IPN-MODIFIED SILICONE THERMOPLASTICS

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The properties of currently available biomaterials tend to fall short of the requirements of many potential medical devices. However, a new process and formulation technology has generated an array of products that may bridge some of these gaps. The technology, which is known as Rimplast (a registered trademark of Petrarch Systems, Incorporated), is based on a reactive polymer and interpenetrating polymer network (IPN) for silicone thermoplastic materials. It is an example of the emerging trend in biomaterial technology in which material development is undertaken with the goal of medical application, in contrast with traditional biomaterial development, in which existing industrial materials were qualified, often clumsily, for medical applications.

Of principal concern for bioengineers are applications in which mechanical properties such as tensile strength, flexural modulus, and fatigue endurance must be combined with good blood-contacting and low physiological-response properties. While exhibiting low mechanical strength, silicones are recognized as possessing these two latter properties. Reviews of silicones in medical applications from the physiological,[1] device,[2] and materials[3] perspectives have been published recently that establish two interesting points germane to the Rimplast polymer systems. The first is that a large portion of the physiological response elicited by silicone rubbers is caused by silica and other fillers within the silicone, not the silicone itself.[4] Second, several polymer systems containing silicone, particularly in the urethane area, have been developed with exceptional blood-contacting properties and reasonably good mechanical properties. The most conspicuous example of this class of material is Cardiothane (formerly Avcothane). While it was originally believed to be a copolymer,[5] later work has shown that the material is more properly considered a blend of about 10% silicone and urethane.[6] Although it indicates the potential of silicone-urethane systems, Cardiothane's nonuniform morphology, poor process parameters, and unattractive economics have disallowed widespread applications. Other polymer systems in which low levels of silicone copolymers have been utilized as additives demonstrate reduced blood-polymer interaction,[7] but it is not clear from the limited data published whether problems of uniform polymer distribution and process-independent properties are resolved. Nevertheless, the introduction of low-molecular-weight species is almost certain to reduce the mechanical properties of the base polymer.

The IPN Process Technology

A block copolymer approach to formulating silicone urethanes is one apparent solution to the dilemma posed by additive and mixture systems. Although the development of several such materials has been reported,[8,9] none of them has been introduced for commercial applications. Rimplast represents a second and unique approach, one in which a polyblend of high-molecular-weight silicone and urethane is converted to an IPN during processing by extrusion or injection molding.

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A simple statement of the IPN process technology is as follows. Reactive silicone components are confined to separate solid pellets of matrix resin (e.g., urethane), which are handled as a homogeneous mix. When the melt state is achieved in conventional injection-molding or extrusion equipment, the confinement of reactive silicones to individual pellets collapses and they begin to react with each other to form a pseudo-interpenetrating polymer network. While it is essential that the reaction is initiated in the melt, it will proceed in the solid state. Within two to three hours of the start of the melt state the property development associated with the formation of the IPN is substantially complete. Little or no difference between this technology and conventional resin processing during extrusion or injection molding is observed.

The chemistry of the process that generates the silicone IPN is a platinum-catalyzed vinyl-addition reaction, stated:

$$\sim(\underset{Me}{\overset{R}{OSi}})_m\sim CH{=}CH_2 + H(\underset{Me}{\overset{R}{SiO}})_n\sim \xrightarrow{P+} \sim(\underset{Me}{\overset{R}{OSi}})_m\sim CH_2\,CH_2(\underset{Me}{\overset{R}{SiO}})_n\sim$$

This chemistry is adapted in a number of ways for specific polymer systems: the *R* substituents are varied to achieve an appropriate degree of compatibility with the matrix resin, the molecular weight and number of reactive groups are varied in order to achieve the desired cross-link density, and finally, the ratio of silicone to matrix polymer is varied.

Table I: Properties of IPN-modified silicone thermoplastics compared to pure silicones and to base polymers.

Compared to Silicones	Compared to Base Polymers
Can be processed on conventional thermoplastic equipment with fewer processing variables than liquid silicone rubber	Silicone release characteristics
Greater strength—tear, tensile, flexural strength increased	Lower wear and friction
Lower mating-surface wear; silica-free formulation reduces abrasion	Improved dielectric properties
Lower oxygen permeability; moisture transmission reduced	Reduced blood/polymer interaction; filler-free silicone surface reduces thrombogenic response
Increased elastic recovery at low extensions	Increased permeability to oxygen—useful in self-supporting enrichment applications
Reduced blood/polymer interaction; filler-free silicone surface reduces thrombogenic response	Improved high-temperature performance
	Increased elastic recovery at high extensions
	Improved solvent and stress-crack resistance

Table II: Properties of seven grades of IPN-modified silicone urethanes.

Property	PTUA102 Aliphatic ether	PTUA103 Aliphatic ether	PTUE101 Aromatic ester	PTUE102 Aromatic ester	PTUE202 Aromatic ether	PTUE302 Aromatic ether	PTUE332 Aromatic ether w/carbon fiber
Silicone, %	10	15	8	10	10	10	10
Hardness, shore	70A	60A	80A (30D)	55D (95A)	55D	60D	70D
Tear strength, pli	300	200	500	750	650	1000	1200
Tensile strength, psi	3000	1500	6500	6000	6000	6000	18,500
Elongation, %	700	1000	520	470	425	400	5
Flexural strength, psi				7300	7000	8000	18,000
Flexural modulus, psi	4000	2000	6000	16,000	15,000	27,000	800,000
Izod impact, ft-lb/in.							
notched	NB[a]	NB	NB	NB	NB	NB	1.6
unnotched	NB	NB	NB	NB	NB	NB	8.0
Water absorption, 24 hours, %	0.3	0.3	0.3	0.3	0.4	0.5	0.4
Specific gravity	1.11	1.10	1.16	1.19	1.12	1.12	1.24
Shrinkage % (⅛-in. section)	1.5–2.0	1.5–2.0	1.0–1.5	1.0–1.5	1.0–1.5	1.0–1.5	1.1–1.4
Process temperature range, °F	300–350	300–350	325–375	325–375	400–450	400–450	420–475

[a]NB = No break.

Test	Result
Agar overlay cytotoxicity	Negative
Systemic injection	
Saline	Negative
Ethanolic saline	Negative
Polyethylene glycol	Negative
Cottonseed oil	Negative
Intramuscular implantation (7 days)	No gross signs of tissue damage
Red blood cell hemolysis	Negative
Blood protein adsorption (60A HTV silicone = 1)	0.7–0.8
Ames/salmonella mutagenicity	Negative

Table III: Results of biocompatibility tests of silicone aliphatic urethane formulation, grade PTUA102.

Properties and Applications

The mechanical and physiological properties of IPN-modified silicone thermoplastics are compared to those of pure silicones and base polymers in Table I. At a minimum, the mechanical properties of the matrix resin are preserved, and in many areas—including wear, lubricity, and abrasion resistance—they are improved. In high cross-link density systems the resilience and resistance to creep (set) of the resins is enhanced. The ready processability of these materials makes them good substitutes for liquid-injection-molded silicone.

IPN-modified silicone polyurethanes can be formulated with a considerable range of properties (see Table II). In the middle range are the materials that were the initial targets for biomedical applications. They demonstrate tear and tensile strengths three to five times that of silicones and wear rates that are lower by a factor of five or six when compared to urethanes and by factors greater than 10 when compared to silicones. At the low-modulus end of the material spectrum are flexible silicone urethanes with durometers as low as 60A, while at the high-modulus end carbon fiber–reinforced high-durometer silicone urethanes with strengths approaching die-cast metals have been achieved.

All clean grades of IPN-modified silicone polyurethanes have demonstrated favorable results in biocompatibility tests. Silicone–aliphatic urethane systems have undergone the most extensive evaluation, and appear to have a significant potential for long-term implant applications. Classic biocompatibility assays such as cytotoxicity, systemic injection of extracts, and implantation tests on the aliphatic urethane–matrix resin selected for hybridization in silicone IPN systems—a methylene bis(cyclohexyl)isocyanate polybutylene ether elastomer manufactured by Thermedics (Waltham, Massachusetts)—have yielded favorable results (Table III).[10] Additional information that contributes to an assessment of the material's positive potential for long-term implants derives from other blood-contact and implant studies. Hemolysis tests, which give a crude gage of blood compatibility, have indicated less than 0.5% hemolysis; blood protein adsorption from heparinized whole human blood has been observed to be 20–30% lower than HTV silicone controls; and a more uniform surface morphology has also been observed. These combined factors suggest the material should exhibit one of the lowest levels of mural thrombosis induced by polymeric implants. Initial tests of highly stressed specimens of silicone–aliphatic urethane tubing implanted for 90 days showed no indication of stress cracking, a frequent problem with conventional urethanes (personal communication with Michael Szycher, Thermedics). Longer implantation studies are underway.

Other studies of silicone–aliphatic urethane formulations have demonstrated negative findings for stone buildup when the material was implanted in dog bladders for 1 week, and in 3 out of 5 specimens when it was implanted in rat bladders for 1 month; the other 2 specimens experienced some stone buildup in the area of the scar (personal communication with Jerald Glantz, American Medical Systems).

Silicone–aromatic urethane materials currently are being evaluated in a wide range of medical device applications. Tests of cytotoxicity, systemic injection of extracts, and short-term implants have been favorable. However, because of the continuing debate on the appropriateness of aromatic urethanes in biomedical devices, neither a favorable nor unfavorable recommendation can yet be made for these formulations. In any case, these materials are not recommended when steam sterilization is included in the intended product's use protocol.

While the Rimplast technology was originally developed with polyurethanes, it has been extended to other thermoplastic elastomers and engineering thermoplastics. Polyester elastomers and EPDM- and SEDS-type block copolymers have now all been used as matrix resins, and silicone-SEDS formulations appear to be excellent candidates for catheter and other disposable applications. Polyamide (nylon) and polyester engineering thermoplastics have also been formulated using the technology. Silicone–nylon 6/6 systems show increased resistance to deflection under load at elevated temperatures and less anisotropic shrinkage, while silicone–nylon 12 materials appear to be excellent candidates for self-supporting medical device applications such as implantable pumps, catheter guides, and connectors (see Table IV). All materials formulated by the technology thus far have demonstrated improved solvent resistance.

Table IV: Properties of three nonpolyurethane IPN-modified silicone thermoplastics.

	PTA6602	PTA1202	PTSEDS[a]
Resin	Nylon 6/6	Nylon 12	SEDS
Silicone, %	10	10	20
Hardness, shore	NA[b]	98A	70A
Tear strength, pli	NA		150
Tensile strength, psi	10,100	5200	1000
Elongation, %	5	20	400
Flexural strength, psi	14,000	8000	NA
Flexural modulus, psi	360,000	200,000	500 psi at 300% elongation
Impact strength, ft-lb/in.			
notched	0.8	0.6	NB[c]
unnotched	15.0	6.4	NB
Water absorption, 24 hours, %	0.6	0.5	0.2
Specific gravity	1.12	1.01	0.95
Shrinkage, % (⅛-in. section)	0.4–0.6	1.0–1.8	not tested
Process temperature range, °F	460–525	375–425	330–360

[a]Developmental properties. [b]Not applicable. [c]No break.

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