DMTA STUDY OF DGEBA-BASED EPOXY ADHESIVES REINFORCED WITH NANO AND MICRO PARTICLES FOR IN-SITU TIMBER BONDING

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Introduction

Bonded-in rods have been used for the repair and upgrading of existing timber structures and in new construction for at least 30 years[1]. An adhesive is expected to hold the materials together and transfer design loads from one adherend to the other within the given service environment. As the temperature rises above the glass transition temperature T_g, the adhesive becomes more rubber-like because bonds between polymer chains become weak and the polymer becomes soft. Thus, knowledge of T_g is essential in the selection of materials for various applications especially for bonded-in timber connection for better service life.

Differential scanning calorimetry DSC which measures the heat flow into and out of a sample as a function of temperature has been extensively used to study the cure kinetics of various thermosetting polymers [2,3]. However, DSC does not provide information on structural changes at the molecular level. By contrast, the DMTA technique imposes a small oscillatory deformation which generates viscoelastic materials properties such as the storage modulus E', loss modulus E' and the mechanical loss, tan δ (E"/E'), which are characteristics of the changes of the material's structure during cure. The objective of this study is to investigate the thermal properties of four solvent free epoxy-based adhesives reinforced with nanosilica, liquid rubber and micro-sized ceramic particles.

Experimental

Materials

Four types of two-part epoxy-based 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 glycidlyether (monofunctional) and hardener, a mixture of polyetheramines. The other three adhesives were formulated from standard adhesive but with the addition of either nanosilica, liquid rubber (carboxyl-terminated butadiene and acrylonitrile (CTBN)) or micro-particles (a mixture of bentonite, quartz and mica) and these adhesives were designated as Nanopox, Albipox and Timberset.

Specimen preparation

The adhesive were mixed manually at a constant speed so that to avoid the formation of air and vapor bubble. Then the adhesive was filled into a rectangular 2-mm-thick, 500-mm-wide and 500-mm-long PVC mould coated with released agent. The adhesive was left to cure for 10 days. After demolding the adhesive plate was cut by diamond saw into 5.0 x 2.0 x 20.0 mm bars.

Apparatus and procedures

The dynamic mechanical properties of the four adhesives were measured with the aid of a Tritec 2000 DMTA analyzer. The specimens were gripped as cantilever beams between two clamps in the DMTA system. A sinusoidally alternating force was applied to the end of each cantilever beam at the centre of the equipment. The first part of the experiment, a multiple thermal scan was conducted with frequencies of 0.316, 1, 3.16,10 and 31.6 Hz. In the second part, a single thermal scan method was used with a constant frequency of I Hz and the temperature was increased up from -50 to 18°C at a constant rate of 2°C/min. To be sure that the results obtained were constant, the experiments were repeated at least three times for each adhesive.

Result and discussion

A dynamic mechanical thermal analysis was carried out on all the adhesive systems. The effect of various frequencies (0.316, 1, 3.16, 10and 31.6 HZ) on their dynamic properties was examined. Figure 1 shows a typical plot at storage modulus and tan δ versus temperature different frequencies.

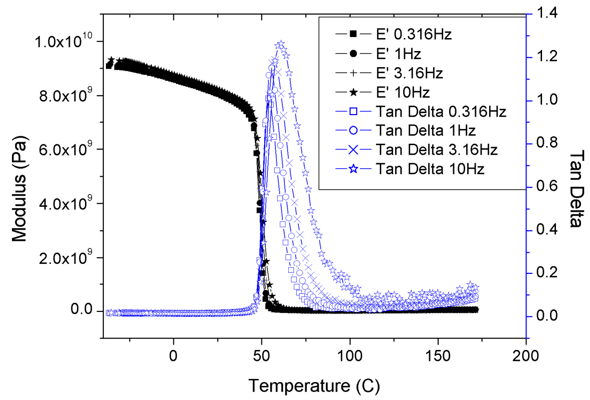

Fig.1: Graph of Modulus and Tan Delta versus temperature at four frequencies for Albipox.

Higher frequencies shifted the storage modulus E', the loss modulus E" and tan δ characteristics toward higher temperatures therefore increasing the glass transition temperature Tg. Although the adhesives are thermosets they are clearly only partially cured before testing and behave in a classic viscoelastic manner. Comparing the dynamic response of the four adhesives as a function of frequency, Timberset is a higher modulus adhesive than the other formulations and was able to respond to a frequency of 31.6 Hz unlike CB10TSS, Nanopox and Albipox. Figure 2 shows the plots of storage modulus E' versus temperature for the different adhesive systems.

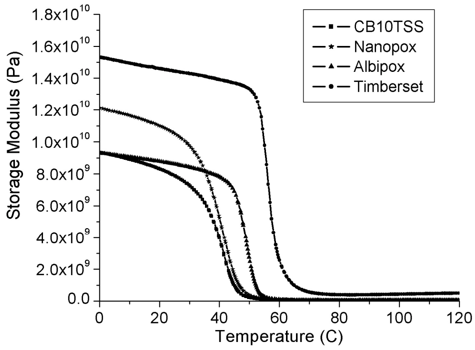

Fig.2: Storage modulus versus temperature for all the adhesives.

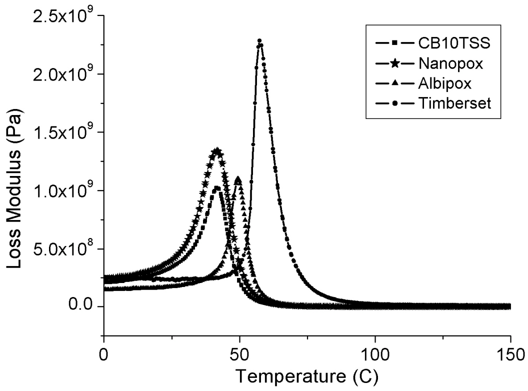

Fig. 3: Loss modulus versus temperature for all the adhesives.

It is seen that, on the whole, their dynamic mechanical behavior 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. Comparing Fig.2 and 3, we notice that the addition of filler increases the storage and loss moduli by the same order of magnitude. At visco elastic and viscous stages, the effect of nanosilica particles on E' is weaker. This means that, at these stages, E' is more dependent on the properties of epoxy than the filler. The ceramic particles in Timberset show considerable stiffening effect on the adhesive, giving the highest value of E'. This fact agrees with the values for the static elastic modulus in authors' previous study on the mechanical properties of these adhesives [4]. At 20°C, the storage modulus of the adhesives decreases in the order of Timberset > Nanopox > Albipox > CB10TSS. The rubbery plateau modulus for Timberset is higher than that other adhesives. In the tan δ peak for Timberset (not shown here) is lower and wider than that of for the other adhesives which reflects the poor adhesion between ceramic particles and the adhesive matrix, but its greater width points to the higher degree of cross-linking [5].Table 1 shows a summary of T_g data for all adhesive investigated together with corresponding value of storage modulus. The T_g was determined from the onset of E' drop .

Table 1:T_g and E' values for all adhesives.

Adhesives	**T_g (°C) onset E'curve**	**E' Mean,GPa**
CB10TSS	31.7	62.7
Nanopox	33.8	7107
Albipox	42.8	80.9
Timberset	53.8	47.1

The addition of liquid rubber and ceramic particles increased the glass transition temperature by 5 to 15°C, respectively, compared to those of CB10TSS and Nanopox. The storage modulus E', similar to the static elastic modulus[4] decreases in the order Timberset>Nanopox>Albipox>CB10TSS.

Conclusion

1. Timberset, containing high-modulus ceramic particles, had the highest storage modulus E', loss modulus E" and glass transition temperature T_g, but the lowest value of tan δ due to poor bonding.
2. The fillers increased T_g significantly by up to 22°C.

References

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