PROCESSING AND PROPERTIES OF NEW POLYIMIDE COMPOSITES WITH HIGH TEMPERATURE ABILITY

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Abstract

The communication present results from work on development and evaluation of new polymeric carbon fiber composites with extreme temperature performance: \(T_g\) up to 360°C is targeted. The anticipated use of such composites is found in aeroengine-applications. In the work we are exploring a new and tailored phenyl ethynyl terminated imide (PETI) formulation, specially developed for the program. The formulation utilizes crosslinkers of the Nexamide\textsuperscript{TM} type (from Nexam Chemical AB, Sweden). The resins are initially evaluated from a processing and property perspective. Both DSC-measurements and rheology characterization are utilized in the development. Suitable RTM-processing schemes are investigated from a viscosity point of view. The schemes are used in the composite sample manufacturing. Besides a processing perspective the study also present the first results on physical behavior of the polymers and their composites.

1. Introduction

Although ceramic and metal matrix composites can be used at several thousand degrees, there is great interest to use polymeric composites in high temperature applications since polymeric composites are more lightweight, have better fatigue properties and are more ductile [1]. One of the major limitations of polymeric composites for structural applications however is the ability of the matrix to withstand and maintain load transfer capability at high temperatures. There are traditional polymers that may be used for composites at relatively high temperatures such as epoxies, phenolics, cyanate esters, benzoxazines and bismaleimides (BMI) [2]. These resin systems are however only in rare cases suitable for continuous use at temperatures above 250°C due to e.g. insufficient thermal oxidative stability or glass transition temperatures (dry or wet). The current study is instead focused on polyimide resin composites. Polyimides are very temperature resistant and stable polymers, available either as thermoplastic or thermosets [3]. During the last years there has been significant development in the area of so-called phenylethynyl-terminated imide (PETI) resins. They combine very high \(T_g\) (up to 375°C) with high toughness and low volatile generation during cure [4-6].

The results presented in the paper is obtained with the framework of a larger collaborative research project with overall objective to “... develop a cost effective organic matrix resin with 360°C temperature capability which exhibits both robust performance and processing characteristics that will enable high rate production of carbon fiber reinforced organic
matrix composite components.”. The project focuses on the development of polyimide resin formulations, the development of composite processing protocols and verification of the properties of the final composites. In the current paper we primarily present results obtained during the development verification of composite processing.

2. Materials

A propriety grade polyimide resin, formulated and currently under development by Nexam Chemicals AB was studied, see Figure 1. The resin, in the current study denoted A64, is a low molecular weight PETI resin. The resin contains a combination of 4-(Phenylethynyl)Phthalic Anhydride (4-PEPA), end-group crosslinker and ethynyl bis-phthalic anhydride (EBPA) main chain crosslinker. The use of optimized combinations of the 4-PEPA and EBPA (both Nexamide™ type) is expected to enable ultimate $T_g$ above 400°C.

![Figure 1 Photograph of uncured A64](image)

Besides the polyimide resin, a low molecular weight reactive diluent was also studied and characterised. The diluent, denoted A57 in the current study was developed by Nexam Chemicals AB. The principle behind the diluent is that it is a low molecular weight phenyl based structure with certain number of reactive sites, capable to react either with the ethynyl groups at the end of the resin or the ethynyl groups incorporated in the main chain during the curing reaction. Prior to curing this compound is expected to act as a diluent lowering the viscosity during processing.

3. Experimental

Differential Scanning Calorimetry (DSC) measurements were conducted in a Perkin Elmer Diamond DSC, using stainless steel sample holders with rubber seals. The tests are conducted according to ASTM standards [7].

The flow behavior and viscoelastic properties of the samples were measured in a controlled stress rheometer C-VOR (Bohlin) with a 25-mm diameter parallel plate configuration. Pot life and gelling time according to definitions given by ASTM D4473 [8] were measured in an oscillation mode. The dependence of shear viscosity on temperature and/or time was measured in a viscometry mode (i.e. continuous shearing). In both modes, the gap distance between the parallel plates was set to 200 μm.
TA Instruments DMA Q800 with 3-point bending fixture was used for DMTA-tests on quasi isotropic carbon fiber composites. The tests were conducted according to ASTM standards [9] with temperature ramp at a heating rate of 1°C/min and a single frequency of 1 Hz.

4. Results and Discussion

Results from DSC heating scans on the resin and the diluent are presented in Figure 2. The graph to the left shows two representative curves obtained with A57. Two thermal processes are evident. A clear and distinctive endothermic melting is observed at 202°C. The diluent is hence solid and cannot be processed in a composite manufacturing process below this temperature. An exothermic curing reaction takes place at higher temperature. The onset of the reaction takes place at around 355°C and the peak reaction rate is obtained at 387°C. Total heat of reactions, $\Delta H$ of 377 J/g and 444 J/g are obtained in the two tests. Values from corresponding tests on A64 are presented in the graph to the right. In contrast to A57, A64 does not show any clear and distinct endothermic melting point during the test. In both tests there are some very small indications of some minor endothermic thermal processes at around 130°C and 180°C respectively. Complementary DSC scans with higher heating rates (50 °C/min) confirms, but does not explain, the difference between A64 and A57 in terms of melting. The onset of the curing reaction of A64, measured according to the procedures of the standard, is at 360°C and the peak reaction rate is reached at 390°C. The total heat of reaction, $\Delta H$ is around 220 J/g i.e. about half the value compared to A57.

![Figure 2 DSC-scan from 30 to 450°C at 10°C/min for Nexamite A57 (left) and A64 (right).](image)

Results from rheometer tests in oscillation mode on the A64 base resin, following ASTM D4473, are presented in Figure 3 and Figure 4. This analysis looks for the crossover of elastic modulus ($G'$) and viscous modulus ($G''$) in a single frequency test as a means to determine the gel point of a curing system. The frequency used is 1 Hz and the measurements were conducted at two temperatures, 290°C and 330°C. These temperatures were selected since they are considered as part of the tentative curing schedule of the systems. Amplitude sweeps at different stress levels were conducted first to ensure that single frequency tests in Figure 3 and Figure 4 are carried out in the linear viscoelastic (LVE) region.

The left graph in Figure 3, where two stress levels within LVE region were applied, shows that the viscous contribution to the response starts to increase almost immediately whereas the elastic component remains constant at least during the first 60 minutes. At longer times the viscous component increases further while the elastic component also starts to increase. There is never any crossover point between the two components i.e. the elastic component never
becomes larger than the viscous. This indicates that no gelation occurs during the first 150 minutes at this temperature. Values of complex viscosities $\eta^*$ were also extracted from the results. An initial $\eta^* \approx 750$ mPa.s was obtained and the time to double this value to $\eta^* \approx 1.5$ Pa.s was 40 minutes. In a complimentary test the sample was kept for 270 minutes without any elastic and viscous crossover and hence no occurrence of gelation.

From the right graph in Figure 3 one notice significantly higher increase rates both for the viscous and elastic component (c.f. time scales in the two graphs). One also notices that a crossover point where the elastic component becomes larger than the viscous occurs after about 18 min. The difference between the two tests is only about 1.2 minutes. Gelation, according to the definition given by the standard, thus occurs at this temperature. This also indicates that the curing reaction of the A64 system occurs already at 330°C which is also supported by the DSC-curves presented in Figure 1. Values of complex viscosities $\eta^*$ were extracted from the results also at this temperature. An initial $\eta^* \approx 200$ mPa.s was obtained and the time to double this value to $\eta^* \approx 400$ mPa.s was 8 minutes.

While oscillation mode may provide useful insight on the gradual transition from a viscous liquid to a viscoelastic solid it is expected that measurements in viscometry mode (continuous shearing) provides more realistic data with respect to the materials behavior during a mold filling and composite impregnation phase. A set of complementary measurements were therefore conducted under steady-state shear at different temperatures. These results are presented in Figure 4 and Table 1. All tests were conducted using a single shear rate of 220 s$^{-1}$. Repeated viscosity measurements at temperatures between 230°C and 350°C for neat A64 resin are presented in Figure 4. It can be seen that viscosity starts out at high values, around 10 Pa.s, at the lowest temperatures but decreases with increasing temperature. The viscosity continuously decreases with increasing temperature up to temperatures around 320°C and remains below 600 mPa.s on a temperature interval between 250°C and 320°C. From this one can conclude that the impregnation during RTM-manufacturing should preferably take place within this temperature interval. Above 320°C the viscosity increases due to chemical polymerization and crosslinking reactions.
When plotted in log scale (not shown here) one notice an almost perfect linear viscosity decrease with increasing temperature in the range between 230°C and 275°C indicating that the viscosity in this interval can be described by a Arrhenius type of temperature dependence [10]. The deviation from an Arrhenius dependency for temperatures above 275°C is explained by the pronounced viscosity increase over time due to chemical reactions e.g. noticed in Figure 2 and Figure 3.

The influence of the reactive diluent, A57, on shear viscosities of A64 is presented in Table 1. Up to 4 parts A57 per 100 parts A64 was considered. From the first column one observe a noticeable reduction in viscosity at 230°C, the lowest temperature. With 4 parts A57 the viscosity is reduced with 50% at this temperature. A less pronounced, but still a significant diluent effect, is observed at 250°C whereas no significant effects are noticed at 270°C and 290°C. From a composite processing view it may be concluded that the use of this type of reactive diluent enhances the processing ability of the resin since it lowers the viscosity and hence contributes to a broadening of the processing window towards lower temperatures.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Viscosity at different temperatures (Pa.s)</th>
<th>230°C</th>
<th>250°C</th>
<th>270°C</th>
<th>290°C</th>
</tr>
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<tr>
<td>A64</td>
<td></td>
<td>9.67±1.06</td>
<td>1.89±0.20</td>
<td>0.55±0.09</td>
<td>0.31±0.05</td>
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<td>A64/A57:100/1</td>
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<td>8.20±0.16</td>
<td>1.72±0.15</td>
<td>0.68±0.11</td>
<td>0.33±0.07</td>
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<td>A64/A57:100/2</td>
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<td>6.04±0.31</td>
<td>1.27±0.01</td>
<td>0.47±0.01</td>
<td>0.31±0.01</td>
</tr>
<tr>
<td>A64/A57:100/4</td>
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<td>4.88±0.41</td>
<td>1.25±0.03</td>
<td>0.52±0.03</td>
<td>0.27±0.02</td>
</tr>
</tbody>
</table>

Table 1. Shear viscosity values at different temperatures for A64 and its mixtures with A57

A typical curing scheme of polyimide resins [4-6] implies subjecting the resin to various temperatures. The first stage is usually at moderate temperatures and intended to melt and create a homogeneous viscous liquid whereas the impregnation and curing are usually performed in subsequent stages with gradually increasing temperatures. In the current study we have used the rheometer to study the viscosity profile of neat A64 resin during a tentative curing profile. The results are presented in Figure 5. The selected temperature profile is
1. isothermal at 250°C for 25 minutes (melting, degassing etc)
2. isothermal at 290°C for 10 minutes (injection and mold filling)
3. ramp temperature with 3°C/min to 340°C (heating of tool to cure temperature)
4. isothermal at 340°C for 30 min (cure)
5. ramp temperature with 3°C/min to final curing/post curing temperature.

Our viscometry tests are stopped around 9 minutes in to the fourth stage, slightly before the resin is completely solidified. From the results we notice that in these tests the initially measured viscosity at 250°C starts out at around 1 Pa.s. After that follows a close to linear viscosity increase lasting throughout the first isothermal stage. At the end of first 25 minutes the viscosity increases about 3.5 times. During injection in to the RTM-tool the resin will almost instantaneously increase its temperature to 290°C. A corresponding 10 times drop in viscosity, down to 350 mPa.s is registered. Again the viscosity continues to increase due to chemical reactions while kept at isothermal conditions. A viscosity of 650 mPa.s is obtained after 10 minutes at 290°C. During the subsequent ramping to 340°C one observes the typical behavior of a curing thermoset during temperature ramping [11] i.e. the viscosity initially decrease due to temperature but with increasing temperature, and hence increasing cure reaction rate, the effect on viscosity due to polymerization and cross linking starts to dominate and an overall increase in viscosity is noticed. The viscosity continues to increase during the isothermal curing stage at 340°C. The experiment is stopped after about 9 minutes at 340°C once the viscosities becomes too high to measure with the current setup implying that the material is very close to solidification/gelation. In general the results from the viscometry are encouraging since they confirm that it is possible to tailor a cure temperature schedule that is suitable from a RTM-composite processing point of view.

The thermal-mechanical behavior of the cured A64 was studied using DMTA measurements on two carbon fiber reinforced composites samples with A64 resin, see Figure 6. The composite is a quasi-isotropic laminates prepared using 8-harness satin weaves based on Cytec T650 carbon fibres. The composite samples were manufactured using RTM following a similar temperature history as in Figure 5 but cured at 340°C for 30 minutes followed by a 2.5
hours post cure at 370°C. $T_g$ determined by the onset of stiffness decrease, of 331°C and 352°C were obtained in the tests. Tan delta peaks were observed at 376°C and 395°C respectively. One sample was subjected to an additional postcure in air for a few hours at temperatures above 400°C. Only a 0.9% weight loss was registered due to this treatment while the $T_g$ of the composite increased significantly above the targeted 360°C.

![Figure 6](image.png)

**Figure 6** Results from DMTA tests on A64 and A57 blend (100:4) sample

5. Conclusions

A newly developed pheneylethynyl terminated polyimide resin system alongside with a phenyl based reactive diluent was studied and characterized in the current work. Rheological studies revealed that a theoretical temperature range for processing the resin in a liquid state is between 230°C to 330°C. In practice the temperature range is however more narrow since the viscosity is high at lower temperatures within the range and the viscosity build up rate is high at higher temperatures. It was also observed that reactive diluents can decrease the viscosities at lower temperatures hence contributing to broaden the processing window. A tentative cure scheme was verified with the use of viscosity characterization. The thermal-mechanical properties of the resin system were verified using DMTA measurement on fiber reinforced composites manufactured with a curing schedule derived with aid from the thermal and rheological measurements. A $T_g$ around 340°C of the composite was obtained after complete cure in the tool (without any further post-cure). This very high $T_g$ confirms the extreme temperature ability of the material system.

6. Acknowledgements

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References


[7] ASTM D3418 - 12e1, Standard test method for transition temperatures and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry


[9] ASTM E1640 - 13 Standard test method for assignment of the glass transition temperature by dynamic mechanical analysis
