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Thermophysical characterization of two-component, nano-heterogeneous epoxy networks

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Abstract

The macroscopic homogeneity of a series of two-component epoxy networks (EN) is indicated by a single glass transition temperature as measured by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). However, the heterogeneity at the nano-scopic length scale of the order of chain persistence length p exists as indicated by a broadening of T_g intervals. With the assumption of this nano-scopic heterogeneity, the composition dependence of the heat conductivity of EN in a broad temperature range was quantitatively analyzed by a step-by-step averaging (SSA) approach.

Keywords: Epoxy resin; Heterogeneity; Heat conductivity; Dynamic mechanical analysis; DSC

1. Introduction

Observation of a single glass transition temperature (T_g) smoothly changing with composition from $T_{g,1}$ for the neat component 1 to $T_{g,2}$ for the neat component 2 can be regarded as an empirical criterion of a homogeneous, single-phase state of a binary polymer blend on the length scale well above the chain persistence length p (e.g. [1–3]). However, there are theoretical reasons [4] to expect the onset of a thermodynamic driving force for transformation of an initially homogeneous melt into a spatially modulated structure of nano-size domains of, say component 1 in a continuous matrix of component 2 on cooling down the blend from $T \gg T_g$ into the region of instability of a single-phase state at $T > T_g$. The predicted composition heterogeneities on the nano-scopic length scale of the order of p are, infact, believed to be responsible for the excess, zero-angle SAXS intensities [5], for the broadening of T_g intervals [5–7] and for the heterogeneous regime of low-temperature chain dynamics [8,9] in the miscible blends of poly(methyl methacrylate) and poly(vinylidene fluoride).

Thus, it is the purpose of the present paper to derive the evidence for nano-scale composition heterogeneities in a series of two-component, copolymerized epoxy networks (EN) through measurements of their thermophysical properties. The possibility of development of structural heterogeneity during cross-linking polymerization was recently discussed by Wen et al. [10,11].

2. Experimental

2.1. Materials

Two epoxy oligomers, i.e. diglycidyl ether of bisphenol-A (DGEBA) (Araldite MY 790-1 from Vantico Ltd. equivalent molecular weight 174, melting point ~40 °C) and diglycidyl ether of poly(propylene glycol) (DGEPPG) (from Aldrich, approximate average molecular weight 380) are used. Hexahydrophthalic anhydride (HHPA) (HT 907, molecular weight 154, melting point ~32 °C) were supplied by Vantico Ltd. 2-Ethyl-4-methyl-imidazole (2,4-EMI or EMI) was purchased from Janssen Chimica, Belgium (purity higher than 99%). All reagents were used as received.

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2.2. Sample preparation

For all mixtures the mole ratio of epoxy group to anhydride group was 1.06:1, and the concentration of the initiator, 2,4-EMI, was 1.2 wt.% of that of HHPA. The compositions of the two-component epoxy networks, represented by the mole ratio of DGEBA to DGEPPG, are 100/0, 90/10, 70/30, 50/50, 30/70 and 0/100, respectively. Thus, the weight ratio of DGEBA/HHPA/DGEPPG/EMI was 120/100/0/1.2 for 100/0 system and 0/100/131/1.2 for 0/100 system. The compositions were also represented by the DGEPPG content, i.e. the epoxy equivalent weight percentage (%EEW) of DGEPPG in the whole epoxy oligomers.

As described in detail elsewhere [12], the mixtures were prepared by a successive loading of 2,4-EMI, HHPA, DGEBA and DGEPPG into an aluminium cup, heating up to 60 °C to completely melt the components, stirring the melts for 2 min, cooling down to room temperature and stirring for additional 3 min to ensure homogeneity. Finally, the mixtures were converted into the grafted epoxy networks of DGEBA and DGEPPG by their preliminary curing at 80 °C (24 h) and final post-curing at 160 °C (1 h).

2.3. Characterization

The glass transition temperatures (T_g) were determined by a Perkin Elmer DSC 7 instrument under N_2 atmosphere from a temperature of at least 60 °C lower than T_g of the fully cured sample to 220 °C at a heating rate of 20 °C/min. The sample was cooled down from the rubbery state to the glassy state at 30 °C/min before the measurement. The breadth of T_g was defined as the difference between the extrapolated onset and endset of the step change in heat capacity during devitrification of the samples.

The dynamic mechanical measurements were performed between 230 and 450 K using an Advanced Rheometric Expansion System (ARES) from Rheometric Scientific in oscillation mode with rectangular geometry at a frequency of 1 Hz and a heating rate of 1 °C/min.

Steady-state heat conductivity λ of disc-like specimens (diameter: 15 mm; thickness: 2 mm) was continuously measured at a heating rate of ca. 4 °C/min in the temperature interval of 143–353 K with an upgraded version of the commercial instrument, IT-λ-400. The standard input data on the temperature differences for a heat sensor and for a sample were complemented by monitoring the sample thickness. Repeated calibrations using standard samples of copper and poly(methyl methacrylate) proved that the experimental data were reproducible within the error limits of 3–4%.

3. Results and discussion

3.1. Nano-scopic heterogeneity

As can be seen from Fig. 1, all studied samples showed a single step in the heat flow versus temperature curves which can be converted into the specific heat capacity jump ΔC_p at the corresponding glass transition temperature T_g. As expected for macroscopically homogeneous systems, the values of ΔC_p changed linearly with composition (Fig. 2a), while the corresponding glass transition intervals for the EN were considerably broader than those for the neat components (Fig. 2b). The latter effect is a clear indication for existence of small- (nano-) scale heterogeneities in the EN.

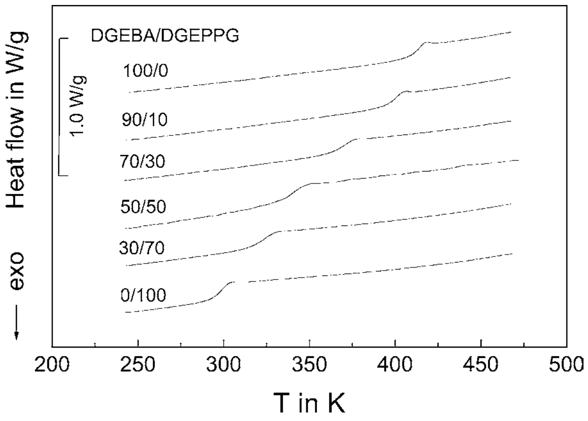

Fig. 1. Heat flow vs. temperature curves for different DGEBA/DGEPPG ratios.

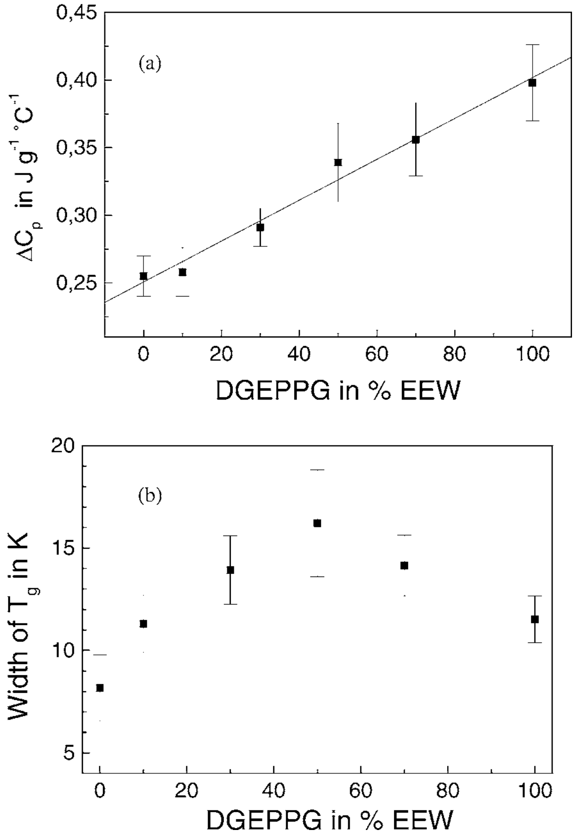

Fig. 2. The heat capacity change at T_g, ΔC_p (a) and the width of T_g (b) from DSC as a function of DGEPPG content. The value of the error bar is estimated from 5 to 10 independent measurements.

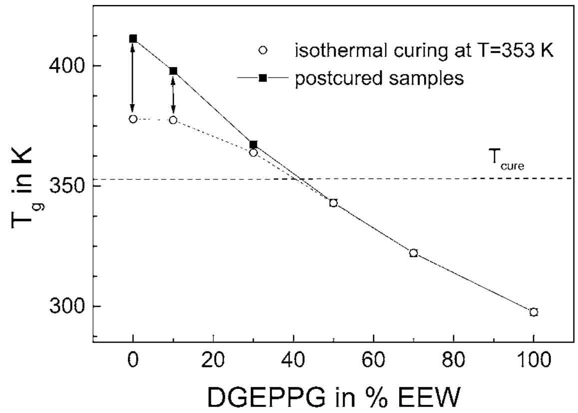

Fig. 3. T_g (measured by DSC) as a function of DGEPPG content after isothermal curing at 353 K (squares) and post-curing at 433 K for 1 h (circles).

For the samples with high DGEBA content (e.g. ratios 100/0 and 90/10) T_g is considerably increased after post-curing (Fig. 3). This indicates that the reaction of these samples was frustrated by the vitrification during isothermal curing.

The T_g values derived from the tan δ versus temperature curves (Fig. 4) are plotted versus composition in Fig. 5, which shows a similar composition dependence as obtained from DSC (Fig. 3). The heights and the half-widths of tan δ maxima for the EN exhibited non-additive composition dependencies (Fig. 6a and b). As argued above, these data can be attributed to structural heterogeneities in the networks. Since all studied samples were optically transparent, the characteristic length of such heterogeneities should be much smaller than the wave length of light (that is, should correspond to the nano-scale).

3.2. Heat conductivity

As typical for non-crystalline polymers [13–16], for all studied samples the initial smooth increase of λ with temperature was followed by a gradual leveling-off on the approach to the respective T_g (Fig. 7). As could be expected [17], the absolute values of λ over the entire temperature intervals tended to increase, the higher the apparent network density (i.e. the higher the DGEBA/DGEPPG ratio); however, the evidence presented above suggests a possibility of small-scale composition heterogeneities (presumably, the mixed microphases of different compositions). In this context, it can be assumed that the EN consist of two mixed microphases enriched with DGEBA and DGEPPG networks,

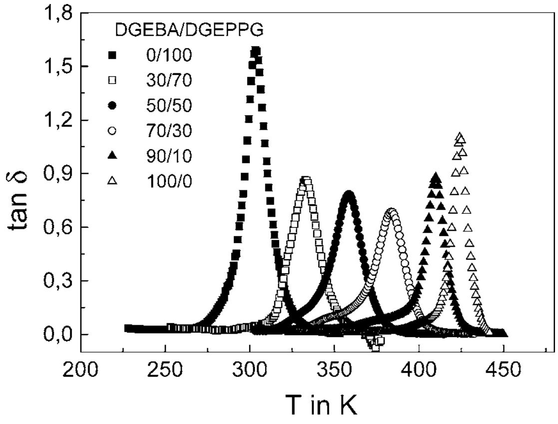

Fig. 4. tan δ vs. temperature curves for different DGEBA/DGEPPG ratios.

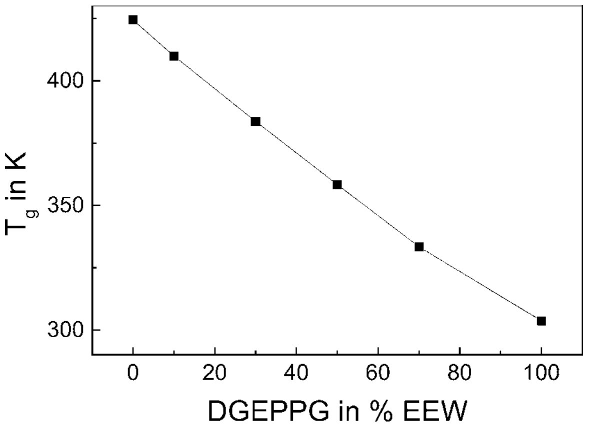

Fig. 5. T_g from dynamic mechanical analysis as a function of DGEPPG content (see Fig. 4).

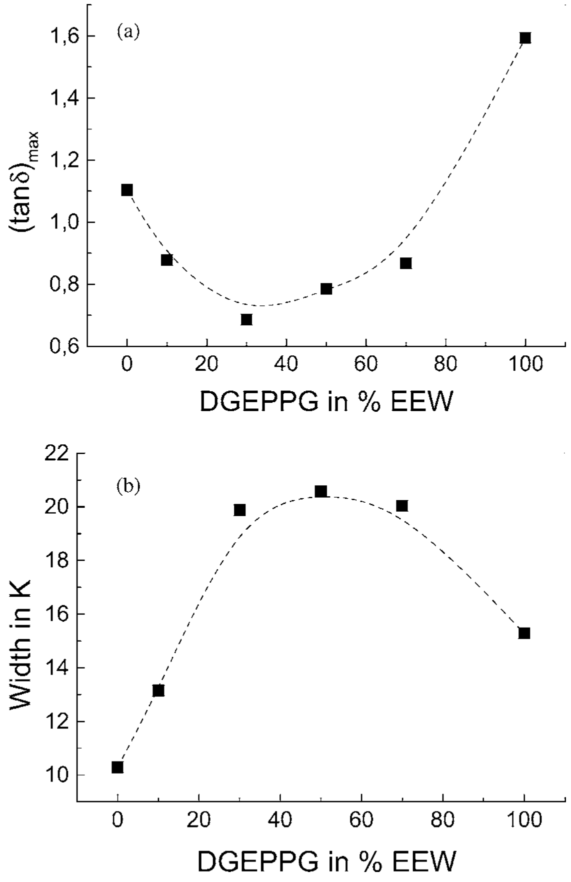

Fig. 6. Maximum value (a) and half height width (b) of the peak in tan δ vs. temperature curves (see Fig. 4) for different DGEPPG contents.

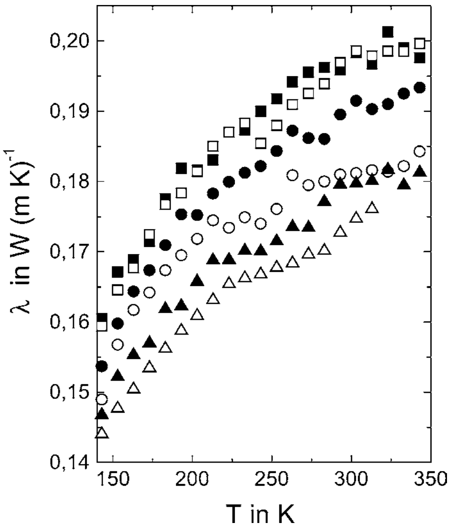

Fig. 7. Temperature dependencies of heat conductivity (λ) for the networks with the DGEBA/DGEPPG ratios (from the top to the bottom) of 100/0, 90/10, 70/30, 50/50, 30/70 and 0/100.

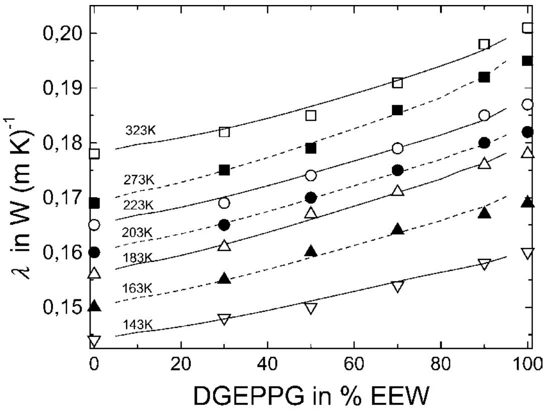

Fig. 8. Best fits of predictions of the SSA approach to the experimental heat conductivities at 323, 273, 223, 203, 183, 163 and 143 K (from the top to the bottom) for different DGEPPG contents.

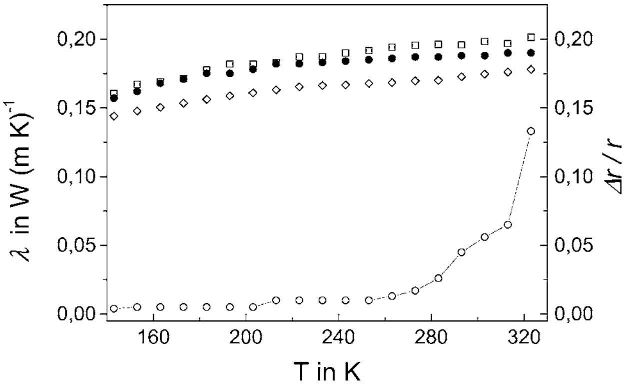

Fig. 9. Temperature dependencies of the heat conductivity of sample 100/0 (open squares), sample 0/100 (open diamonds) and BI (solid circles), and of the reduced BI thickness (open circles).

respectively (components 1 and 2), and of the “boundary interphase” of the nominal composition. This assumption will be used for a quantitative treatment of composition dependence of the heat conductivity data within the frame of the step-by-step averaging (SSA) approach [18]; the essentials of this approach are outlined below.

A unique feature of the structural model adopted in the SSA model [18] is the possibility to account explicitly for the smearing out of a sharp (i.e. of zero thickness) interface between components 1 and 2 into a “physical” boundary interphase (BI) structurally different from the matrix component 2. It is assumed that even at the relatively low nominal content φ of the disperse component 1, the isolated particles of size $2r$ coated with a BI of thickness Δr can coalesce into isolated clusters (IsC) containing a constant limiting volume fraction $\varphi^* \gg \varphi$ of component 2. The effective concentration φ' of such IsC with $\varphi^* = \text{const}$ will increase with the nominal component 1 content φ until an infinite cluster (InC) spanning the entire system is formed at the percolation threshold $\varphi' = \varphi_c$. The bulk representative elements (BRE) of the InC are Voronoi polyhedra constructed by the intersection of planes drawn normal to the vectors connecting the centers of particles at their midpoints. In this fashion, the InC is sectioned into a system of different Voronoi polyhedra with the number of faces dependent on the coordination number $N_c = f(\varphi^*)$ of corresponding particles. The effective properties of a disordered system of such BRE are calculated assuming its identity to the appropriately chosen, “mutually adequate” (as concerns isotropicity, mechanical stability, geometrical equivalence, etc.) one with an ordered structure (e.g. a spherical particle embedded into a cube).

The calculations were carried out for variable values of the effective heat conductivity and reduced thickness of the BI (λ_{BI} and $\Delta r/r$, respectively) at fixed values of $\varphi_c = 0.15$, $\varphi^* = 0.60$ and $t = 1.8$ (critical exponent for conductivity [18]). The quality of theoretical fits to the experimental heat conductivities of EN can be assessed from the representative plots in Fig. 8; the best-fit values of λ_{BI} and $\Delta r/r$ are shown in Fig. 9.

As could be expected, the apparent heat conductivity of the BI lied in between those for the neat EN components; the reduced BI thickness remained negligibly thin over the major part of the temperature interval of measurements, while a sharp upswing was observed on the approach to the T_g of neat DGEPPG network (Fig. 9). Further experiments are definitely needed to check whether this latter effect is the artefact of the fitting procedure or the manifestation of a certain real structural change in the studied EN.

4. Conclusions

The thermophysical properties of a series of two-component, copolymerized epoxy networks are investigated in this study. The macroscopic homogeneity of the epoxy networks is indicated by a single glass transition temperature as measured by DSC and DMA, while the heterogeneity at the nano-scopic length scale exists as indicated by broadening of T_g intervals. With the assumption of this nano-scopic heterogeneity, the composition-dependent heat conductivity of the epoxy networks in a broad temperature range was quantitatively analyzed by a step-by-step averaging approach. The reduced thickness of the assumed "physical" boundary interphase between the two neat components was derived from theoretical fits of the experimental data. This thickness remained negligibly thin over the major part of the temperature interval of measurements, while increased sharply on approaching T_g of neat DGEPPG network.

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