

Study on the Properties and Application of Epoxy Resin/Polyurethane Semi-interpenetrating Polymer Networks

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SYNOPSIS

Damping properties of epoxy resin/polyurethane (EP/PU) semi-interpenetrating polymer networks (IPNs) were studied by the dynamic mechanical analysis (DMA) method. It shows that the semi-IPNs have excellent damping properties at ordinary temperature. The maximum value of $\tan \delta$ is about 1 when the weight composition of EP/PU is 70/30. Tensile tests also indicate that the system has good tensile strength and elongation at break at this ratio. The effects of structure on the properties of the semi-IPNs are discussed. Applied to the cavitation corrosion resistant coating, the semi-IPNs show good cavitation corrosion resistance. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

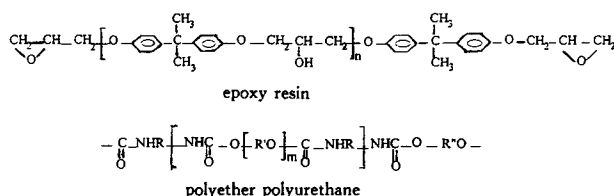
In the research field of interpenetrating polymer networks (IPNs), it is very important to study the effects of interpenetration on the properties of polymers.¹⁻⁵ Because of the polyurethane's linear network with excellent elasticity, abrasive resistance, and damping property, and the epoxy resin's cross-linked network with good adhesion to metals and high mechanical strength, epoxy resin/polyurethane (EP/PU) semi-IPNs were prepared. The glass transition behavior and morphology of the semi-IPNs have been studied before. The results showed that

the compatibility between the two polymers is best when the weight composition of EP/PU is 70/30.¹ In this paper we will discuss further studies on the damping properties, mechanical properties, and application of the semi-IPNs.

EXPERIMENTAL

Materials

We chose EP-014 epoxy resin and polyether polyurethane as the two components, which are described as follows:



Diaminodiphenylmethane (DDM) was used as curing agent and dimethyl formamide (DMF) as solvent.

Preparation

EP/PU semi-IPNs were obtained as follows: After dissolving the EP-014 and PU in DMF at some ratio, we added DDM to the mixture while stirring. Then the mixture was poured into a polytetraflu-

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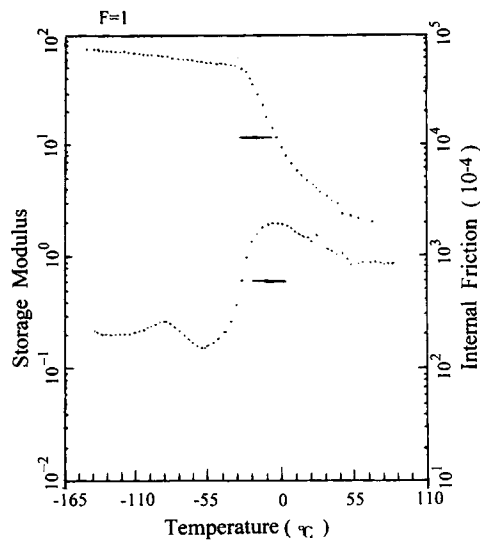


Figure 1 DMA trace of PU.

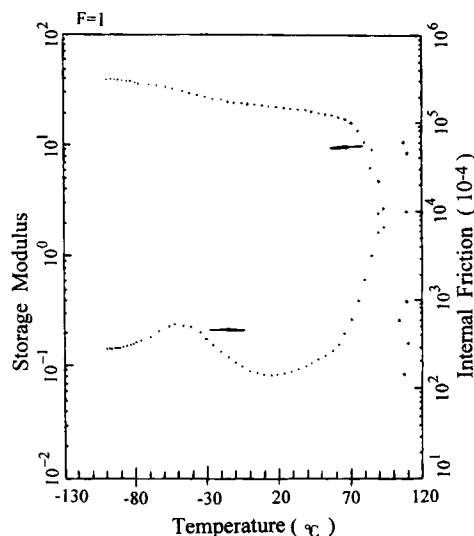


Figure 2 DMA trace of EP.

oroethylene mold, volatilized, and heated to 150–160°C. The blends were cured at this temperature for 1 h.

Methods

The damping properties were detected by multi-function internal friction apparatus (MFIFA-1) at 1 Hz. The heating speed was 3°C/min. Mechanical properties were tested by an Instron materials testing system at 10°C. The cavitation corrosion resistant property was tested with WH-1 cavitation apparatus.

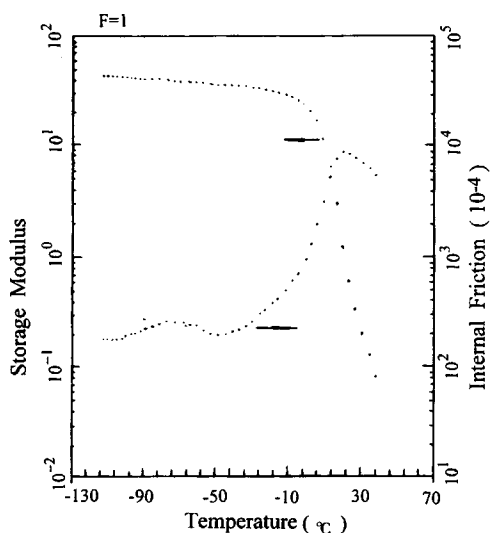
RESULTS AND DISCUSSION

Damping Properties

Because of their excellent viscoelasticity, polymer materials can absorb and diffuse the energy of vibration as heat. We call this process internal friction, which endows damping properties to materials. The higher the internal friction, the better the damping property.

Figures 1 and 2 show traces of dynamic mechanical analysis (DMA) of PU and EP, respectively. Figure 1 shows that PU has high internal friction at relatively low temperatures. As we know, PU has a block structure. The two peaks correspond to the glass transition of soft segments and rigid segments whose concentration was 30–

50 wt % in PU. The low activation energy of the soft segments' motion makes it easy for soft segments to move at a very low temperature, -88°C . However, the movement of the rigid segments is difficult at such a low temperature because of its high activation energy. Therefore, the internal friction, $\tan \delta$, of PU is low at -88°C . We found that PU shows greater internal friction at -5°C .



(a) 70/30

Figure 3 DMA traces of the semi-IPNs of EP/PU with different weight compositions.

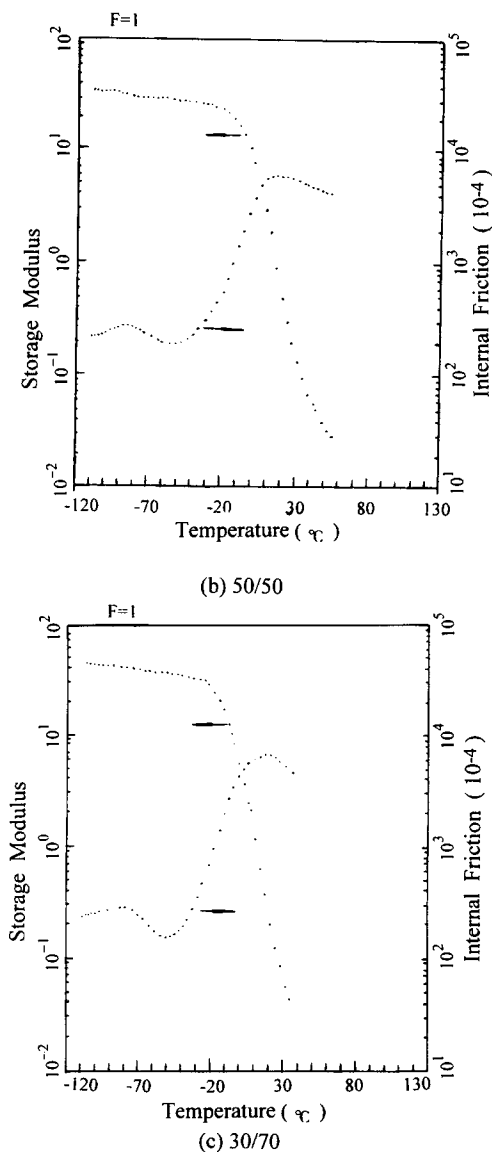


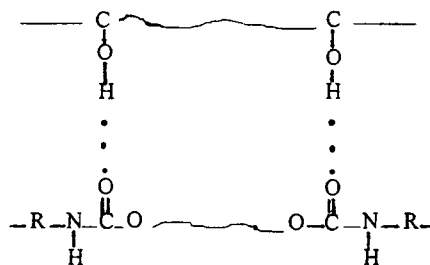
Figure 3 (Continued from previous page)

This corresponds to the molecular friction when both soft and rigid segments move.

One can see that high internal friction of EP takes place at high temperature (Figure 2). So it is not suitable to use EP as a damping material at ordinary temperatures. But high temperatures may worsen the mechanical properties of these materials.

The DMA traces of EP/PU semi-IPNs with different weight compositions are given in Figure 3, which shows that the semi-IPNs embody relatively high internal friction at ordinary temperatures. This indicates that the forming of IPNs im-

proves the materials' damping properties. We found that the maximum of $\tan \delta$, the internal friction, which approaches 1, takes place when the weight composition of EP/PU is 70/30. This is because the interpenetration improves the compatibilities of EP and PU. The entanglement of polymer chains and the hydrogen bond formed in the interface between two polymers makes it possible for longer segments to move with PUs molecular chains at its glass transition temperature, which moves to a higher temperature when semi-IPNs form. The hydrogen bond can be specified as follows:



Meanwhile, it is possible that the work imposed on the crosslinked networks of EP can be liberated as heat through physical crosslinking points between two polymers and PU linear networks. Therefore, the semi-IPNs have good damping properties at normal temperatures.

In sum, the semi-IPNs can be applied to damping materials at ordinary temperatures when proper compositions are chosen.

Mechanical Properties

The results of tensile tests are listed in Table I, which shows that the stress at auto break reaches its maximum at ratio 70/30. Because the interpenetrating between EP and PU improves their compatibilities, fills the defects existing in the single polymer, and increases the effective crosslinking density, the strength of the polymers increases. Table I also shows that the breaking energy increases greatly when semi-IPNs form. The rubbery PU can absorb much energy when being stretched. The larger the areas of interpenetrating surface of PU, the more energy PU can absorb.^{6,7} Then the breaking energy is greater. In addition, we have studied the morphology of the EP/PU semi-IPNs before⁸ and have found that they have a cellular structure, where PU forms the cell and EP forms the cell wall. The PU particles whose sizes are about 1–2 μm act as stress concentration points which can initiate and

Table I Mechanical Properties of EP/PU Semi-IPNs with Different Weight Ratios

Weight Ratio	100/0	70/30	50/50	30/70	0/100
Strain at auto break (%)	2.01	211.90	105.10	160.10	218.51
Stress at auto break (MPa)	29.11	37.67	22.45	15.29	11.67
Energy to break point (J)	0.025	1.806	1.140	1.637	2.033

stop the development of crazes and crackles, thus enhancing the breaking strength of IPNs. Comparing the semi-IPNs with different weight compositions, we found that the value of stress at auto break reaches its highest when the ratio of EP/PU is 70/30.

Table I also shows that the forming of semi-IPNs greatly improves the toughness of EP. When the weight ratio of EP/PU is 70/30, the breaking elongation of semi-IPNs reaches 211.9%. This results from the effects of PU's plasticization. The soft linear chains of PU are linked to the EP crosslinked networks by physical crosslinking points. Then the slide of molecular chains can take place in the tensile fields without destroying the structure. Thus the semi-IPNs show both high elongation and high strength at break.

From the discussion above, we reach the same conclusion as before, which is that the compatibilities of EP and PU are best when the weight ratio of EP/PU is 70/30 and the two polymers show good synergism when the semi-IPNs form.⁸

Application

As to hydrodynamic machines, such as water turbine pumps, the damage of cavitation corrosion is an urgent problem. Such corrosion is caused by the form-

ing and bombing of bubbles which develop because of the subatmospheric pressure when the fluid scours the turbine. Therefore, many dens form in the surface of the turbins and cause the loss of materials.⁹

In order to solve this problem, we apply the EP/PU semi-IPNs to a kind of cavitation-corrosion-resistant coating. In terms of the mechanism of cavitation, the protective coating requires certain properties, such as good adhesion to metals, abrasive resistance, water resistance, elasticity, toughness, and damping property, which may be achieved through the synergism of EP and PU in semi-IPNs.

The strength of cavitation of different materials was tested; the results appear in Table II. The cavitation strength is measured by the weight loss of materials per testing time. The higher the value, the worse the material's cavitation-corrosion resistance.

One can see that the coating of EP/PU semi-IPNs shows good cavitation-corrosion resistance, better than those of two other polymers, carbon steel ZG30 and low-alloy steel ZG40Cr, and approaching those of martensitic stainless steel ZG1Cr18Ni9Ti and ZG0Cr13Ni4Mo.

As we know, the damage of cavitation results from the vibration energy of the shock wave. If materials absorb the energy and cannot liberate it effectively,

Table II Strength of Cavitation Corrosion of Different Materials

Materials	Cavitation Strength (mg/h)	Note
Coating of PU	29.2	
Coating of PPS	39.2	
Coating of semi-IPN	3.9	
ZG30	16	Annealed
ZG40Cr	8.1	Normalized and tempered
ZG1Cr18Ni9Ti	2.38	Water quenched
ZG0Cr13Ni4Mo	1.34	Normalized and tempered

the plastic deformation of materials takes place; pits, which lead to the stripping of materials, are formed in the surface. When the EP/PU semi-IPN is used as face coatings, the interpenetrating between linear networks and crosslinked networks makes the energy transfer and liberation easier. Instead of plastic deformation, elastic deformation which can be recovered occurs. This prevents the materials from corrosion.

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