

Effect of NBR on Epoxy/Glass Prepregs Properties

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ABSTRACT: Solid acrylonitrile-butadiene rubber (NBR) was used in epoxy resin for toughening and also for increasing the tack of epoxy/glass prepregs. The NBR used in this study was a rubber with 33% acrylonitrile content. The changes in thermal and mechanical properties such as glass transition temperature (T_g), curing characteristics and lap-shear strength have been studied. For this purpose, three types of prepregs with two levels of NBR content of 3 and 5%, were prepared. Prepregs were made by solvent type impregnation apparatus. In this method, resin impregnates satin textile glass fiber under the controlled and constant condition of line speed and oven tem-

perature. Prepregs were B-staged for about 3%. The cure characterization, T_g and flow behavior were evaluated using differential scanning calorimetry and rheological analysis. Results showed that increasing the rubber content caused the following effects: (a) delay in gel time of prepregs, (b) increase in activation energy of prepregs, and (c) decrease in total heat of curing reaction. It is interesting that NBR increased the tack of epoxy/glass prepreg but, had no effect on its resin flow behavior. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1597–1603, 2012

Key words: NBR; epoxy; prepreg; glass fiber; composites

INTRODUCTION

Epoxy/glass prepregs are widely used in the commercial airplanes, sports, and marine industries. One of the most important characteristic of prepregs is tack. Conventionally, prepreg tack has been defined as the capability of two prepreg plies to adhere to each other.^{1,2} Tack is one of the properties of prepreg that should be optimized. Accordingly, Seferis and coworkers recommended that prepreg tack is considered to be a bulk property rather than a surface property, depending on viscoelastic and surface characteristic of the individual prepreg plies.^{3–4} Matrix modification is one acceptable method to improve prepreg tack. On the other hand, epoxy resins used as matrix in epoxy/glass prepregs are characterized with outstanding performances such as toughness, rigidity, high temperature performance, chemical resistance, adhesive properties, and reactivity with a wide variety of chemical curing agents. The resin forms a highly crosslinked network structure having relatively high stiffness and glass transition temperature (T_g) with high chemical resistance. However, the inherent toughness of epoxy network is low.^{5–8}

It is now well established that the addition of low molecular weight liquid rubbers such as carboxyl terminated butadiene acrylonitrile, CTBN, or hydroxyl terminated poly butadiene, HTPB, are popularly used

as a modifier to epoxy resins. These rubbers could improve fracture toughness and interfacial adhesion of epoxy resins. It has been shown that the acrylonitrile content has a strong influence on solubility of rubber in epoxy resin and therefore is an important factor for the microstructure of rubber-toughened epoxies.^{7,9,10} Although liquid CTBN rubbers with low molecular weights and terminal functional groups are the most frequently used modifiers for toughening epoxy resins to date, no attempt has been made to use solid acrylonitrile butadiene rubber (NBR) with high molecular weight and no terminal functional groups to toughen epoxy and to improve the tack of epoxy/glass prepregs. Athwart CTBN and HTBN liquid rubbers, solid NBRs are readily available materials in the market at a much lower price.⁹

This work investigates the effect of solid NBR on epoxy resin properties such as glass transition temperature, cure behavior, and morphology. Its effect on epoxy/glass prepreg properties such as gel time, tack and lap shear strength are also investigated. Viscoelastic properties and thermal analysis of modified prepregs have also been studied.

EXPERIMENTAL

Materials

The epoxy resins used in this study were a combination of two epoxies based on diglycidyl ether of bisphenol-A included to, Epiro01 (EEW 530–560) and Epiro04 (EEW 225–230) manufactured by Khuzestan Petrochemical Company of Iran. The curing

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TABLE I
Resin Compositions

Formulation	Epiro01 (phr)	Epiro04 (phr)	NBR (%)	Monuron (phr)	DICY (phr)	Solvent (%)	Viscosity at 25°C (cp)
NBR0%	60	40	0	2	4	25	500
NBR3%	60	40	3	2	4	27	513
NBR5%	60	40	5	2	4	30	522

agent and the accelerator used were dicyandiamide and monuron, respectively manufactured by Merck and Aldrich Companies. The industrial type of methyl ethyl ketone was used as the solvent.

The elastomer used in formulation was solid NBR produced by Polymeria Europa with 33% acrylonitrile [Europerene (n33 45)]. The reinforcement used was a 8H satin glass fabric with an area density of 300 g/m². Resin formulation components and their compositions are shown in Table I. We would like to mention that the NBR which was used in this study has high molecular weight, and this caused a significant increase in resin viscosity and made difficulties in process capability of resin system such as fibers impregnation. On the other hand, the solubility of NBR in epoxy resin in high concentrations of NBR is very difficult. For this reason, we did not use higher NBR contents in this study.

Prepreg

A solvent type prepreg manufacturing process was used to prepare the experimental prepreg samples. The resin systems used for solution impregnation contained ~ 25% solvent to achieve a viscosity about 500cp at 25°C for impregnation. The processing parameters for all samples were 0.88 m/min line speed and 110°C average oven temperature. The nominal resin content was set at 40 ± 2 wt %.

EXPERIMENTS

Differential scanning calorimetry

DSC was performed using DSC200F3 equipment made by Netzsch Company, Germany. Dynamic-heating experiments were conducted in the flowing nitrogen environment (50 mL/min) and calibrated with an Indium standard. The uncured resin samples of 12 ± 2 mg sizes were placed in an aluminum pan with a pierced lid and placed opposite to the empty reference pan in the DSC chamber. The DSC was then set for temperature range of 25–300°C with heating rate of 5°C/min. The heating rate of 10°C/min was used for the second run for the determination of T_g . The sampling time was set to 6 s per point.

Scanning electron microscopy

SEM was performed using a VEGA model SEM made by TESCAN Company to examine the fracture surfaces of toughened epoxy matrices. The samples were coated with a gold sputter layer and the SEM filament voltage was set at 20 kV.

Rheological analysis

A MCR300 Rheometer made by Anton Paar Company was used to determine the rheological behavior of prepreg during curing process. The rheometer was used in parallel-plate configuration with aluminum discs radius of 25 mm. Data was generated with the disc oscillating at 1.0 Hz. The isothermal testing temperatures were chosen according to the DSC curing characteristics of prepreps. The dynamic temperature ramp was 10°C/min from 30°C to 220°C.

Tack

Quantitative tack measurements were performed on the three prepreg systems. This test was performed according to the method, which was developed by Seferis and coworkers.^{1–3} To perform the tack test, five plies of 5 cm by 5 cm of prepreg were laid up and bonded between two metal tabs, and subjected to a compression-to-tension cycle. In a standard cycle, the prepreg is compressed to 267 N at a displacement rate of 1 mm/min, held at 267 N compression for 30 s, and then pulled apart in tension at a constant displacement rate of 1 mm/min. Previous research¹ has indicated that the most representative tack value is the toughness factor (eq. 1). The toughness factor is defined as the amount of energy under the tensile portion of the stress/strain curve up to the maximum load.¹

$$\text{Toughness factor} = \int_{\varepsilon_{0\%, \text{tensile}}}^{\varepsilon_{\text{max}}} \sigma d\varepsilon \quad (1)$$

where, $\varepsilon_{0\%}$ = strain at zero load during the tensile loading

ε_{max} = strain at maximum load

σ = stress

Lap shear strength

For investigation, the lap shear strength of prepregs, aluminum plates series 5000 of 25×102 -mm dimension and 2-mm thickness were used. Aluminum surface should be prepared for adhering prepreg part, so involved treated with sand blasting paper no. 150 then degreasing with distilled water and acetone and dried in oven for 2 h. Then, one ply of prepreg of 25×17 mm was cut and put on treated part of aluminum. The overlap length was 13 mm by 25 mm. Samples cured in a hot press at 25 bar and 140°C for 45 min. After curing, samples were cooled to room temperature. The samples pulled to failure using a tensile instrument machine manufactured by Santam Company (STM-150), with a cross head speed of 1.3 mm/min and load cell of 2000 kg, and the maximum force to failure was recorded. The lap shear strength calculated by dividing the maximum force to the overlap area.

RESULTS AND DISCUSSION

Evaluation of cure parameter and T_g of resin formulations

The DSC thermograms of resin formulations are shown in Figure 1. The endothermic peaks in the first part of DSC thermograms would be due to the solvent evaporation. As can be seen in Figure 1, the area under the exothermic peaks (the heat of curing reaction, ΔH) becomes smaller with the addition of rubber indicating the elution effect of rubber and decreasing in cross link density. Dilution increased with the addition of rubber caused the decreasing of reaction groups.

The effect of NBR content on resin curing parameters and the T_g of cured resin is shown in Table II. Curing process for all samples was complete because no residual exothermic peak was discerned. As shown in Table II the T_g of cured formulations changed with the addition of NBR content. The addition of 3% NBR,

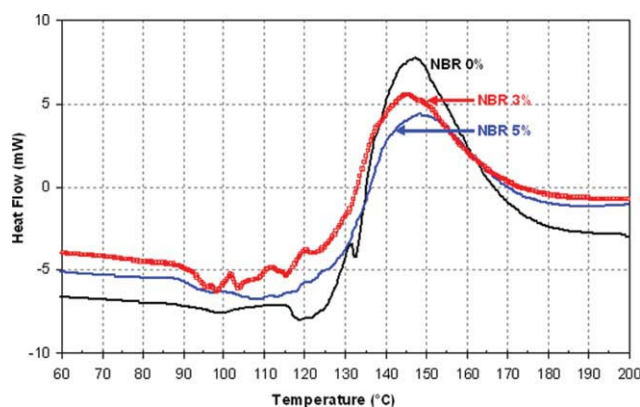


Figure 1 DSC diagrams of neat and modified epoxy resin formulations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
DSC Results of Neat and Modified Epoxy Resin Formulations^a

Formulation	T_i ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	ΔH (J/g)	T_g ($^\circ\text{C}$)
NBR0%	126	147	184	147	104
NBR3%	123	146	182	99	107.5
NBR5%	119	149	182	91	100.9

^a T_i , T_p and T_f stands for initiation, peak and final cure temperatures, respectively.

increased the glass transition temperature that should be attributed to the chemical interaction between the cyanide groups of rubber and hydroxyl groups in the epoxy molecular chain. These interactions can restrict the chain segment movements and increase the glass transition temperature.⁹ However, the addition of 5% NBR decreases the reaction groups caused by decreasing in crosslink density and decreasing the T_g .

On the other hand, thermal evaluation of resin curing of prepreg showed that with the addition of NBR in resin formulation, the T_g of resin formulation decreased. This reduction in T_g of epoxy matrix may be due to the T_g of neat NBR (about -20°C) as can be seen in Figure 2.

SEM

The fractured surfaces of the specimens were examined using SEM. As shown in Figure 3, the neat epoxy matrix shows smooth and glassy fractured surface that indicates brittle failure and no plastic deformation. But the fractured surfaces of the modified epoxies show two distinct phases, a continuous epoxy matrix and the dispersed rubber phase. Two phase morphology that can be seen in SEM micrographs agree with the results of T_g calculation according to the FOX equation¹¹ as shown in Table III.

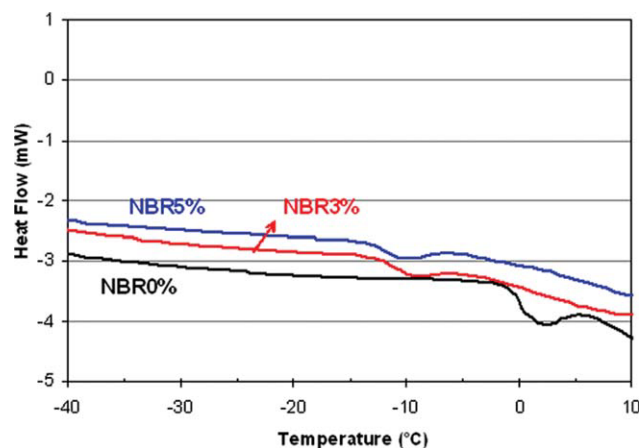


Figure 2 DSC thermograms of prepregs for determination of glass transition temperature of uncured matrix system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

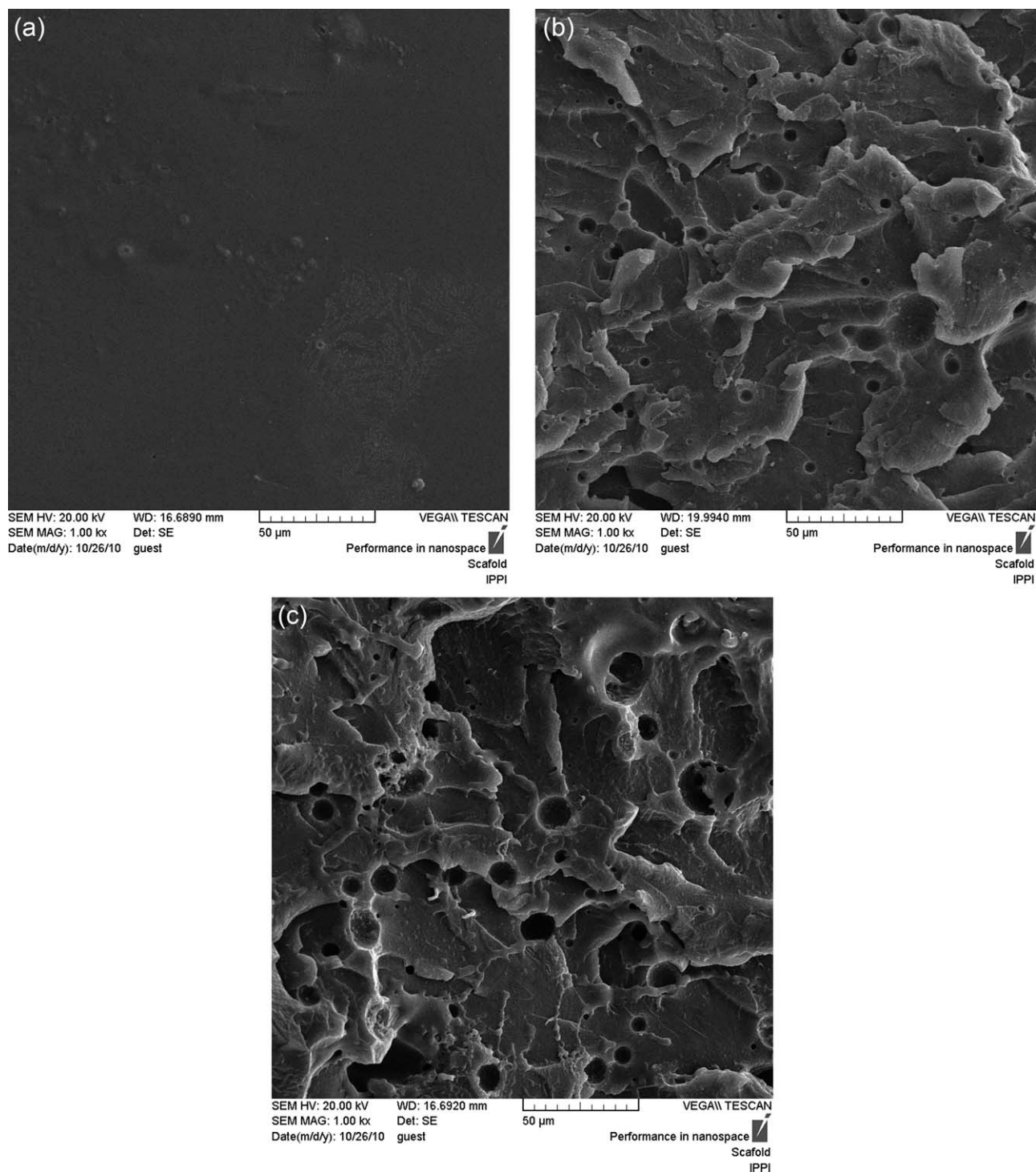


Figure 3 SEM micrographs of (a) neat epoxy, (b) epoxy blend with 3% NBR, and (c) epoxy blend with 5% NBR.

In Figure 3, the holes show the elastomeric particles. The size and the heterogeneity of the precipitated rubbery domains increase with the increase in rubber content. The increase in domain size with the incorporation of solid rubber with high molecular weight is attributed to the coalescence of the dispersed rubber particles, which depends on the viscosity and elasticity ratio.

Rheological measurements

The viscosity profiles at isothermal temperature of 125°C for three kinds of prepreps are plotted in Figure 4. This figure shows that the gel time of prepreps is affected by the addition of NBR. The gel point in the cure process is closely related to the rheological properties. It indicates the beginning of cross linking for the cure reaction where the resin system changes from liquid to rubbery state.

TABLE III
Glass Transition Temperatures of the Cured Epoxy Resins Modified with NBR Obtained from DSC Measurements and FOX Equation

Formulation	$T_g, ^\circ\text{C}$	
	FOX equation	Experimental
NBR0%	–	104
NBR3%	133	107
NBR5%	153	101

The gel time can be determined according to the different criteria. In this study, the determination of gel time was based on the time required for the viscosity to reach a very large value or tends to infinity.¹²

Table IV depicts the gel times of prepregs in two different temperatures that shows a small increase in gel time with the addition of NBR content. It shows that the chemical reactions are delayed with inclusion of rubber thus, the dilution effect happened. This result can be attributed to the lower activity of modified epoxy due to an increase in viscosity. With the addition of rubber, the dilution effect due to decreasing in concentration of reacting species happened. The activation energy for curing kinetic could be determined from the gel times. According to eq. (2), the apparent activation energy (E_a) can be calculated¹³ from the slop of the curve of $\ln(T_{gel})$ vs. $1/T$ as shown in Figure 5.

$$\ln(t_{gel}) = C + \frac{E_a}{R} \cdot \frac{1}{T} \quad (2)$$

According to the data of Table V, the activation energy of prepregs increased with increasing in NBR content. The increase of resin viscosity due to the addition of solid rubber is a reason of the increase in E_a .

Dynamic rheological measurements were carried out for three different prepregs to characterize the

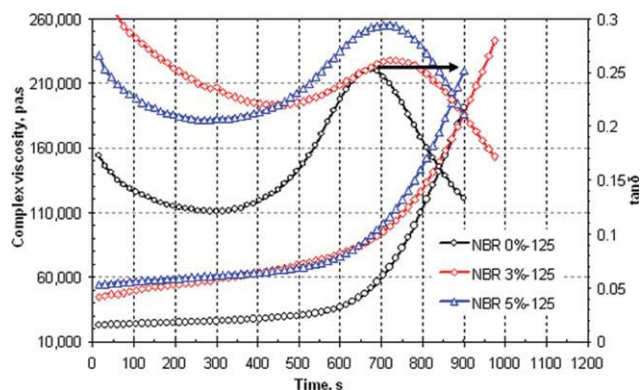


Figure 4 Isothermal rheological curves at 125°C for three types of prepregs. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE IV
Gel Time of Prepregs Calculated from the Isothermal Rheological Measurements

Formulation	Gel time	
	at 125 °C (sec.)	at 135 °C (sec.)
NBR0%	570	360
NBR3%	600	375
NBR5%	610	400

viscoelastic properties such as storage modulus and complex viscosity during the curing process and evaluate the flow behavior of prepregs under cure conditions. The variation of complex viscosity versus temperature is shown in Figure 6. The viscosity profile in the dynamic cure process is different from that in the isothermal cure process. As the temperature increases, the viscosity decreases and reaches to a minimum value and then increases gradually. As shown in Figure 6, the decrease in viscosity of NBR modified prepregs was lower than pure prepreg because of the greater viscosity of NBR and its better heat stability in this temperature. The minimum viscosity increased by the addition of NBR content. At the minimum viscosity, the epoxy resin system had the greatest flow capability. The minimum viscosity has an important effect on the application of epoxy prepreg. If the minimum viscosity would be too low, it may cause the epoxy resin to distribute unevenly among the reinforced fibers before it gets fully cured. Figures 7 and 8 show the effect of NBR on prepreg loss and storage modulus. The variations of loss modulus with temperature are similar to the viscosity profiles. These results are useful for investigation and optimization of the prepreg production and the final composites processing conditions.

Tack

The toughness factor or tack is the energy required to separate the prepreg stack after it has been

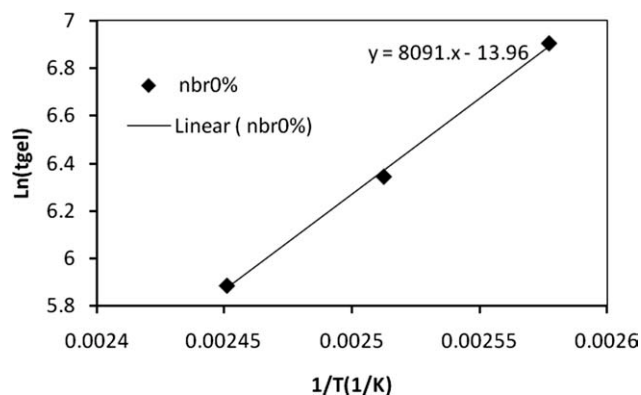


Figure 5 $\ln(T_{gel})$ vs $1/T$ for the calculation of E_a .

TABLE V
E_a and C Calculated from Equation 2

Parameter	NBR0%	NBR3%	NBR5%
E _a (kJ/mol)	67.2	71.4	72.4
C	-13.9	-15.1	-15.3

compressed for a period of time and the compressive stress has been removed.³ The comparison between the tack of three types of prepregs is shown in Figure 9. It can be seen that the prepreg tack increases with the increase in NBR content. These observations imply that the prepreg tack is related to the viscoelastic properties and the surface characteristics of prepregs and influence by all components of the system. The addition of solid NBR content with high molecular weight to epoxy/glass prepreg caused by the increase in modulus of prepreg plies in testing temperature ($25 \pm 3^\circ\text{C}$). This increase in modulus leads to a larger cohesive strength of prepreg plies, which, in turn causes a better stability of the bonding between plies and the energy required to separate the prepreg stacks is increased. In addition, acrylonitrile groups of NBR on one prepreg ply made strong bonds with the same groups and hydroxyl groups on adjacent ply therefore caused an increase in separation energy. For these reasons, tack is increased by the increase in NBR content.

Lap shear strength

Prepreg adhesion bonding to metals is an important mechanical property because they can be used to fabricate aluminum honeycomb sandwich structures. Lap shear test was used for the evaluation of shear strength of prepregs joints with aluminum. Figure 10 shows the effect of NBR content on lap shear strength of epoxy/glass prepregs. It can be seen that

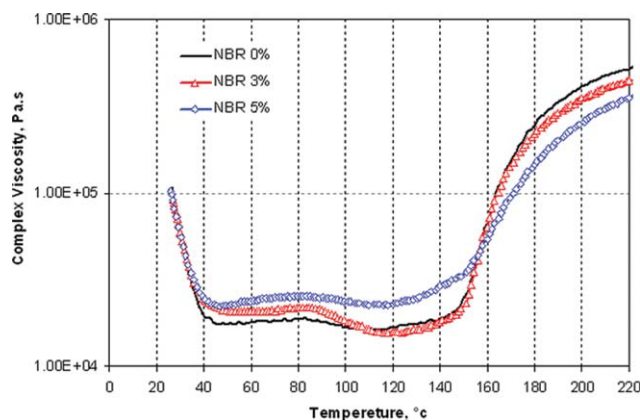


Figure 6 Complex viscosity versus temperature for unmodified and modified prepregs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

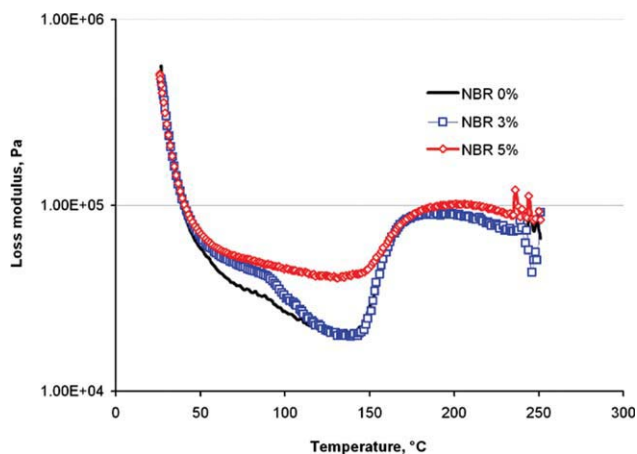


Figure 7 Loss modulus versus temperature for unmodified and modified prepregs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

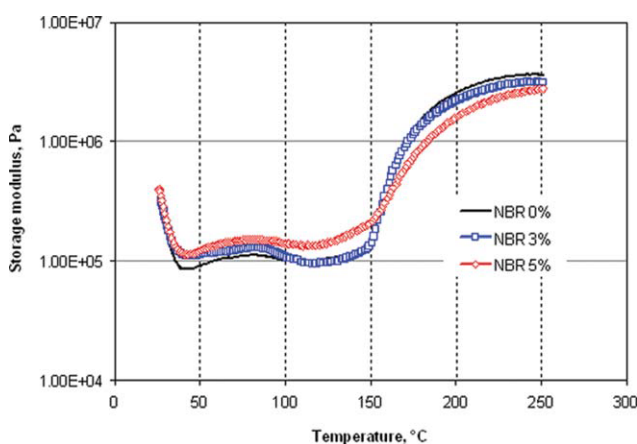


Figure 8 Storage modulus versus temperature for unmodified and modified prepregs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

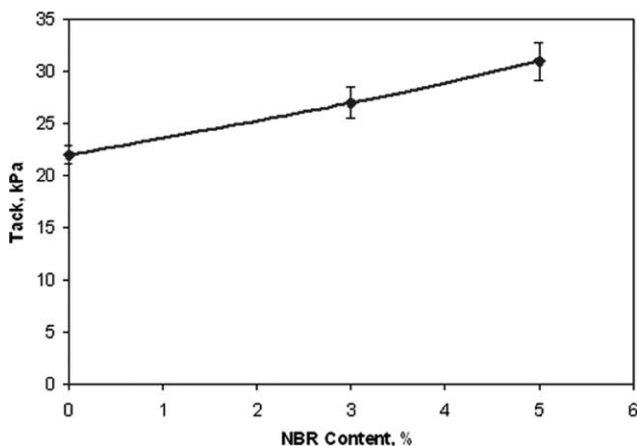


Figure 9 Effect of NBR content on the tack of prepregs.

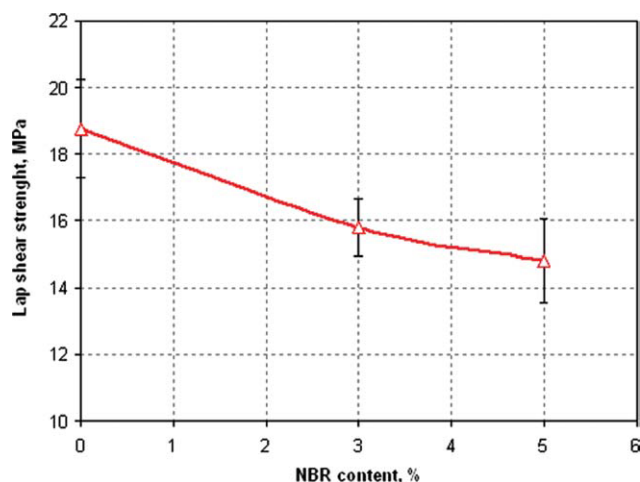


Figure 10 Effect of NBR content on the lap shear strength of prepregs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the lap shear strength decreases with the addition of NBR content.

Aliphatic hydroxyl and ether groups that are present in the initial resin chain and in the cured polymer, serve as sites for the formation of strong electromagnetic bonding attractions (hydrogen bonds) between epoxy and metal oxides.^{14,15} With the addition of NBR, the concentration of these groups on prepreg surface and the formation of strong chemical bonds decreases, therefore the lap shear strength of prepreg ply decreased. On the other hand with the addition of NBR, crosslinking density decreased due to the decreasing in the strength of formed bonds.

CONCLUSIONS

Solid NBR has been incorporated into an epoxy resin matrix. The inclusion of rubber as observed from the DSC analysis caused changes in the T_g of the cured resin. That shall be attributed to the change in crosslink density. Two phase morphology and increase in the size of elastomeric domains with the inclusion of

greater weight percentage of rubber has been demonstrated by the SEM micrographs.

As observed from the rheological measurements of prepregs, the rubber was caused a delay in curing polymerization and hence delays in gel time due to the increase in resin viscosity and the reduction in concentration of reacting species and crosslink density

The tack of prepregs increased by the inclusion of solid rubber. This is due to the increase in resin viscosity and more interfacial interactions resulted in the increase in adhesion bond strength of prepreg plies.

Lap shear strength of prepregs decreased by the addition of rubber due to the decrease in prepregs hydroxyl groups and crosslink density of final cured epoxy resin.

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