Abstract— CB10TSS thixotropic and room temperature cured epoxy based adhesive specially formulated for in-situ bonding of pultruded rod into timber for repair and strengthening of timber structures. The glass transition temperature for CB10TSS is 31.7°C which considered low for outdoor exposure. Therefore CB10TSS was modified by reinforcing it with nano- and micro-particles and denoted as Nanopox (CB10TSS/nanosilica), Albipox (CB10TSS/liquid rubber) and Timberset (CB10TSS/ceramics). Thermal properties of epoxy adhesives were studied by using dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). Albipox showed significant improvement in the glass transition temperature but Timberset has the highest Tg, due to high modulus of ceramic particles. A second scan for all the adhesives increased Tg which shows that the room temperature cured adhesives are not fully cross-linked. In DSC scan, typical graphs of heat flow versus temperature able to describe more characteristic of the curing behavior such as a sharp and deep endothermic dip at Tg which corresponds to a rearrangement of the molecules and the wide and shallow endothermic dip at around 100°C is associated with moisture in the adhesive.

Index Term— cure behavior, in-situ timber bonding, particle reinforcement, thermal properties

This work was supported by Malaysian Government and the adhesives was supplied by Rotafix Ltd.

Z. A. is with Faculty of Civil Engineering, Universiti Technology Mara Malaysia, 40450 Shah Alam, Selangor, Malaysia, phone: 60355435236, Fax: 60355435275, e-mail: zakiyahah@hotmail.com

M. P. A. is with Materials Research Centre, Department of Mechanical Engineering, University of Bath, BA2 7AY, UK, e-mail: m.p.ansell@bath.ac.uk.

D. S. is with Rotafix (Northern) Limited, Rotafix House, Abercraf, Swansea, SA9 1UR, UK, e-mail: daverotafix@aol.com.

S. B. Author, Jr., was with Rice University, Houston, TX 77005 USA. He is now with the Department of Physics, Colorado State University, Fort Collins, CO 80523 USA (e-mail: author@lamar.colostate.edu).

T. C. Author is with the Electrical Engineering Department, University of Colorado, Boulder, CO 80309 USA, on leave from the National Research Institute for Metals, Tsukuba, Japan (e-mail: author@nrim.go.jp).

I. INTRODUCTION

Structural adhesives are distinguished from other adhesive by being high strength materials that are designed to support loads. They are often subjected to severe environmental conditions for example in external construction application. For such applications, the adhesives used are required to possess excellent properties in terms of mechanical and thermal properties. Several approaches have been used to enhance the properties epoxy resins which include chemical modification of the epoxy backbone to make it more flexible structure, increasing the molecular weight of the epoxy, lowering the cross-link density of the matrix, incorporation of a dispersed toughener phase in the cured polymer matrix, and incorporation of inorganic fillers into the neat resin.

The addition of fillers in the epoxy based adhesive has primary intention in improving the toughness and the mechanical properties. However the presence of the fillers will affect the curing characteristics of the adhesive which can lead to an increase or decrease the mechanical properties of the adhesive. Incorporation of nanofillers/nano-reinforcements into thermosets such as epoxy has attracted considerable interest indicated by the recent increase in the number of publications [1,2,3,4,5]. Research results show that the microstructure and properties of composites, such as thermal stability and rigidity are affected by modifier particle, particle size; concentration and particle shape [3,5,6]. Calabrese and Valenza [7] added CTBN to DGEBA-DGEBF epoxy resin there was an increase of the curing rate and they concluded that it was due to the catalytic effect of the CTBN carboxyl (-COOH) end groups on the cure process. Recent study by Thomas et al [8] on the thermal properties of epoxy based adhesive by varying the percentage of CTBN (5-20%) found that as the percentage of CTBN increases, the Tg and the storage moduli of the modified epoxies with lower content of CTBN are greater while that of a 20 phr blend is lower than that of the neat resin. At lower concentration, the phase separated CTBN leads to improved fracture toughness of the epoxy network. At a higher concentration, the liquid rubber flexibilizes the epoxy matrix and reduces the cross-linking density. The decrease in the storage modulus is attributed to the lowering of the cross-linking density and plasticization effect of the liquid rubber into the epoxy matrix.
As glass transition temperature is an important property of an adhesive as the mechanical properties of an adhesive are affected by the degree of cross-linking during the curing process it is necessary to follow the curing process by a suitable thermal analysis technique. This study reports the curing behavior and glass transition temperature of thixotropic and room temperature cured epoxy based adhesive reinforced with nano and micro-particles.

II. EXPERIMENTAL PROCEDURES

A. Materials

Four types of adhesive were used in this study. The first type is the standard adhesive (CB10TSS) which is a mixture of diglycidylether of bisphenol-A (DGEBA) with reactive diluent glycidylether (monofunctional), silica fume particles and hardener, a mixture of polyetheramines and thixotropic ingredients. This CB10TSS is considered the standard adhesive. The other three adhesives were formulated by modifying the standard adhesive with the addition of either nano silica, liquid rubber (carboxyl-terminated butadiene and acrylonitrile (CTBN)) or micro-particles (ceramics particles, a mixture of bentonite, quartz and mica) and these adhesives were designated as Nanopox, Albipox and Timberset.

B. Preparation of specimens and experimental methods

Specimen preparation

The adhesives were mixed manually and then the mixture was transferred into plastic rectangular mould of 3 mm thick, 500 mm wide and 500 mm long coated with release agent. Another glass plate was placed on top of the mould and weights were added to apply some pressure in order to achieve a flat surface. The adhesive was left to cure for 10 days.

Dynamic mechanical thermal analysis (DMTA)

The dynamic mechanical properties of the four types of adhesives were measured using a Tritec 2000 DMTA analyzer. The samples of the adhesive as prepared were cut into bars with dimensions of approximately 5.0 mm width x 3.0 mm thickness x 20.0 mm length using a diamond cutter. The sample was gripped as a cantilever beam at the center of the equipment at a constant frequency of 1 Hz and the temperature was ramped up at a constant rate of 2°C/min from -50°C to 180°C.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry was conducted using a TA Instruments differential scanning calorimeter, Model 2910 with a controlled cooling accessory. A cured adhesive sample previously prepared as a thin plate was cut as a disc with a mass between 10 to 20mg and was used in all experiments and was placed in a closed aluminum pan.

The sample was heated at 30°C and left to equilibrate for 2 mins and then quenched to a temperature of -30°C. The sample was then immediately reheated and the dynamic scan was performed at a heating rate of 2°C/min in the temperature range from -30°C to 180°C with a nitrogen flow rate of 25ml/min. Then the post-cured sample was cooled at 20°C/min down to –30°C and a second scan was carried out at a constant rate of 2°C/min until a temperature of 180°C was reached in order to determine the glass transition temperature of the post-cured sample.

C. Scanning Electron Microscopy

The specimens before and after tested using DMTA were broke by hand into two parts. The fracture surface of adhesives was inspected in a JEOL JSN6310 scanning electron microscope (SEM) equipped with a computer image analysis system, after gold coating.

III. RESULTS AND DISCUSSION

A. Cure behavior of the adhesives analysed using DMTA

Cure behavior after first scanning

Fig.1 shows the plots of storage modulus E' versus temperature for the adhesives. The whole curve of the dynamic storage modulus versus temperature consists of three stages. (The curve for Timberset is used as an example to explain the general characteristics). The stages are: glassy (0 - 55°C); viscoelastic (55 - 65°C) and rubbery (55 - 120°C). In the first stage, due to the macromolecular chains [9] the modulus of Timberset is between 14 to 17GPa, which is a high range of stiffness. In the second stage, the molecular chains start to move freely, and the modulus decreases rapidly to 1GPa. In the third stage, molecular deformation is dominated by viscous flow and the dynamic modulus falls to a value close to zero.
It is seen that, on the whole, the dynamic mechanical behavior of the four adhesives is similar. The differences are in the low temperature modulus and the temperature of the main transition from elastic to viscoelastic behavior, which are related to the types of nano- and micro-filler as the based adhesive are the same.

The E’ curves show that the addition of filler gives higher E’ values compared to standard adhesive (CB10TSS). In the low-temperature stage, the addition of nanosilica has increased the E’ value of CB10TSS but in the visco-elastic and viscous stages the effect of nanosilica particles on the modulus of the CB10TSS weakens. This can be seen in the E’ values of the nanosilica filled epoxy (Nanopox) which is almost the same as the standard adhesive, CB10TSS in the viscoelastic region. This indicates that during this stage the modulus is mainly dependent on the properties of the epoxy rather than the fillers. The ceramic particles in Timberset stiffen the adhesive (Fig. 1), giving the highest value of E’. This observation agrees with the values for the static elastic modulus reported in the authors’ previous work [10]. At 20°C, the storage modulus of the adhesives decreases in the order of Timberset > Nanopox > Albipox > CB10TSS. The dynamic modulus was found to be higher than static modulus by a factor of 0.23 to 3 times higher[10]. The rubbery plateau modulus for Timberset is found to be higher than the other adhesives. The addition of high modulus ceramics particle has allowed Timberset to retain a higher modulus even at a temperature above the glass transition. The modulus in the rubbery plateau region is proportional to either the number of crosslinks or the chain length between entanglements [11]. For the three adhesives other than Timberset the storage moduli are similar and very small in the rubbery zone.

The loss modulus, E‖, is related to the amount of energy lost due to viscous deformation. The E‖ curves for the adhesives are shown in Fig. 2. According to Barral [12], small loss factor peaks can be explained by a relaxation in which the epoxy network loses mobility and free volume as it cools down towards the equilibrium glassy state and, as a result, the ability to dissipate energy is reduced.

If there is compatibility between the filler and matrix interaction, the peak maximum of the E‖ curve will shifts towards a lower temperature which can be seen for CB10TSS, Nanopox and Albipox. On the other hand, Timberset has the highest E’ peak and is shifted towards a higher temperature. This indicates less compatibility between the epoxy matrix and the ceramic particles because a higher temperature is required to increase mobility. The loss modulus is also increased in the same order as storage modulus. Timberset is again seen to have the highest E” peak value at 58.13°C (Fig.2) which means there is large amount of damping in the material as a result of the high fraction of filler particles.

The tan δ curves for the adhesives are shown in Fig. 3. The very slight difference between the heights of the tan δ peaks for CB10TSS and Nanopox points to the same order of damping capabilities. However, the tan δ peak of Albipox is seen to be slightly higher. This is probably due to the nanoparticulate rubber content.

In Albipox, the rubber particles react with the epoxy forming an interphase of amorphous nature and it has the highest tan δ peak. Even though SEM micrograph are not able to image the interphase, it is known that CTBN possesses reactive-end groups which will phase-separate during cure and induce a high reactivity with the epoxide ring of the epoxy molecule [13]. This may increase the intensity of the tan δ peak (bigger lag
between stress and strain because of the viscoelastic nature of the rubber).

The tan δ peak for Timberset is lower and wider than that for the other adhesives. Its lower height reflects the poor adhesion between the ceramic particles and the adhesive matrix (see Fig. 4), but its greater width points to the higher degree of cross-linking [14].

This observation is supported by the results of bending tests for different curing times [10] where the flexural strength of Timberset did not change over the period of time from 7 to 40 days, which is also indicative of a fully cross-linked structure. The lower damping capacity of Timberset suggests that the interaction with the heavily fillers ceramic filler effectively lowers the polymer mobility.

 Cure behavior after second scanning

Fig. 5 shows typical plot of the dynamic properties versus temperature for CB10TSS, Nanopox, Albipox and Timberset after first and second temperature scanning. The first run was from −50 to +180°C. In general the $E'$ curve, $E''$ and tan δ peaks have shifted to the right, therefore the post-curing effect has increased the $T_g$ values. When a polymer is cross-linked, covalent bonds are formed between the polymer chains, which bring them closer together. This reduces the free volume and causes an increase in the glass transition temperature [13].

B. Cure properties of adhesives analyzed using DSC

The cured CB10TSS, Nanopox, Albipox and Timberset were subjected to Differential Scanning Calorimetry (DSC) to evaluate their thermal properties and different heating rates were used as described below.

 Cure behaviour after first run

The thermograms of all adhesives are shown in Fig. 6. The thermograms for all the adhesives generally show similar behaviour. For CB10TSS, there is a slight drop in heat flow at 5°C followed by a sharp endothermic peak at 47°C. After this endotherm, a broad endotherm is observed at around 110°C which is due to moisture loss and beyond that a small sharp exotherm is observed at around 160°C. For Nanopox, there is a small endothermic peak at slightly below 10°C followed by a sharp endothermic peak at 58°C. After this endotherm, a broad endotherm is also observed followed by small exothermic peaks.

The Albipox behaviour is very similar to CB10TSS except for a sharp and deep endothermic peak at about 47°C. For Timberset, a few small steps were observed at 10°C followed by a jump in heat flow at about 25°C and subsequently followed by the sharp endotherm at the peak temperature of 58°C beyond which there is a shallow exotherm at around 120°C.

It is interesting to note that for all adhesives, lower temperature peaks or shoulders were observed preceding the dominant endotherm and this may be associated with formation of chemical bonds [15]. In this case, these lower temperature peaks and shoulders may be attributed to the type of fillers added because Timberset shows multiple peaks and shoulders which may be related to the different chemical composition of the ceramic components. These small peaks or shoulders remain after the second scan (see Fig. 7).

From Fig. 6 one can see the differences in the depth and width of the endothermic peaks at $T_g$. Since Timberset is
heavily filled adhesive with micro-ceramic particles therefore more energy is being absorbed to increase the mobility as compared to CB10TSS which shows very shallow dip. Hence the endothermic peak corresponds to a rearrangement in the molecules to relieve stress frozen in below Tg. These stresses are trapped in the material until enough mobility is obtained at Tg to allow the chains to move to a lower energy state [16].

For Nanopox, there is obvious formation of endothermic/exothermic transitions above the Tg (as indicated in the box in Fig. 6) which might be due to the formation of new compounds as a result of degradation of cured adhesive molecules or might be due to the oxidation of degraded products.

Cure behaviour after second run

Fig. 7 shows the thermograms after second scanning. It can be seen that the sharp endothermic peaks at Tg in Fig. 6 have disappeared leaving very shallow peaks and Tgs have shifted to a higher value which indicates that the adhesives have reached the full state of cure. When comparing the E’ values at 20°C, the E’ values for CB10TSS and Nanopox after second scanning decrease but the E’ values for Albipox and Timberset remain the same. The E” curve peaks also shift towards higher temperatures therefore there is reduction in viscoelastic flow.

![Thermograms obtained by DSC at 2°C/min on the adhesives after the second run.](image)

<table>
<thead>
<tr>
<th>Adhesives</th>
<th>First run</th>
<th>Second run</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E’ onset</td>
<td>E’ peak</td>
</tr>
<tr>
<td>CB10TSS</td>
<td>31.7</td>
<td>43.2</td>
</tr>
<tr>
<td>Nanopox</td>
<td>33.8</td>
<td>42.2</td>
</tr>
<tr>
<td>Albipox</td>
<td>42.8</td>
<td>48.6</td>
</tr>
<tr>
<td>Timberset</td>
<td>53.8</td>
<td>58.1</td>
</tr>
</tbody>
</table>

Comparing the Tgs during first run and second run, The Tgs after second run is higher than first run. These results suggest that the Tg of the room temperature cured adhesives will slowly increase with time as more cross-links are developed.

From Table I, the values of Tg measured using the different techniques in DMTA produce different values of Tg. The value from the tan δ peak is found to be higher than the other Tg values. Tan δ is an indicator of how efficiently the material loses energy to molecular rearrangements and internal friction and the ratio of E” to E’ is independent of geometry effects [11]. For this reason many other studies have used Tg from tan δ peaks [12, 17]. For all the adhesives, the Tg from tan δ peak is found to be higher than the other Tgs but the storage modulus corresponding to tan δ peak decreases significantly thus proving that at this temperature the polymer is already in a rubbery state (see Fig. 5) in which the molecular chains are highly mobile. At this stage the molecular chain slips pass each other and the viscous flow leads to an irreversible deformation.

Another definition of Tg is the temperature of the E” peak. E” is a measure of dissipated energy, therefore the temperature of E” peak is a possible measure of the glass transition temperature. Fig. 5 shows that the E” peak temperature corresponds to an E’ value which lies in the middle of the visco-elastic range of temperatures and at this temperature, the storage modulus is lower than the E’ value measured at the onset E’ temperature.

Therefore, the temperature of the onset E’ gives the lower limit of the viscoelastic temperature range. Below this temperature, the material possesses the stiffness to resist deformation and also possesses the flexibility as not to shatter under strain which is important for timber structures. Thus, it is reasonable for this temperature to be taken as the upper limit for the working glass transition temperature. If Tg is used based on the tan δ peak, it will overestimate the value of Tg and this may affect the bonding integrity and the strength of the bonded member in a timber structure. Therefore Tg based on the onset of E’ will be used to compare with Tg from the DSC method later.

The Tg increases significantly in the order of Timberset > Albipox > Nanopox > CB10TSS. Compared to the standard adhesive, CB10TSS, the increase in Tg for Timberset is 22.1°C,
Albipox is 11.1°C and the smallest increment is for Nanopox by 2.1°C.

**Determination of glass transition temperature using DSC**

The Tg was determined from the midpoint value of the jump in heat flow and also the point of inflection. The construction of the lines was done by the TA Instrument software. The analyses of DSC thermograms are summarized and presented in Table II.

<table>
<thead>
<tr>
<th>Adhesives</th>
<th>Tgm (a) (°C)</th>
<th>Tgi (b) (°C)</th>
<th>Tgm (c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB10TSS</td>
<td>39.5</td>
<td>43.7</td>
<td>49.8</td>
</tr>
<tr>
<td>Nanopox</td>
<td>39.5</td>
<td>42.5</td>
<td>49.0</td>
</tr>
<tr>
<td>Albipox</td>
<td>51.5</td>
<td>52.6</td>
<td>65.2</td>
</tr>
<tr>
<td>Timberset</td>
<td>53.6</td>
<td>55.0</td>
<td>85.7</td>
</tr>
</tbody>
</table>

(a) Tgm - glass transition temperature at the midpoint
(b) Tgi - glass transition temperature at the point of inflection
(c) Tgm - glass transition temperature at the midpoint after second run

The Tg from Table II, it is seen that the Tg based on the point of inflection is higher than Tg based on the midpoint of the sudden drop in heat flow. As the Tg based on the point of inflection may fall outside the sudden drop range, the Tg based on the midpoint was used. Again, it can be seen that the Tgs after second run is higher than the Tgs after first run. The Tg of the adhesives are in the order of Timberset > Albipox > Nanopox > CB10TSS. The addition of ceramic particles increases the Tg of Timberset by 14°C. The addition of the rubbery phase in Albipox increases the Tg by 12°C. The Tg for Nanopox is the same as the Tg for CB10TSS.

It is seen that Tg values from the DMTA analysis are lower than Tg from DSC analysis by more than 5°C. However, they still have the same order of Tg values for all the adhesives: Timberset > Albipox > Nanopox > CB10TSS.

Other studies have also reported that Tg values from DSC measurements are higher [11]. Overall, the construction for obtaining Tg from DMTA data is more straightforward than that for DSC data.

**IV. CONCLUSION**

The thermal properties of adhesives reinforced with nano- and micro-fillers were investigated using DMTA and DSC techniques. The following results were obtained.

- Timberset, containing high-modulus ceramic particles, has the highest storage modulus E', peak loss modulus E" and glass transition temperature Tg, followed by Albipox, CB10TSS and Nanopox.
- In DMTA tests, Timberset has a higher crosslink density than Albipox, CB10TSS and Nanopox demonstrated by a wider tan δ peak and higher storage modulus in the rubbery region. The smaller tan δ peak reflects the high cross-link density and possibly the poor adhesion between the ceramic particles and the matrix.
- In DMTA tests, the glass-transition temperature is best defined as the temperature of the onset of the E' drop (tangent construction). The measurement of Tg based on the tan delta peak corresponds with a very low value of storage modulus, when the polymer is in the viscoelastic or rubbery state. Such a physical state is not associated with a polymer at its glass transition.
- In DMTA tests, the addition of micro-fillers and nano-fillers increased the Tg in the order of Timberset > Albipox > Nanopox > CB10TSS. The presence of ceramic particles in Timberset improves the Tg by about 22°C compared to CB10TSS. The nano-rubbery phase in Albipox improves the Tg by 11°C compared to CB10TSS. There is not much difference in the Tg values of Nanopox and CB10TSS.
- In DMTA tests, a second scan for all the adhesives increased Tg which shows that the room temperature cured adhesives are not fully cross-linked.
- In the first DSC scan, typical graphs of heat flow versus temperature show a sharp and deep endothermic dip at Tg which corresponds to a rearrangement of the molecules to relieve stress frozen in below Tg. The wide and shallow endothermic dip at around 100°C is associated with moisture in the adhesive. After a second scan the endothermic dip at Tg and the broad endothermic dip at 100°C disappear because the adhesive is only partially cured at room temperature.
- In DSC tests, Tg is measured as the midpoint value of the initial drop in the heat flow versus temperature characteristic. The Tg of the adhesives are in the order of Timberset > Albipox > Nanopox > CB10TSS.

**REFERENCES**


