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Dynamic Mechanical Properties of N-Phenylnadimide Modified PMR Polyimide Composites

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DYNAMIC MECHANICAL PROPERTIES OF N-PHENYLNADIMIDE
MODIFIED PMR POLYIMIDE COMPOSITES

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INTRODUCTION

Studies on the relationship between the structure of high temperature resistant polymers and their mechanical properties present a considerable challenge to polymer chemists. This is because the structures of these polymers are little known and difficult to determine, due to their intractable nature. This characteristic severely restricts the applicability of most of the current available techniques for structural determination. Dynamic mechanical measurements, however, can provide insights into such structure-property relationships. The use of this technique has been described in the studies of a series of linear condensation type polyimides¹⁻³ and an acetylene-terminated polyimide, viz. Thermid 600⁴.

In this paper, the dynamic shear properties of newly developed Celion 6000/N-Phenylnadimide (PN) modified PMR polyimide composites were investigated. For comparison purposes, the state-of-the-art Celion 6000 graphite fiber/PMR-15 composite was also investigated. The objective is to correlate the mechanical properties with the structure of a highly crosslinked PN modified PMR polyimide. The temperature-frequency dependence of the shear properties for the composite systems was determined. The activation energies for the α , β , and γ relaxation processes in the matrix resins were also determined. The influence of N-phenylnadimide on the rigidity of the PMR-15 polyimide system is discussed.

MATERIALS AND METHODS

A PN modified PMR polyimide matrix resin consists of four monomer reactants: N-phenylnadimide (PN), monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), dimethyl ester of 3,3', 4,4'-benzophenone-tetracarboxylic acid (BTDE), and 4,4'-methylenedianiline (MDA)⁵. Their chemical structures are shown in Figure 1. In this study, three PN modified resin compositions were evaluated, along with the control, PMR-15. Table 1 shows the compositions of these four resin systems. The unidirectional composite materials were compression molded, following a previously established processing cycle⁵. All composite systems were cured at 316° C for 2 hours under 3.45 MPa pressure. To obtain similar resin contents for the molded composites, a different pressurization temperature was employed for each composite system⁵. The fiber content of the composite systems including the control varied from 58 to 60 volume percent as determined by the H₂SO₄/H₂O₂ digestion method. The composites were examined by ultrasonic C-scan for voids and defects prior to the dynamic mechanical testing. None of the composites showed any detectable voids and defects.

The dynamic shear measurements were performed using a Rheometric dynamic spectrometer, Model 7700. Rectangular composite specimens having a length of 63.5 mm, width of 12.7 mm, and thickness of 1.3 mm with the fiber axis perpendicular to the specimen length were subjected to forced torsional

oscillations. The specimens were clamped to the fixtures in the chamber and the temperature of the chamber was allowed to equilibrate to -150°C , using liquid nitrogen as a cooling agent. As soon as the equilibrium temperature of the chamber reached -150°C , measurements were made at a constant strain of 0.1 percent and a constant frequency, using a temperature sweep mode. The temperature of the specimens was raised from -150° to $400^{\circ}\text{C} \pm 2^{\circ}\text{C}$ at a heating rate of $2^{\circ}\text{C}/\text{minute}$. The storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) were recorded and plotted against temperature at each 2°C interval. For experiments to determine the frequency dependence of the dynamic shear properties, three decades of frequency varying from 0.2 to 100 cycle/second were employed. Unless specified, the frequency used was 1 cycle/second. Two to four specimens per composite system were tested to determine the reproducibility of the measurements.

RESULTS AND DISCUSSION

Temperature Dependence of G' , G'' , and $\tan \delta$

Figure 2 illustrates a typical dynamic shear spectrum for Celion 6000/PMR-P1 composite. Three parameters: storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$), were recorded. In the glassy state of the matrix resin, the G' values declined slightly from 7×10^{10} to 3×10^{10} dyne/cm² over the temperature range from -150° to 320°C . Near 330°C , however, a marked decrease of the G' values was seen, indicating that the matrix undergoes a glass-rubber transition. In the glass-rubber transition region from 330° to 360°C , the G' values decreased from 3×10^{10} to 5.3×10^9 dyne/cm². At 385°C - a temperature 40°C above the glass transition temperature (T_g) of the matrix - the G' reached a plateau, giving an equilibrium G' (G_r') value of 2.5×10^9 dyne/cm².

Three well-defined transition peaks can be seen in the G'' and $\tan \delta$ curves. The transition peaks are associated with three relaxation mechanisms of the matrix resin and are assigned as α , β , and γ peaks. The temperatures of maximum losses for these relaxations are designated as $T_{\alpha\text{max}}$, $T_{\beta\text{max}}$, and $T_{\gamma\text{max}}$. They occurred around 343° , 100° , and -115°C , respectively, in the G'' curve. While the $T_{\beta\text{max}}$ and $T_{\gamma\text{max}}$ were seen at about the same positions, $T_{\alpha\text{max}}$ occurred approximately 20°C higher in the $\tan \delta$ curve than in the G'' curve. The $T_{\alpha\text{max}}$ of the G'' curve was defined as the glass transition temperature (T_g) of the polymer⁶. Other composite systems exhibited similar dynamic mechanical spectra as that shown in Figure 2. Table 2 summarizes the temperatures of maximum mechanical losses for the four composite systems studied. Excellent reproducibility (maximum error 5%) of the dynamic mechanical spectrum was obtained for the PMR-P1 composite system.

Comparison of the dynamic shear spectra for the PN modified PMR composite systems with that of the control, as seen in Figure 3, reveals that a great deal of similarity exists in their dynamic mechanical behavior. Of particular importance is that neither additional relaxation peaks nor unusual dynamic shear behavior was observed in the spectra of the modified composite systems. This suggests that the PN modified PMR polyimides, like PMR-15, are homogeneous polymeric materials and contain no detectable quantities of a second phase polymeric material which could be formed from the homopolymerization of PN.

Figure 3 also shows the effects of PN concentration on the dynamic shear properties of the composite systems. When PN was increased from 0 to 7.8 mole percent, the glass transition temperature of the composite decreased

from 345° to 330° C. This behavior was also found in the previous study⁵. A similar trend was also observed for T_βmax (from 102° to 85° C) and T_γmax (from -112° to -120° C). Furthermore, the intensities of the three relaxation peaks were enhanced. These findings suggest that a polymer having a reduced crosslinking density is produced,^{4,7,8} when PN is added to the PMR-15 composition.

Activation Energies of α, β, and γ Relaxations

Figure 4 shows the variation of tan δ with temperature at various frequencies for Celion 6000/PMR-P1 composite. When the frequency was stepwise increased from 0.2 to 100 cycle/second, the T_αmax, T_βmax, and T_γmax of the tan δ curve progressively shifted to higher temperatures. In the range of frequencies studied, the T_αmax increased from 358° to 380° C, T_βmax from 90° to 123° C, and T_γmax from -120° to -95° C. This behavior was also observed for the other three composite systems.

Figure 5 shows the frequency in logarithm scale as a function of reciprocal absolute temperature for the T_αmax, T_βmax, or T_γmax of the four composites studied. As evident from Figure 5, the dependence of the T_αmax, T_βmax, and T_γmax on the frequency used follows an Arrhenius relation:

$$\log \text{ frequency} = \frac{-E_a}{2.303 R T_{\max}} + C$$

where E_a is the apparent activation energy, R is the gas constant, T_{max} is the absolute temperature for T_αmax, T_βmax, or T_γmax, and C is a constant⁷⁻⁹. From the slopes of the straight lines shown in Figure 5, the activation energies for the α, β, and γ relaxation processes were estimated and are given in Table 3. It should be noted that each data point in Figure 5 represents a single experiment. Because of the limited data obtained, the precision for the values of the activation energies given in Table 3 was not determined. The data of Table 3 seem to indicate the trend that as the PN content increased, the activation energies decreased. The decrease appears to level off between 5.2 to 7.8 mole percent PN used in the matrices. Since an activation energy measures the average potential barrier restricting the mobility of the particular group of atoms, the magnitudes of the activation energies presented in Table 3 seem to be consistent with the following assignments¹⁰⁻¹¹. The α relaxation of the present polyimide networks is due to the segmental motions of large groups involving several main chains; the β relaxation is attributable to the coordinated motions of small groups within a main chain; and the γ relaxation arises from the rotational motions of small groups around single bonds.

Lowering the energies required to activate the molecular motions for PN modified PMR polyimides is a good indication that the modified polymers are more flexible and have greater mobility than the unmodified PMR-15 system¹⁰⁻¹¹. This is in agreement with the previous findings on the variations of the glass transition temperature and the damping peak magnitude with the content of PN.

Formation of Copolymer

On the basis of the interpretation of the dynamic mechanical data, the present study suggests that PN copolymerizes with the PMR-15 prepolymer to give a copolymer. Figure 1 shows the proposed structure of a PN modified PMR polyimide. The PMR-15 structural unit (shown in X bracket) consists of a long chain terminated by four crosslinking sites. The PN structural unit

(shown in Y bracket) contains a short phenyl side group and two crosslinking sites. When the PMR-15 structural units are replaced with the PN units, a randomly arranged copolymer is produced which would have increased free volume between crosslinks. This would reduce the crosslinking density and enhance the mobility between chain segments. This is consistent with what was observed in the dynamic mechanical data. The PN modified PMR polymer systems exhibit (1) lower glass transition temperatures, (2) lower activation energies of the relaxation motions, and (3) higher damping peak heights, compared to the unmodified PMR-15 system. It seems reasonable to expect that if a homopolymer of PN were produced and present with a PMR-15 Polymer, distinctly different dynamic mechanical behavior due to a homopolymer of PN would have been observed. This is because the structure of a low molecular weight linear homopolymer of PN¹² differs considerably from the structure of a high molecular weight crosslinked polymer of PMR-15. As mentioned previously, the dynamic mechanical spectra for the modified composite systems closely resemble that of the control. No additional relaxation peaks or unusual dynamic mechanical parameters were observed in the modified specimens. This suggests that a single phase, rather than a two-phase, polymeric materials were formed from the modified formulations, as from the unmodified PMR-15.

As noted above, PN in the absence of other monomers forms a low molecular weight, rather than a high molecular weight, homopolymer¹². Such a low molecular weight material is expected to be thermo-oxidatively unstable at 316° C. Our previous study showed that the composites based on PN modified PMR polyimide resins reinforced with Celion 6000 graphite fibers exhibited outstanding thermo-oxidative stability at 316° C for 1500 hours⁵. This behavior is inconsistent with the formation of a PN homopolymer. Also, the polymer of PN is known to be readily soluble in organic solvents, for example, chloroform¹³. The absence of a chloroform extractable substance from the PN modified composites provided additional evidence against the formation of a PN homopolymer.

SUMMARY OF RESULTS

This investigation has shown: (1) norbornene end-capped addition polyimides undergo α , β , and γ relaxations in the regions of 360° C, 100°, and -120° C, respectively; (2) activation energies for the above three relaxations were estimated to be 232, 60, and 14 kcal/mole, respectively, for PMR-15; (3) addition of N-phenyladimide to the PMR-15 composition causes (a) lowering the activation energies of the three relaxations, (b) decreasing the glass transition temperature, and (c) increasing the intensities of the three damping peaks, compared to those of PMR-15; and (4) formation of a more flexible copolymer from N-phenyladimide and PMR-15 prepolymer is consistent with the dynamic mechanical data obtained.

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TABLE 1. COMPOSITIONS OF PMR POLYIMIDES

Resin	PN Mole % ^a	Monomer, g ^b			
		PN	NE	MDA	BTDE
PMR-15 (Control)	0.0	0.0000	3.8329	5.9742	7.8711
PMR-P1	0.6	0.0867	3.8329	5.9742	7.8711
PMR-P6	5.2	0.9333	3.8329	5.9742	7.8711
PMR-P7	7.8	1.400	3.8329	5.9742	7.8711

$${}^a\text{PN mole\%} = \frac{\text{moles of PN}}{\text{moles of (PN + NE + MDA + BTDE)}} \times 100$$

^bQuantities used for preparing a 7.6cm by 20cm by 0.13cm cured composite.

TABLE 2. TEMPERATURES OF MAXIMUM MECHANICAL LOSSES FOR PMR POLYIMIDES^a

Resin	Temperature of Maximum G''/Tanδ, °C		
	T _{αmax} (T _g)	T _{βmax}	T _{γmax}
PMR-15 (Control)	345/371	101/102	-113/-112
PMR-P1	343/364	100/97	-115/-116
PMR-P6	338/358	84/85	-120/-120
PMR-P7	330/355	84/85	-120/-120

^aDetermined at 1 cycle/second frequency

TABLE 3. ACTIVATION ENERGIES FOR PMR POLYIMIDES

Resin	Activation Energies (Kcal/mole)		
	α	β	γ
PMR-15 (Control)	232	60	14
PMR-P1	224	53	13
PMR-P6	183	45	9
PMR-P7	181	49	9

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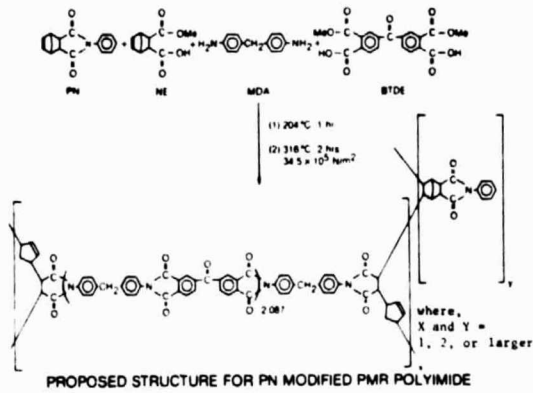


Figure 1 - Synthetic reaction for PN modified PMR polyimide.

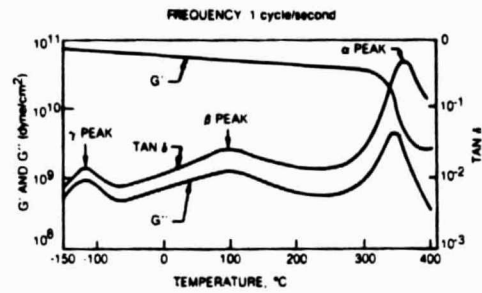


Figure 2. - Typical dynamic shear properties of Celion 6000 PMR-P1 composite.

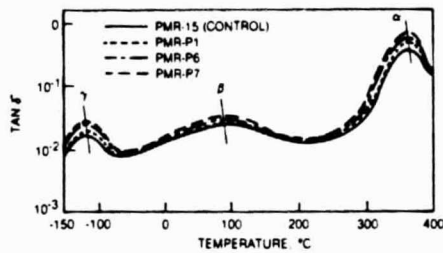


Figure 3. - Effects of N-phenylnadimide content on positions and magnitudes of tan δ peaks for PN modified PMR polyimides.

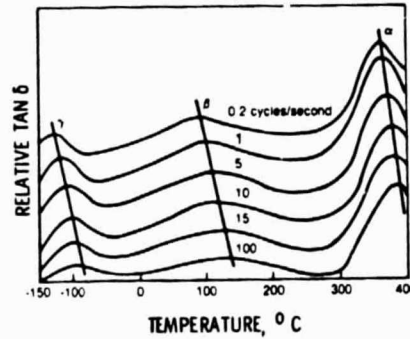


Figure 4 - Frequency - temperature dependence of tan δ for Celion 6000 PMR-P1 composite.

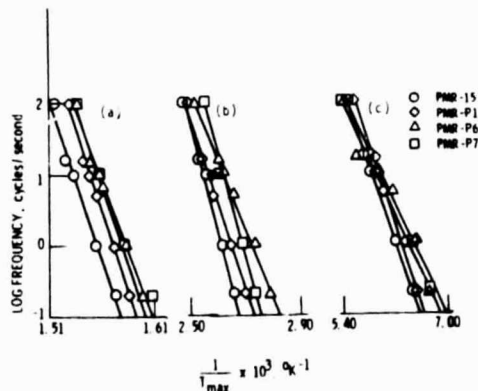


Figure 5. - Log frequency versus $(1/T_{max}^0 K)$ for PN modified PMR polyimides. (T_{max}^0) refers to temperature of maximum tan δ loss in constant frequency experiments. (a) α -, (b) β -, (c) γ -relaxation.