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RHEOLOGICAL, PROCESSING, AND 371 °C MECHANICAL PROPERTIES  
OF CELION 6000/N-PHENYLNADIMIDE MODIFIED PMR COMPOSITES

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The rheology, processing, and chemistry of newly developed N-phenylnadimide modified PMR (PMR-PN) polyimide resins are reviewed. The 371 °C performance of their composites reinforced with Celion 6000 graphite fibers is also reviewed, along with the state-of-the-art Celion 6000/PMR-15 composite. The effects of the 371 °C exposure in air for up to 300 hr on the composite glass transition temperatures, weight loss characteristics, and dimensional stability are presented. The changes in the composite 371 °C interlaminar shear and flexural properties are also presented. In addition, composite interfacial degradation as a function of exposure time at 371 °C was followed by scanning electron microscopy. The results suggest that the composite materials can be used at 371 °C for at least 100 hr.

INTRODUCTION

High-performance polymer matrix composites constitute a class of engineering materials that have significant potential for application in advanced aircraft engines. In the past 10 years considerable effort has been made toward the design and fabrication of a variety of advanced composite components which operate at a temperature range of 260 to 316 °C (ref. 1). A significant improvement in engine efficiency could be achieved by extending the use temperature of advanced composites up to 371 °C. Thus far, most high-temperature polymer matrix composite studies have been conducted at temperatures of 316 °C and below. Composite performance above 316 °C, however, has not been extensively investigated (refs. 2 and 3). Because of this lack of property data at temperatures above 316 °C, composite applications at higher temperatures, such as 371 °C, cannot be assessed realistically at the present time.

In 1981, a new series of N-phenylnadimide (PN) modified PMR polyimides (ref. 4) was reported. These are designated as PMR-P1, -P2, etc., where P1, P2, etc., refer to a formulation containing a given quantity of PN. Collectively, they are designated as PMR-PN. Initial studies revealed that the composites prepared from these matrices and Celion 6000 graphite fibers exhibited excellent processability and thermo-oxidative stability at 316 °C in air for up to 1500 hr (ref. 4). Composite dynamic mechanical properties were also investigated from the viewpoint of clarifying the resin chemistry (ref. 5).

This paper reviews the rheology, processing, chemistry, and 371 °C properties of PMR-PN resins and their composites reinforced with Celion 6000 graphite fibers. Data are presented on the physical, thermal, and mechanical properties of the composites aged at 371 °C in air.

## RESULTS AND DISCUSSION

### Rheological and Processing Characteristics

**Resin rheology.** - The modified resins are prepared from in-situ thermal polymerization of four monomer reactants: the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE), 4,4'-methylenedianiline (MDA), the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), and N-phenylnadimide (PN). Their chemical structures along with the idealized cross-linked polyimide structure are shown in figure 1. Table I gives the chemical compositions of the modified (PMR-PN) and unmodified (PMR-15) PMR polyimides investigated. This table shows that the PN contents in the four PMR-PN formulations are relatively low compared to the amounts of the other three monomers.

Despite relatively low quantities of PN employed, PN exerts a significant influence on the rheological properties of PMR-PN resins and composites as explained below. Further, the flow properties of the modified resins exhibited a strong dependence on the stereochemistry of PN which exists in two isomeric forms: endo and exo. As seen in figure 2, the use of endo-N-phenylnadimide in PMR-P1 formulation (curve c) causes a decrease while the use of exo-N-phenylnadimide in the same formulation (curve a) causes an increase in the minimum viscosity of PMR-15 (curve b). This behavior can be attributed to the melting-point difference between these two isomers as shown in figure 3. The endo-isomer shows a sharp endotherm at 145 °C due to melting, while the exo-isomer shows a considerably higher melting temperature (195 °C). The exotherms at 360 and 367 °C for exo- and endo-PN, respectively, are due to their polymerization reaction.

Therefore, to obtain improved flow, the use of the endo-form of PN, rather than the exo-isomer, is recommended. For this reason, PMR-PN resins reported hereafter use the endo-form of PN to improve their flow characteristics.

Figure 4 shows the influence of endo-PN concentration on the dynamic shear viscosity of the imidized molding powders (ref. 4). In comparing curves b through g with curve a, it can be seen that the PMR-PN samples exhibited lower shear viscosities than PMR-15 over the temperature range of 238 to 303 °C. The minimum viscosities for the PMR-PN samples ranged from 1769 dyne/cm<sup>2</sup> for PMR-P1 to 884 dyne/cm<sup>2</sup> for PMR-P5, compared with a value of 2940 dyne/cm<sup>2</sup> for the control PMR-15. This represents a decrease of 40 to 70 percent in the minimum viscosity of PMR-15. Figure 5 shows that the addition of the first 4 mole percent of PN (PMR-P1) to PMR-15 causes a significant and disproportionate reduction in the minimum shear viscosity. A linear correlation between the minimum viscosity and PN concentration appears to exist in the PN concentration range of 4 to 20 mole percent.

**Processing characteristics.** - The resin flow characteristics in composites are known to have significant effects on composite processing and properties. A plot of the resin flow in Cellion 6000/PMR-PN composites as a function of the PN concentration is shown in figure 6. Note that, in order to provide a valid basis for comparing resin flow behavior, all of the composites were molded using the same cure cycle (ref. 4). From figure 6, it is evident that the PMR-PN composites, like the PMR-PN molding powders discussed previously, exhibited improved resin flow compared to PMR-15 composite. These results indicate that PN is an effective flow-modifying agent. This can be attributed to the fact that PN exists in the liquid

state up to the cure temperature (316 °C). These results also suggest that the flow properties of PMR-PN resins and composites can be tailored to meet specific processing requirements by adding small quantities of PN.

Studies reported in reference 4 showed that resin flow in compression-molded PMR-PN composites could also be controlled by varying the pressurization temperature in the cure cycle. For example, increasing the pressurization temperature from 232 °C for PMR-15 to 282, 288, 293, and 299 °C for PMR-P1, -P2, -P3, and -P4 composite systems, respectively, reduced the composite resin flow to about 3 percent, which is equivalent to the resin flow of PMR-15 composite.

#### Postulated Structure of PMR-PN Polyimides

As mentioned previously, figure 1 shows the chemical structures of four monomer reactants, PN, NE, MDA, and BTDE, used in the synthesis of PMR-PN polyimides. It is postulated that the three monomers, NE, MDA, and BTDE, first react to form a PMR-15 imide prepolymer through an amic acid intermediate. It is further postulated that the imide prepolymer can undergo a crosslinking reaction with itself and with PN to give a crosslinked homopolymer or copolymer system. The presence of a copolymer as an integral part of the polymer system is supported by the dynamic mechanical properties reported previously (ref. 5).

The incorporation of PN into the PMR-15 polymer network could result in a change in the basic structure of PMR-15 which, in turn, could alter the chemical properties of PMR-15. The idealized structures of PMR-15 and PMR-PN polyimides are shown in figures 7 and 8, respectively. In PMR-15 the molecular structure between the crosslinking sites consists of several aromatic and imide functionalities. A molecular model (not shown) of the idealized structure of PMR-15 demonstrated that there is considerable steric crowding and interaction between neighboring chains. This steric crowding can be substantially reduced, when some of the PMR-15 chain groups are replaced with the pendant phenyl group from PN. With such a replacement, not only would the steric crowding be reduced, the crosslinking density would also be reduced because there are only two crosslinking sites in each PN, while there are four in each PMR-15 structural unit. Thus, the replacement would lead to a copolymer having increased flexibility due to decreased crosslinking density and possibly increased free volume. This hypothesis is consistent with the physical and mechanical properties determined in the previous studies (refs. 4 and 5).

#### Effects of 371 °C Postcure and Aging on Physical, Thermal, and Mechanical Properties of Celion 6000/PMR-PN Composites

Physical properties. - The effects of 16- and 30-hr postcures at 371 °C on composite weight loss and dimensional changes of the composite systems are listed in table II. Approximately 2 percent weight loss was experienced by all composites after 30 hr of postcure. All composites exhibited 1 percent shrinkage in the transverse direction to the fibers, and as expected, nondetectable dimensional change in the longitudinal direction for either 16- or 30-hr postcure. Weight losses at 371 °C for exposure times up to 300 hr are shown in figure 9. After 300 hr, PMR-P1 and PMR-P2 exhibited the lowest weight losses (~5.7) compared to the control system PMR-15 (7.2).

Thermal properties ( $T_g$ ). - Figure 10 shows the effects of 371 °C exposure in air on the glass transition temperature ( $T_g$ ) of the composites. The lower initial  $T_g$  for PMR-PN systems compared to the  $T_g$  of PMR-15 system may be explained on the basis of a lower crosslink density for PMR-PN relative to PMR-15 as discussed previously. The attainment of maximum  $T_g$  for the PMR-PN and PMR-15 composites follows a stepwise process and occurs in two distinct stages: (a) stage one occurs within the first 30 hr of postcure in which a rapid increase in  $T_g$  occurs. The rate constant ( $k_1$ ) for this step varied from 2.0 °C/hr for the control (PMR-15) to 1.5 °C/hr for the P-4 specimen; (b) stage two occurs between 30 to ~160 hr; the rate constant  $k_2$  was found to be 0.11 °C/hr, which is approximately 14 times slower than  $k_1$ . This may be explained by a decrease in concentration of crosslinkable groups with time and/or by a quenching effect due to molecular immobility. The dependence of  $T_g$  on the exposure time can be expressed by the following equation:

$$T_g = k_1 \ln t + C \quad (1)$$

where  $k_1$  is the rate constant for either stage one or stage two,  $t$  is time, and  $C$  is a constant. Normally, a postcure time of 10 hr at 316 °C is employed for PMR composite materials intended for use at 316 °C. The results presented in figure 10 and equation (1) suggest that longer postcure times at 371 °C are required, if the materials are to be used at 371 °C. The composites attained a  $T_g$  of 371 °C after a postcure time of 50 hr or longer at 371 °C.

Mechanical properties. - Figures 11 and 12 show the 371 °C mechanical properties of the composites, after a 30-hr 371 °C postcure, followed by exposure up to 100 hr in air at 371 °C. Even though testing temperature (371 °C) was above or close to the glass transition temperatures, most of the composite materials exhibited good mechanical properties at 371 °C during the first 100 hr of exposure. Thus, a 30-hr postcure time appears to be adequate for attaining a useful level of mechanical properties at 371 °C. Prior to exposure at 371 °C, PMR-PN composites exhibited lower flexural strengths (fig. 11), but somewhat higher interlaminar shear strengths (fig. 12), compared to the control. After the 100-hr exposure, all PMR-PN composites exhibited higher flexural and interlaminar shear strengths than the control specimen PMR-15, particularly the PMR-P1 and PMR-P2 composite systems. The increase in the 371 °C flexural and interlaminar shear properties during the 50-hr exposure interval from 50 to 100 hr indicates that the useful lifetime of PMR-PN composite materials may be greater than 100 hr. This is supported by the thermogravimetric analysis (TGA) data of PMR-P1 resin shown in figure 13 which shows that PMR-P1 resin aged for 100 hr at 371 °C in air is more thermo-oxidatively stable than both the unaged and 371 °C, 200-hr aged samples.

In addition to the mechanical properties presented previously, the trend for the higher thermo-oxidative stability of PMR-P1 and PMR-P2 composite systems at 371 °C is further supported by the weight loss data presented in figure 9 and the fiber retention comparison illustrated in figure 14. Thus, the thermo-oxidative stability of the PMR-PN composite systems follows the order (from ref. 4)

$$\text{PMR-P1} \sim \text{PMR-P2} > \text{PMR-P3} \sim \text{PMR-15} > \text{PMR-P4}$$

Scola reported that the thermo-oxidative degradation of Celion 6000/PMR-15 at 335 °C occurs only at exposed composite surfaces and that oxidative degradation and pyrolysis do not occur within the bulk of the composite system (ref. 3). Figure 15 shows the SEM micrographs of PMR-P1 composites aged at 371 °C for time periods up to 200 hr. The micrographs shown were taken near the exposed surfaces of the

composites. No matrix or interfacial degradation was observed as a result of the 30-hr postcure at 371 °C in air (fig. 15(a)). However, some matrix degradation occurred between 0 and 120 hr at 371 °C in air (fig. 15(b)). Continued exposure to 200 hr resulted in extensive matrix and interfacial degradation (figs. 15(c) and (d)). The other PMR-PN composite systems exhibited similar interfacial characteristics as that of PMR-P1 during the thermo-oxidative treatment.

The minimal degradation as assessed by SEM analysis and the high level of mechanical properties of the composites after 100 hr at 371 °C in air suggest that the 371 °C useful life of the PMR-PN composites is at least 100 hr.

### CONCLUSIONS

PMR-PN resins exhibit higher resin flow characteristics than the unmodified PMR-15 system. Addition of PN does not compromise the elevated temperature properties of PMR-15; in fact, the results indicate that the 371 °C shear and flexural properties of the PMR-P1 and PMR-P2 modified systems after 100 hr aging at 371 °C are superior to those of PMR-15. The addition of PN appears to be a technically sound approach for attaining PMR-polyimide formulations with improved processing characteristics without sacrificing the thermo-oxidative stability of the resin and composite systems.

### REFERENCES

1. Serafini, Tito T.; Delvigs, Peter; and Alston, William B.: PMR Polyimides - Review and Update. NASA TM-82821, 1982.
2. Pike, R.A.; and DeCrescente, M.A.: Elevated Temperature Characteristics of Borsic and Graphite Fiber/Polyphenylquinoxaline Resin Composites. The Wide World of Reinforced Plastics. Society of the Plastics Industry, New York, 1974, Section 18F.
3. Scola, Daniel A.: A Study of the Thermo-Oxidative Process and Stability of Graphite and Glass/PMR Polyimide Composites. 27th National SAMPE Symposium and Exhibition, SAMPE, Azusa, CA, 1982, pp. 923-939.
4. Pater, Ruth H.: Novel Improved PMR Polyimides. Technology Transfer, SAMPE, Azusa, CA, 1981, pp. 38-52.
5. Pater, Ruth H.: Dynamic Mechanical Properties of N-Phenylindimide Modified PMR Polyimide Composites. NASA TM-83051, 1983.

TABLE I. - COMPOSITIONS OF PMR-PN POLYIMIDES

Resin system	Monomer (mole)				PN mole percent <sup>a</sup>
	NE	MDA	BTDE	PN	
PMR-15 (control)	2	3.087	2.087	0.0	0.00
PMR-P1	↓	↓	↓	.041	0.57
PMR-P2	↓	↓	↓	.099	1.36
PMR-P3	↓	↓	↓	.136	1.87
PMR-P4	↓	↓	↓	.177	2.41

<sup>a</sup>PN mole percent = moles of PN/moles of (NE+MDA+BTDE+PN).

TABLE II. - EFFECTS OF 317 °C POSTCURE ON PHYSICAL PROPERTIES OF CELION 6000/PMR-PN POLYIMIDE COMPOSITES

Composite property	Postcure time, hr	Resin system				
		PMR-15 (control)	PMR-P1	PMR-P2	PMR-P3	PMR-P4
Weight loss, percent	16	1.6	1.6	1.6	1.6	1.7
	30	2.1	2.0	2.1	2.2	2.3
Transverse shrinkage, percent	16	0.9	0.9	1.0	1.0	1.0
	30	0.9	1.0	1.1	1.1	1.1

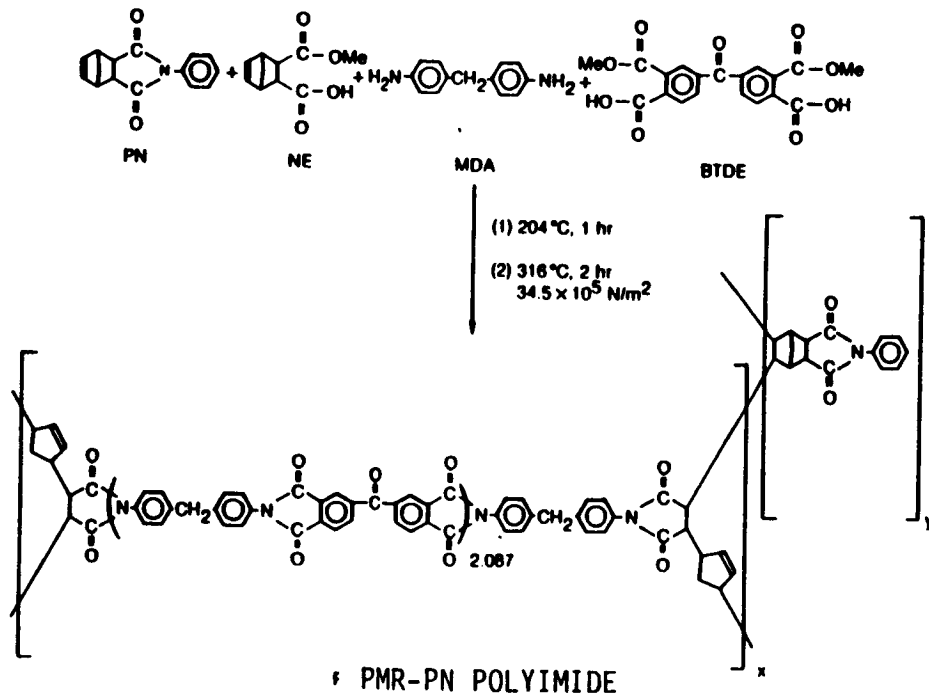


Figure 1. - Synthetic reaction for PMR-PN polyimides.

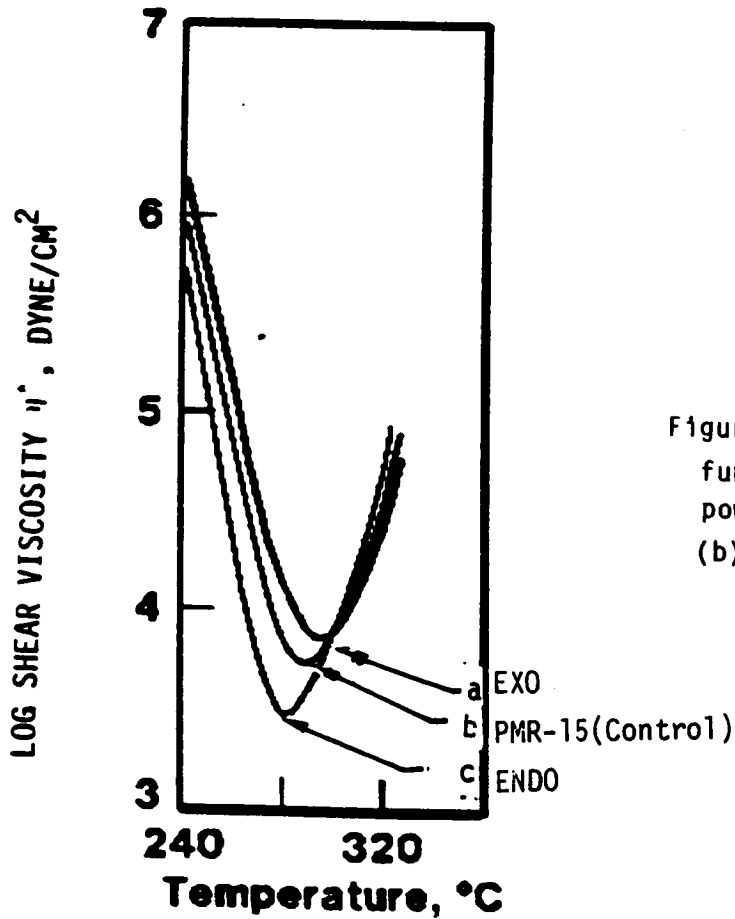


Figure 2. - Log shear viscosity as function of temperature for molding powders. (a) PMR-P1 using exo-PN. (b) PMR-15. (c) PMR-P1 using endo-PN.

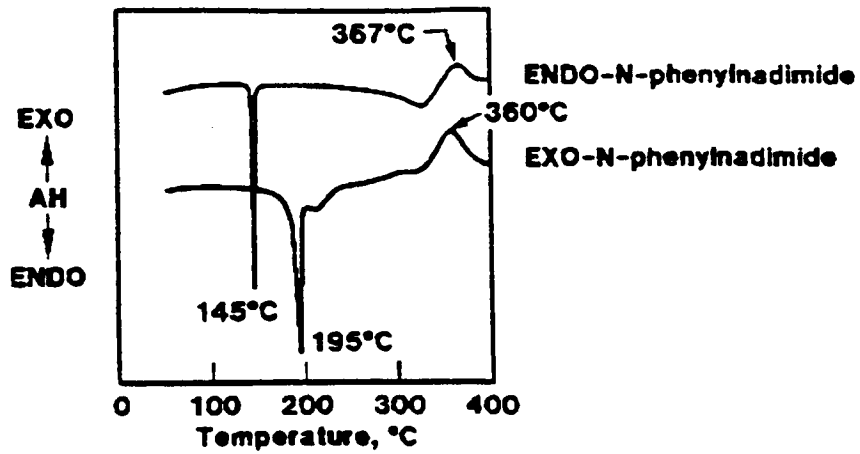


Figure 3.- Differential scanning calorimetry scans of endo- and exo-PN.

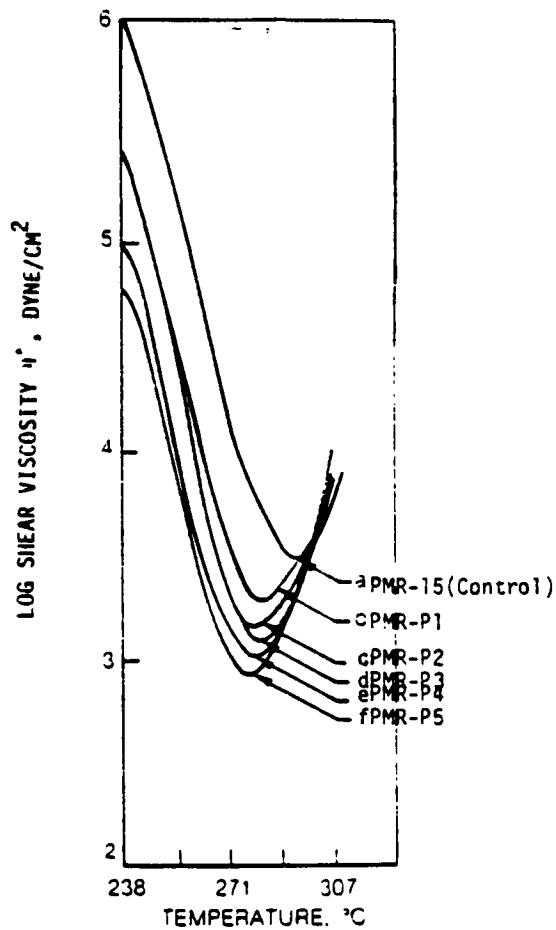


Figure 4. - Log shear viscosity as function of temperature for PMR-PN molding powders.



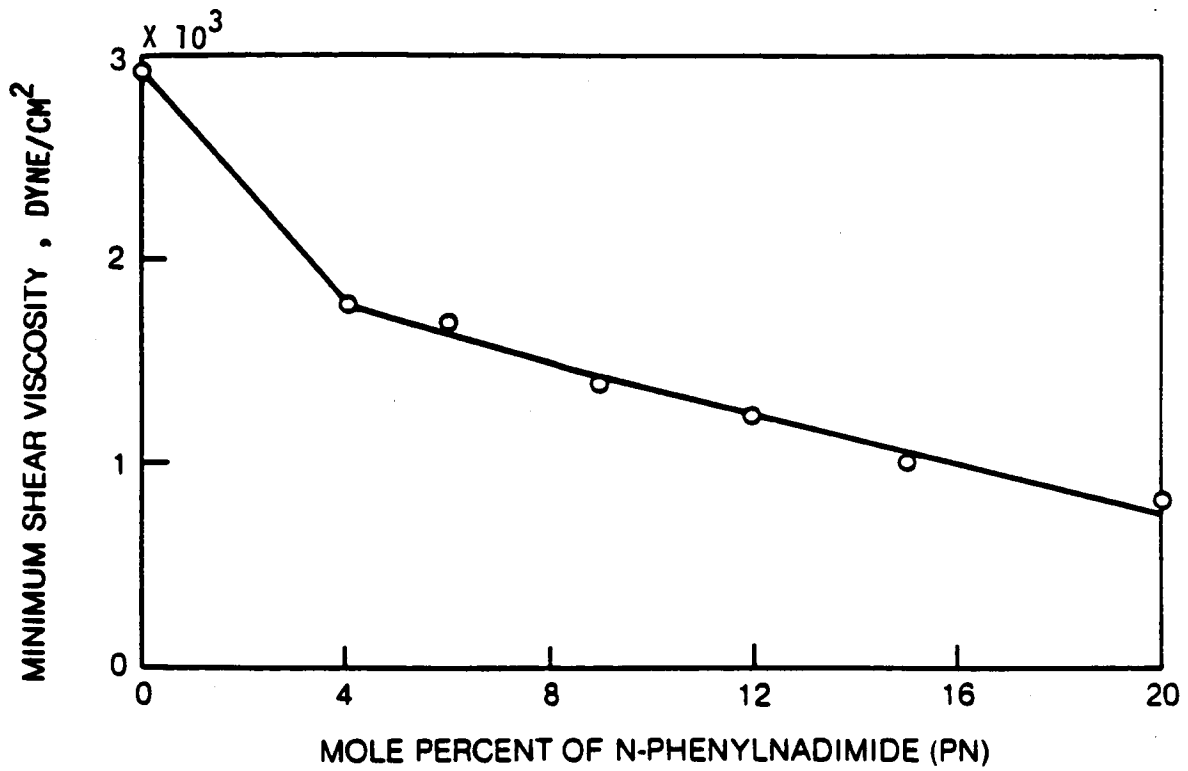


Figure 5. - Minimum shear viscosity as function of PN concentration for PMR-PN molding powders.

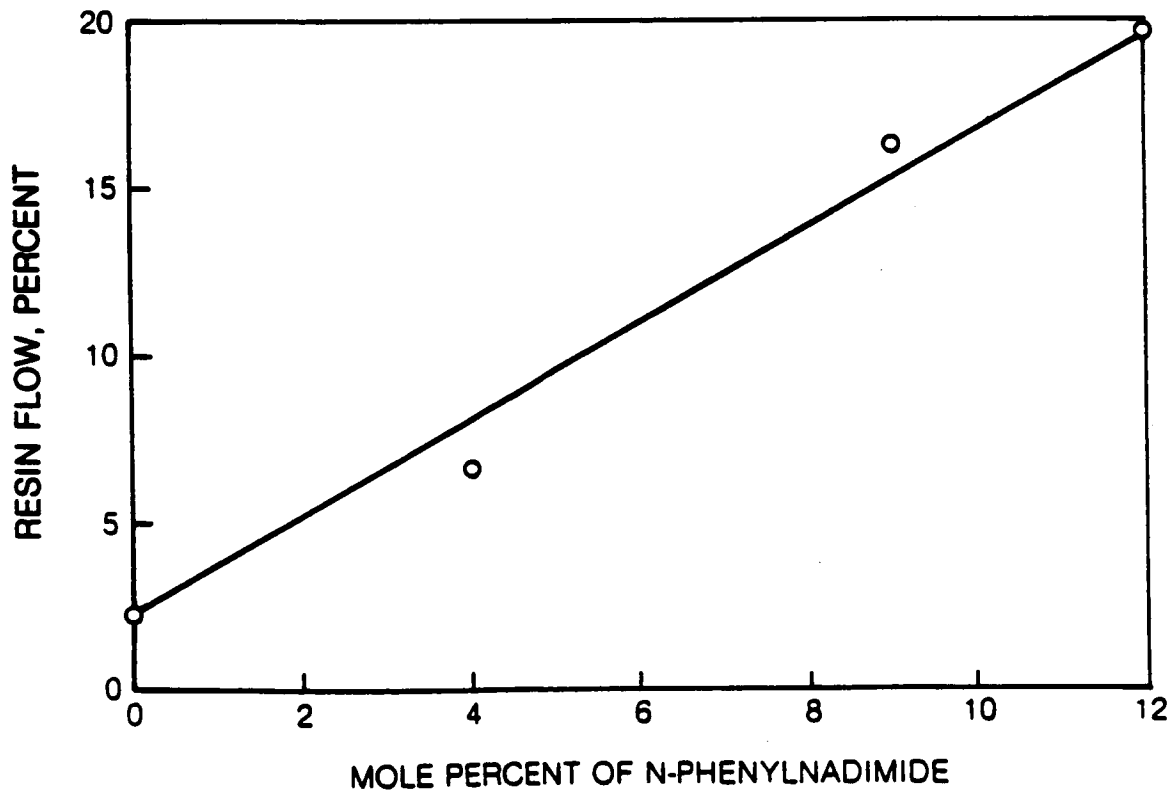


Figure 6. - Resin flow as function of PN concentration for Celion 6000/PMR-PN composites.

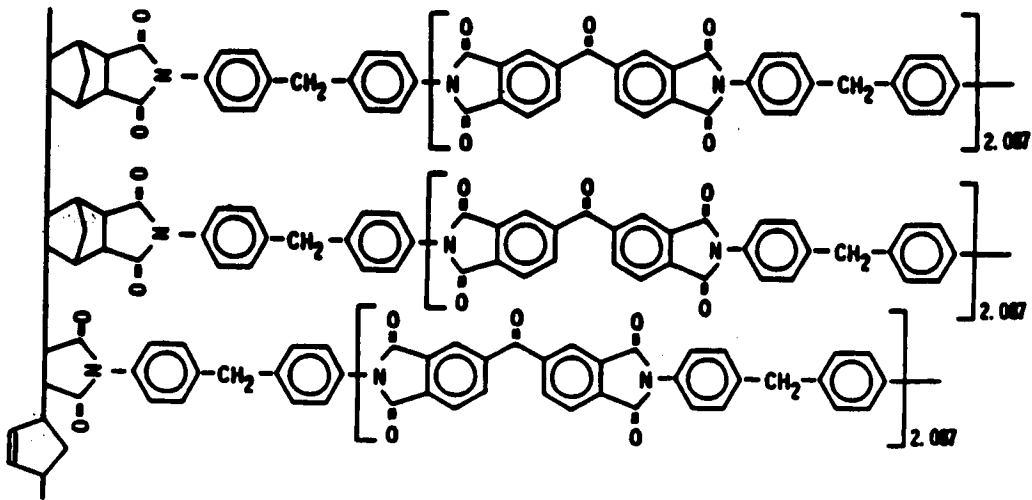


Figure 7. - Idealized structure for PMR-15.

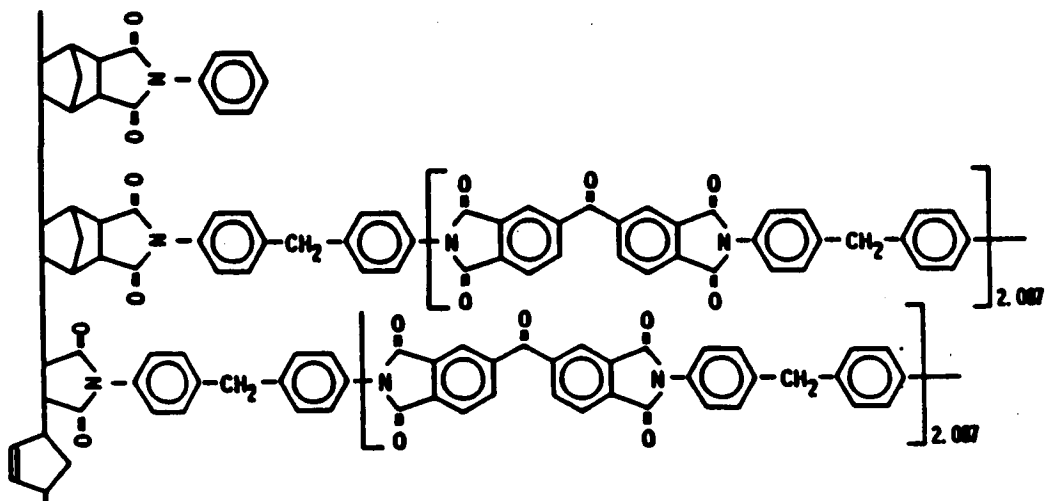


Figure 8. - Idealized structure for PMR-PN polyimide.

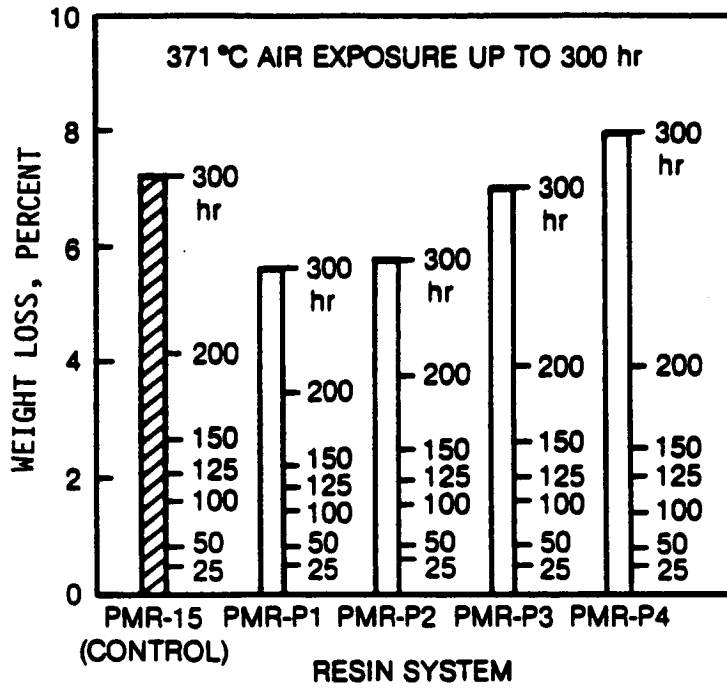


Figure 9. - Weight loss of postcured Celson 6000/PMR-PN composites.

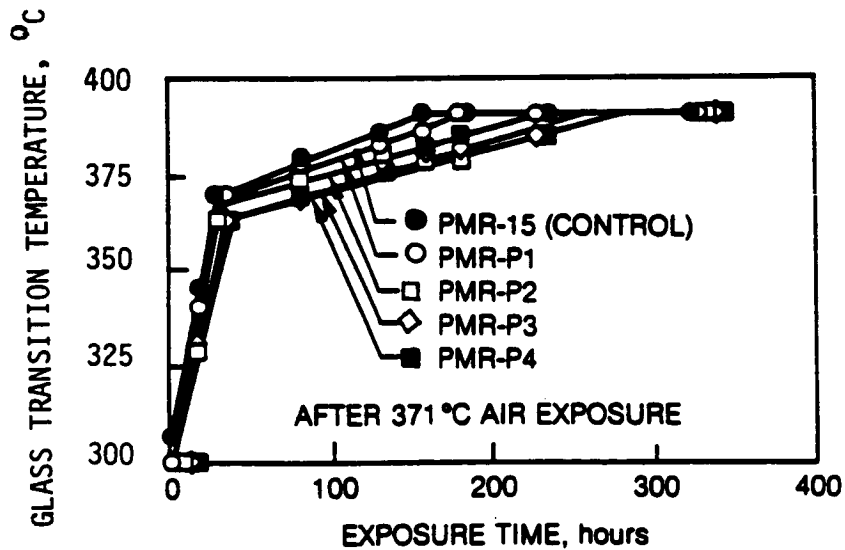


Figure 10. - Glass transition temperature as function of exposure time for as fabricated Celson 6000/PMR-PN composites.

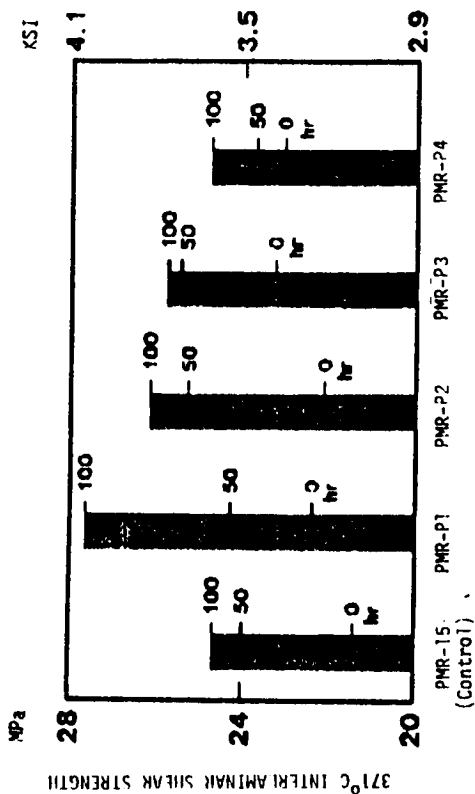


Figure 12. - Interlaminar shear strength of postcured Cellation 6000/PMR-PN composites at 371 °C.

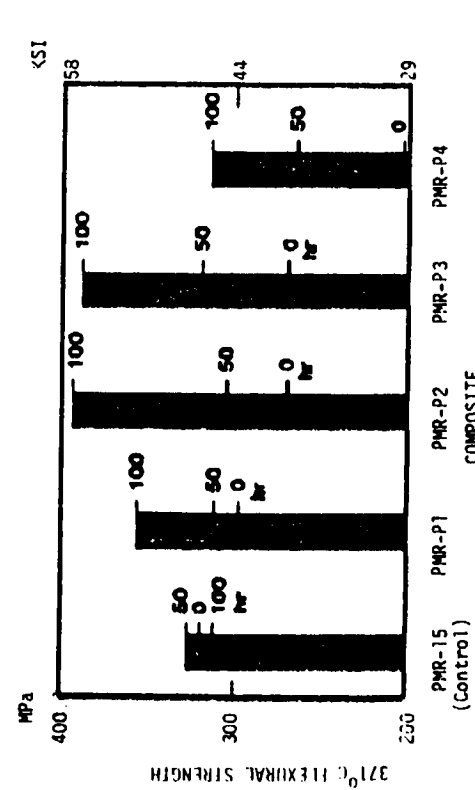


Figure 11. - Flexural strength of postcured Cellation 6000/PMR-PN composites at 371 °C.

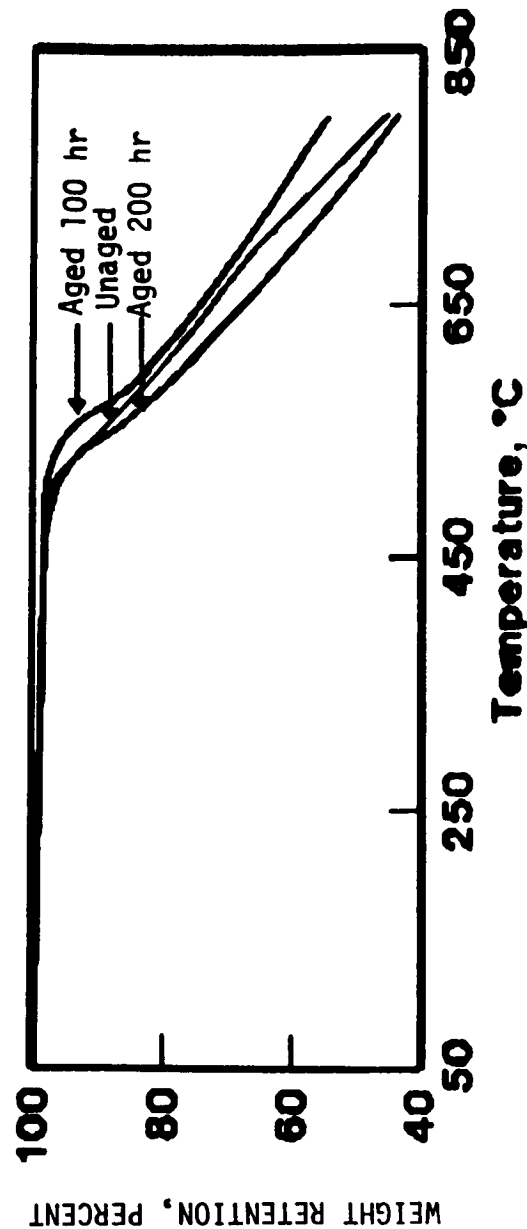
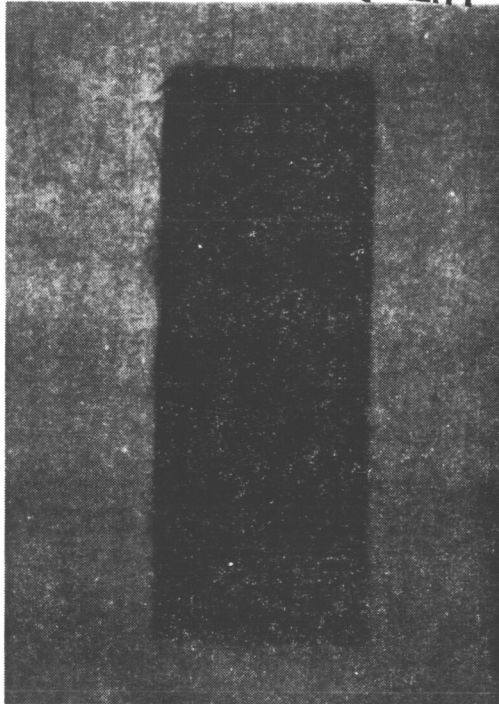


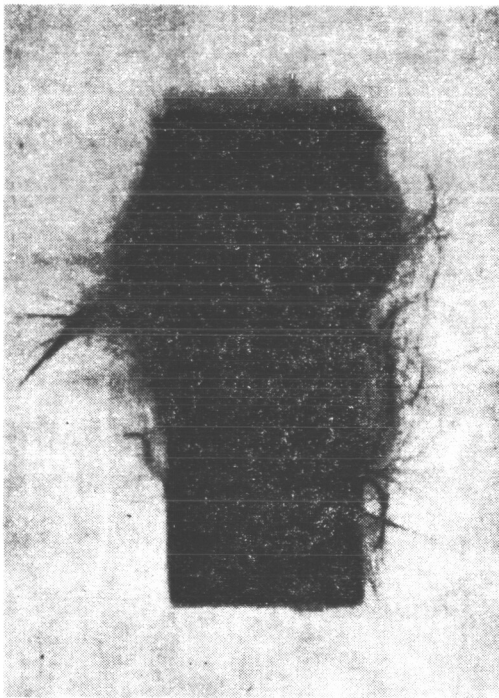
Figure 13. - Thermogravimetric analysis curves for PMR-P1 resin exposed in air at 371 °C.

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A. CELION 6000/PMR-P1

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B. CONTROL CELION 6000/PMR-15

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Figure 14. - Comparison of fiber retention characteristics for Celion 6000/PMR-P1 and control PMR-15 composites after a 30 hr postcure followed by a 200 hr exposure in air at 371 °C.

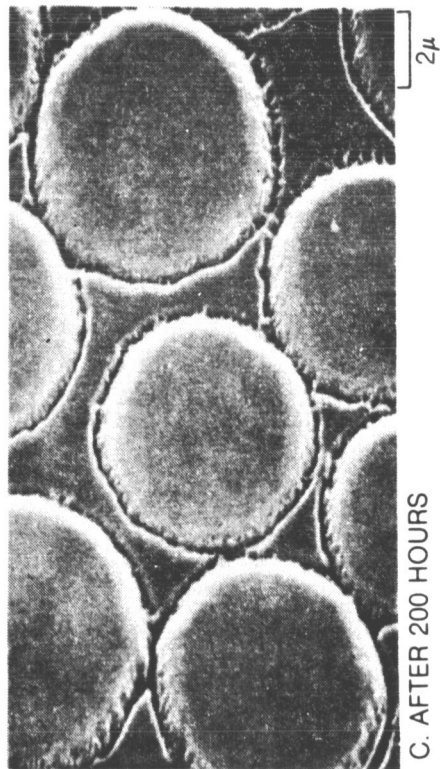
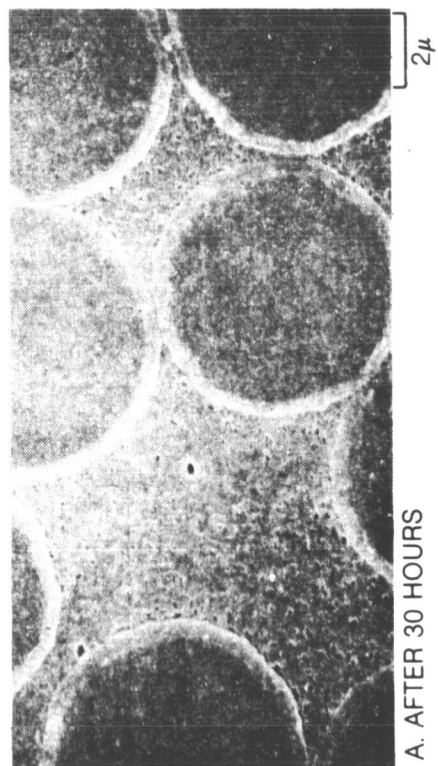
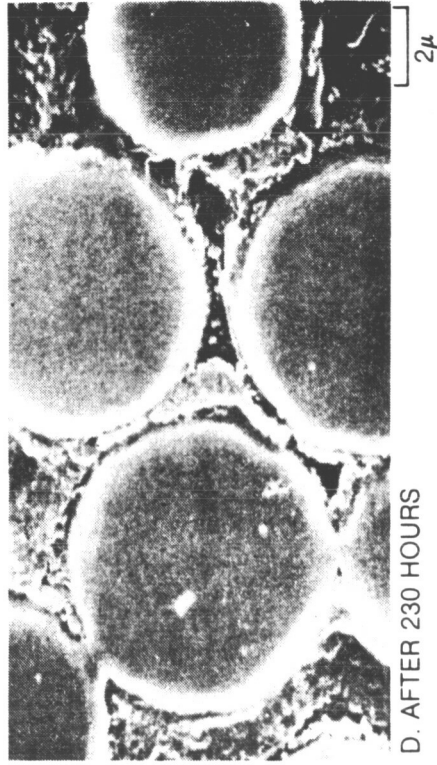
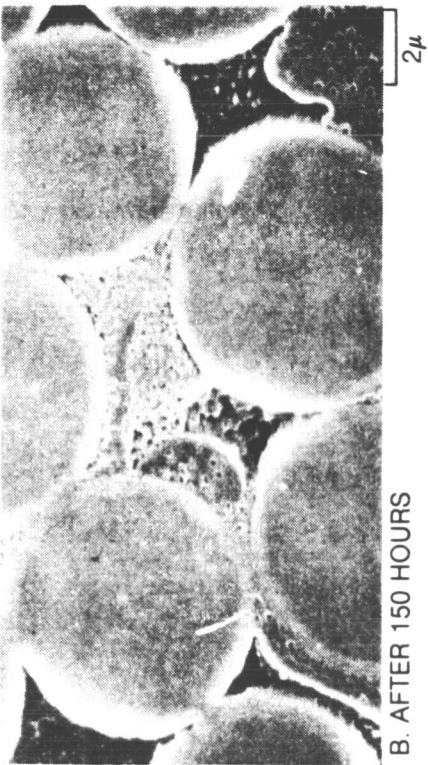


Figure 15. - SEM photomicrographs of Celion 6000/PMR-PI composites after a 30 hr postcure followed by exposure in air at 317 °C for 120, 170, and 200 hr, respectively.