CURE KINETICS AND PHASE MORPHOLOGY OF CNT MODIFIED MULTI-PHASE EPOXY NANOCOMPOSITES

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Abstract

This work is focused on the preparation and characterisation of high performance multiphase epoxy nanocomposites containing functionalised carbon nanotubes (CNTs) and phase-separating thermoplastic (TP) microparticles. Two epoxy systems with different number of functional groups were employed as the matrix. Analysis of the curing reaction in ternary nanocomposite systems indicated a decrease in the activation energy in comparison with the neat epoxy material. This could be attributed to the catalytic effects of the functionalised nanotubes. TP-rich particles with varying particle sizes are formed in two systems, which is believed to be caused by the differences between viscosities and crosslink densities of the epoxy materials. Although based on microscopic analysis, CNTs are mostly well dispersed, the rather inevitable formation of the secondary agglomerations lead to the non-uniform distribution and irregular shape of TP-rich phase.

1. Introduction

Epoxy resins are extensively used in the fabrication of fibre reinforced polymer (FRP) composites as well as in adhesive compounds. However, the brittleness of cured epoxy results in relatively poor matrix-dominated properties of the FRP composite such as fracture toughness and damage initiation. A practical approach to address the brittleness of epoxies is incorporating nonhomogeneities in their structure [1,2]. Various types of inclusions have been used for this purpose with varying degrees of success. Among these inclusions, engineering thermoplastics (TP) have offered an effective means for enhancing the fracture toughness of epoxy materials without any significant deterioration of other mechanical properties, which is commonly the case with rubber modification. Nanoscale inclusions, such as carbon nanomaterials, can potentially offer great advantages in improving strength and damage behaviour of epoxy resins [3]. More importantly, the simultaneous addition of both thermoplastic and carbon nanomaterials, to the matrix, could provide a higher degree of freedom in formulating multi-phase thermosetting matrices with superior fracture toughness without adversely effecting other mechanical properties.

It has been well established that the mechanical properties of cured epoxy resins depend on their structures as well as the curing conditions [4,5]. Therefore, it is necessary to study the effects of the particle modification on cure kinetics of epoxy resin following the addition of the thermoplastic and CNTs in order to understand the relationship between chemical structure and properties of modified epoxy based composites. In this particular case, the thermoplastic and epoxy blend is a homogeneous solution before curing. During curing, phase separation occurs mainly as a consequence of the decrease in the entropy of mixing. This leads to the formation of two separate phases (i.e., a TP-rich phase and epoxy-rich phase). The resulting microstructure is of great importance as far as the toughness properties of the resulting multiphase system are concerned [6,7]. Therefore, the influence of CNTs on the final phase morphology should be further clarified. In the present study, multi-phase epoxy resin nanocomposite systems containing functionalised multiwall carbon nanotubes (CNTs) and an engineering thermoplastic, polyetherimide (PEI), were manufactured. Cure kinetics following addition of CNTs and PEI was studied using differential scanning calorimetry (DSC) analysis. The effect of CNTs on phase morphology of the nanocomposite is also discussed.

2. Experimental

Two types of epoxy monomers, diglycidyl ether of bis-phenol A (DGEBA) and tetraglycidyl-4, 4’-diaminodiphenylmethane (TGDDM) were used. Both systems were cured using a high temperature hardener, 4, 4’-Methylenebis [3-chloro-2, 6-diethylaniline] (MCDEA). Dichloromethane (DCM) was chosen to dissolve PEI. COOH functionalized multi walled carbon nanotubes (CNTs) with the length of 10-30 μm were employed.

For the fabrication of CNTs and PEI modified ternary nanocomposite, CNTs were added to the epoxy monomers with stirring at 120°C overnight to detangle the highly entangled CNTs. The ultrasonication was further conducted to improve dispersion of the nanotubes. In the meantime, the thermoplastic pellets were dissolved in DCM. CNT/epoxy monomer solutions were then mixed with this thermoplastic solution. DCM was removed by keeping the solution at 180°C for at least 3 hrs and a subsequent degassing. Following addition of the stoichiometric amounts of MCDEA, one part of the liquid nanocomposite blend was immediately cooled down to room temperature to avoid curing before further analysis, while the other part was poured into a preheated rectangular mould with a depth of 4 mm. The liquid was then cured at 170°C for 1hr, at 200°C for a further 2hrs and at 220°C for another 2hrs. The resulting nanocomposites are referred to as TCNT/PEI (TGDDM as matrix) and DCNT/PEI (DGEBA as matrix), hereafter. The TP and nanotube contents in the nanocomposite were 10 and 0.3 wt%, respectively. Binary CNT/epoxy systems with a nanotube content of 0.3 wt% and PEI/epoxy blends with 10 wt% of PEI were prepared in the same fashion. The PEI/epoxy blends based on TGDDM and DGEBA epoxy resins are referred to as TPEI and DPEI, respectively.

Curing kinetics of nanocomposite was studied with a dynamic DSC (Perkin Elmer). The uncured samples were heated from 20 to 380°C at increasing heating rates (5, 10, 15, 20 and 25°C/min). The weight of the samples was kept at around 6-7 mg. A scanning electron microscope (SEM, JEOL) was used to investigate the phase morphology of modified epoxy resins of the cryo-fractured surfaces. All selected specimens were sputter-coated with gold to prevent the build-up of electrical charges during microscopy. Hot-stage optical microscopy was used for direct observation of the phase separation process. A droplet of sample was squeezed between two glass slides. The sample was then placed inside the hot stage at a temperature of 200°C. The phase separation process was then recorded with a transmission optical microscope (Nikon).

3. Results and discussion

Fig. 1(a) shows the dynamic DSC diagrams of TCNT/PEI conducted at various heating rates. All DSC curves show a broad exothermic peak at a temperature range of 200-350°C which corresponds to the curing reaction. Further addition of the thermoplastic, carbon nanotubes, and the combined incorporation of PEI and CNTs do not seem to have a noticeable impact on the reaction mechanism between epoxy and amine groups. Kissinger’s [8] method is employed to obtain the activation energy, E_a, of the curing reaction from the DSC results,

$$E_a = -R \times \frac{\mathrm{d}\left(ln\left(\frac{\beta}{T_P^{\,2}}\right)\right)}{\mathrm{d}\left(\frac{1}{T_P}\right)} \tag{1}$$

where R is the gas constant, β is the heating rate, T_p is the peak temperature of the DSC curve. The experimental data fits quite well, indicating the applicability of the Kissinger equation (Fig. 1(b)). The activation energies of different epoxy systems are shown in Fig. 1(c). In TGDDM systems, due to the high functionality, the existence of PEI chains hinders the curing reaction leading to an increased activation energy [9]. However, with addition of the CNTs, the activation energy decreases, presumably as a result of the catalytic effects of the functionalised CNTs on the curing reaction. In DGEBA systems, adding TP phase has an insignificant influence in activation energy. This may be explained by the fact that DGEBA shows a relatively lower functionality, so existence of thermoplastic plays a lesser role in affecting the reaction. Incorporation of CNTs in the case of bifunctional epoxy resin, causes a further decrease in activation energy which, similar to the case of the tetrafunctional epoxy, is attributed to the catalytic effects on curing reaction.

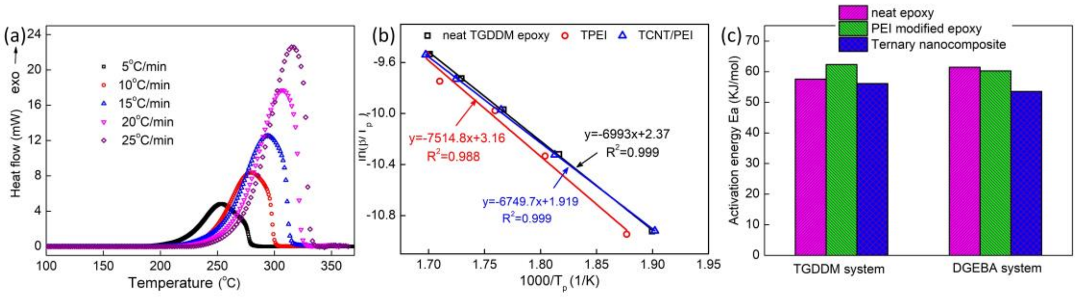

Figure 1. (a) DSC scanning of uncured TCNT/PEI nanocomposite, (b) the linear fitting by the Kissinger equation and (c) the activation energy of curing for different epoxy resin systems.

SEM images of the cryo-fracture surfaces are presented in Fig. 2. In both tetrafunctional and bifunctional neat epoxy resins, a typical featureless fracture surface is observed. However, after introducing the thermoplastic phase, the two epoxy materials show quite different phase morphologies. Micron-sized TP particles can be clearly seen on the fracture surface of DPEI, whereas in TPEI system, the TP particles are significantly smaller as specified by red arrows in Fig. 2(c) and (d). The rather significant difference in the TP particles size in the two systems could be related to the corresponding differences in viscosity and crosslink density between the two epoxy monomers. The tetrafunctional epoxy material, TGDDM, has a significantly higher viscosity and crosslink density in comparison with the bifunctional DGEBA. This could impede the growth of phase separating TP particles by limiting diffusion of the polymer chains [10]. In nanocomposite systems containing CNTs, although most of CNTs are well dispersed in the matrix, (arrows in Fig. 2(e) and (f)), agglomerations as large as 2 to 3 µm could be identified in both systems (highlighted by yellow arrows). Fracture surfaces of the DCNT/PEI system reveal that the formation of the TP particles does not have any noticeable effect on the secondary agglomeration of CNTs as the size of agglomerates in DCNT/PEI is comparable with that of nanocomposite only containing CNTs. In TCNT/PEI systems, further addition of CNTs does not impact the TP particle size.

Microscopic observation of the phase separation process for DCNT/PEI system is shown in Fig. 3. Initially, except for the dark CNTs agglomerates, the matrix presents a clear solution. After nearly 14 minutes, a visibly co-continuous morphology starts to appear, indicating the onset of phase separation. With the curing proceeding, the co-continuous structure becomes coarser. Then about 16 min later, this co-continuous structure seems to break up into small droplets, dispersed in the epoxy-rich matrix. The resulting morphology seems to freeze at around 24 min indicating the termination of the process.

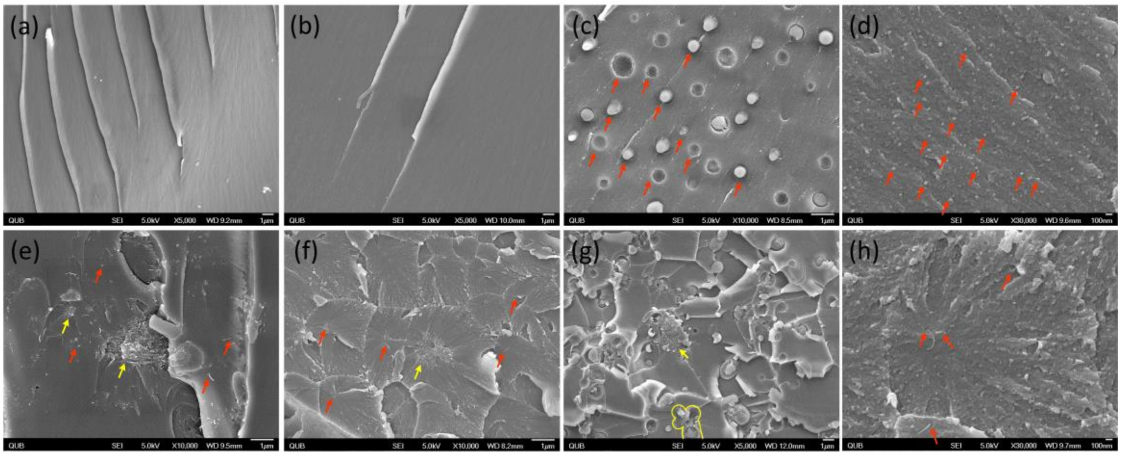

Figure 2. SEM micrographs of the cryo-fractured surfaces: (a) neat DGEBA epoxy, (b) neat TGDDM epoxy, (c) DPEI, (d) TPEI, (e) DCNT, (f) TCNT, (g) DCNT/PEI and (h) TCNT/PEI.

As mentioned earlier, carbon nanotubes could reduce the activation energy of the curing reaction. This results in the acceleration of the crosslinking reaction, and hence advancing the onset of phase separation. However, phase separation and growth of the TP particles near the large nanotube agglomerates seems to be suppressed by the high local viscosity. That will contribute to the creation of smaller particle size of the thermoplastic. This is not the case in locations with well (better) dispersed CNTs where TP particles would even find a chance to connect into larger domains.

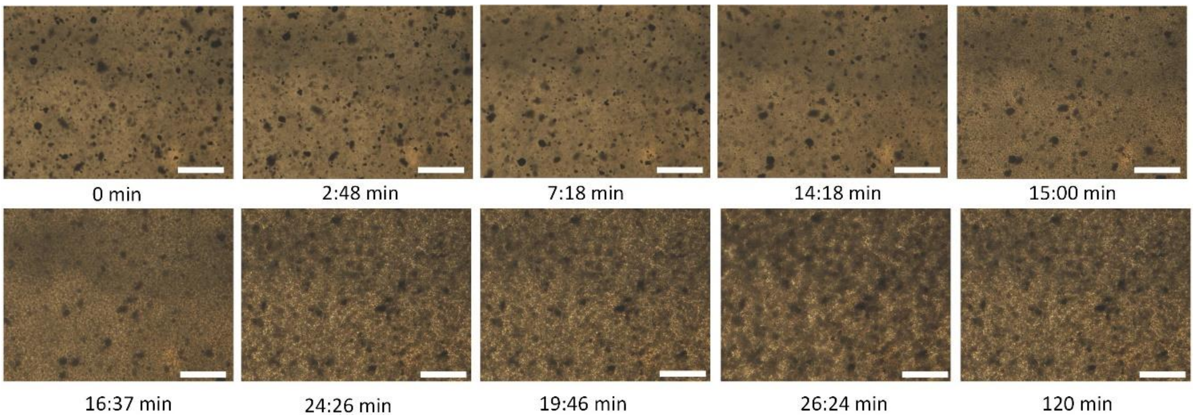

Figure 3. The evolution of phase morphology of ternary nanocomposite during different times at 200ºC (scale bar 50 μm).

4. Conclusions

The activation energy of curing of TGDDM is higher after introducing PEI because the existence of PEI hinders the reaction of this high functionality epoxy, while the catalytic effect brought by the functionalised CNTs lowers the activation energy of curing of the ternary nanocomposite. For DGEBA, with the addition of PEI, no significant variation is observed due to the relatively low functionality. Further introduction of CNTs leads to an even lower activation energy. Although some CNTs agglomerations can be identified, most CNTs can be well dispersed in the nanocomposite with or without PEI. Nano-sized and micron-sized PEI-rich particles are formed in TGDDM system and DGEBA system, respectively, which is because of the differences of viscosity and crosslink density of two epoxy resins. The further addition of CNTs leads to the non-uniform distribution and irregular shape of the micron PEI-rich particles.

Acknowledgments

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