Structural relaxation of hybrid composite of phenol formaldehyde

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Glass-palm fibre reinforced hybrid phenol formaldehyde (PF) composites have been studied at constant heating rate by using differential scanning calorimetry (DSC). Sample under investigation is annealed for different times and temperatures. Glass transition temperature \( T_g \), crystallization temperature \( T_c \) and heat absorbed \( \Delta H \) in glass transition region have been calculated for glass-palm fibre reinforced hybrid phenol formaldehyde composite. It is found that \( T_c-T_g \) and \( \Delta H \) are maximum at annealing time of 60 min and temperature of 60°C. This composite is found to be more thermally stable at these annealing time and temperature due to structural relaxation.

The use of the polymeric materials is increasing day by day because of their cost-effectiveness, availability of raw materials in abundance and lot of processing techniques by which they can be manufactured. Because of the insulation characteristics, some composites also find application in electrical laminates.

Phenolic resins matrices are used as an industrial material because of their good heat resistance, electrical insulation, dimensional stability and chemical resistance. But it is inherently brittle due to its higher crosslinking density. The thermal properties such as thermal conductivity and thermal diffusivity of phenolic resins can be modified by reinforcing them with different type of materials such as ceramics, elastomers and fibres.

The utilization of lignocellulosic materials especially wood and natural fibres as reinforcements in resin matrix has received much attention recently. These natural reinforced thermoset composites have received considerable attention as they demonstrate excellent mechanical properties, dimensional stability and remarkable economical advantages. Several reports proved that toughness along with other mechanical properties of the phenolics has been improved by the incorporation of natural fibres.

Oil palm empty fruit bunches are obtained after the extraction of oil from the seeds. This leaves lot of empty fruit bunches. These are of no use and degraded very slowly. Before the degradation this empty fruit bunches creates environmental problems. So, the utilization of these fibres as reinforcement in polymers has economical as well ecological importance. The reinforcement of the glass fibre in PF matrix produces composites with impact strength comparable to the thermoplastics. These glass fibres are manufactured as continuous filaments. According to Vinson and Chou each fibre in the hybrid composites has been selected to set off the poor qualities of other fibres.

The PF resins are amorphous in nature. Therefore, the prepared hybrid composites are also amorphous materials. The DSC thermograms of the amorphous composite show endothermic reaction defined as glass transition and then further heating with constant heating in DSC it shows an exothermic reaction indicating clearly the crystallization mechanism through nucleation and growth process. Accordingly, a knowledge of the nucleation activation energy as a function of temperature is essential for predicting phase transformation and microstructure in these materials. The nucleation is necessary parameter for anticipating the stability of the glass in a particular application, such as for optical fibres and laser operations, where crystal nucleation and growth severely degrade the properties of glass or amorphous materials.

In the present study, resole type phenol formaldehyde (PF) resin matrix is reinforced with different weight percentage of two type of fibres, i.e., oil palm fibre and E-glass fibre resulting in the hybrid composite. In order to understand degradation mechanism, structural relaxation in these composites has been in-
vestigated through the study of glass transition stability and heat absorbed in the glass transition region at different temperatures and for different annealing times using differential scanning calorimetry (DSC) thermograms at heating rate of 20 K/min.

Experimental Procedure

Sample Preparation

Phenol formaldehyde resole type resins, procured from coast polymers Pvt. Ltd (Kollam, Kerala, India), having 50±1% solid content, has been used as the matrix for the composites formation. The oil palms empty fruit bunches are supplied by oil palm India Limited (Kottayam, India).

The fibres were processed from the empty fruit bunches by the retting process. Pithy materials were removed, washed and dried at 60°C. Fibres were then fed into chopper and cut into 40.0 mm long fibres and randomly oriented mats were prepared.

Hand lay-up, which is the simplest among all the methods to fabricate fibre-reinforced plastic, has been used for the composite fabrication. The mould was given a thin coating of a release agent such as polyvinyl alcohol solution, oil or wax. This was done to prevent the fabricated article from sticking to the mould. The mould was then coated with the resin matrix. Glass fibre mats and oil palm fibre mats were arranged in such a manner so that to get maximum intermingling in the preparation of the hybrid composites. Thermosetting resin was then brushed onto the reinforcing materials. This process was repeated till the desired thickness of the material was reached.

Measurements

Differential scanning calorimetry (DSC) scans of all samples for different annealing times and temperatures have been recorded at heating rate 20 K/min using a Rigaku 8230B DSC connected to a thermal analysis station. Equipment (DSC) was calibrated prior to the measurement, using high purity standards of Pb, Sn and In with well-known melting point. The results obtained for the standard materials were within in 3% of the values given in literature. The temperature precision of the instrument is ±1°C. Samples of masses approximately 10 mg were scanned over a temperature range from room temperature to 450°C at heating rate of 20 K/min for relaxation studies. This heating rate has been selected to obtain good quality of thermogram in DSC. The samples have been annealed for 10, 30, 50, 60 and 120 min at 40, 50, 60 and 70°C temperatures.

Results and Discussion

The thermal behaviour of the composite having 4% of glass, 45% of oil palm fibre and 51% of PF has been investigated using the differential scanning calorimetry (DSC). Typical DSC trace of the system for the abovementioned compositions at a constant heating rate 20 K/min, for annealing time 10 min and annealing temperature 40°C is shown in Fig. 1. The endothermic and exothermic peaks are evident in the DSC thermograms in the temperature range of investigation. From the analysis point of view the DSC thermograms are divided into two parts, the first one corresponds to the glass transition region represented by the endothermic reaction and the other part is related to the crystallization process as indicated by exothermic peak of the DSC curve. The glass transition temperatures (T_g) and the onset crystallization temperatures (T_c) are defined as the temperature which corresponds to the intersection of the two linear portions adjoining the transition elbow of the DSC traces in the endothermic and exothermic direction respectively. Fig. 1 also shows the peak value of glass transition temperature (T_gp) and peak of crystallization (T_cp). Studies of thermal properties of these composites with varying fibre and formaldehyde have also been made in detail separately. From DSC thermograms glass transition temperature (T_g), crystallization temperature (T_c) and T_c-T_g have been determined at annealing time 10, 30, 50, 60 and 120 min and annealing temperature 40, 50, 60 and 70°C as listed in Table 1. It is found from Table 1 that T_c-T_g is maximum at annealing time 60 min and annealing temperature 60°C.

![DSC thermogram on heating rate 20 K/min, at annealing time 10 min and annealing temperature 40°C](image-url)
Table 1—Glass transition temperature \( T_g \), crystallization temperature \( T_c \) and \( T_c - T_g \) with annealing time and temperature

<table>
<thead>
<tr>
<th>Annealing time (min)</th>
<th>( T_g )</th>
<th>( T_c )</th>
<th>( T_c - T_g )</th>
<th>( T_g )</th>
<th>( T_c )</th>
<th>( T_c - T_g )</th>
<th>( T_g )</th>
<th>( T_c )</th>
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Table 2—Heat absorbed \( (\Delta H) \) in glass transition region with annealing time and temperature

<table>
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<tr>
<th>Annealing time (min)</th>
<th>( 40^\circ C )</th>
<th>( 50^\circ C )</th>
<th>( 60^\circ C )</th>
<th>( 70^\circ C )</th>
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<td>138</td>
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<td>136</td>
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</table>

The values of the heat absorbed in glass transition region for each annealed sample have been calculated by area between endothermic curve and the base line of the DSC thermogram at fixed heating rate for each sample using equation,

\[
\Delta H = \frac{kA}{m}
\]

where \( k \) is the instrument constant, which is found to be 1.5, \( A \) is the area of the curve in endothermic region and \( m \) is the mass of sample. Heat absorbed in glass transition region is listed in Table 2. It is found from Table 2 that \( \Delta H \) is maximum for annealing time 60 min and at annealing temperature 60°C. Maximum value of the \( T_c - T_g \) and \( \Delta H \) for all the annealing temperature below glass transition region at an annealing time of 60 min is indicative of the fact that the sample annealed for this particular time is most thermally stable.

Glassy materials being in metastable non-equilibrium state relax toward the equilibrium structure by minimizing their excess enthalpy, \( H_{\text{excess}} \), at every temperature with time. These processes, which are thermally activated are termed as relaxation processes. These can be investigated by measuring the changes of various properties, such as thermal properties with different annealing time and temperature. The basic thermodynamic quantity, which has been used so far for relaxation studies is specific heat. Heats absorbed \( (\Delta H) \) in glassy region and \( (T_g - T_c) \) are also thermodynamic quantities, which are studied for the said purpose. Recovery of the total excess enthalpy \( H_{\text{excess}}(T_c, t) \), by structural relaxation is a commonly observed phenomenon. Three characteristic groups of structural relaxation processes are recognized. These are topological short range order (TSRO) processes representing cooperative reorganization of topology of longer structural unit, the chemical short range ordering (CSRO) process representing chemical ordering inside the structural elements and the glass transition process representing softening of translational modes of structural elements.

In general, all polymers in glassy region exhibit two relaxation processes, one is \( \alpha \)-process and other is \( \beta \)-process. \( \alpha \)-processes are because of large-scale micro-Brownian motion of chains and are prohibited to be slow below glass transition temperature \( T_g \), whereas \( \beta \)-processes, due to limited motions of chains, are normally observed in the glass transition state and above glass transition region. Then at temperature below \( T_g \), large-scale micro-Brownian motion corresponds to large degree of freedom to absorb some heat energy. Above temperature \( T_g \), these are limited and the corresponding absorbed heat contents goes down. If the polymer is annealed near \( T_g \) it
would have maximum absorbed heat energy, which goes on decreasing with temperature. The relative magnitude of heat absorbed with time depends upon the fact whether \( \alpha \)-process or \( \beta \)-process\(^{35}\) dominates at a particular temperature in reference to time.

It has also been found in our case that heat absorbed increases and becomes maximum at a particular time \( t=60 \) min at which the contribution of \( \alpha \)-process are maximum and \( \beta \)-process are minimum and large-scale brownian motions of the chain dominates. As soon as, the annealing time is greater than the characteristic time \( t_0 \) the saturation prohibition of \( \alpha \)-process is reached and the \( \beta \)-process is then start dominating. It is clear from Table 2 that for all the annealing temperatures the characteristic time for structural relaxation is same. Thus, a glassy polymer having fixed fibre concentrations shows structure relaxation at characteristic time \( t_0 \) for all the annealing temperatures, which of course depends upon the relative concentration of fibres, in the hybrid composites.

**Conclusions**

Systematic investigation of the kinetic parameters and the effect of annealing on the thermal behaviour of the material under consideration suggests that structural relaxation depends upon the annealing temperature. However, in all the cases this annealing temperature is below the peak glass transition temperature \( (T_g) \). Besides, for a given sample composite the annealing time of the samples at all the temperatures below glass transition region is a measure of its thermal stability.

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**References**