John Wiley & Sons

ethyl, and butyl) methacrylates were prepared by using tetraethylene glycol dimethacrylate as crosslinker. The IPNs based on PMMA have shown higher tensile strength compared with others. Dynamic mechanical analysis (DMA) showed that the IPNs have superior damping properties than SBR (Figure 3.4). Because of IPN formation, $\tan \delta$ peak shifted inward between SBR and acrylates when IPN was forming. Moreover, the peaks were broadened because of micro heterogeneous phase separation. At higher concentration of methacrylate, splitting in $\tan \delta$ peak was noticed because of phase separation.

3.2.2.2 BR-Based IPNs BR is a synthetic rubber that is a polymer formed from the polymerization process of the monomer 1,3-butadiene. Cured BR imparts excellent abrasion resistance (good tread wear), and low rolling resistance (good fuel economy) due to its low glass transition temperature (T_g). It is the second largest volume synthetic rubber produced, next to SBR. Seventy percent of total production is used in tire compounds with another 20% being used for modifying plastics [12].

Ghosh and Ray [8] used BR to prepare BR/PS semi- and full-PNs by sequential polymerization method to modify PS, respectively. Dicumyl peroxide

(DCP) was used to form the initial PBR network. The semi-IPNs were formed by allowing the initially formed BR network to swell in styrene monomer and then completing polymerization of the monomer through the swollen network. For full-IPN formation, low doses of divinylbenzene (DVB) were used in the monomer styrene and copolymerization of the styrene-DVB system in the swollen BR network subsequently. Effects of variation of DCP dose, DVB dose, and PBR/PS blend ratio on the physico-mechanical properties of the blends were examined. Analysis of the micrographs (Figure 3.5) shows that the effect of variation in blend ratio points to a critical ranges of BR/PS blend ratio around 50 : 50 to 40 : 60. Around this blend ratio, the phase morphological pattern undergoes a notable change akin to phase inversion. For full IPNs when PS has high content (>50%), the PS phase distributed as continuous long ridge-like or fibrillar structures. For BR>50%, the elastomer phase is apparently the continuous phase. The full-IPNs exhibited higher tensile strength and modulus, while the semi-IPNs exhibited greater toughness.

Xue *et al.* [13] report on the synthesis and characterization of a novel simultaneous pseudo-IPN (semi-IPN) based on crosslinked CR and BR. They mixed proportional amounts of linear CR (potassium iodide pretreated in benzene and dimethyl sulfoxide-mixed solvent) and BR (which was dissolved in dry benzene) to give the desired compositions followed by adding the diamine crosslinking agent for CR. Subsequently, the mixtures were sufficiently stirred and then were carefully poured into aluminum dishes and placed in an oven to obtain solidified films. All IPNs studied (scanning electron microscopy or SEM and differential scanning calorimetry or DSC) revealed two distinct glass transitions and a melting point that corresponded to the linear PB component which suggest microphase separation in the IPNs. Pure crosslinked CR exhibits a uniform morphology (Figure 3.6a). IPN-1 showed a complex morphology with a small number of micrometer-sized disperses spherical domains and some large irregular “holes” (Figure 3.6b). IPN-2 and IPN-3 showed interesting wormlike disperse fibrous domains. The average thickness of the dispersed fibrous domains decreases as the weight fraction of PB component increases (Figure 3.6c and d). For ultimate mechanical properties of the IPNs, the tensile strengths and elongations at break are decreased as the content of BR increased. The pseudo-IPN structure could be an effective way to combine two rubbers.

3.2.2.3 CR-Based IPNs Polychloroprene (poly(2-chloro-1,3-butadiene)), CR, is an elastomer widely used in the electrical and automobile industries. CR is not characterized by one outstanding property, but its balance of properties is unique among the synthetic elastomers. It has outstanding physical

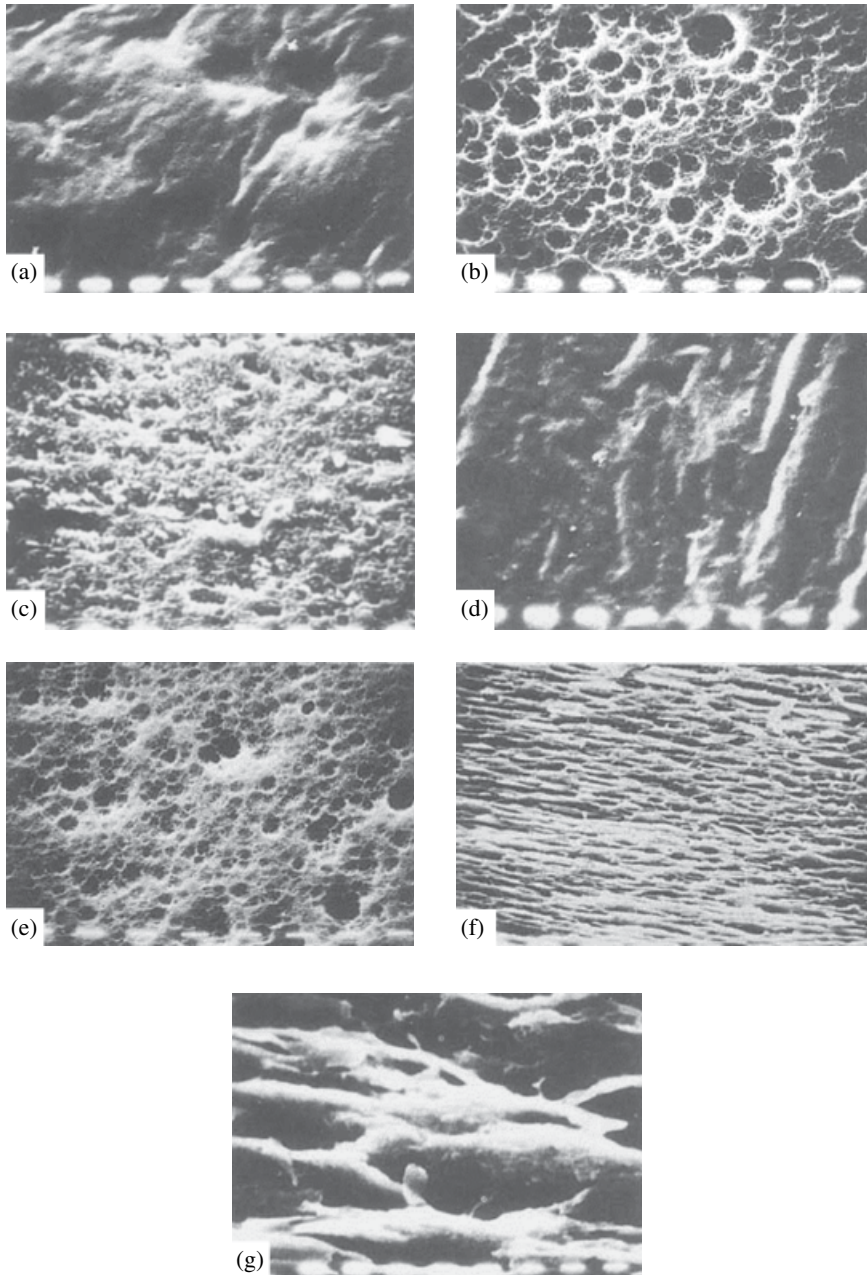


FIGURE 3.5 Scanning electron micrographs of BR/PS FIPNs and semi-IPNs (800 \times). Semi-IPNs, DCP 0.05 phr, DVB 0 wt % (a) 70 : 30, (b) 50 : 50, and (c) 20 : 80. Full-IPNs, DCP 0.05 phr, DVB 5 wt %, (d) 70 : 30, (e) 50 : 50, and (f) 20 : 80. Full-IPNs, DCP 0.05 phr, DVB 5 wt %, (6400 \times) (g) 20 : 80. Source: Ghosh and Ray [8]. Reproduced with permission of Springer

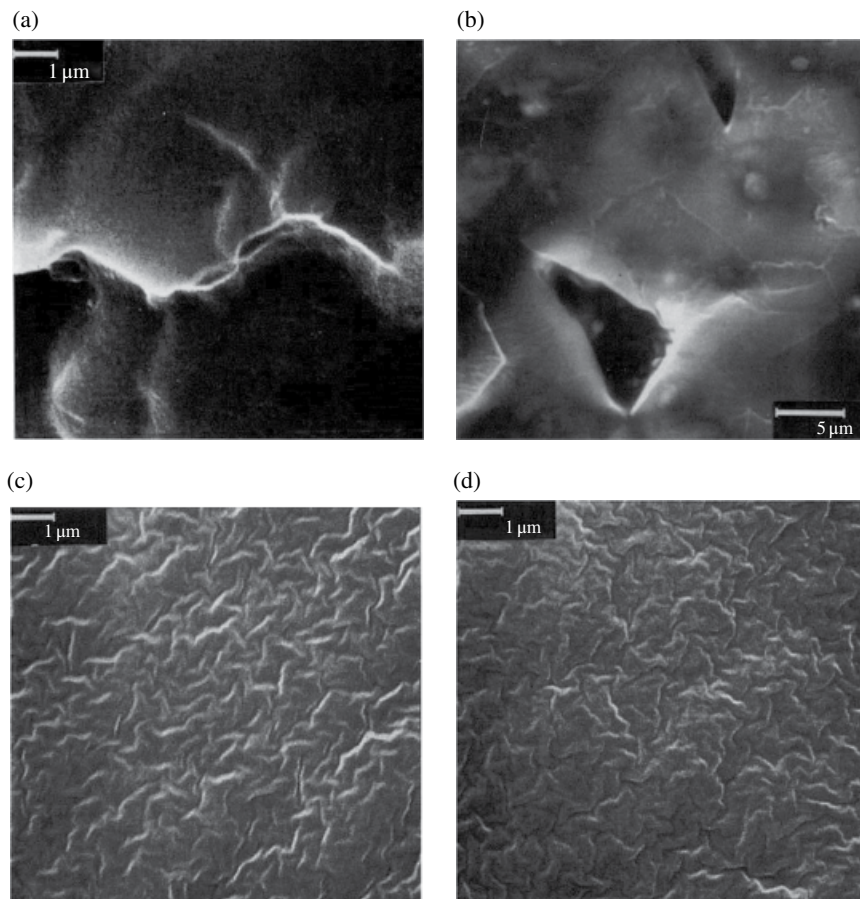


FIGURE 3.6 SEM of CR and pseudo-IPN: (a) CR, (b) IPN-1(CR/BR = 75 : 25), (c) IPN-2 (CR/BR = 50 : 50), and (d) IPN-3 (CR/BR = 25 : 75). Source: Xue, Chen, and Frisch [13]. Reproduced with permission of John Wiley & Sons

toughness, a wider operating temperature range, and excellent resistance to ozone, sun, and general weather conditions [14].

Besides the previously discussed CR/BR semi-IPN [13], Xue and Frisch [15] also prepared CR/poly(carbonate-urethane) (PCU) simultaneous IPN (SIN). In this study, the crosslinking of poly(chloroprene) (CR) use ethylene glycol dimethacrylate (EGDMA) and benzoyl peroxide (BPO) under mild temperature conditions. The effect of composition on the phase morphology of full-IPNs of CR/PCU has been studied by DSC (Figure 3.7) and SEM. The microphase separation of the component networks in the IPNs occurred in samples whose weight percentage of the CR component was 50% and higher.

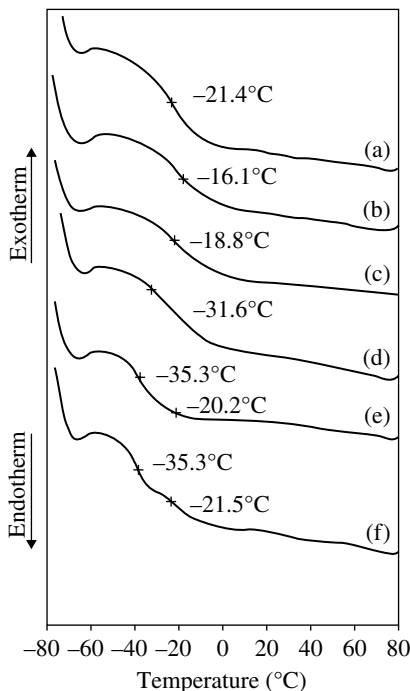


FIGURE 3.7 DSC thermograms of full-IPNs of crosslinked CR/PCU: (a) 15/85, (b) 25/75, (c) 30/70, (d) 40/60, (e) 50/50, and (f) 75/25 wt% composition. Source: Xue and Frisch [15]. Reproduced with permission of John Wiley & Sons

Rajalingam and Radhakrishnan [16] reported on another polychloroprene-based semi-IPN with the formation of castor oil (CO)-based PUs as adhesive. Polychloroprene was the first synthetic elastomer to be used as an adhesive for leather, rubber, and so on. Similarly, thermosetting and thermoplastic PUs are also used as adhesives for these materials. Results showed that the order of peel and shear strength is leather–leather > leather–rubber > rubber–rubber.

Latex IPNs (LIPNs) have been prepared using a crosslinked polychloroprene latex as the seed emulsion, followed by the *in situ* polymerization of styrene, typically with a 10% DVB crosslinker by Burford and Vo [17]. They found that the type of initiator contributed significantly in the morphology development of the LIPNs. For the water-soluble initiator ($K_2S_2O_8$), domain structures predominated for 70/30(Neoprene/XPS), whereas PS-rich shells and domain structures have been found in 60/40(Neoprene/XPS) and lower ratios of Neoprene/XPS. For the oil-soluble initiator (AIBN), larger domain sizes have been found in all cases, with thinner and less continuous shells for the 50/50 ratio. The reason is the different hydrophobic nature of the employed initiators.

Damping materials are an important application for synthetic rubber-based materials. Ping and Wang [18] report the dynamic mechanical and thermal decomposition behavior of CR/polybutyl methacrylate (PBMA) SIPNs. By varying the swelling time in the solution of butyl methacrylate and BPO, CR/PBMA SIPNs with different composition (20, 26, and 44% PBMA) were obtained. The IPNs show broader temperature distribution in loss factor. For IPNs with 44% PBMA, $\tan \delta$ above 0.3 from -49 to 104°C was observed, which indicated an excellent damping property. The thermal decomposition is influenced by the components. Both the decomposition rate and initial decomposition temperature decreased.

3.2.3 Specialty Rubber-Based IPNs

3.2.3.1 NBR-Based IPNs NBR is a synthetic rubber copolymer of acrylonitrile (ACN) and butadiene synthesized by emulsion polymerization technology. Its physical and chemical properties vary depending on the polymer's composition of nitrile; this form of synthetic rubber is generally resistant to oil, fuel, and other chemicals (the more nitrile within the polymer, the higher the resistance to oils but lower the flexibility of the material) but always had problems with ultraviolet light and ozone attack [19]. Therefore, NBR is always used in binding with other polymers to avoid its disadvantages and to modify other polymers with its advantages. NBR-based IPNs are studied by many researchers.

NBR/Polymethacrylate IPNs Polyalkyl methacrylates such as poly(*n*-butyl methacrylate) (PBuMA), poly(ethyl methacrylate) (PEMA), and PMMA are well known for their good mechanical properties, but these have some drawbacks such as poor low-temperature resistance to solvents [20]. They are brittle in nature and they are incompatibly immiscible with synthetic rubbers thermodynamically. Therefore, rubber/polyalkyl methacrylate IPNs are used to conquer their drawbacks.

As early as 1983, Adachi and Kotaka [21] synthesized two types of IPNs consisting of incompatible NBR and PMMA: one was semi-IPNs in which only NBR was crosslinked, and the other was full-IPNs in which both NBR and PMMA were crosslinked. For a full-IPN, the NBR film was allowed to swell in an MMA monomer solution containing 0.1 mol% EGDMA and 1 wt% AIBN as a crosslinking agent and initiator, respectively. After swollen, the film was then heated at 70°C for 180 min to complete the PMMA network formation. Then the IPNs were dried in vacuo at 60°C for 4 days. For the semi-IPN preparation, the procedure was the same as the full-IPN preparation, except that the

MMA monomer mixture contained only 1 wt% AIBN and no EGDMA. Heterogeneous and fairly homogeneous structures containing a continuous NBR phase for semi- and full-IPNs have existed, respectively. The damping properties are especially studied. For the full-IPNs, as the PMMA content increases, the $\tan \delta$ peak of the NBR component shrinks but its position does not change, while another peak nearly 400 K (PMMA) gradually becomes larger and shifts to high temperature. When the content of PMMA is 52%, the value of $\tan \delta$ is almost constant over the temperature range 250–400 K, which shows good damping properties. To explore damping properties of NBR-based IPNs, Patri *et al.* [22] prepared sequential IPNs based on NBR and various types of polyalkyl methacrylates such as PBuMA, PEMA, and PMMA. And the compositions of the IPNs are varied by varying the reaction parameters such as swelling time and concentration of crosslinker. The results showed that the dynamic modulus and loss tangent of the IPNs decrease with increase in bulkiness of the ester group of the acrylates (Table 3.2). In addition, the tensile properties of the IPNs also show similar trend.

Similar to the earlier discussion, Manoj and coworkers [23–25] studied a series of IPNs based on carboxylated nitrile rubber (XNBR) and poly(alkyl methacrylates) such as PMMA, PEMA, and PBuMA. The compositions of the IPNs were varied by changing the swelling time of the rubber in the methacrylate monomer. The IPNs showed broad $\tan \delta$ values as shown in Figures 3.8 and 3.9, which indicates the probable use as vibration and acoustic

TABLE 3.2 Damping Characteristics of NBR/Polyalkyl Methacrylate IPNs

Composition	%TEGDM ^a	$\tan \delta_{\max}$	1/2 Peak Width of $\tan \delta$ Curve (°C)
NBR	—	1.4	15
<i>NBR/PBuMA</i>			
85/15	2	0.61	26.5
80/20	4	0.63	30.0
80/20	6	0.45	30.0
65/35	8	0.43	43.0
<i>NBR/PEMA</i>			
50/50	2	0.46	58.0
50/50	4	0.38	76.0
<i>NBR/PMMA</i>			
70/30	4	0.45	32.0
65/35	6	0.36	57.0
65/35	8	0.34	75.0

Source: Patri *et al.* [22]. Reproduced with permission of John Wiley & Sons

^aTetraethylene glycol dimethacrylate (TEGDM) was used as crosslinker for acrylates during IPN synthesis.

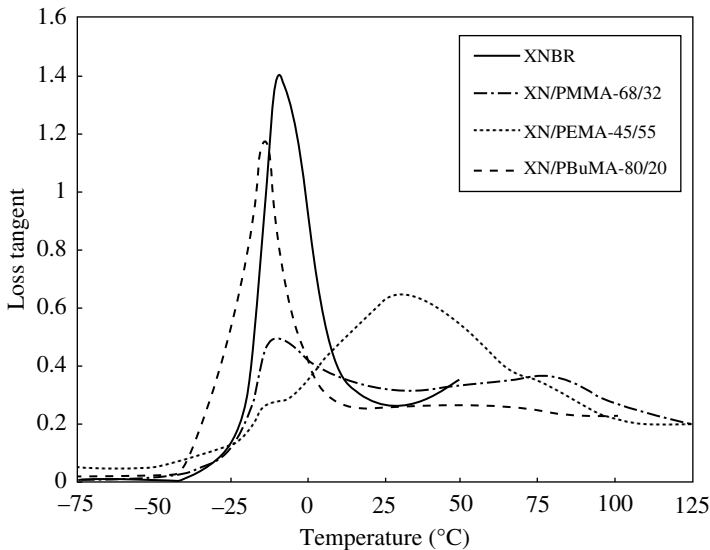


FIGURE 3.8 Plot of loss tangent versus temperature of XNBR and the IPNs. Source: Manoj *et al.* [23]. Reproduced with permission of John Wiley & Sons

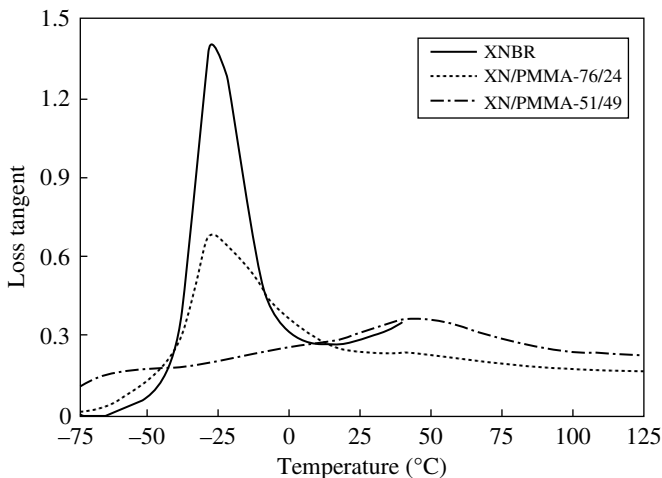


FIGURE 3.9 Plot of loss tangent versus temperature of XNBR and the IPNs. Source: Manoj *et al.* [24]. Reproduced with permission of John Wiley & Sons

dampers. For the superior mechanical properties, especially damping properties, NBR/polyalkyl methacrylate IPNs are extensively studied—some details, for example, morphology (Figure 3.10) of the IPNs—are given by Samui *et al.* [26, 27]. SIPNs of 83/17 and 62/38 compositions (NBR/MMA) show uniform distribution for both phases. For damping properties of poly-methacrylate/NBR IPNs [26–28], similar results were obtained.

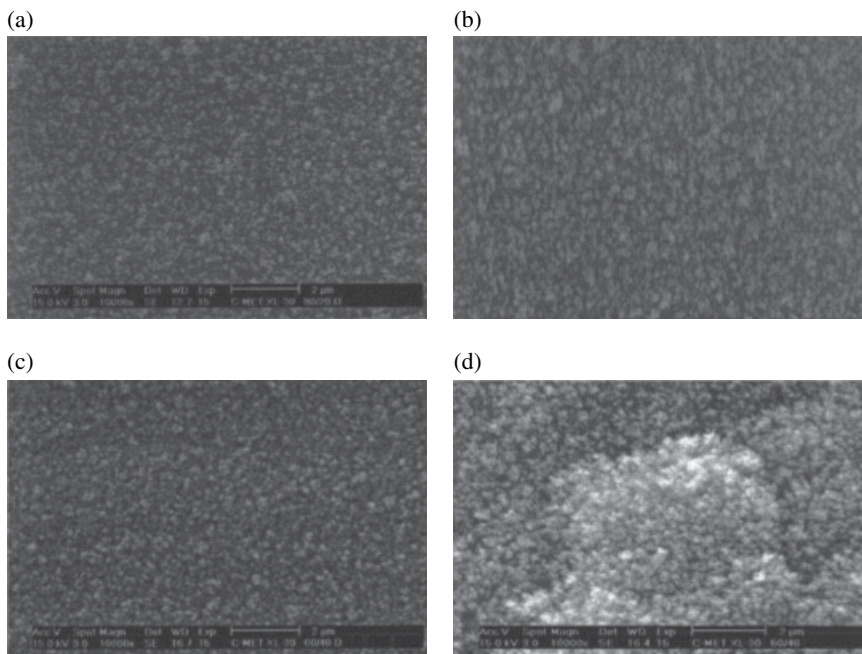


FIGURE 3.10 SEM micrographs of NBR-PMMA IPNs synthesized by single-step (SIPN) and multistep modes: (a) 83/17 SIPN, (b) 82/18 MIPN, (c) 62/38 SIPN, and (d) 62/38 MIPN. Source: Samui *et al.* [26]. Reproduced with permission of John Wiley & Sons

NBR/Fluoroelastomer IPNs Besides the formation of the IPNs with polyalkyl methacrylates, the NBR/fluoroelastomer (FKM) IPNs were prepared by molten blending at a high temperature [29]. Combination of the two highly immiscible polymers (FKM and NBR) by IPN technology might enhance the low-temperature flexibility of FKM and obtain the best compromise in compound process ability and cost. The respective chemical crosslinking of two components occurred in the IPNs. The morphology study shows that dark NBR domains (stained with O_sO_4) exist in the bright continuous phase of FKM when the component ratios are 90/10, 80/20, and 70/30 (w/w) FKM/NBR samples as shown in Figure 3.11. In the case of 70/30 FKM/NBR composition, there exist two transitions at -19 and -23°C , and the value of T_g between -18.5 and -24.5°C (Figure 3.12) shows that the microphase separation of the IPNs between the FKM and NBR phase has existed. This can be the directions for damping material design. The IPNs show better mechanical properties when the two components are in good intermixing. As the NBR content increases, the NBR phase becomes more and more agglomerate and the microphase separation becomes serious. Then the mechanical properties

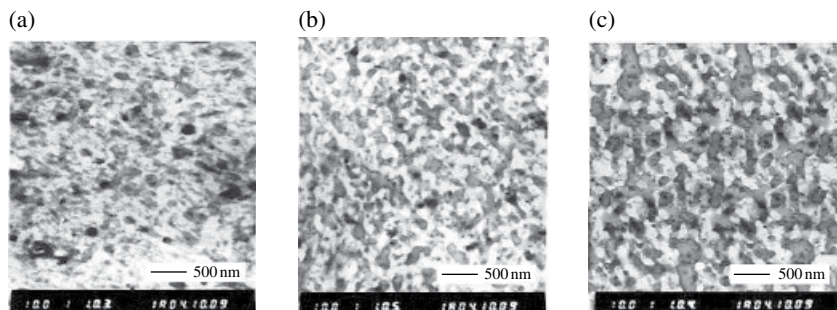


FIGURE 3.11 TEM of different component ratios of FKM/NBR IPNs: (a) 90/10, (b) 80/20, and (c) 70/30 FKM/NBR at magnification of 10000. Source: Chen *et al.* [29]. Reproduced with permission of Springer

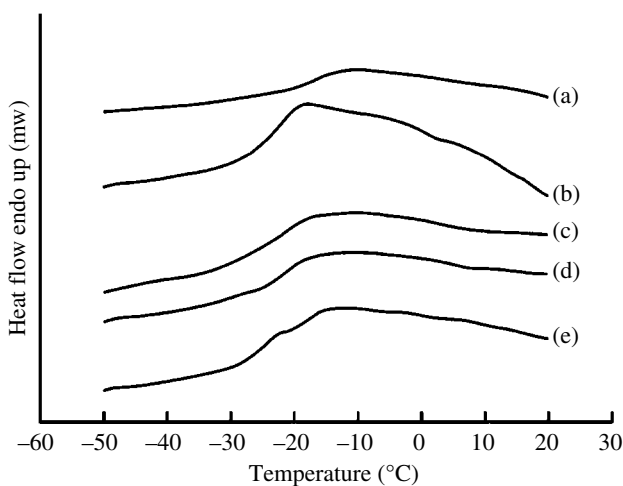


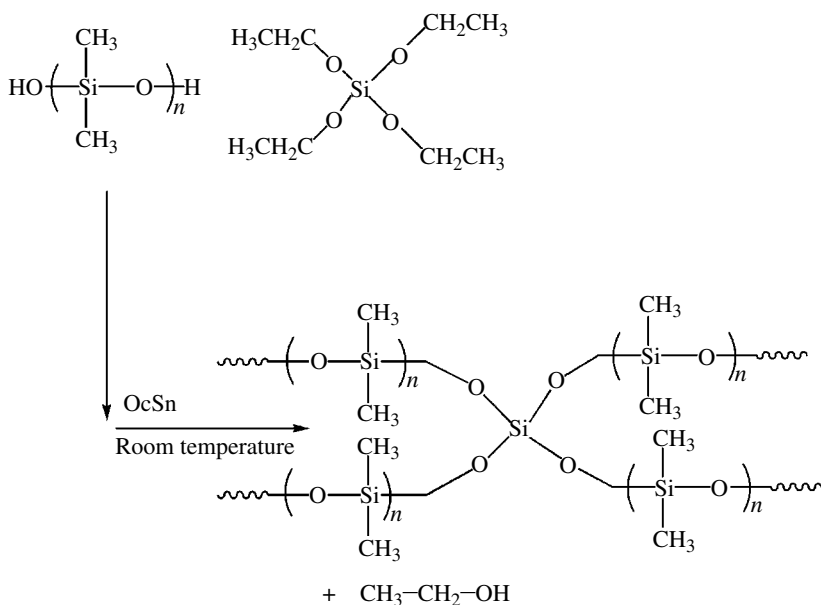
FIGURE 3.12 DSC curves of FKM/NBR IPNs: (a) 100/0, (b) 0/100, (c) 90/10, (d) 80/20, and (e) 70/30 FKM/NBR. Source: Chen *et al.* [29]. Reproduced with permission of Springer

decrease. For all the IPNs, the mechanical properties nearly consistent with the law: under a certain ratios of the component, the mechanical properties attain best and then decrease with the change of microphase separation.

3.2.3.2 Silicone Rubber-Based IPNs Silicone rubber is an elastomer composed of silicone-itself polymer-containing silicon together with carbon, hydrogen, and oxygen that differ from other polymers in that their backbones consist of Si–O–Si units. It has extensively been researched in recent years for their unusual properties such as high thermal and oxidative stability, chemical resistance, excellent dielectric, low glass transition temperature, low surface

energy, high permeability and biocompatibility [30]. It is resistant to temperatures from -55 to $+300^{\circ}\text{C}$, while still maintaining its useful properties. However, their mechanical strengths are rather poor because of nonpolar siloxane bond in the main chain. In order to improve the mechanical strength or to use their advantages effectively, many modifying methods have been found such as interpenetrating with other polymers that are extensively researched.

Silicone Rubber/Poly Methacrylate IPNs He *et al.* [31, 32] synthesized polydimethylsiloxane (PDMS)/PMMA IPNs by *in situ* sequential synthetic method with the following steps. A mixture of α,ω -dihydroxy-PDMS, crosslinker (using tetraethyl orthosilicate (TEOS) to form full-IPNs or using trimethoxysilylpropyl methacrylate (TMSPM) to form graft IPNs) stannous octoate, MMA, 1,1,1-trimethylolpropane trimethacrylate (TRIM), and AIBN was poured into a mold. The ratio $K = [\text{SiOR}]/[-\text{SiOH}]$, where $\text{R} = \text{CH}_3$ or C_2H_5 , which represents the number of alkoxy functions per hydroxyl function, was varied from 1 to 4. The PDMS network was formed first at room temperature (Scheme 3.1). After gelation of the medium, the temperature was raised to 60°C to initiate the copolymerization of the methacrylic monomers. The resulting IPN was cured overnight at 75°C and post-cured under vacuum at 120°C for 3 h. The studies showed that when PDMS networks are prepared in the presence of monomers that are able to undergo radical polymerization,



SCHEME 3.1 The PDMS network formation

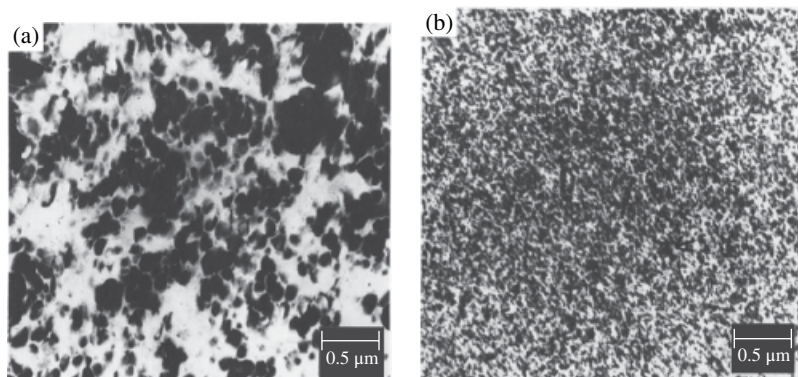


FIGURE 3.13 Transmission electron micrographs ($\Delta E = 165$ eV) of 30/70 PDMS/PMMA IPNs: (a) $M_{n, \text{PDMS}} = 4200$ g mol⁻¹ and (b) $M_{n, \text{PDMS}} = 860$ g mol⁻¹. Source: He *et al.* [32]. Reproduced with permission of Elsevier

deactivation of the catalyst can be avoided either by eliminating oxygen from the reaction medium or by adding a radical inhibitor. Therefore, it becomes possible to synthesize IPNs based on PDMS and vinyl polymers *in situ*. The morphology (Figure 3.13) study showed that the first-formed network (PDMS) constitutes the continuous phase. Increasing the level of crosslinking by decreasing the molar mass of the PDMS precursor leads to more dispersion and reduction of the size of the methacrylic domains. And the formation of PDMS/PMMA IPNs improves the poor mechanical properties of the silicone network. For example, when the PMMA content is 30%, the tensile modulus increases from 2 to 47 MPa, and the tensile strength increases from 0.15 to 3.23 MPa. In addition, the surface properties are PDMS-like, and the gas permeability of these materials remains high.

Latter, Hou and Kuo [33] used linear PMMA as the guest polymer and silicone as the host polymer to prepare a novel PMMA/silicone semi-IPN. The silicone network formed by the self-condensation reaction among the pendant-reactive methoxysilane groups on the polymethylphenylsiloxane (DC3074). PMMA and DC3074 were miscible at any blended ration, but phase separation occurred when the silicone network formed. DSC was used to investigate the T_g of the IPNs (Table 3.3). An inward-shift T_g for the pure component in the blends and a particular broad T_g were observed in the 50/50 blend. The SEM morphology confirms the results shown in Figure 3.14. The crosslinked silicone was transparent and shown to be a uniform morphology (Figure 3.14e). The PMMA/silicone (75/25) and (50/50) blend both exhibited a heterogeneous morphology consisting of dispersed spherical particles that comprise PMMA. In the 50/50 blend, the boundary of the two domains

TABLE 3.3 Glass Transition Temperatures of the PMMA/Silicone IPNs Measured from DSC

PMMA/Silicone	T_{g1} (K) ^a	T_{g2} (K) ^a
100/0	382.1	—
75/25	372.9	329.2
50/50	368.8	327.8
25/75	377.6	326.9
0/100	—	321.9

Source: Hou and Kuo [33]. Reproduced with permission of Elsevier
^a T_{g1} is the glass transition temperature for the PMMA-rich domain and T_{g2} for silicone-rich domain.

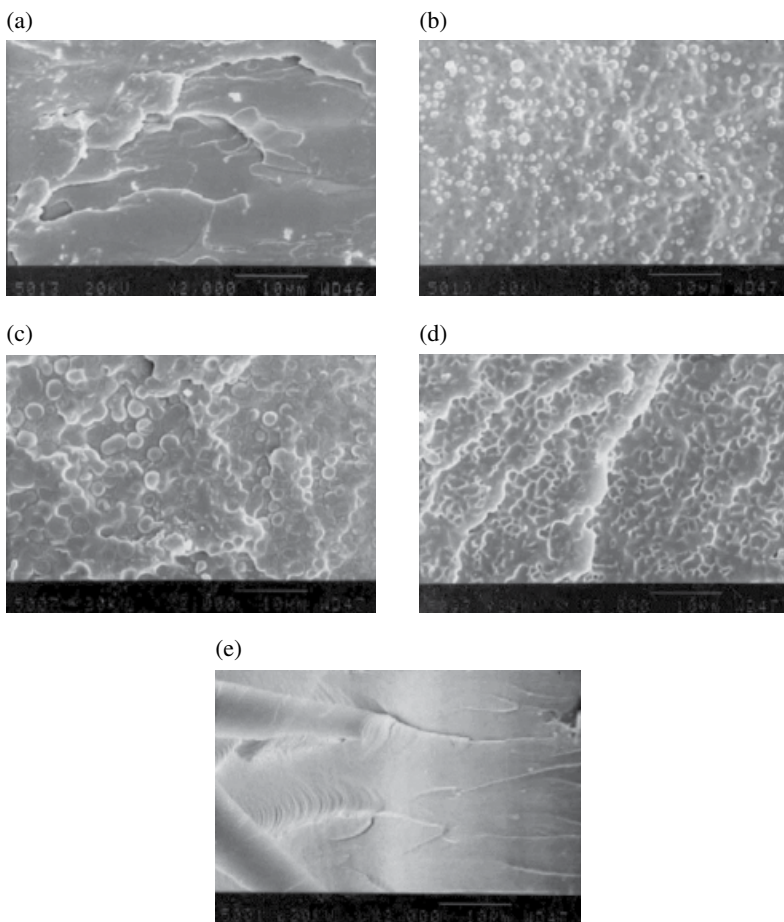
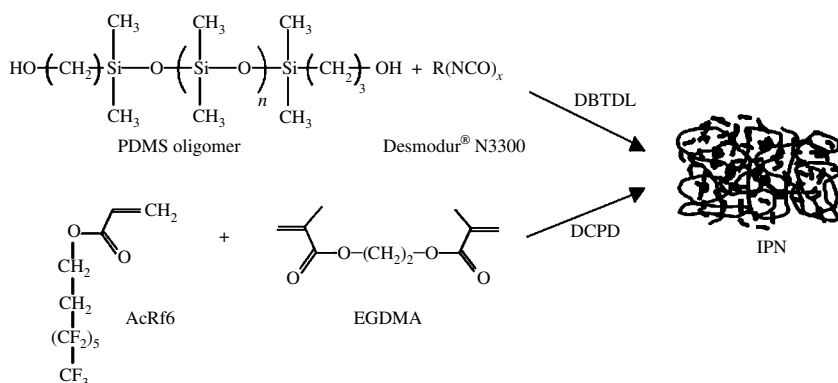


FIGURE 3.14 SEM of micrographs of the fracture surfaces of PMMA/silicone semi-IPN. (a) Pure MMA, (b) 75/25, (c) 50/50, (d) 25/75, and (e) pure crosslinked silicone. Source: Hou and Kuo [33]. Reproduced with permission of Elsevier

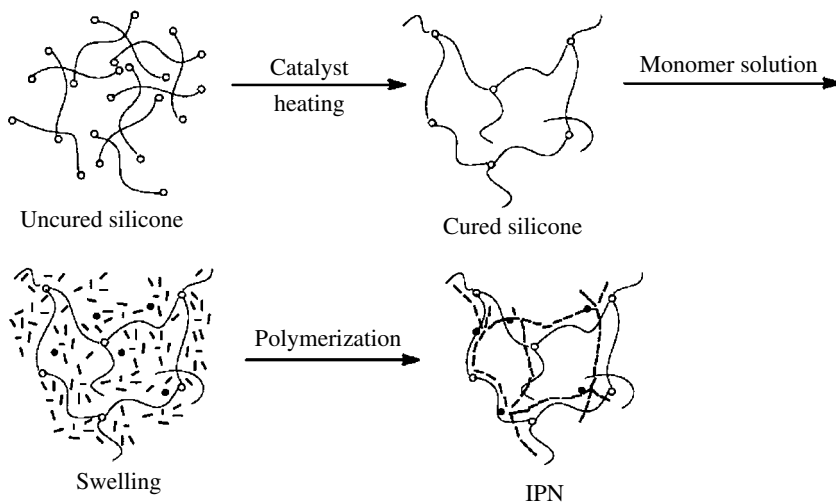
is less distinguishable, which indicated better compatibility of the PMMA and crosslinked silicone network than that of the other ratios.

The polymethacrylates can be modified by special organic functional groups before forming IPNs with the silicone rubber. Darras *et al.* [34] synthesized IPNs based on PDMS and poly(fluorinated acrylate) (polyAcRf6) shown in Scheme 3.2. The IPNs with different relative weight proportions of the fluorinated versus silicone partners were characterized by DMTA. The IPN mechanical relaxations are very broad, which indicated good damping properties of the formed IPNs. Vuillequez *et al.* [35] reported on an IPN combining a PU methacrylate (PUMA) network and a silicone network. The silica's presence increases the thermal stability and surface hardness and T_g decrease with increasing silica content. The facility modification of methacrylate monomer is conducive to the design and improvement of these IPNs.

As state previously, besides the mechanical and thermal properties, damping properties are important properties of synthetic rubber-based IPNs. The damping properties of silicone rubber/polyacrylate IPNs are studied by many researchers [36–38]. Abbasi *et al.* reported the preparation of the IPNs from poly(2-hydroxyethyl methacrylate) (PHEMA) and PDMS by sequential method [36]. The HEMA monomer was polymerized with simultaneous crosslink formation in the presence of the swollen silicone rubber (Scheme 3.3). The study discovered the optimum conditions for the preparation of silicone rubber/PHEMA IPNs that contain about 33% PHEMA. These compositions were reported as an optimum composition in which the obtained biomaterial has a good biocompatibility as well as elastomeric properties. Then, the damping factor ($\tan \delta$) and tensile properties for the PDMS/PHEMA IPNs and their variations with the structural composition were evaluated [37]. The results for the IPNs were compared with corresponding



SCHEME 3.2 Synthesis pathway of PDMS/polyAcRf6 IPNs. Source: Darras *et al.* [34]. Reproduced with permission of Elsevier



SCHEME 3.3 Schematic diagram of the synthesis of silicone rubber/poly(HEMA) sequential IPN. Source: Abbasi, Mirzadeh, and Katbab [36]. Reproduced with permission of John Wiley & Sons

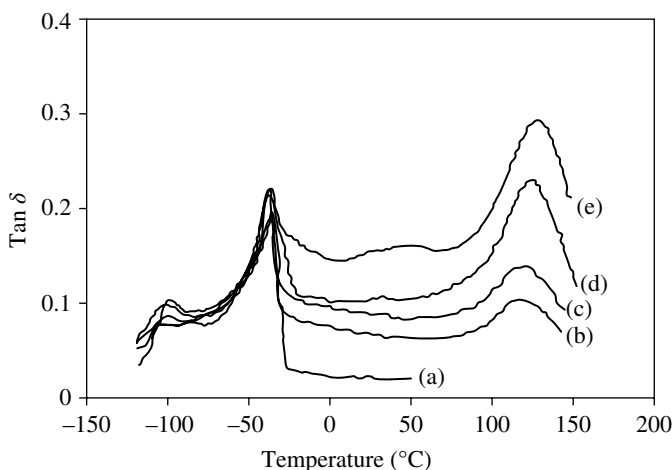


FIGURE 3.15 The $\tan \delta$ versus temperature for the PDMS/PHEMA IPNs having PHEMA contents of (a) 0 wt%, (b) 10.8 wt%, (c) 19.5 wt%, (d) 30.4 wt%, and (e) 38.8 wt%. Source: Abbasi, Mirzadeh, and Katbab [37]. Reproduced with permission of John Wiley & Sons

physically blended systems. As can be seen from the curves (Figure 3.15) of temperature dependence of the $\tan \delta$ for the IPNs (and physical blends) with a large content of PHEMA show a pronounced maximum in the region of α -transition of PHEMA, and for the IPNs with a small content of PHEMA, the

curves show a low and wide maximum (Figure 3.15). The shape of the temperature dependencies of the $\tan \delta$ for both systems is typical for two-phase polymer systems with incompatible components. The investigated systems are two-phase systems, but the shift of the maximum $\tan \delta$ for the PHEMA in the IPN on the temperature scale from its position for pure polymer, as well as its broadening, indicates an incomplete phase separation in the IPN formation. Furthermore, the $\tan \delta$ curve for the IPN having 40 wt% hydrogel content shows another maximum occurring at approximately 50°C. For tensile properties, the IPNs have higher tensile strength and higher elongation at break values than those for physical blends. Wang *et al.* [38] prepared silicone rubber/polyacrylate sequential IPNs by silicone rubber sheet dipped into the solution composed of different acrylate monomers and BPOs for different times at room temperature and then acrylate polymerized at 80°C for 2 h. Similarly results that the loss factor of the IPNs is improved after interpenetrating with polyacrylate ether were obtained.

Silicone Rubber/EP IPNs Kumar and coworkers [39,40] developed a novel siliconized epoxy interpenetrating coating system using EP as base, hydroxyl-terminated polydimethylsiloxane (HTPDMS) as modifier, γ -aminopropyltriethoxysilane (γ -APS) as crosslinking agent, and dibutyltin dilaurate (DBTDL) as catalyst. It is observed that the thermal stability of epoxy coating systems is enhanced when siloxane is incorporated to them, for the siloxane bond energy is significantly greater than those of carbon-carbon and carbon-oxygen bonds. There is a slight decrease in the glass transition temperature observed for silicone-modified epoxy coatings, and all siliconized epoxy coating systems exhibit single glass transition temperature (T_g), which in turn confirms the presence of intercrosslinked network structure. The heterogeneous morphology shown in Figure 3.16 also confirms the existence of intercrosslinking network structure in siliconized epoxy coating systems. The siliconized epoxy coatings can be effectively used as thermal barrier coatings.

Dhoke *et al.* [41] also studied the heat-resistant IPN prepared from epoxy and silicones using a crosslinking agent and a catalyst. For heat-resistant property, the silicone resins withstood up to 533 K, whereas the epoxy coating performed well up to 423 K. But the IPNs remained stable up to 478 K. The heat-resistance property of the EP was improved by the silicone resin through the formation of the IPN. To further enhance the heat-resistance property and other properties of the IPNs, modifiers such as black pigments like graphite, silicon carbide, and carbon black can be used for their shape, size, conducting nature, and heat stability property [42].

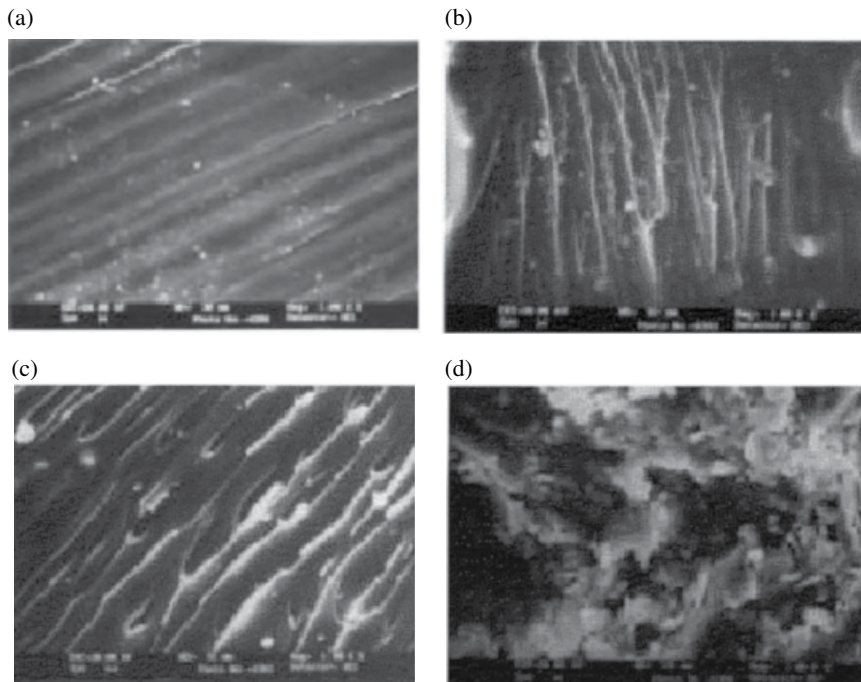


FIGURE 3.16 SEM of micrographs of the fractured surface of the unmodified epoxy (a) and siliconized epoxy coating systems having 5% (b), 10% (c), and 15% (d) siloxane content. Source: Kumar and Narayanan [39]. Reproduced with permission of Elsevier

The Formation of Silicone Rubber-Based IPNs with Other Polymers Miyata *et al.* [43] prepared PDMS/PS IPN membranes by the bulk copolymerization of styrene and DVB in the PDMS networks. All the PDMS/PS IPN membranes had a microphase-separated structure in which PS domains exist in a continuous PDMS phase (Figure 3.17). When an aqueous ethanol solution was permeated through the PDMS/PSt IPN membranes by pervaporation, the PDMS/PS IPN membranes exhibited ethanol permselectivity, regardless of the PDMS content. And the mechanical properties of the PDMS/PS IPN membranes could be improved by the introduction of PS without lowering the ethanol permselectivity of the PDMS membrane. A functional membrane was obtained.

An IPN combining a hydrophobic polymer (PDMS) and a hydrophilic polymer (polyvinylpyrrolidone or PVP) was synthesized in different solvents by Hillerstrom *et al.* [44]. The choice of solvent during polymerization of the IPN was affecting both the wettability and transparency of the PVP/PDMS IPN. The PVP/PDMS IPNs turned hydrophilic in all the solvents used in their study, but the transition from a hydrophobic to a hydrophilic PVP/PDMS IPN

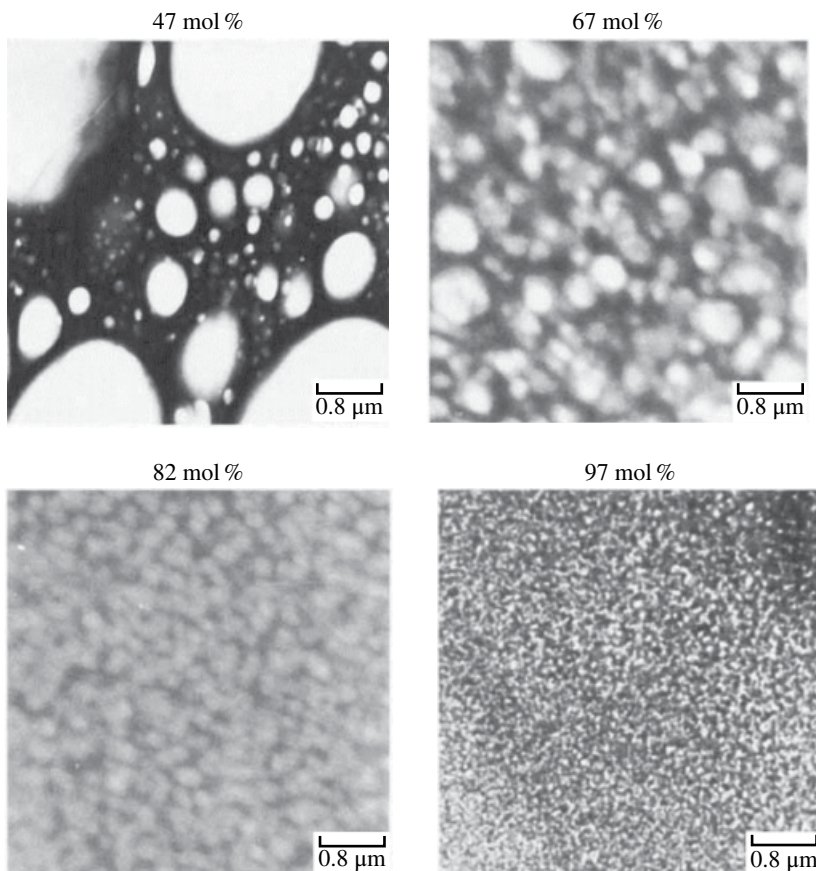


FIGURE 3.17 Transmission electron micrograph of the PDMS/PS IPN membranes with different PDMS contents. Source: Miyata *et al.* [43]. Reproduced with permission of John Wiley & Sons

occurred at lower PVP concentration if a solvent with similar solubility parameter as PVP was chosen. The properties of the PVP/PDMS IPN can be tuned by the selection of the solvent used during polymerization.

Kirubakaran *et al.* [45] reported on high-temperature-resistant IPNs prepared by blending silicone resin polymer with the organic polymers such as polypyrrole (PPy) and polythiophene (PTh). The IPNs with a molar ratio of silicone–PPy/PTh of 0.346 : 0.569 exhibited excellent heat-resistance properties. The thermal stability of silicone–PTh IPN was found to be significantly higher than that of the Silicone–PPy IPN. The atomic force microscopy (AFM) study (Figure 3.18) shows that surface profile of silicone–PTh is much more regular than that of silicone–PPy, indicating that the silicone-containing

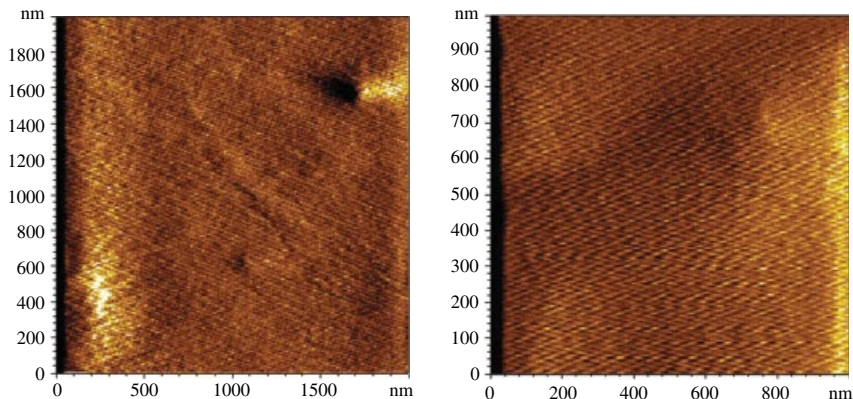


FIGURE 3.18 AFM images of silicone-PPy and silicone-PTh IPN. Source: Kirubaharan *et al.* [45]. Reproduced with permission of John Wiley & Sons

polymer matrices form new hybrid structured polymer systems when compared with the silicone resin. The heterogeneity of silicone-PTh IPN is higher when compared with that of the silicone-PPy IPN. It is the confirmation for the influence of PPy/PTh on silicone polymer to form smooth heterogeneous microstructures.

3.2.3.3 PU-Based IPNs PUs are organic polymers that contain the urethane group in the structure. They are typically made by the reaction of a polyol with a diisocyanate. They are a group of organic polymers that are normally grouped with rubbers. They are flexible and elastic polymers that are widely used in coatings, adhesives, thermoplastic elastomers, and composites. Nevertheless, pure PU has some disadvantages, such as low mechanical strength and poor heat resistance, and its applications in structural materials are thus limited [46]. Like the rubbers mentioned earlier, PUs often are combined with high mechanical plastic polymers such as epoxy, PS, and PMA in blending and especially in IPN form to improve their properties.

PU/EP IPNs EP has been employed in many kinds of structural composites for their high modulus and strength. However, such resins suffer from brittle behavior, which restricts their application in some applications [47]. PU/EP IPNs that integrated the advantages of PU and EP were first reported by Frisch *et al.* in 1974, and then their properties were extensively researched.

Hsieh and Han [48, 49] introduced PU based on poly(butylene adipate) (PU(PBA)) and poly(oxypropylene) (PU(PPG)) polyols into the diglycidyl ether of bisphenol A (DGEBA) (epoxy) to form graft IPNs. The tensile strength in PU(PPG)/epoxy and PU(PBA)/epoxy systems increases with increasing PU

content. Because the IPN formation leads to more intimate interpenetration between the PU and epoxy, the tensile strength increased. Maximum values emerge at PU/epoxy ratios between 19/81 and 27/73. The toughness of epoxy resin can be improved. These graft-IPNs can have a morphology ranging from rubber particles dispersed in the rigid matrix (extensive phase separation) or a more homogeneous solution of PU and epoxy. The impact strength of the IPNs improves much more with homogeneous morphology than that of with the phase-separation system.

Wang and coworkers [47, 50] prepared a series of poly(tetramethylene glycol) (PTMG) and polycaprolactone (PCL)-based PU/EP graft IPNs and their mechanical properties, damping properties, and thermal stability were systematically studied in terms of composition and the value of the PU isocyanate index (R). For PU(PTMG)/EP IPNs [51], when PU(PTMG) was incorporated, the tensile strength decreased, but the elongation of the IPN increased with increasing PU content. With the value of PU isocyanate index increasing, the tensile strength was improved while the elongation was impaired. The impact strength of the IPNs was relatively good when the IPN is formed. The research highlight is the damping properties. The damping properties of the EP matrix can be improved by forming a graft IPN with PU(PTMG). The damping temperature range became broader and the glass transition temperature T_g became lower with the increase of PU content (Figure 3.19), and the maximum value of $\tan \delta$ increased with the increase of the value of the isocyanate (Figure 3.20). Investigation of the morphologies revealed that a heterogeneous microstructure existed in the PU (PTMG)/EP IPNs. And, the microstructure became more heterogeneous with the increase

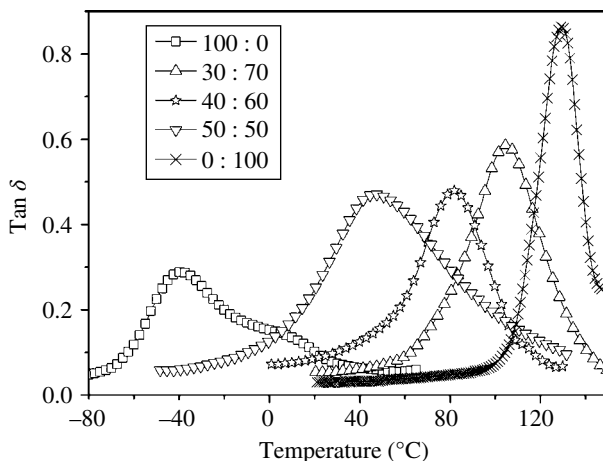


FIGURE 3.19 DMA traces of PU/EP IPNs with different component ratios at 10 Hz ($R = 2$). Source: Wang *et al.* [47]. Reproduced with permission of Springer

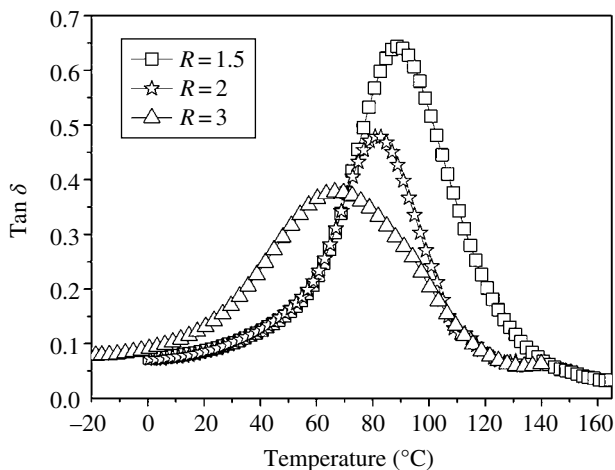


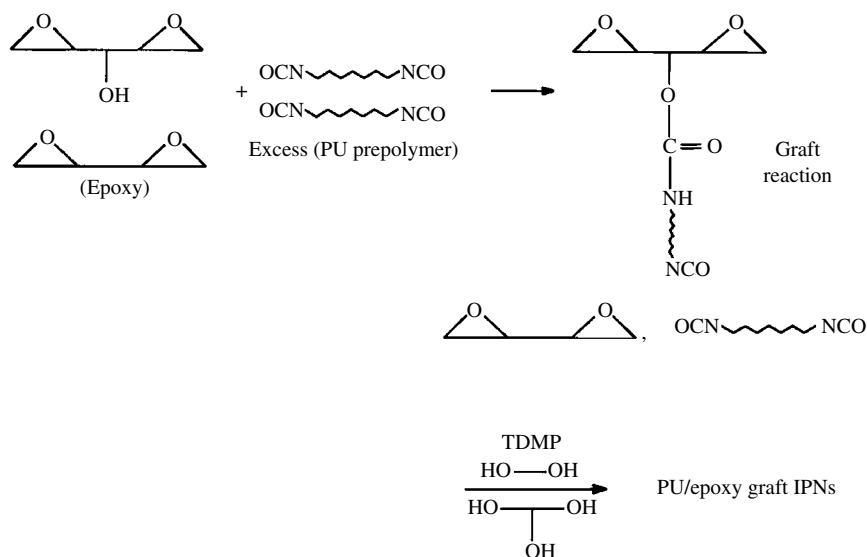
FIGURE 3.20 DMA traces of 40 : 60 PU/EP IPNs with different values of isocyanate index at 10 Hz. Source: Wang *et al.* [47]. Reproduced with permission of Springer

of PU content, which was the elucidation of the variation of the properties of the PU/EP IPNs. The formation of PU (PCL)/EP IPNs showed similar results in mechanical properties and better damping properties because the more hydrogen bonds exist in them [50].

The mechanical, thermal, and damping properties of poly diols-based PU/EP IPNs were also studied by Chen *et al.* [52], Bakar *et al.* [51], Cristea *et al.* [53], and others. The overall performance of the materials is improved when the IPNs are formed. Besides the poly diol-based PU rubbers, the poly triol-based PU rubbers are studied especially the CO-based PU and the PU(CO)/EP IPNs. CO is one of the more widely used natural products in the polymer field. It contains hydroxyl groups as well as carbon–carbon double bonds: it is especially well suited to a wide range of chemical modifications [54]. The PUs obtained from CO are typically water resistant and flexible due to the presence of a long fatty acid chain and lend themselves to thermosetting-type structures due to their trifunctional nature [55].

Raymond and Bui [2] prepared graft IPNs from DGEBA cured with 1.5% 2,4,6-tris(dimethylaminomethyl) phenol (DMP-30) and CO cured with 2,4-toluene diisocyanate (TDI) at NCO/OH = 1.50, following a sequential method (Scheme 3.4). Good interpenetration existed between the two networks and some degree of grafting existed between the two phases. Therefore, graft IPNs of 20% PU provided better heat resistance than that of cured epoxy as well as large synergistic effects on the tensile properties. However, their impact energy obtained from instrumented impact testing did not show much

enhancement except for a narrow PU composition gap between 25 and 30%. Similar mechanical results were obtained by Chen *et al.* [56], and the damping properties of the IPNs were further studied extensively. The damping properties of EP matrix can be improved by forming graft IPNs with PU. With the increase of the PU content, the damping properties of the IPNs increased, whereas the glass transition temperature decreased (Figure 3.21). Further, the



SCHEME 3.4 Scheme of the grafting process between epoxy and PU prepolymer. Source: Raymond and Bui [2]. Reproduced with permission of John Wiley & Sons

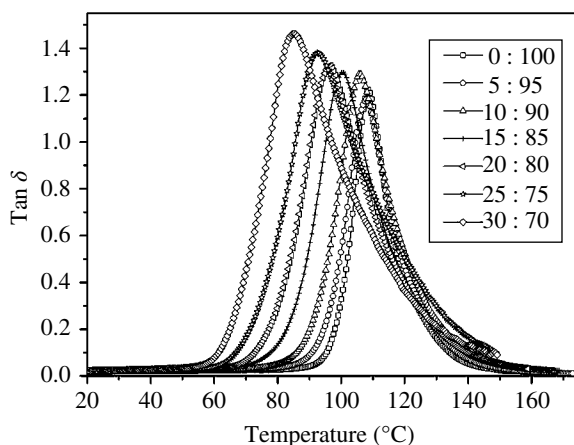


FIGURE 3.21 DMA curves of PU/EP IPNs with component ratios from 0 : 100 to 30 : 70 at 10Hz. Source: Chen *et al.* [56]. Reproduced with permission of John Wiley & Sons

damping properties can be improved by modifiers—both organic [57, 58] and inorganic [59]. In addition, the PU/EP IPN composites showed better damping properties under higher frequencies.

PU/PS IPNs As early as 1975, Kim *et al.* [60] prepared the SIN-type IPNs composed of a PS network (crosslinked with DVB) and a PCL glycol-PU network (crosslinked with trimethylolpropane (TMP)). Phase separation was observed in PU/PS IPNs due to the incompatibility of each network. The continuous phase is PS at PU compositions of less than 75%. Enhanced tensile strength was observed because of the reinforcing effect of the rigid dispersed phase and the effect of increased permanent chain entanglement due to interpenetration. Valero *et al.* [55] also prepared the SIN from pentaerythritol-modified CO-based PU and PS. Due to permanent chain entanglements, a maximum in mechanical properties was observed at around 20% of PS (Figure 3.22). At concentrations above the 20% PS content, phase separation occurred, which presents a broad glass transition temperature area. Compositions (90% PU/10% PS) that are rich in PU show a continuous matrix with dispersed PS. Intermediate compositions (60% PU/40% PS) show signs of the existence of two continuous phases (Figure 3.23).

Gomza *et al.* [61] synthesized PU/PS sequential semi-IPNs (SIPNs) based on network PUs with various M_c (the molecular masses of chain segments between crosslinks) values and the linear PS. The network PU was synthesized from poly(oxypropylene glycol) (POPG) with $M = 500$ (PU-500), 1000 (PU-1000), or 2000 (PU-2000), triisocyanate adduct of TDI, and TMP in butyl acetate at 60°C. Then, the PU network was allowed to swell to equilibrium in a monomer (styrene) containing the dissolved radical initiator (AIBN), and then polymerization was carried out at 60°C. The structural features of them were studied by DSC and small-angle X-ray scattering. The studied SIPNs are composed of microregions of two basic types. The first type includes microregions, which conserve the features of the microphase-separated structure of PU, and the second type involves domains enriched in PS. Further, with an increase in the M_c of the PU constituent (the PU-2000-PS SIPN), the interference maximum appears. The research is beneficial for understanding of the microstructure of PU/PS SIPNs.

PU/Polymethacrylate IPNs For complementary properties of polymethacrylates with polyurethane and as incompatible pair, the combination of polyurethane and poly methacrylates with IPN technology has become a research focus in the IPN study. Xiao *et al.* [62] prepared two types of IPNs by simultaneous polymerization. The first type consisted of PU(PTMG)/PMMA, and the second one consisted of PU/poly(methyl methacrylate-*co*-methacrylic

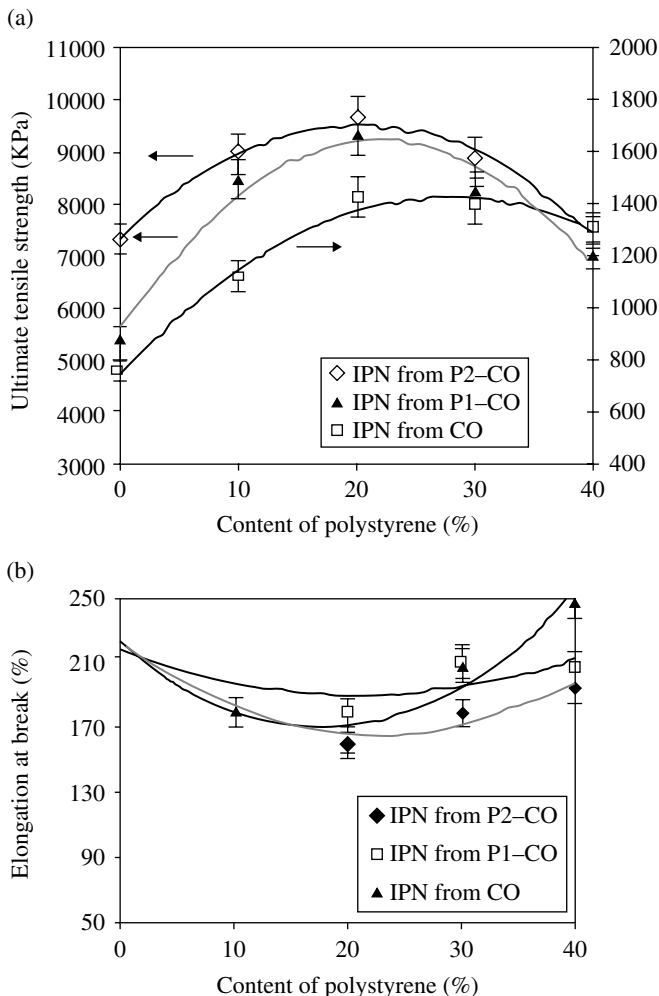


FIGURE 3.22 Mechanical properties of IPNs. (a) Ultimate tensile strength and (b) elongation % at break (P1-CO (molar ratio pentaerythritol/ castor oil=0.2), P2[0.4]). Source: Valero *et al.* [55]. Reproduced with permission of Springer

acid) (P(MMA-MAA)) of constant composition (90/10) and (80/20) by weight, respectively. The mechanical properties, particularly the modulus of both types of IPN, increase with increasing NCO/OH ratio and decrease with increasing MW of the polyol in the PU. Phase compatibility improves and phase separation decrease in both types of IPN with increasing NCO/OH ratio and decreasing MW of the polyol used in the PU. Increasing the NCO/OH ratio and decreasing the MW of the polyol in the PU component could improve the interpenetration which is the explanation for the results.

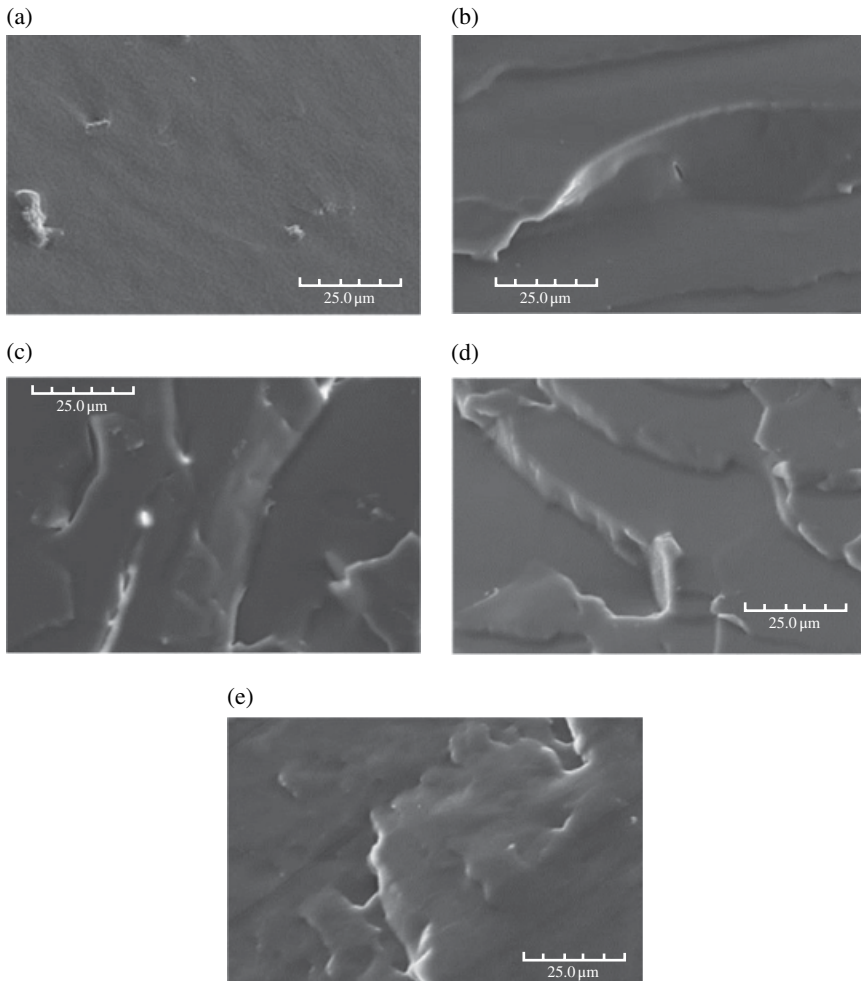


FIGURE 3.23 SEM of SIN-P1-CO, with various levels of PS at NCO/OH = 1: (a) PS0PU100, (b) PS10PU90, (c) PS20PU80, (d) PS30PU70, and (e) PS40PU60. Source: Valero *et al.* [55]. Reproduced with permission of Springer

Akay and Rollins [63] evaluated the damping properties of a variety of simultaneous and sequential IPNs based on a PU(POPG) network and PMMA in linear and network forms. The IPNs produced broad transitions of various types depending on the composition shown in Figures 3.24. The plots clearly show that at the extreme IPN compositions, that is PU/PMMA ratios of 80/20 and 20/80, single relatively sharp $\tan \delta$ curves were obtained and at the intermediate IPN compositions broad $\tan \delta$ curves were obtained. The elastic modulus, hardness and the tensile strength of the IPNs increase with increasing

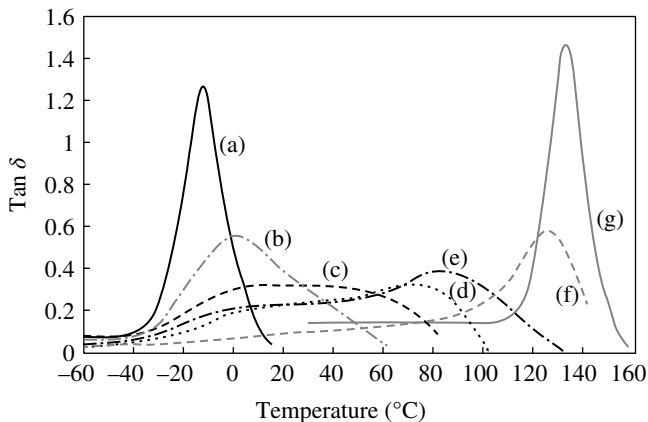


FIGURE 3.24 Dynamic mechanical properties for simultaneous full-IPNs with PU/PMMA compositions: (a) 100/0, (b) 80/20, (c) 70/30, (d) 60/40, (e) 50/50, (f) 20/80, and (g) 0/100. Source: Akay and Rollins [63]. Reproduced with permission of Elsevier

PMMA content. The distribution of the component polymers in the IPNs appears to be more homogeneous than in the sequential IPNs.

Kong *et al.* [64, 65] prepared semi- and full-IPNs using PU produced from a canola oil-based polyol with primary terminal functional groups and PMMA. For both types of IPNs, the reaction rates increase with the increases of PU content. With the same components, the reaction rates of full IPNs are faster than those of semi-IPNs. Both types of IPNs show two-phase systems with incomplete phase separation. However, the process of phase separation is more developed in the semi-IPNs compared with the full-IPNs as full-IPNs exhibit better compatibility because of the enhanced interpenetration shown in Figure 3.25. The original PMMA was rather brittle, and the PU was rubbery but fairly weak, while the mechanical properties of the IPNs are superior to those of its constituent polymers. The combination of PU with PMMA is useful in extending the elastomeric properties of PU and mitigating the brittleness of PMMA.

The Formation of PU-Based IPNs with Other Polymers The PU either can form IPNs with many other polymers including other synthetic rubbers to improve their properties such as PU/poly(cis-1,4-polyisoprene) IPNs [9], and CO-based PU/CR IPNs [16] in the preceding narrative. In addition, Parthiban *et al.* [66] prepared semi-IPNs using CO-based PU and chlorinated rubber. The toughness of chlorinated rubber can be improved by interpenetrating it with CO-based PU. These systems may be used in the coating industry, and

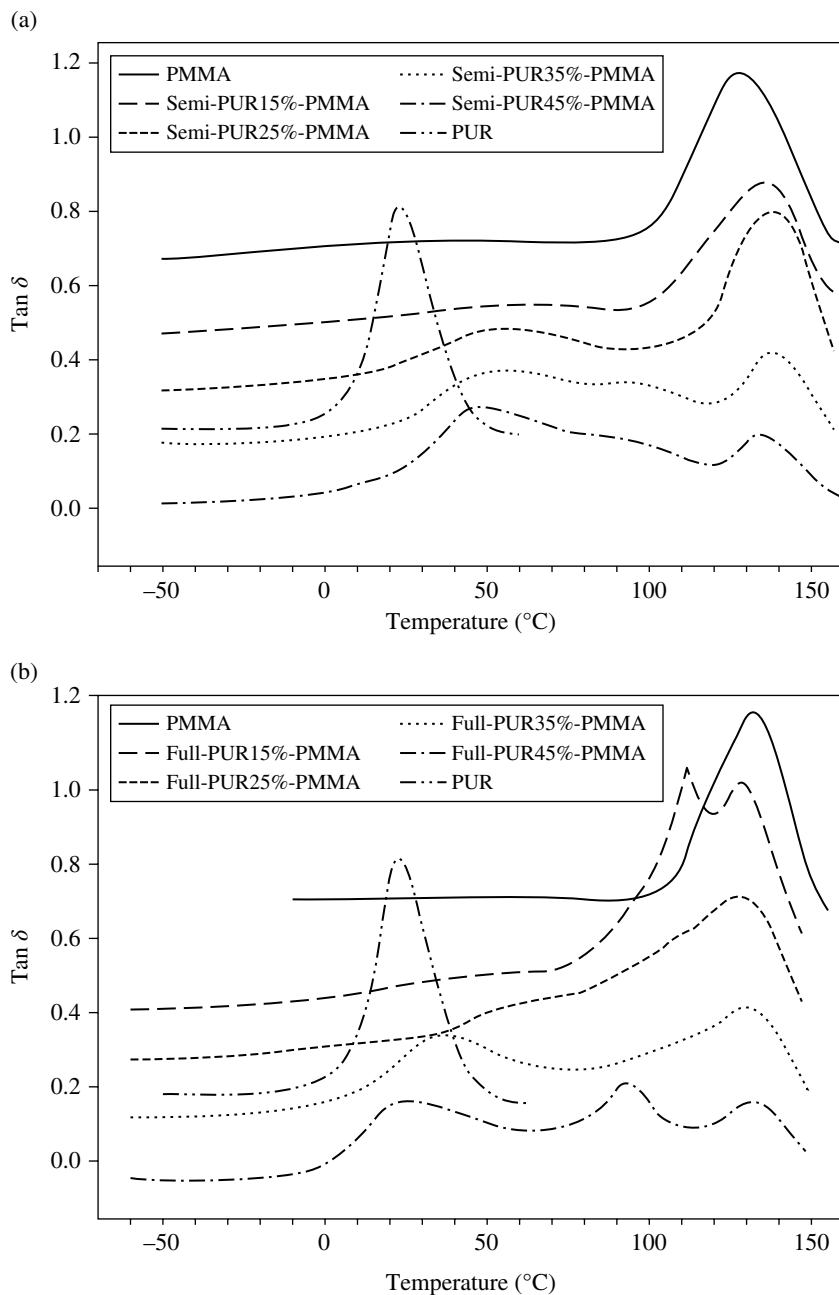


FIGURE 3.25 The dependences of $\tan \delta$ on temperature for IPNs with different PU content (a) semi-IPNs and (b) full-IPNs. Source: Kong, Tan, and Narine [65]. Reproduced with permission of John Wiley & Sons

further the flame resistance of the PUs would be improved by the presence of chlorinated rubber. Semi-IPNs of acrylamide-based PUs were synthesized from different NCO-terminated polyurethane prepolymers derived from PTMG by Merlin and Sivasankar [67]. The IPNs showed better thermal stability, compatibility, tensile, and elongation properties compared to the individual polyacrylamide network.

3.3 SUMMARY AND CONCLUSIONS

The IPNs prepared from commonly used synthetic rubbers such as SBR, BR, CR, NBR, silicone rubber, PU, and so on, and other rigid plastic polymers (high mechanical strength but brittle) such as PS, PMMA, EP, and so on, represent one of the fastest-growing fields in polymer science. The morphology, phase separation, mechanical properties, damping properties, thermal properties, and other properties of the IPNs are extensively researched. Synthetic rubbers usually are incompatible pairs with rigid plastic polymers. The IPN technology can combine them together with intimate interpenetration. The toughness of rigid plastic polymers can be attained by the intimate interpenetration. In contrast, the strength of the rubber improves. Thus, the strength of the IPNs is better than the individual rubber networks, and the toughness of the IPNs is better than the individual rigid polymer networks. Varying degrees of phase separation will occur resulting in a two-phase polymer system according to the nature and composition of component polymers. They can have a morphology ranging from rubber particles dispersed in the rigid matrix (extensive phase separation) or a more homogeneous solution. The impact strength of the IPNs improves much more with homogeneous morphology than that of with the phase-separation system. However, the broad glass transition region comes from the micro heterogeneous phase separation. Proper phase separation in the IPNs leads to good damping properties. The synthetic rubber-based IPNs conquer many drawbacks of the rubbers and exhibit better overall mechanical, thermal, and damping properties, which can be used in many applications. However, the research about many synthetic rubbers needs further study, for example, the IPNs prepared from the rubbers IR, EPDM, IIR, and FKM that also have excellent properties, are scarcely reported. Moreover, the morphology control, damping optimization, and so on for specific applications when the IPNs are formed should be further studied. The research of synthetic rubber-based IPNs will continue to receive attention from both academia and industry.

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