

The Stability of Poly(ether urethane)/Polydimethylsiloxane Interpenetrating Polymer Networks

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SYNOPSIS

Interpenetrating polymer networks (IPNs) are a special type of polymer blend consisting of two polymer networks synthesized and/or cross-linked independently within each other. One potential approach for the preparation of composite materials from polymers having desirable physical characteristics obtained by modifying their surfaces with physiologically acceptable polymers involves IPN technology. An IPN based on a poly(ether urethane) and polydimethylsiloxane has been synthesized and characterized using optical microscopy, dynamic mechanical analysis, and scanning electron microscopy. The stability of poly(ether urethane)/polydimethylsiloxane composites were studied in hydroxyl radical aqueous solutions over 30 weeks. The data suggest that these composites have good potential for biomedical applications. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The stability of synthetic polymers used for manufacturing replacements of human organs or their components is a critical property of such materials as it determines the long-term function of a specific biomedical device. Recent studies¹⁻⁴ in our laboratory on the mechanisms of polymer degradation in implantable devices suggests that the hydroxyl radical is one of the main causes of polymer degradation in implantable devices. *In vivo*, the hydroxyl radicals can be generated by transition metal ions, peroxide, and superoxide species during the respiratory burst of phagocytic cells in acute or chronic inflammation sites.

Biodegradation can be virtually eliminated by the covalent bonding or grafting of the more physiologically inert silicone polymer to the surface of polymers in implantable devices. The blood compatibility is thought⁵ to be maximized within a narrow range of surface-free energies (20–30 dyne/cm)⁶ that give rise to favorable interaction with plasma proteins. The blending of polydimethylsiloxane with poly-

mers of high surface tension values produces films with high polydimethylsiloxane surface concentrations,⁷⁻⁹ which provides surface tension values around 22 dyne/cm, thought by some to be optimal for medical application. This approach appears to be capable of modifying surface properties without impairing the properties of the bulk.

Interpenetrating polymer networks (IPNs) are a special type of polymer mixture consisting of two polymer networks synthesized and/or cross-linked independently within each other. On a molecular level, they can be viewed as interlocked macrocycles of two species that are chemically not bonded to each other, yet are physically inseparable. Polymer mixtures are often thermodynamically unstable and, therefore, will phase-separate, the extent of which in IPNs will depend on the degree of the interlocking.

One potential approach for the preparation of composite materials from polymers having desirable physical characteristics obtained by modifying their surfaces with physiologically acceptable polymer involves IPN technology. The synthesis of IPNs of polyurethane with a silicone polymer takes advantage of the excellent physical properties and manufacturability of polyurethanes and the favorable

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biological and elastomeric properties of silicone rubber.

A blend of polysiloxane and a polyurethane was converted into a semi-IPN during processing by Arkles.^{10,11} The polysiloxane network was formed by a platinum-catalyzed vinyl addition. Hourston and co-workers have published¹²⁻¹⁵ on urethane-siloxane IPNs.

An IPN based on a poly(ether urethane) (PU) and polydimethylsiloxane (PDMS) has been synthesized and characterized using optical microscopy, dynamic mechanical analysis, and scanning electron microscopy. The homonetworks of PU and PDMS as well as the IPN containing 85% w/w of PU has been synthesized and their stability in hydroxyl radical aqueous solutions was studied over 30 weeks to evaluate the stability of PU/PDMS composites and their potential for biomedical applications.

EXPERIMENTAL

The polyurethane network (PU) was prepared from Adiprene L-100 (Uniroyal Chemicals), an isocyanate-terminated prepolymer based on toluene diisocyanate and tetramethylene glycol, which was chain extended using poly(propylene glycol) (1025) (BDH Chemicals) and cross-linked trimethylolpropane (Aldrich). The polysiloxane network (PDMS) was synthesized from an α - ω -dihydroxy-PDMS (Dow Corning) that was cross-linked with tetraethyl orthosilicate (Aldrich). There was no possibility of indiscriminate cross reactions between the two prepolymers as this had been checked previously.¹⁶ In the preparation of both the homonetworks and the IPN, stoichiometric quantities of the prepolymers and the cross-linking agents were used in all cases, and dibutyltin dilaurate (Sigma Chemicals) was used to catalyze the homonetwork-forming processes of PU and PDMS. Stannous octoate (Sigma Chemicals) was used to catalyze both of these independent network-forming processes of the IPN containing 85% w/w of PU.

Adiprene L-100 was heated to 60°C to depolymerize any oligomers formed during storage and then cooled to room temperature. The two homonetworks were prepared by mixing the prepolymers with their cross-linking agents and the appropriate amount of catalyst and with 10% w/w of tetrahydrofuran to facilitate mixing and to promote homogeneity. A high-speed mechanical mixer was employed to achieve the best possible degree of mixing. The amounts of catalyst used for the PU and the

PDMS homonetworks were 0.001 and 3.2% w/w, respectively. Mixtures were degassed and poured into aluminum molds with Perspex lids and allowed to cure at room temperature. After 48 h, the cured sheet was removed from the mold and placed in a vacuum over at room temperature for a week¹⁷ prior to testing to ensure total cure and removal of residual tetrahydrofuran.

The procedure for the preparation of IPNs was identical to that for the homonetworks. For the IPNs, the amount of catalyst was varied to 1% of stannous octoate to ensure that the system could be degassed properly and that the materials gelled after approximately the same time of reaction.

Hydroxyl radicals (HO \cdot) were generated by the reaction of aqueous solutions of H₂O₂ (3 wt %) with either ferrous sulfate (FeSO₄) or cobalt nitrate [Co(NO₃)₂] in distilled water. All media had the same concentration of HO \cdot by using constant amounts of all chemicals. Samples of PU, PDMS, and IPN containing 85% w/w of PU were immersed in Fe(II)/H₂O₂ and Co(II)/H₂O₂ solutions and stored in glass bottles in a 37°C incubator for a period of 30 weeks. Each medium was replaced twice a week to maintain the generation of fresh hydroxyl radicals. For each incubation time, 10 specimens were recovered, washed several times with distilled water, and vacuum-dried for 1 week at room temperature before being subjected to various analyses.

Electron spin resonance spectroscopy (ESR) was used to check the presence of HO \cdot radicals in both Fe(II)/H₂O₂ and Co(II)/H₂O₂ solutions. ESR spectra were recorded, at 77 K, using either a Bruker ER200-SRC spectrometer with a nuclear magnetic resonance gaussmeter (Bruker ERO-35M) and frequency counter (Systron Donner 6245A) or Bruker ER300 spectrometer at microwave powers varying from 2 mW to 2 μ W. A suitable spin-trap, α -(π -pyridyl-1-oxide)-*N*-*tert*-butylnitron (POBN) (Aldrich, UK), was used for detecting hydroxyl radicals in aqueous solution at pH 6-7. All ESR spectra measurements were carried out in a Bruker Quartz flat cell.

Optical microscopy was conducted using a Nikon Model L-Ke microscope fitted with a microflex PFM photomicrographic attachment. Magnifications up to \times 400 were obtainable. All dynamic mechanical measurements were made with a Polymer Laboratories dynamic mechanical thermal analyzer at a frequency of 10 Hz and a heating rate of 3°C/min.

Scanning electron microscopy (SEM) using a Jeol JSM-25C microscope was used to study the morphology of the specimens. The samples were

mounted and sputter-coated with gold using an EM scope sputter coater. Surfaces and cross sections of the specimens were prepared as photomicrographs.

RESULTS AND DISCUSSION

The PU and PDMS homonetworks were transparent, whereas the IPN was white. The optical microscopy of the IPN containing 85% of PU indicated a two-phase structure where the PU network is the continuous phase and the PDMS is the discrete phase with the average domain size of about 12 μm .

The dynamic mechanical behavior of the PU homonetwork is shown in Figure 1. The glass transition, T_g , is apparent at -19°C in the $\tan \delta$ -temperature plot that corresponds to a previously published¹⁴ value. The dynamic mechanical behavior of the PDMS network is shown in Figures 2 and 3. The transition at -25°C in the $\tan \delta$ -temperature plot, corresponding to the catastrophic fall in E' , is associated with crystalline melting.^{18,19} The T_g at -105°C shows a low $\tan \delta$ value as reported by Hourston and co-workers¹⁴ because the amorphous content is quite low in this crystalline material. There is also a small peak at -39°C resulting from a cold-crystallization process.¹⁸

The dynamic mechanical behavior of the IPN containing 85% w/w of PU is shown in Figures 4

and 5. The similarity of the behavior of this IPN to that of the PU homonetwork may be observed. The PDMS crystalline melting is no longer observed, which supports the contention that at 85% w/w of PU it is the PU that is the continuous phase. The T_g of PDMS for the IPN containing 85% w/w of PU is broad and small, as shown in Figure 4, whereas this low temperature is highlighted more in the E'' temperature plot, as in Figure 5.

The main features of the dynamic mechanical behavior of the PU and PDMS homonetworks and the IPN containing 85% w/w of PU specimens were monitored in both hydrolytic and free-radical systems (Table I) to study the effect of the introduction of hydroxyl radicals on these materials. The similarity of the dynamic mechanical behavior of IPN in various media indicates its ability to withstand the rigors of the harsh environment of the hydroxyl radicals over the period of 30 weeks. The dynamic mechanical characteristics of the IPN are shown in Figure 6.

In general, the glass transition temperatures of the PU and PDMS homonetworks, -19 and -105°C , respectively, have not suffered any noticeable change after incubation in different media. There was also a lack of change in T_g values of the IPN containing 85% w/w of PU in different media except the PDMS, where the T_g value was decreased to -125°C in the IPN compared with the value of

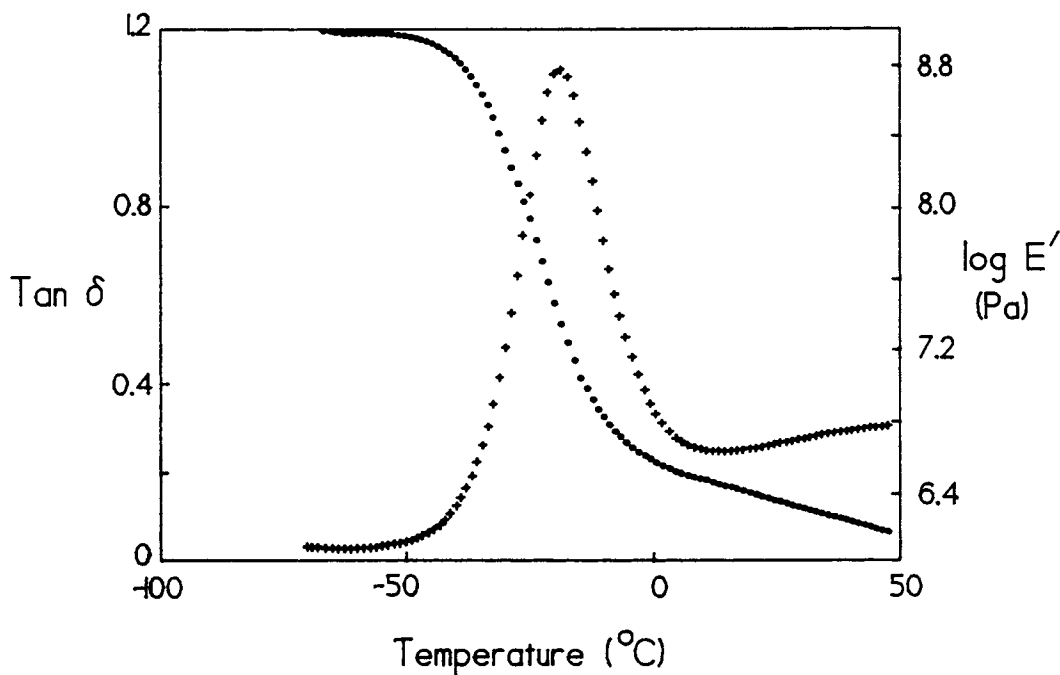


Figure 1 $\tan \delta$, E' temperature plots of PU homonetwork.

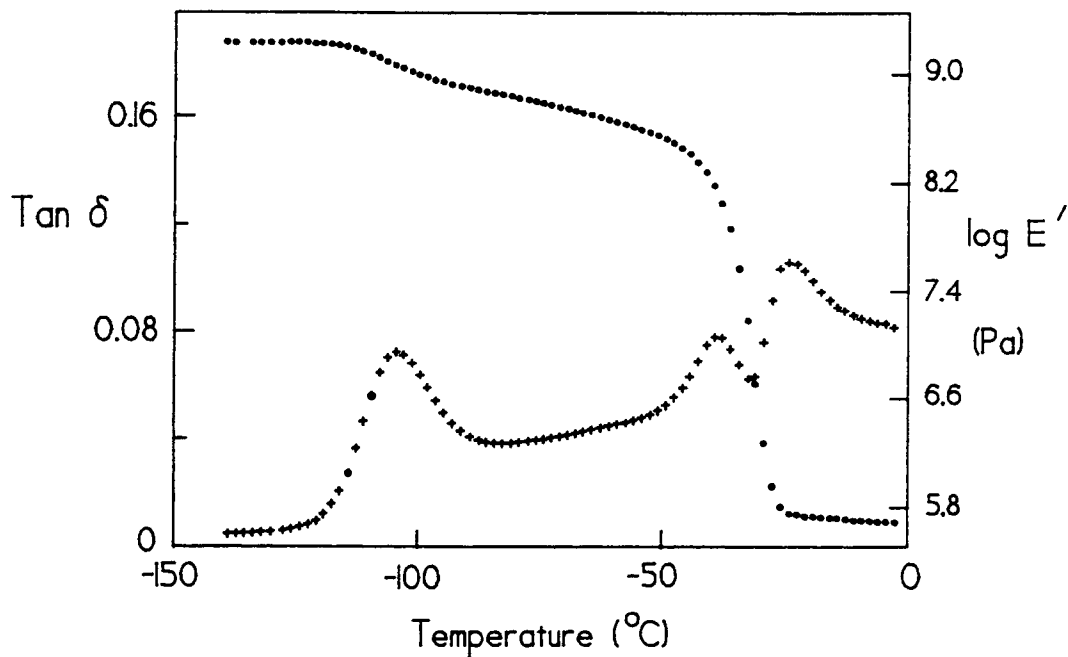


Figure 2 $\tan \delta$, E' temperature plots of PDMS homonetwork.

-105°C in the network. This decrease could be caused by PDMS homonetwork being more crystalline than is the PDMS in the IPN.

The results obtained by SEM enabled observation of the physical characteristics of the external and

internal morphologies of the PU and PDMS homonetworks and the IPN containing 85% w/w of PU after 30 weeks of incubation in various aqueous environments.

Scanning electron micrographs of the surface and

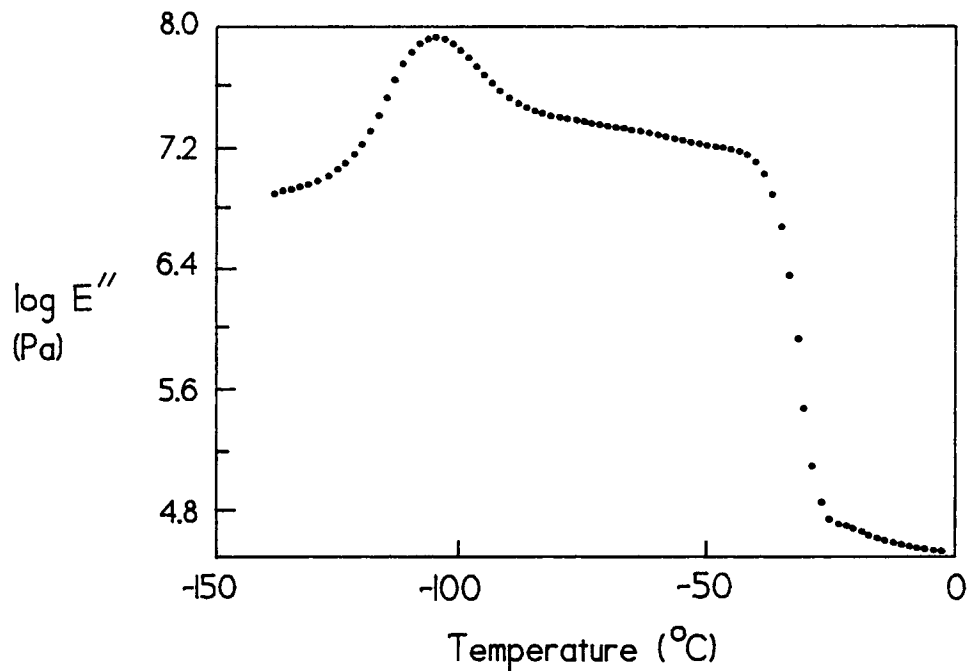


Figure 3 E'' temperature plot of PDMS homonetwork.

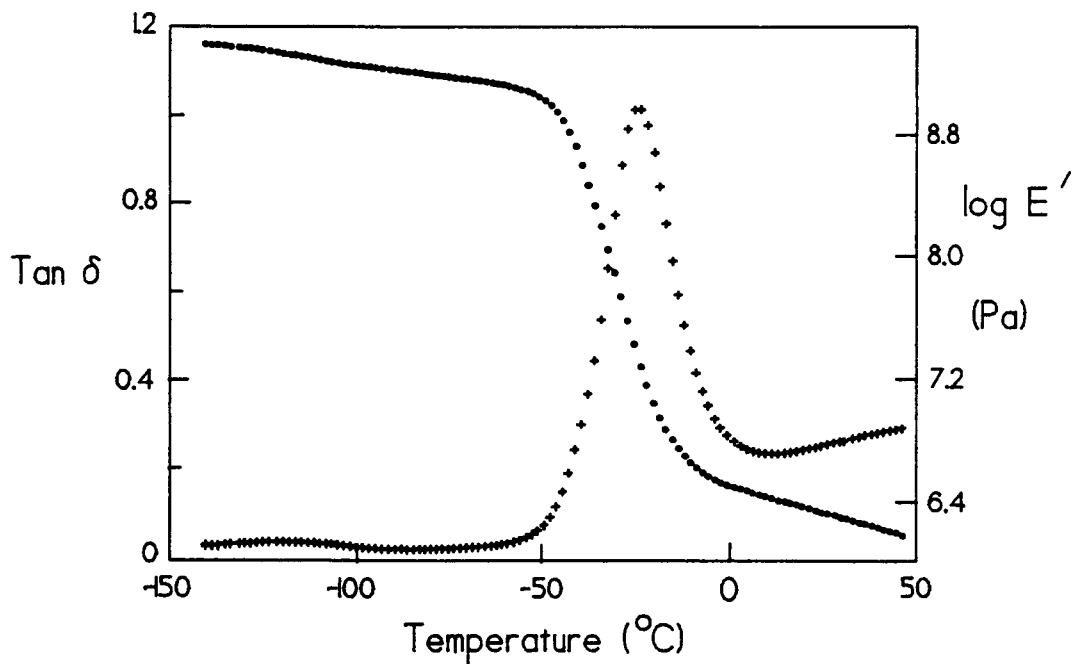


Figure 4 $\text{Tan } \delta, E'$ temperature plots of the IPN containing 85% w/w of PU.

cross section of the PU and PDMS homonetworks specimens indicate that prior to any treatment the materials were generally smooth, except for debris and depressions caused by mold and/or the cutting of the specimens.

The micrographs of PU homonetwork specimens after 30 weeks of incubation in $\text{Fe(II)/H}_2\text{O}_2$ and $\text{Co(II)/H}_2\text{O}_2$ aqueous hydroxyl radical solutions at 37°C indicate that no apparent change in the cross-section topography was observed following the in-

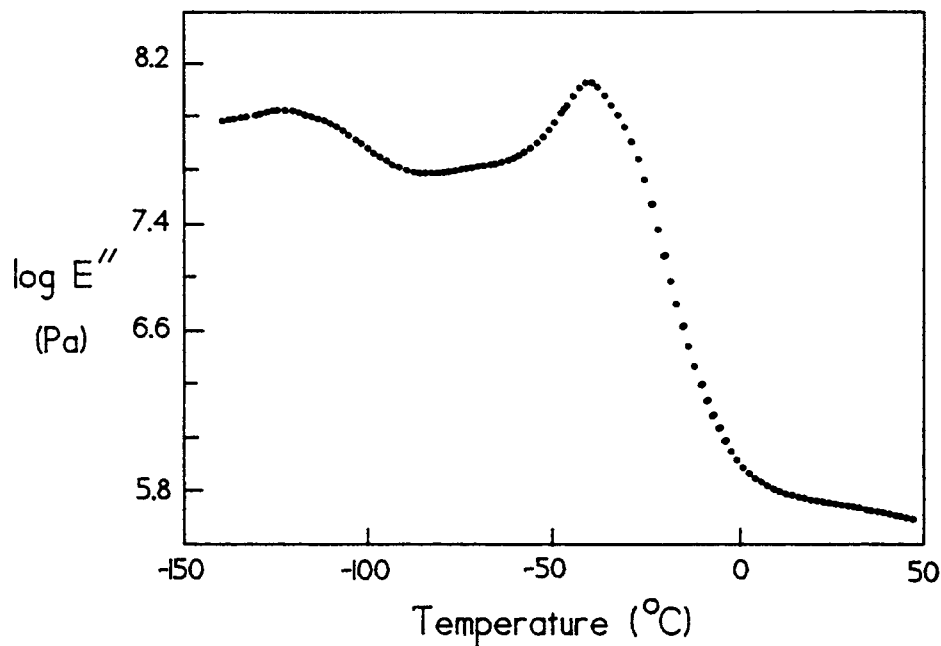


Figure 5 E'' temperature plot of the IPN containing 85% w/w of PU.

Table I The Main Features of the Dynamic Mechanical Behavior of the PU and PDMS Homonetworks and the PU/PDMS IPN Containing 85% w/w of PU after 30 Weeks of Incubation at 37°C

Homonetwork or IPN	Glass Transition (°C)			
	Control	H ₂ O	Fe(II)/H ₂ O ₂	Co(II)/H ₂ O ₂
PU	-19	-19	-20	-20
PDMS	-105	-105	-106	-105
IPN				
85% PU (T_g)	-23	-19	-19	-19
15% PDMS (T_g)	-117	-124	-124	-125

T_g measured to $\pm 1^\circ\text{C}$.

cubation of the PU homonetwork specimens, whereas the micrograph of surface morphology shows some roughness and the emergence of small troughs as sign of the degradation, possibly due to the effect of the hydroxyl radicals.

The micrograph of the surface of PDMS homonetwork specimens after 30 weeks of incubation in Fe(II)/H₂O₂ and Co(II)/H₂O₂ aqueous hydroxyl radical solutions at 37°C shows the removal of a large amount of debris from the surface, possibly due to the cleaning effect of the hydroxyl radical solutions, whereas the micrograph of the cross sec-

tion does not indicate any changes in the topography following the incubation in the hydroxyl radical solutions. These results indicate that the aqueous hydroxyl radical solutions have relatively little effect on the PDMS homonetwork specimens.

The micrographs of the surface and cross section of the IPN containing 85% w/w of PU specimens are shown in Figure 7(a) and (b), respectively. There are some debris and voids on the surfaces. The micrographs of the cross section of IPN as shown in Figure 7(b) and (d) reflect the continuous phase of PU and the disperse phase of PDMS with

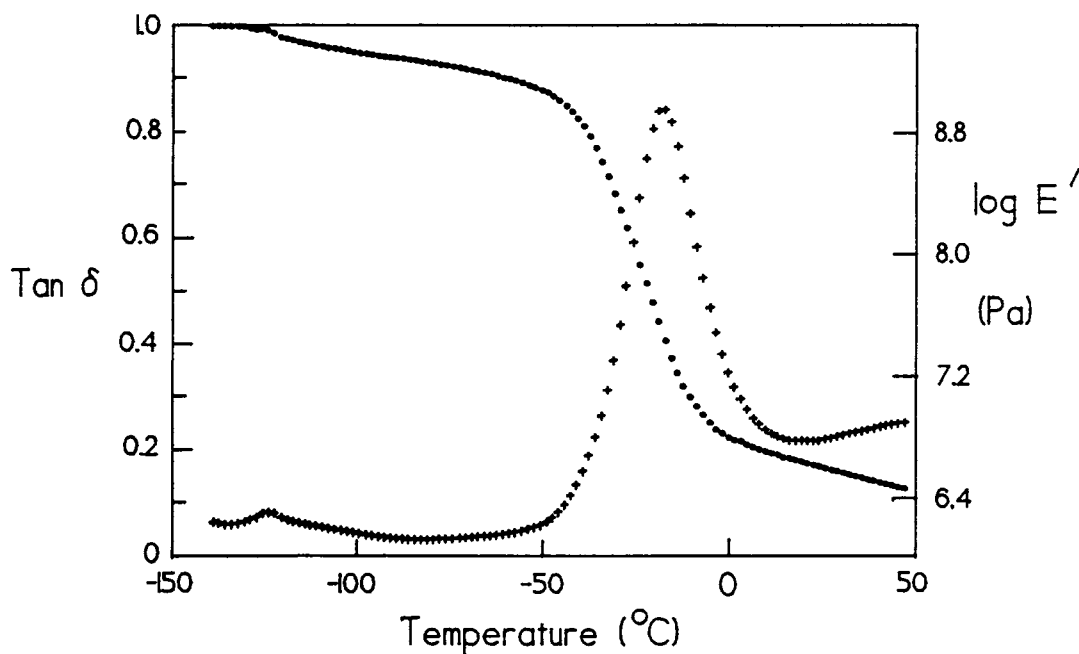


Figure 6 $\text{Tan } \delta$, E' temperature plots of the IPN containing 85% w/w of PU after 30 weeks of incubation in distilled H₂O.

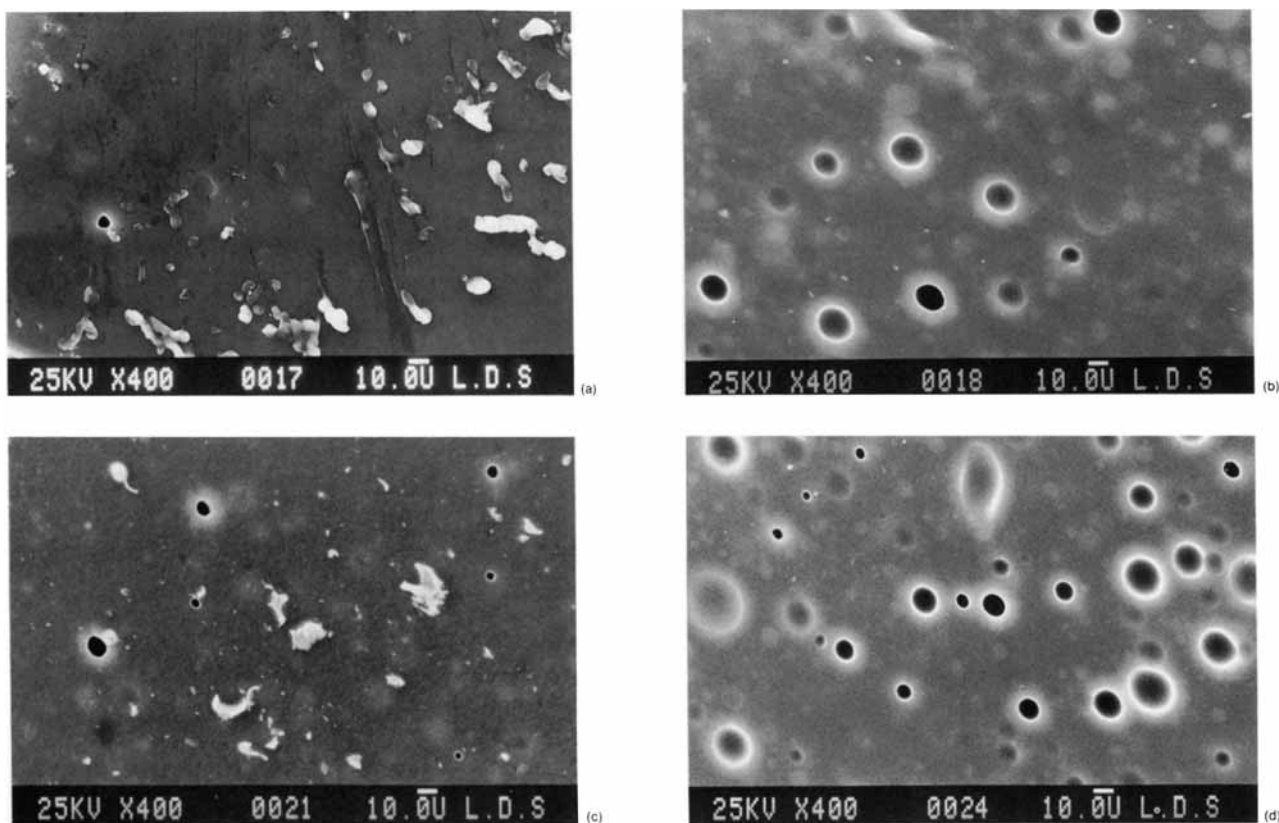


Figure 7 Scanning electron microscopy of (a) surface and (b) cross section of virgin IPN containing 85% w/w of PU and (c) surface and (d) cross section after 30 weeks of incubation in Fe(II)/H₂O₂ and Co(II)/H₂O₂ solutions, respectively.

the average domain size of about 12 μm . However, the micrographs of the surface of IPN as indicated in Figure 7(a) and (c) do not show the phases of the two components clearly. Figure 7(c) and (d) exhibit the micrographs of the IPN material after the treatment with Fe(II)/H₂O₂ and Co(II)/H₂O₂ aqueous hydroxyl radical solutions at 37°C, respectively. There is no apparent effect of the oxidizing agent on the surface morphology or the phase-separation structure. The surface and the bulk of IPN material has exhibited a good tolerance against the most reactive radicals.

CONCLUSIONS

The PU and PDMS homonetworks and the IPN containing 85% w/w of PU have been studied to evaluate aspects of the biocompatibility of this poly(ether urethane)/polydimethylsiloxane IPN. These materials were incubated over the period of 30 weeks in Fe(II)/H₂O₂ and Co(II)/H₂O₂ aqueous hydroxyl radical solutions. Optical microscopy, dy-

namic mechanical analysis, and scanning electron microscopy were used to study the influence of hydroxyl radicals on the morphology and physical characteristics of the IPN material and the homonetworks.

There were no apparent effects of the strong oxidizing agent on the surface morphology of the IPN material. These results suggest that PU/PDMS IPN containing 85% w/w of PU has good potential for biomedical applications. Further detailed work is continuing to determine the effect of the free radicals on the chemical characteristics of the surface and the bulk of the PU/PDMS IPN material.

Long-term implantable prostheses that require high tensile strength, excellent tear resistance, excellent flex fatigue, and low profiles may benefit from these PU/PDMS IPNs materials.

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