ABSTRACT

Phenolic/glass prepregs are widely used in manufacturing of structural composites. In this work, four types of glass/phenolic prepregs, each with a resin content of about 40 wt% were prepared by using resole and novolak phenolic resins and satin glass fibre fabric. They were B-staged or pre-cured at 100°C, 110°C and 120°C in a laboratory-scale prepreg production machine at different processing conditions. The manufactured prepregs were characterized in terms of their volatile content, resin content, conversion or the degree of pre-cure, tack and flow behaviour to provide qualitative and quantitative assessments of prepreg processing, structure and properties. The optimum processing conditions were determined and the results show that the level of pre-cure or conversion was in the range of 2 to 55% having significant effect on tack and flow properties of the prepregs. The resole prepreg containing 15% novolak resin (Re15N) showed the maximum tack of 19.8 kPa which was found to be at 6.5% of pre-cure. Nonetheless, the volatile content of prepreg was very critical and had a dual effect on tack and processing condition. We studied the rheological properties of these prepregs by using a parallel plate rheometer. The novolak prepreg displayed a distinct rheological behaviour and by using a mixture of both resole and novolak resins a suitable processing condition was achieved.

INTRODUCTION

There is a trend towards more extensive use of pre-impregnated or prepreg unidirectional and woven materials for the fabrication of larger composite component parts in the aerospace, sports and marine industries [1,2]. By using prepregs in the manufacture of composites, it is possible to produce very accurate and well-controlled composites. Therefore, the use of prepregs has increased significantly in the last few decades. Tack, drape and flow values have been used to examine the suitability of prepregs. Prepreg tack characterizes the ability of two prepreg plies to adhere to each other. Although the loss of tack is tolerated in flat laminates, it is a problem in the manufacturing of parts with complex contours. In addition, the current commercial prepregs often exhibit major fluctuations in tack strength not only from point-to-point within a
Sheet but from sheet to sheet as well. Apart from difficulties associated with handling and laying-up of the prepregs with irregular tack values, a laminate constructed from such sheets would have a large number of interlaminate voids [3]. This problem is surmounted to some extend by a special prepreg production machine.

Thermoset prepregs with desirable tack and drape properties enable manufacturers to produce composites with complex shapes [3,4]. Tack is one of the prepreg properties that has to be monitored besides parameters such as resin content, fibre area weight, degree of impregnation, content of volatile materials and sample thickness [3]. Tack can be controlled by degree of pre-cure and matrix formulation.

In the case of a solvent-type prepregs, the impregnated reinforcement usually passes through a heating oven to reduce the solvent content. The mixture would continue to react and lose solvent to a degree determined by the storage and handling environments. It is suggested that, to a certain degree, tack can be adjusted by controlling the volatile content of a prepreg. Though, a higher volatile content can increase the tackiness, it may also affect the viscosity profile during curing process and resulting in development of pores in the laminates [4,5].

Although commercial prepregs are being used for few decades, however, prepregnation process [6,7] and matrix formulation development especially in prepreg manufacturing have not been analyzed in significant detail. From this point of view, papers published on phenolic-based prepregs are exceptional [8,9]. Phenolic composites have high thermal and fire resistance [10] and for this reason, they are widely used in specific applications, which necessitate further investigations.

In this work, we describe the effects of resin type and its level of pre-cure in providing a new phenolic/glass prepreg product with optimum flow and tack properties. Resin type and level of pre-cure are the parameters that the prepreg manufacturer has explicit control over them [11,12]. For this reason, the level of pre-cure in relation to tack, volatile content and flow of the woven phenolic/glass prepreg products were tested to determine the optimum value for prepreg production. To the best of our knowledge, no published work is found on this important aspect of prepreg formation.

**EXPERIMENTAL**

**Materials**

The resins used were a resole type phenolic resin (Iran Ayegh Electric Co., Iran) and a novolak type phenolic resin (Moheb Co., Iran). The viscosity of resole resin at 25°C was 245 mPa.s which was supplied with 80±2 wt% solid content in ethanol as the solvent of the resin. The novolak resin was in powder form with about 8 wt% hexa content. The reinforcement was a satin E-glass fabric with an area density of 300 g/m² with trade name of TG-300-30A supplied by Polotsk-Steklovolono, Belarus.

**Prepregs Preparation**

The phenolic/glass prepregs were produced by using a resole type and a novolak type of resins and their mixture and a satin E-glass fabric. Four types of resin systems were prepared with different resin systems each having about 60±2 wt% fibre content. The different types were (a) pure resole resin, (b) 85 wt% resole plus 15 wt% novolak, (c)70 wt% resole plus 15 wt% novolak, (d) pure novolak resin which was dissolved in 25 wt% ethanol. The viscosity of all four resin systems was adjusted at 245 mPa.s at 25°C by adding required amount of ethanol. Hereafter, they are designated as Resole, Re15N, Re30N and Novolak, respectively.

A laboratory-scale prepreg preproduction machine, developed in Iran Polymer and Petrochemical Institute was used to produce prepregs of 100 mm width. The general layout of this vertical solvent-type impregnator is illustrated in Figure 1. As can be seen, the continuous reinforcement passes through the impregnation bath and enters into the heating oven at a constant velocity. In order to achieve a high conversion in the prepreg production, it is necessary to increase the temperature profile of heating column or decrease the line speed. In this work, we changed the line speed from 0.4 m/min to 1 m/min (residence time of 2 to 5 min) and the temperature profile of heating column increased from
100°C to 120°C. The prepregs were kept in a freezer at -15°C after rolling the prepregs by the assistance of two release films, in order to prevent any possible further curing reactions.

Each prepreg was prepared with five different degrees of conversion. Therefore, 20 phenolic/glass prepregs were prepared in order to evaluate the effects of resin type and processing conditions.

Characterization
A Brookfield rotational viscometer (DVII+, USA) was used to measure the viscosity of phenolic resins according to the ASTM D 2196. The gelation time was determined for each phenolic resin according to the ASTM D 4640 by placing approximately 0.5 g of the resin on an electric hot plate at constant desired temperature under continuous agitation. Using a stopwatch, the time taken for the resin to become a soft elastic rubbery solid is reported as the gel time.

The reported results are the average of three measurements.

DSC Analysis
The DSC tests were performed on a NETZSCH DSC 200 F3 (Germany) instrument. Dynamic-heating experiments were conducted under 50 mL/min nitrogen flow. Each resin sample of 12±2 mg was placed in an aluminum pan with a pierced lid and placed opposite to the empty reference pan in the DSC chamber. The DSC was set up for temperature range of 25°C -300°C with heating rate of 10°C/min.

Prepreg Tack Test
The prepreg test was carried out according to a procedure developed by Putnam et al. [13]. To perform this test, five square-shaped samples of 5×5 cm dimensions were cut from prepregs, and they were stacked on each other and placed between the two tabs
of the tensile apparatus. The complete surfaces of the first and fifth layers were accurately adhered to both tabs by using a quick-set epoxy glue. To perform the tack test, the specimen was subjected to compression-tension cycles. The prepreg was subjected to a pressure of 267 N at a displacement rate of 1 mm/min, held at 267 N compression for 30 s and then it was pulled apart in tension at a constant rate of 1 mm/min. At the end, the layers were separated. The value of the prepreg tack, termed as toughness factor was calculated using the recorded stresses and strains through eqn (1).

\[ \text{Toughness factor} = \int_{\varepsilon_{\text{0%}, \text{tack}}}^{\varepsilon_{\text{max}}} \sigma \, d\varepsilon \]  \hspace{1cm} (1)

Figure 2 shows a typical stress/strain test curve obtained during a tack test.

**Degree of Pre-cure, Resin Content, Volatile Content and Flow of Prepregs**

The volatile content (V%), resin content (R%) and also the conversion or the degree of pre-cure (C%) of the prepreg were determined according to ASTM D 3529 and ASTM D 3530 tests procedures which the details have been reported elsewhere [9].

Prepreg flow test was performed according to ASTM D 3531. A weighed specimen consisting of two plies of 50 mm² at 0° to 90° cross-plied was sandwiched between bleeder material and release film. The sandwich was heated to 160°C in a hot press, which provided a pressure of 700 kPa (100 psi). The pressure was held for 15 min or until the resin underwent curing. The cooled sandwich assembly was removed from the press, and the overflown resin was wiped out from the edges of the specimen before being reweighed. The change in weight as a percentage of the original weight was expressed as the resin flow.

**Lap Shear Test**

Lap shear test was performed according to the ASTM D1002. Aluminium was used as a substrate for measuring the lap shear strength of phenolic/glass prepregs. The aluminium strips (25 × 102 × 2 mm) were cleaned with acetone to remove oily contamination followed by abrading the area to be bonded to a 150-mesh emery paper. Subsequently, the strips were cleaned using acetone with a brush to remove particle or dust and dried in an air oven at 110°C for 5 min. Finally the strips were cooled to room temperature.

The lap shear specimens were prepared as follows: a piece of prepreg (25 × 17 mm) was applied uniformly over a cleaned surface of an aluminium strip and another strip was placed over the prepreg. The overlap length was 13 mm. The bonded specimens were put in a hot press at 30 bars and allowed to cure at 150°C for 30 min. Length and width of the bonded area were measured using a digital caliper. A specimen was placed in the grips of a tensile testing machine (Santam STM150, Iran). Load was applied to the specimen at 1.3 mm/min and the load-at-failure was recorded. The lap shear strength was calculated by the ratio of failure force to the bonded area. The reported results are the average of five tested specimens.

**Rheology**

The rheological data in this research was obtained by using a parallel plate rheometer (Anton Paar, MCR 300, Austria). To establish the profile of viscosity of the prepregs, the heating rate of 5°C/min with a constant frequency of 0.2 Hz and strain of 0.18% were used [2]. In addition, the isothermal rheological data were studied at constant temperatures of 130°C and 145°C.
RESULTS AND DISCUSSION

DSC Analysis
Figure 3 shows the DSC thermographs of resole and novolak resins used in this work at heating rate of 10°C/min. The endothermic peak at 55°C in the DSC curve of novolak resin can be regarded as its melting point. The endothermic peak in resole resin around 120°C might be due to the evaporation of residual solvent, which is usually water. Water is the byproduct of the condensation reaction of phenol and aldehyde.

Figure 3 shows that the curing of resole is initiated at 136°C and the curing of novolak is initiated at 135°C. These values were chosen as the point where the exotherm curve deviates from the baseline towards the higher values. The peak temperature of novolak and resole resins occurred at 165°C and 208°C, with the final curing temperatures of 180°C and 260°C for the respective resins. Novolak resin has a very narrow exothermic peak, but the resole resin displays a broad curing behaviour. A shoulder is observed on the left hand side of exothermic peak of resole resin. This implies that the curing of resole resin might consist of two reactions. Figure 3 also shows that resole resin needs more time to cure completely. Since the curing of phenolic resin involves a condensation of reaction and two reactions namely evaporation of a byproduct, e.g., water or ammonia, and curing takes place simultaneously, it is difficult to explore their curing reaction mechanism in

![Figure 3](image)

**Figure 3.** DSC thermograms of phenolic resins at heating rate of 10°C/min.

Based on these data, for the production of laboratory-scale prepregs, the temperature profile of heating column was maintained at 120°C rather than the conventional temperature of 100°C. At this temperature although ethanol is evaporated rapidly, the curing of resin is initiated slowly and the precuring or B-staging of resins can be completed under controlled condition.

Volatile Content and Prepreg Flow Test
Figure 4 shows the effect of conversion on volatile content and flow of Re15N prepreg. As expected, the volatile content and flow of prepreg decrease with higher degree of conversion. Up to the conversion of 25%, the flow decreased rapidly and then its rate slowed down. Volatile content and resin flow fluctuations are not significant after 25% conversion.

The variation of flow as a function of conversion up to 16% of conversion for four prepreg specimens are shown in Figure 5. It can be seen that the resole-based prepreg has the high resin flow. In contrast, the prepreg-based novolak resin has the lowest resin flow. It must be noted that novolak prepreg is not tacky at the lowest degree of conversion as it is a solid material. This is due to the solid state of as-received novolak resin. Figure 5 shows that by increasing the amount of novolak resin, the resin flow of prepreg decreases significantly; implying that the flow of prepreg can be adjusted and controlled by resin formulation.

![Figure 4](image)

**Figure 4.** Resin flow and volatile content vs. conversion for Re15N prepreg.

details [14].
Prepregs Tackiness

The tack value of prepregs was assessed using the above mentioned test and calculated by eqn (1) for all four types of resin systems. The profile of tack values of Re15N prepreg versus conversion is shown in Figure 6. It can be observed that the prepreg tack is very small at very low and very high pre-cure stages, and the maximum measured value was found to be at 6.5% of pure cure. This is due to the fact that at low levels of pre-cure, the matrix viscosity is low, therefore its liquid strength is low. In other words, the low levels of pre-cure resin result in having insufficient strength to provide adequate peel resistance. At high levels of pre-cure, the resin is able to form strong bonds and therefore its viscosity is extremely high to be able to wet-out the adherent. Such behaviour has already been reported in case of phenolic [9] and epoxy [12] prepregs.

The tack properties of two other formulations namely resole and Re30N showed similar behaviour. The maximum amount of tack for resole prepreg was 8.9 kPa. This value for Re15N prepreg was 19.8 as the highest tack value compared to Re30N and novolak prepregs which were 2, and 0 kPa, respectively.

Rheological Analysis

Figure 7 shows the variation of complex viscosity with curing time for Resole, Re15N, Re30N and novolak prepregs at 130°C and 145°C. This figure shows the viscosity increment with time due to the resin incremental cross-linking. It is observed that the samples at 145°C have faster curing reaction, as indicated by the sharper slope of the curves resulting in full cross-linking compared to reaction temperature of 130°C. Therefore, the sample reaches a complete cure in a shorter time at 145°C. In addition, the curing rate of novolak prepregs is faster than the resole type prepregs. These results are in agreement with the DSC data (Figure 3). It can be seen that by adding 15 and 30 wt% novolak to resole, the curing rate of the system gradually increases.

One of the most efficient and accurate ways for measuring the gel time of a prepreg is by isothermal rheological methods [2]. From this point of view, the gel time is the time required for viscosity to reach a very large value or infinity. Figure 7 demonstrates that...
it is difficult to determine the gel time of these phenolic prepregs from isothermal rheological data, particularly for pure novolak or novolak-resole prepregs. This might be due to their fast curing rates. Therefore, the gel time of these resins was measured by employing an electric hot cure plate.

Figure 8 shows the gel times of four resin systems studied in this work as a function of temperature. It may be observed that the gel time decreases as the temperature increases. Novolak resin has the lowest gel time in comparison with other systems. The resin comprised of pure resole has highest gel time. The gel time of resole resin is more temperature dependent than the novolak resin.

From the relationship between the gel time at different temperatures it can be written \[2\]:

\[
\ln t_{gel1} - \ln t_{gel2} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

where, \(E_a\) is activation energy and \(R\) is the universal gas constant. Activation energy, \(E_a\), can be determined by plotting \(\ln (t_{gel})\) against \(1/T\). The activation energy of four phenolic systems was calculated and the results are presented in Table 1. It can be seen that the activation energies of resole and novolak resins are 50.3 and 43.8 kJ/mol, respectively. This means that resole prepreg needs more heating for B-staging or curing than the novolak prepreg.

Figure 9 shows the viscosity profile of phenolic/glass prepregs versus temperature for resole, Re15N, Re30N and novolak. As can be seen, the increase in temperature lowers the viscosity until reaching a minimum point. From this point onwards, the curing reaction takes place and an increase in the complex viscosity is observed due to the formation of a

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**Table 1. Activation energy of different phenolic resins.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_a) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resole</td>
<td>50.3</td>
</tr>
<tr>
<td>Re15N</td>
<td>49.0</td>
</tr>
<tr>
<td>Re30N</td>
<td>44.4</td>
</tr>
<tr>
<td>Novolak</td>
<td>43.8</td>
</tr>
</tbody>
</table>

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**Figure 10. Plots of storage modulus (G’), loss modulus (G”) and tan δ vs. temperature for resole/glass prepreg.**
cross-linked structure. The interesting point is that the novolak prepreg has the lowest viscosity. This is an important aspect from the processing point of view. This system shows high fluidity. Resole prepreg has higher viscosity which means lower fluidity of the resole system. It shows that novolak prepreg has higher cure rate than resole-based prepregs.

The development of the storage modulus (G’), loss modulus (G”) and tan δ during the consolidation process are very significant for recording reference data for the gel region. The G’ is the elastic character of the prepreg and reflects the energy that can be recovered. The G” represents the viscous part of prepreg and reflects loss energy by dissipation. The data for resole and novolak prepregs are presented in Figures 10 and 11, respectively. Some researchers [2,15,16] have defined the cross-over point of G’ and G” graphs as gel temperature. Figure 10 shows that there is not any cross-over point for resole system. For novolak prepreg (Figure 11) there is no clear indication of cross-over point. These observations imply that this subject needs further investigation in order to establish a reliable criterion for the determination of gel temperature and gel point particularly for phenolic/glass prepregs.

Rimdusit et al. [17] have modified the processability and thermo-mechanical properties of a phenolic resin system that seems to be suitable for making prepregs involving a ternary system of benzoxazine, epoxy, and phenolic novolak resins. They have shown that this resin system has relatively long shelf-life at room temperature up to 270 days.

**Lap Shear Test**

The lap shear strengths of four prepregs were measured and the obtained results are reported in Table 2. It can be seen that resole based prepregs have the highest shear strength and Re15N is the best prepreg system. In all samples, the surface of bonded area after testing showed adhesive failure.

**CONCLUSION**

In this work, we prepared phenolic/glass prepreg samples of each 100 mm width on laboratory-scale. The tack, volatile and resin content, flow, gel time, shear strength and rheological properties of these prepregs were characterized. The highest tack and shear strength were obtained for Re15N, a resole prepreg. It means that by using a mixture of resole and novolak resins it is possible to increase tack and reduce the volatile content and achieve high shear strength. The results also showed that by controlling the pre-cure process or conversion of prepreg, volatile content and flow of prepregs can be controlled. Fluctuations of these properties with conversion are not so significant after 25% of pre-cure. The novolak prepreg displays very distinct rheological behaviour and by using a mixture of resole and novolak resin, an optimum processing condition can be achieved.

**REFERENCES**

1. Hayaty M, Beheshty MH, Esfandeh M, Cure


