

Polysiloxane–Thermoplastic Interpenetrating Polymer Networks

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Polysiloxane–thermoplastic interpenetrating polymer networks (IPNs) are a unique class of polymer–polymer composites that significantly extend the process and mechanical property range of silicone elastomers and allow modification of the behavior of thermoplastics. The materials are characterized by reactive processing consistent with traditional thermoplastic technology and the development of physical properties consistent with semi-IPNs generated from polysiloxanes cross-linked in a variety of thermoplastic matrices, including polyurethanes, polyamides, and polyolefins. The semi-IPNs are prepared by melt-mixing hydride- and vinyl-functionalized polysiloxanes with thermoplastics and inducing cross-linking with a platinum catalyst in a second melt-process step. Polysiloxane composition, cross-link density, and total content affect the process and mechanical behavior of the semi-IPNs. Polysiloxane–thermoplastic IPNs may be used in biomedical materials, gears and bearings, and applications in which the dimensional stability of crystalline resins must be enhanced.

INTERPENETRATING POLYMER NETWORKS (IPNs) are a special class of polymer blends in which the polymers exist in networks that are formed when at least one of the polymers is synthesized or cross-linked in the presence of the other. Classical or true IPNs are based solely on thermosetting polymers that form chemical cross-links. More recently, two classes of thermoplastic IPNs have been developed. *Apparent IPNs* are based on combinations of physically cross-linked polymers. *Semi-IPNs* are based on combinations of

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cross-linkable and nonreactive linear polymers. Polysiloxane (silicone) interpenetrating polymer networks have had a significant role in the development of thermoplastic semi-IPNs.

The first attempts to commercialize thermoplastic IPNs were based on apparent-IPN technology. In contrast to the true IPNs or semi-IPNs, in which the cross-links that stabilize the polymer networks are chemical (i.e., covalent bonds), the apparent IPNs are stabilized by physical or virtual bonds (i.e., glassy regions of block copolymers, ionic domains of ionomers, or crystalline regions in semicrystalline polymers). A series of apparent IPNs of styrene-ethylene-butylene-styrene (SEBS) block copolymers and crystalline thermoplastics (polyamides and polyesters), offered by the Shell Chemical Company, was developed by Davison and Gergen (1, 2). These normally incompatible resins have been blended in combination with polypropylene or mineral oil to form co-continuous, interpenetrating phases. The IPN structure is stabilized by the physical cross-links in the styrene end blocks of the copolymers and the crystalline regions of the thermoplastic resin. The polymer networks prevent gross phase separation and lead to extended load sharing between the polymer phases. Thermoplastic ionic IPNs have also been reported (3).

The semi-IPNs are intermediate systems in which a thermosetting polymer network is formed within a thermoplastic polymer; the coexisting structures are stabilized by physical cross-links in the thermoplastic phase. Wertz and Prevorsek (4, 5) have used dicyanatotobisphenol A as a thermosetting monomer that is first mixed in the melt state with a thermoplastic matrix resin and later cross-linked during injection molding to develop resins offered by Allied-Signal Corporation. Silicone-thermoplastic semi-IPNs (Rimplast) (6, 7) are formed by a similar reaction-molding process, but the thermosetting polymer network is formed by the addition of functionalized silicone oligomers that have been predispersed in a thermoplastic resin.

The different chemical structures of thermoset true IPNs and thermoplastic apparent and semi-IPNs can be represented conceptually as line drawings (Figures 1-3). True IPNs consisting of two, totally continuous, interlocking networks are shown in Figure 1A. Figure 1B is a geometrical abstraction of a true IPN. Neither phase can be extracted from the IPN. The semi- or pseudo-IPNs represented in Figure 2 consist of one chemically cross-linked phase within a linear thermoplastic polymer matrix. The thermoset phase cannot be extracted from the IPN. Physical cross-links in the crystalline regions of the linear thermoplastic are reversibly broken at elevated temperatures, and these breaks allow the materials to flow. Figure 3 depicts the physical cross-links of the styrene end blocks of the structured SEBS rubber as circles. Because there are no chemical cross-links in the apparent IPNs, either resin phase can be extracted independently.

The preservation of thermoplastic character in the semi-IPNs is of great commercial value. The requirements of thermoplastic processing demand

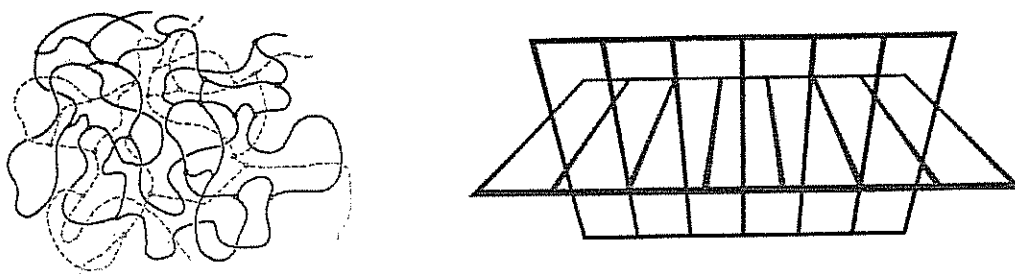


Figure 1. True IPNs. The different polymer systems are cross-linked to themselves but not to each other. The polymers thus form networks that interpenetrate each other. (A) Traditional three-dimensional depiction; (B) geometrical abstraction, in which the cross-links are depicted as junctions of vertical and horizontal lines.

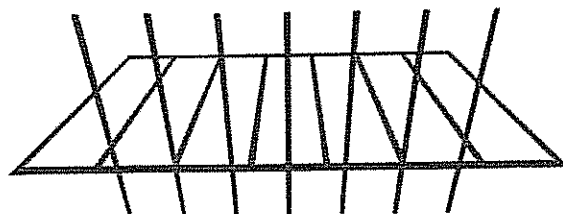


Figure 2. A semi-IPN. Only one polymer is cross-linked. The other thermoplastic polymer is so long that the polymers cannot disentangle.

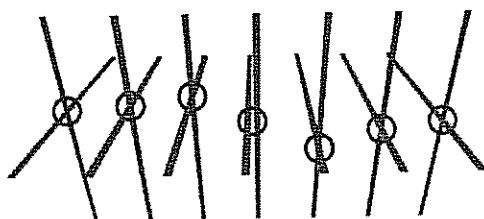


Figure 3. An apparent IPN. None of the polymers is cross-linked, but a third polymeric component, which is compatible with the other two polymers and is usually a block copolymer, holds the system together.

homogeneous rheology. At the same time, requirements for network formation, that is, the development of distinct domains, demand heterogeneous morphology. In many ways, the balance between the two requirements, homogeneous rheology and heterogeneous morphology, defines the synthetic challenge and performance parameters of the thermoplastic IPNs.

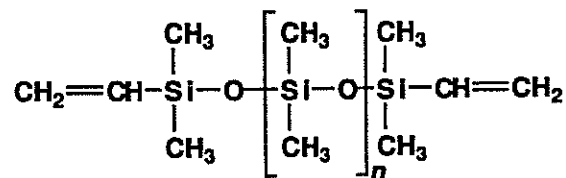
Although chemical structures are used to classify IPNs, the morphology of a polyblend defines it as an interpenetrating polymer network. The net-

work structure imposes compatibility between otherwise incompatible resins; this compatibility allows the expression of both components. However, molecular interpenetration of the two phases in the network can lead to composite properties that are not anticipated. The properties of an IPN are not strictly additive functions of component properties; phase morphology and phase interactions that promote interfacial bonding can lead to unexpected increases in impact strength, modulus, and heat deflection temperatures. Many of these changes can be associated with changes in crystallinity.

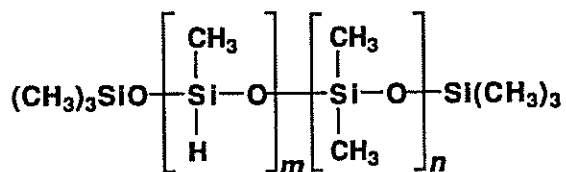
Silicone-Thermoplastic Semi-IPNs

Chemistry and Processing. The silicone-thermoplastic semi-IPNs have two indirect antecedents: the full IPN silicone-urethane systems reported by Frisch (8) and Hourston (9), which are not amenable to thermoplastic processing, and semi-IPNs of cross-linked silicone in a silicone fluid matrix, which are used in prosthetic gels (10) and for which homogeneous morphology precludes the development of enhanced mechanical properties. In silicone-thermoplastic semi-IPNs, hydride- and vinyl-functionalized silicone fluids are intimately blended in the melt state with a thermoplastic resin. Examples of the silicones are given in structures 1-4. No reaction takes place among the fluids during this extrusion step. A catalyst is then applied topically to the resin-blend pellets. When the pellets are remelted in a forming process (e.g., profile extrusion or injection molding), the heat-activated catalyst mixes with the vinyl- and hydride-functionalized silicone fluids and initiates a vinyl-addition (hydrosilylation) reaction, and a high-molecular-weight cross-linked siloxane network is developed in the finished part (Figure 4).

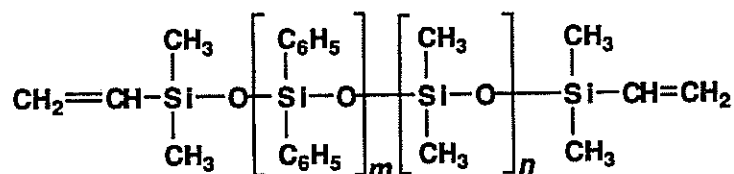
The addition polymerization of silicone-thermoplastic semi-IPNs is ideal



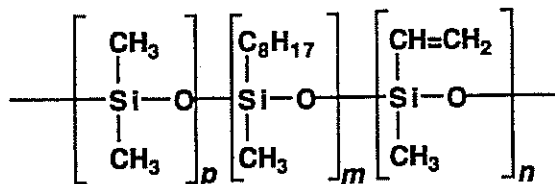
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4

for a continuous reaction-molding or extrusion process. Although the reaction is initiated in the melt at elevated temperature, it will proceed in the solid state. The reaction is fast and will proceed to completion, and no chemical byproducts are formed. Conventional thermoplastic injection-molding machines or extruders can be used in forming the IPNs; no special devolatilization is needed. The rheology of a typical system is shown in three stages (Figure 5): unmodified base polymer, base polymer-silicone polyblend, and silicone semi-IPN. In general, the melt viscosity of the base polymer-silicone polyblend is lower than that of the basic polymer and that of the developed semi-IPN.

A silicone semi-IPN modified thermoplastic urethane illustrates this technology. The following composition is mixed in the melt state by pumping a preblend of the silicones into a counter-rotating twin-screw extruder with

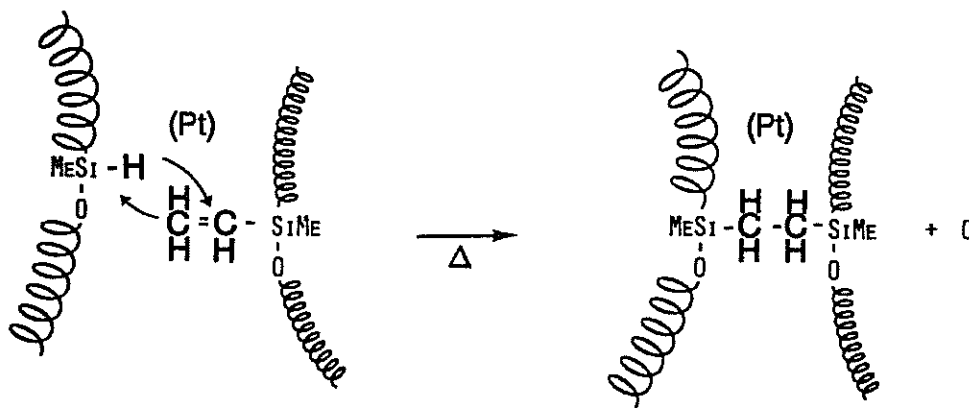


Figure 4. Addition vulcanization of polymer.

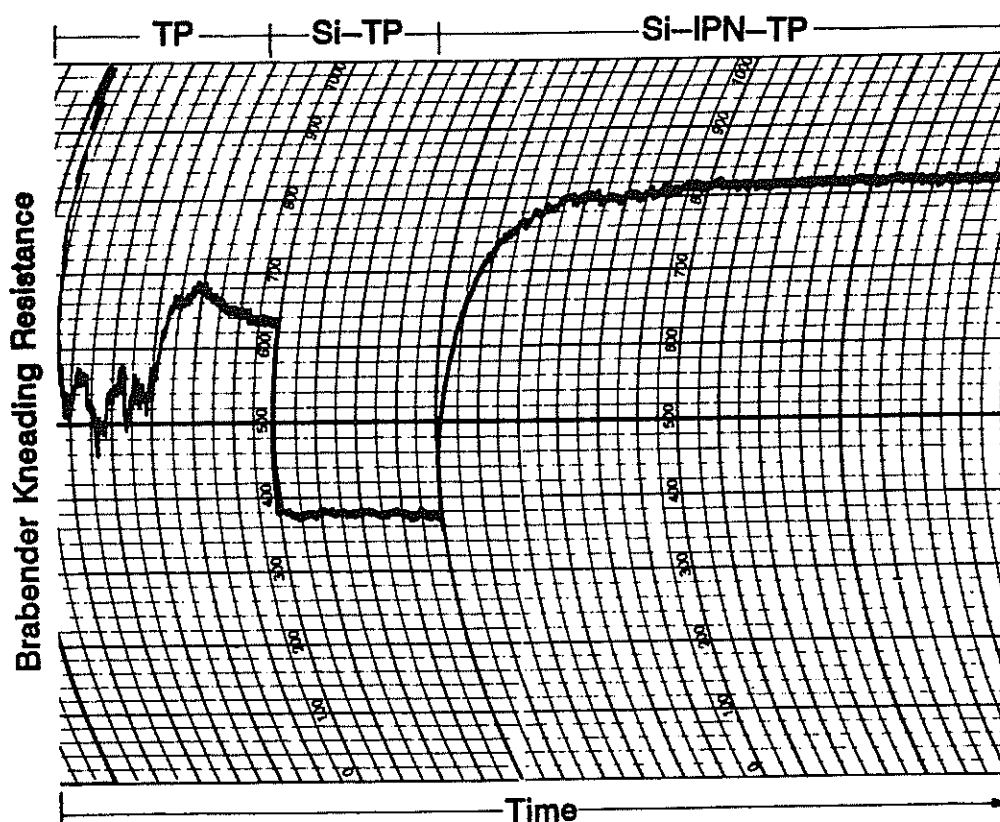


Figure 5. Typical changes in rheology accompanying the transition from a thermoplastic (TP), to a silicone-thermoplastic polyblend (Si-TP), and to a silicone-interpenetrated thermoplastic (Si-IPN-TP) for polypropylene.

thermoplastic urethane at melt temperatures of 210–215 °C: 7500 g of polyether urethane (Pellethane 2103; Dow Chemical Company), 2450 g of poly(dimethylsiloxane-*co*-diphenylsiloxane) (15–17%; vinyl dimethylsiloxane terminated; 5000 ctsks.), and 50 g of poly(diphenylsiloxane-*co*-methylhydro-siloxane) (30–35% methylhydro-siloxane; copolymer terminated; 30 ctsks.)

The mixture is pelletized, and 1 g of a platinum-tetramethyl-tetravinylcyclotetrasiloxane complex (2.5% Pt) is tumbled onto the pellets and then deactivated by the addition of 0.05 g of 3-methylisobutynyl alcohol. The apparently homogeneous material contains two unreacted silicones in a thermoplastic urethane matrix.

The polysiloxane network is formed during part fabrication. In injection molding, the acetylenic alcohol, which acts as a fugitive inhibitor of the vinyl-addition reaction, is volatilized at low temperature as the pellets enter the feed throat. The platinum complex is activated at the process temperature of the urethane (170–185 °C). The vinyl-addition reaction is initiated by the melt state, and the parts generated demonstrate mechanical properties consistent with the formation of a silicone IPN. The fabricated parts are translucent. The physical properties of this formulation (PTUE 205) are given in Table I.

Table I. Properties of Silicone-Urethane IPNs

Property	Aliphatic Ether (PTUA 102)	Aromatic Esters			Aromatic Ethers				
		PTUE 101	PTUE 102	PTUE 102	PTUE 202	PTUE 203	PTUE 205	PTUE 302	PTUE 332 ^a
Hardness (shore) ^b	70A	80A (30D)	55D (95A)	55D	87A	55A	60D	70D	
Tear strength (kN/m)	52.8	88.0	132.0	114.4	88.0	52.8	176.0	211.2	
Tensile strength (MPa)	20.7	44.8	41.4	41.4	18.6	13.8	41.4	127.6	
Elongation (%)	700	520	470	425	1300	900	400	5	
Flexural strength (MPa)			50.3	48.3			55.2	124.1	
Flexural modulus (MPa)	27.6	41.4	110.4	103.5		13.8	186.2	5517.6	
Izod impact (J/m)									
Notched	NB	NB	NB	NB	NB	NB	NB	85	
Unnotched	NB	NB	NB	NB	NB	NB	NB	427	
Water absorption after 24 h (%)	0.3	0.3	0.3	0.4	0.4	1.04	0.5	0.4	
Specific gravity	1.11	1.16	1.19	1.12	1.11		1.12	1.24	
Shrinkage of a 1/8-in. (0.32-cm) section (%)	1.5-2.0	1.0-1.5	1.0-1.5	1.0-1.5	1.5-2.0		1.0-1.5	1.1-1.4	
Process temperature range (°C)	165-190	165-190	165-190	205-232	205-232	190-220	205-232	215-245	

^aThe urethane is an aromatic ether with carbon fiber.

^bShore is a standard measure of hardness for rubber recognized by ASTM. There are several scales, including A and D, which cross over.

^cNB indicates no break.

The technology of silicone–thermoplastic semi-IPNs is highly flexible because IPN compositions and morphology can be varied. The four main factors controlling IPN morphology and properties are (1) base component composition, (2) total IPN content, (3) polymer compatibility and interfacial tension, and (4) cross-link density. Because the silicone network forms independently of the matrix resin, theoretically, an IPN can be developed in any thermoplastic polymer. Those desirable features of silicones, including physiological, release, wear, and thermal properties, can be translated into thermoplastics and thermoplastic elastomers. Some resins that have been transformed into semi-IPNs include the following:

- Polyethylene
- Polypropylene
- Polyamide (6, 6,6, 6,12, 11, 12)
- Polyacetal
- Poly(butylene)(terephthalate)
- Polyurethane
- Styrene block polymers
- Polyolefin elastomers
- Polyester elastomers
- Melt-processable fluorocarbons

Intrinsic Properties. IPN properties can also be tailored by varying silicone concentration. In some systems, dramatic changes in polymer morphology and crystallinity have been observed in loadings as low as 3%. At the other end, polysiloxane loadings of up to 55% have been achieved. Some successful semi-IPN formulations are the following:

- Poly(caprolactam-*inter*-dimethylsiloxane-*co*-vinylmethylsiloxane)
- Poly(propylene-*inter*-dimethylsiloxane-*co*-octylmethylsiloxane-*co*-vinylmethylsiloxane)
- Poly(styrene-*block*-butadiene-*block*-styrene-*inter*-dimethylsiloxane-*co*-diphenylsiloxane-*co*-vinylmethylsiloxane)

The chemical compatibility of the network and matrix polymers determines the extent of solubility of one resin in the other and, hence, the degree of molecular interpenetration. The backbone substitution groups of the silicone prepolymers are carefully chosen to achieve an appropriate degree of compatibility with a specific matrix polymer (11). Although most silicone oligomers are not highly soluble in high-molecular-weight thermoplastic resins, total incompatibility would lead to gross phase separation (i.e., delamination) during fabrication. At the other extreme, fully soluble silicones result in

alloys in which morphology consistent with network formation is not observed. An example of a low-cross-link-density siloxane acting as a plasticizer is shown in Table II for a silicone–aliphatic urethane system. As phenyl groups are introduced into the silicone, solubility increases, network properties diminish, and physical and thermal properties decrease radically.

Various degrees of phase separation have been observed in IPN composites (12). The final structure consideration, cross-link density, in conjunction with the intrinsic compatibility of the polymers, determines the domain size of the reacting phase. Increasing cross-link density leads to smaller domains and greater phase continuity in the cross-linking phase and an increase in “trapped” matrix polymer chains. The greater degree of molecular interpenetration in highly cross-linked systems results in network-imposed compatibility.

Cross-link density in silicone–thermoplastic semi-IPNs is controlled by the molecular weight and number of reactive groups of the silicone oligomers. Highly branched and lightly branched siloxane networks of distinctly different behavior have been developed in the silicone–thermoplastic semi-IPN series. Although every semi-IPN base polymer system develops a distinct morphology, the case of nylon 6,6 is instructive. No dominant structures are observed for the highly branched polymers in scanning electron micrographs (SEMs). The polymer with higher cross-link density presumably forms a more rigid, extended network throughout the matrix thermoplastic. The highly branched networks exhibit greater phase separation. In SEMs of 10% of a lightly branched silicone in nylon 6,6 IPNs, the silicone networks form spherical domains ranging from 6 to 12 μm in diameter. These structures are absent in the highly cross-linked system (Figure 6.) Even in the case of the lightly branched silicone, the majority of the silicone is not involved in gross phase separation, but in the fine structure as demonstrated by the silicon EDX (X-ray dispersive microscopy).

Changes in the crystallization behavior of the thermoplastic phase of the IPN have been observed in DSC (differential scanning calorimetry) experiments (13). In Figure 7, a series of DSC scans on silicone–nylon 6,6 composites of various silicone contents are presented. The characteristic melt peak of the nylon matrix is observed in all of the thermograms, but a second, slightly lower temperature melt peak becomes more pronounced as the concentration or the cross-link density of silicone polymer in the IPN is

Table II. Comparison of IPN-Modified and Unmodified Aliphatic Ether Urethanes

<i>Material</i>	<i>Tensile Strength (MPa)</i>	<i>Elongation (%)</i>
Unmodified urethane	33.1	800
Urethane–poly(dimethylsiloxane) (10%) IPN	20.7	700
Urethane–poly(phenylmethylsiloxane) (10%) IPN	6.2	1000

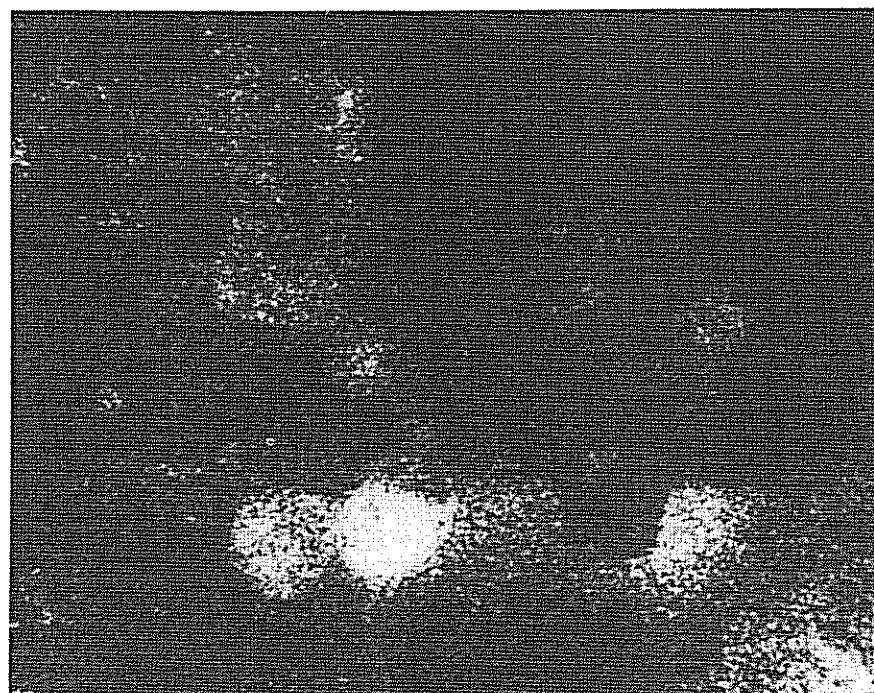
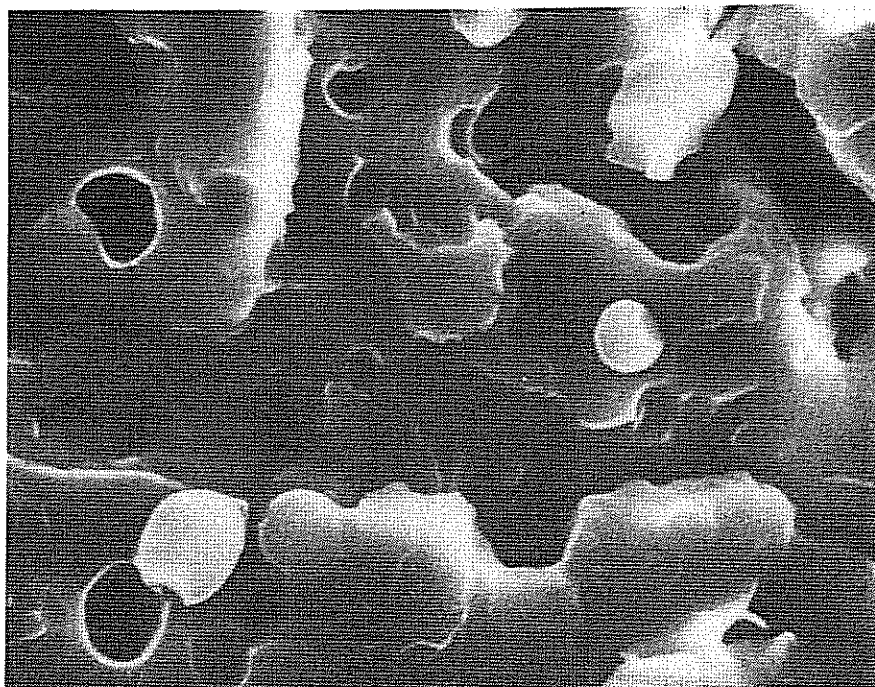


Figure 6. 6,6-Polyamide-i-low cross-link PDMSO at 1000 \times magnification. (Top) Scanning electron micrograph; (bottom) EDX Si.

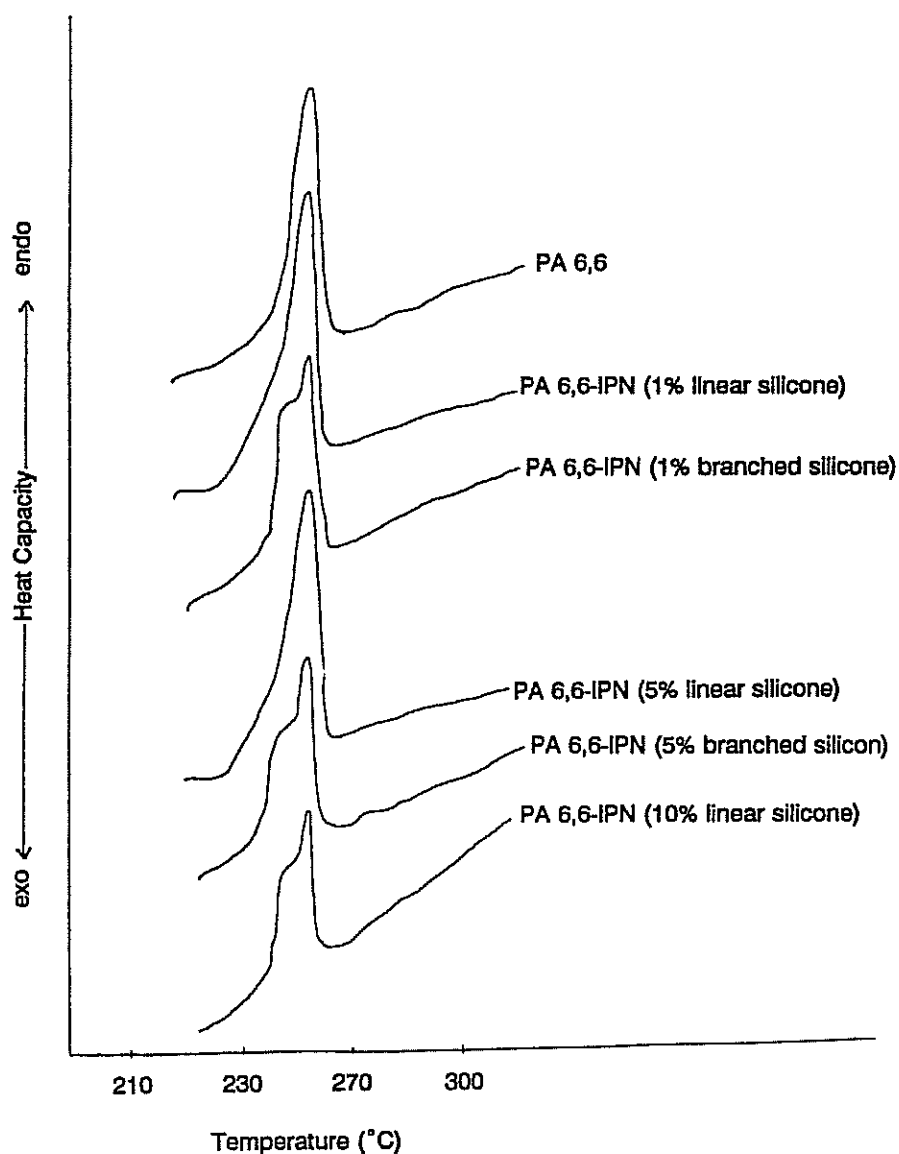


Figure 7. DSC thermograms of nylon 6,6 IPNs. PA is polyamide.

increased. Although double-melting endotherms have been observed in nylon 6,6 (14), they were attributed to a reorganization phenomenon during the DSC scan; the lower melting peak decreased in size and increased in temperature with increased annealing time, results suggesting that a secondary, less-ordered crystalline phase was being converted to a more favored form.

The double-melt endotherms of the silicone-nylon 6,6 IPN do not disappear with thermal cycling. Instead the peaks are further resolved in the DSC when samples are scanned to 50 °C above the melt point, cooled slowly to room temperature, and rescanned (Figures 7 and 8). The stability of the melt endotherm associated with the presence of IPN suggests the presence of an interpenetrated polymer phase of various crystalline structures.

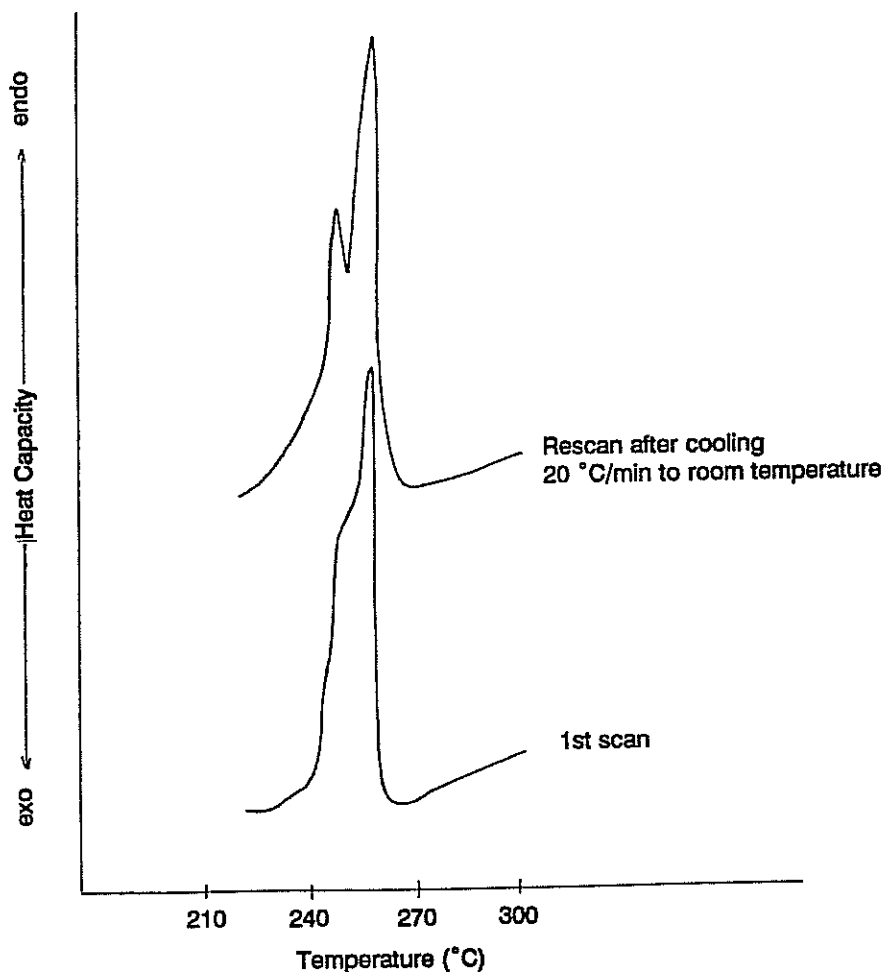


Figure 8. Multiple DSC thermograms of 30% glass fiber-reinforced, highly branched silicone-nylon 6,6 IPN.

Extrinsic and Mechanical Properties. The technology of silicone-thermoplastic semi-IPNs was originally developed with thermoplastic polyurethanes for biomedical applications (15). Silicone rubbers possess the good blood-contacting and low-physiological-response properties required in biomaterials but lack high tensile strength and modulus and are difficult to process. Silicone-polyurethane IPNs provide a range of favorable property combinations in easily injection-molded materials. The mechanical and physiological properties of these IPNs can be compared with those of pure silicones and base polymers:

- Compared with pure silicones
 1. Processing on conventional thermoplastic equipment with less processing variables compared with liquid silicone rubber systems

2. Greater tear, tensile, and flexural strengths
 3. Lower mating surface wear (Silica-free formulation reduces abrasion.)
 4. Lower oxygen permeability and reduced moisture transmission
 5. Increased elastic recovery at low extensions
 6. Reduced blood-polymer interaction (Filler-free silicone surface reduces thrombogenic response.)
- Compared with thermoplastic urethane
 1. Silicone release characteristics
 2. Lower wear and friction (Wear is reduced by a factor of 5-6; the coefficient of friction is reduced by 20-30%.)
 3. Improved dielectric properties
 4. Reduced blood-polymer interaction (Filler-free silicone surface reduces thrombogenic response.)
 5. Increased permeability to oxygen, which is useful in self-supporting enrichment applications
 6. Improved high-temperature performance
 7. Increased elastic recovery at high extensions

In the IPNs, the mechanical properties of the matrix resin are preserved, and wear, lubricity, and abrasion resistance are improved. In systems with high cross-link densities, the resilience and resistance of the resins to creep (set) is enhanced. The properties of a series of thermoplastic-polyurethane IPNs (TPU-IPNs) are listed in Table I.

Applications. The silicone-aromatic urethane grades demonstrate tear and tensile strengths 3 to 5 times those of silicones and wear rates that are lower by a factor 5 or 6 when compared with urethanes and by factors greater than 10 when compared with silicones. The silicone-aromatic urethanes are currently being evaluated in a wide range of medical device applications. The silicone-aliphatic urethane systems may have significant potential for long-term implant applications. Silicone-thermoplastic semi-IPNs have been extended to other thermoplastic elastomers and engineering thermoplastics for use in the medical industry.

Silicone-SEBS IPNs are the only sterilizable thermoplastic systems that resist coring and are capable of self-sealing after being pierced with hypodermic syringes. These IPNs are used in injection sites both because they allow dual-shot fabrication and because they are free of contamination from vulcanization aids found in their natural rubber predecessors.

Silicone–nylon 12 IPN is a candidate material for self-supporting medical devices such as implantable pumps, catheter guides, and connectors.

Silicone–thermoplastic semi-IPNs and fiber-reinforced IPNs based on high-modulus-engineering thermoplastic matrices have also been developed (16, 18). Initially these materials were of interest as internally lubricated composites for bearing applications, in which the IPN combined the high-modulus and high temperature properties of the engineering thermoplastic with the improved tribological properties and release characteristics of a silicone. The mechanical, friction, and wear properties of nylon 6,6 and several silicone–nylon 6,6 IPNs are shown in Table III. As the volume fraction of silicone or the cross-link density increases, a higher continuity IPN is formed, and wear resistance and coefficients of friction improve dramatically. Tensile strengths are maximized, and flexural-modulus values are unchanged at low silicone concentrations. The heat deflection temperatures of all of the IPNs are greater than that of nylon 6,6; the greatest increase is seen in the highly branched silicone networks, in which a more rigid structure is formed.

The mechanical properties of a 30% glass fiber-reinforced silicone–nylon 6,6 IPN approximate that of a conventional glass-reinforced composite (Table III). Strength and stiffness are reduced slightly in the IPN composite, but increases in elongation and Izod impact strengths indicate an increase in ductility. By contrast, low-molecular-weight silicone fluids are often used in combination with polytetrafluoroethylene (PTFE) as internal lubricants for engineering thermoplastics. Although silicone fluids are good lubricants, they tend to reduce the mechanical properties of the composite, and they migrate to the molded surface and contaminate surface mounts or trap abrasive wear debris.

The silicone–thermoplastic IPN composites exhibit superior mechanical properties (Table IV), and the network structure of the silicone prevents migration. The value of the IPN has been demonstrated in a molded journal bearing for use in high-speed paper-handling equipment. For example, part wear was reduced to a greater extent in a PTFE-lubricated, silicone–nylon 6,6 IPN bearing, compared with an uncross-linked silicone fluid, PTFE-lubricated nylon bearing, which attracted abrasive paper dust to the wearing surfaces.

Unique crystallization behavior leads to an unusual apparent property advantage of the silicone–thermoplastic semi-IPNs: low and uniform shrinkage behavior (17). This characteristic is of particular value in crystalline thermoplastic resins, like nylons, polyesters, polypropylene, and acetal, that exhibit high and nonuniform mold shrinkage rates. Shrinkage differential leads to part warpage, a condition that is further aggravated in fiber-reinforced composites. The IPN greatly stabilizes the mold shrinkage behavior in both fiber-reinforced and nonreinforced composites.

Results of a study of mold shrinkage and warpage are shown in Table

Table III. Properties of Silicone-Polyamide IPNs

Property	Modified Nylon 6,6						Modified Nylon 12		
	Nylon 6,6	PTA 6601	PTA 6602	PTA 6631	Nylon 12	PTA 1201	PTA 1202	PTAE 1201 ^a	
Silicone content (%)	0	5	10	3	0	5	10	5	
Other materials				13% PTFE					
Tensile strength (MPa)	81.4	86.2	69.6	68.9	38.6	51.0	35.9	37.9	
Elongation (%)	60	20	5	20	20	8-10	8-10	275	
Flexural strength (MPa)	103.5	109.7	96.6	105.5	48.3	57.2	55.2	15.2	
Flexural modulus (MPa)	2830	2830	2480	2690	1206	1489	1379	2414	
Izod impact (J/m)									
Notched	48	48	43	43	107	37	32	NB	
Unnotched		1121	800	694		1708	342	NB	
Heat distortion temperature at 1.82 MPa (°C)	66	93	74	102	125	150	135		
Wear factor (10 ⁻¹⁰ in. ³ /min) ^b	200	155	20	25		195			
Coefficient of friction									
Static (μS)	0.20	0.19	0.09	0.11		0.18			
Dynamic (μD)	0.28	0.19	0.12	0.18		0.17			
Specific gravity	1.14	1.13	1.12	1.21	1.02	1.02	1.01	1.01	
Shrinkage (%)	1.2-2.0	0.5-0.7	0.4-0.6	0.5-0.7	0.7-0.8	0.5-0.7	0.5-0.7	0.5-0.7	
Water absorption after 24 h (%)	1.2	0.8	0.6	0.6	0.25	0.15	0.12		
Process temperature range (°C)	245-275	235-275	235-275	235-275	180-210	180-210	180-210	180-210	

^aPTAE 1201 is an elastomer with a hardness of 60D.^b10⁻¹⁰ in.³/min is equivalent to 1.64 × 10⁻⁹ cm³/min.

Table IV. Properties of Nylon 6,6 Resin and Silicone-Thermoplastic Semi-IPNs

<i>Property</i>	<i>ASTM Method</i>	<i>Nylon 6,6 (Unmodified)</i>	<i>RL-4610 (Linear Silicone)</i>	<i>RL-4620 (Linear Silicone)</i>	<i>R-5000 (Branched Silicone)</i>
Specific gravity	D792	1.14	1.13	1.12	1.13
Mold shrinkage of a 1/8-in. (0.32-cm) section (%)	D955	0.015	0.012	0.008	0.006
Tensile strength (MPa)	D638	81.4	86.2	69.6	76.6
Tensile elongation (%)	D638	60	20	5	20
Flexural modulus (MPa)	D790	2827	2827	2483	2827
Izod impact strength (J/m)					
Notched	D256	48	48	48	48
Unnotched	D256	>2135	1120	800	1067
Heat distortion temperature at 1.82 MPa (°C)	D648	66	71	82	93
Wear factor (10 ⁻¹⁰ in. ³ /min) ^a		200	155	12	100
Coefficient of friction					
Static (μS)		0.20	0.19	0.07	0.14
Dynamic (μD)		0.28	0.19	0.08	0.16

^a10⁻¹⁰ in.³/min is equivalent to 1.64 × 10⁻⁸ cm³/min.

Table V. Mold Shrinkage and Warpage of Nylon 6,6 and Silicone-Nylon 6,6 IPN Composites

<i>Code</i>	<i>Material</i>	<i>Mold Shrinkage (%)</i>	<i>Warpage^a</i>
R-1000	Nylon 6,6	0.015	0.050
RL-4620	Nylon 6,6-linear silicone IPN	0.008	0.018
R-5000	Nylon 6,6-branched silicone IPN	0.006	0.010
RF-1006	Nylon 6,6-30% glass fibers	0.004	0.270
RF-5006	Nylon 6,6-branched silicone-30% glass fibers	0.003	0.035

^aWarpage of an injection-molded disk (4 by 1/16 in.; 10.2 by 0.16 cm).

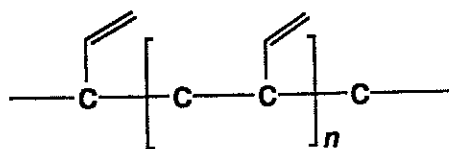
V. A series of 4-in. (10.2-cm)-diameter, 1/16-in. (0.16-cm)-thick edge-gated disks were injection molded under normal nylon-processing conditions. Warpage in the lightly branched and highly branched IPN parts were 2.5- and 5-fold lower, respectively, than the warpage in molded nylon 6,6 resin. The warpage in the 30% glass-reinforced nylon 6,6 IPN was 10-fold lower than that in a 30% glass-reinforced nylon 6,6 composite. The greater dimensional control afforded by the IPN enables crystalline matrix composites to be used in high-tolerance moldings.

A 30% glass-fiber-reinforced, PTFE-lubricated, nylon 6,6 IPN was molded in a high-tolerance gear designed for use in the business machine industry. Although excellent chemical resistance and high fatigue endurance limits of glass-reinforced nylon made it an attractive candidate, total composite error (TCE) for molded glass-reinforced nylon was 0.0055", which

corresponds to a class 6 American Gear Manufacturing Association (AGMA) rating. The nylon IPN exhibited lower TCE (0.0028"), produced a class 8 AGMA gear with an overall shrinkage comparable with that of 30% glass-reinforced polycarbonate. The internal lubrication and isotropic shrink characteristics of the silicone-thermoplastic semi-IPN resulted in a high-quality gear with the desired chemical resistance and fatigue endurance.

Hybrid and Secondary Cross-Linked Silicone IPNs

Hybrid versions of silicone-thermoplastic semi-IPNs have been developed (19). A hybrid interpenetrating network is one in which the cross-linked network is formed by the reaction of two polymers with structurally distinct backbones. Hydride-functionalized siloxanes can be reacted with organic polymers with pendant unsaturated groups such as polybutadienes (5) in the presence of platinum catalysts. Compared with the polysiloxane semi-IPNs discussed earlier, the hydride IPNs tend to maintain mechanical and morphologically derived properties, whereas properties associated with siloxanes are diminished. The probable importance of this technology is in cost-effective ways to induce thermoset characteristics in thermoplastic elastomers.

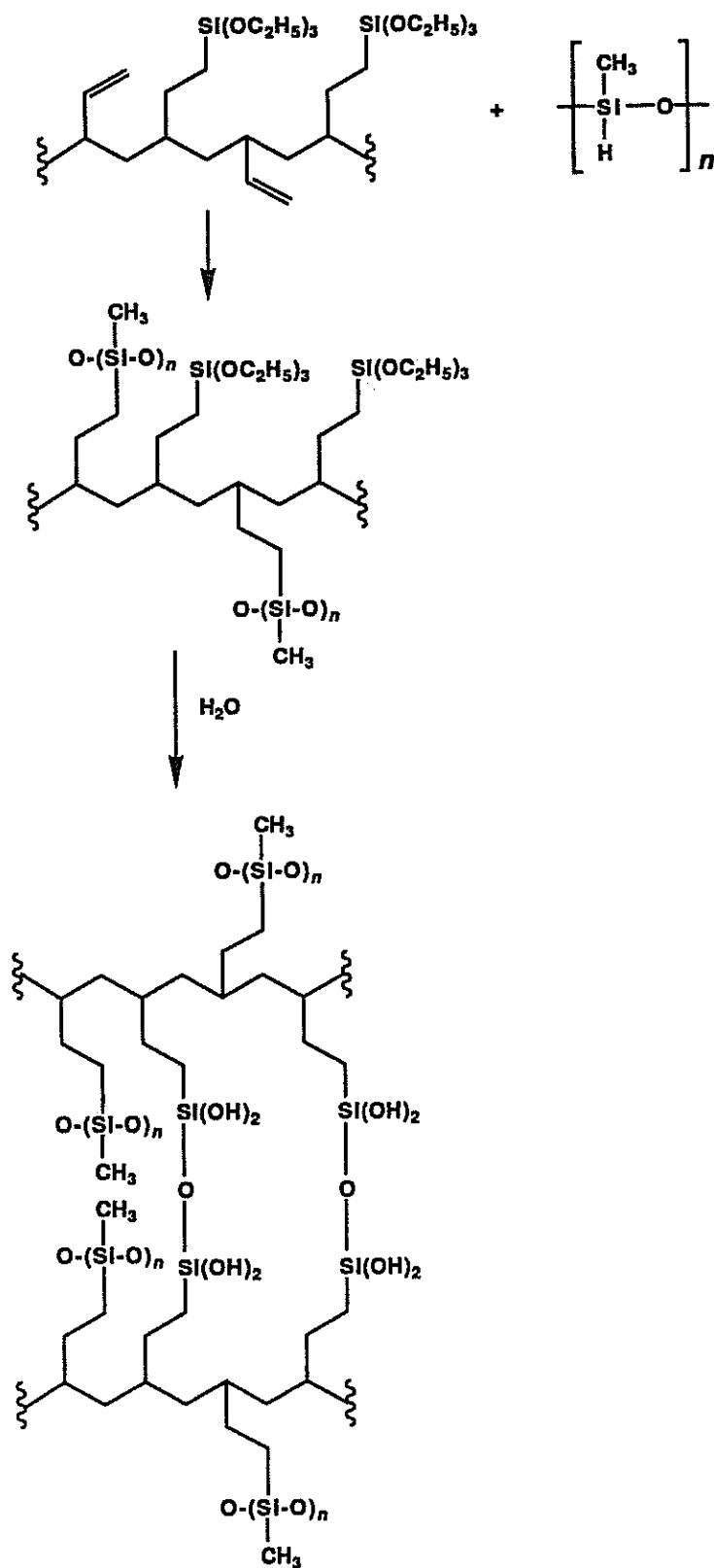


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Another variation of silicone-thermoplastic semi-IPN technology is the use of secondary cross-linking (20). The incorporation of multiple alkoxy silane groups into the interpenetrating network allows a staged cross-linking reaction. The first reaction is the platinum-catalyzed vinyl-addition reaction. The second cross-linking is a hydrolysis condensation that takes place after the thermoplastic processing. This technology is anticipated to be useful in wire and cable insulation and to displace earlier technology, which utilizes peroxide grafting of vinyl silanes (Scheme I).

Conclusion

The silicone semi-IPN structure imparts unique behavior to thermoplastic composites without affecting mechanical strength and stiffness. Apart from the direct effects associated with the incorporation of thermoset character into a thermoplastic, the structure has particular value by functioning as (1) a nonmigrating internal lubricant, (2) a shrinkage and warpage modifier, (3) a flow modifier, and (4) a release agent. As a polymer-polymer composite,



Scheme I

the IPN expresses the strengths of its components, as well as unique thermal, mechanical, and physiological characteristics. The silicone semi-IPN structures present a new avenue for developing thermoplastic elastomers with the mechanical and thermal properties of compression-molded cross-linked rubbers. Because of their synthetic flexibility, silicone IPNs have a broad range of possibilities. Their importance lies not only in these possibilities but also in the examples they provide of what the technology of reactive processes and interpenetrating polymer networks has to offer.

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