Erratum

Fang, D. P., Riccardi, C. C. and Williams, R. J. J. 'Rubber-modified epoxies: *in situ* detection of the phase separation by differential scanning calorimetry' *Polymer* 1993, **34**, 3960.

Because of a printing error, the last page of this article was omitted. The publishers would like to apologize for any confusion, and have pleasure in reprinting the missing page below.

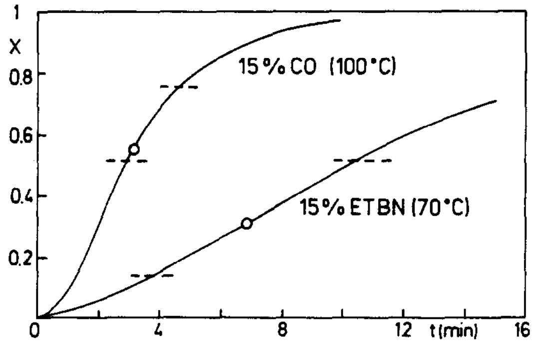

Figure 3 Conversion *versus* time curves obtained from isothermal d.s.c. scans for epoxy–amine formulations containing 15 wt% CO (cured at 100°C) and 15 wt% ETBN (cured at 70°C). Circles indicate the cloud points as determined by light transmission. The dotted bars indicate the phase separation range observed in d.s.c. scans (see *Figure 4*)

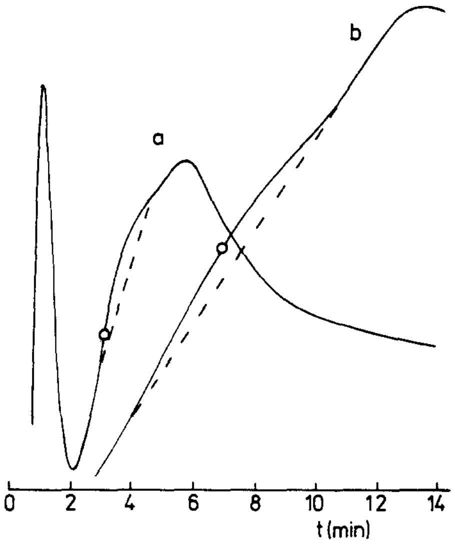

Figure 4 D.s.c. thermograms of modified epoxy–amine formulations using the unmodified formulation in the reference pan. Modifier: (a) 15 wt% CO cured at 100°C; (b) 15 wt% ETBN cured at 70°C. Circles indicate the cloud points as determined by light transmission

The heat (J g^{-1}) evolved in the phase separation process is estimated as:

$$-\Delta H=(-\Delta H)_0-(-\Delta H)_1=1.0 \tag{8}$$

This result is close to the experimental one taking into account the approximations used.

Reactive formulations

Both formulations B and C (see Experimental section) were homogeneous solutions that were phase-separated in the course of polymerization. *Figure 3* shows conversion *versus* time curves (obtained from isothermal d.s.c. scans) for the CO-modified system (B), polymerized at 100°C, and the ETBN-modified system (C) cured at 70°C. Cloud points are indicated by circles. The corresponding cloud-point conversions are $X_{CP}=0.55$ (for CO) and $X_{CP}=0.32$ (for ETBN).

The heat evolved during the epoxy–amine reaction is ~ 470 J g^{-1} (d.s.c. scans). Then, the possibility of detecting the heat associated with the phase separation process (a few J g^{-1}) is not a trivial task. In order to increase the sensitivity of this last process, isothermal d.s.c. scans were performed taking the pure epoxy–amine system as a blank. Thus, one d.s.c. pan contained the CO- or ETBN-modified formulations and the other contained a mass of the pure epoxy–amine system with the same amount of epoxy equivalents as in the modified formulation. Even in the case where the modifier does not exert any influence on the polymerization kinetics (specific rate constants and activation energy), conversion *versus* time curves are shifted due to the dilution effect and the increase in the initial concentration of hydroxyl groups acting as a catalyst in the epoxy–amine addition reaction[10]. Therefore, d.s.c. thermograms showed positive and negative peaks of small amplitude, depending on the prevailing cure rate at a given time.

Figure 4 shows the resulting d.s.c. thermograms. The presence of shoulders is marked on both the thermograms shown. These shoulders represent an exothermic process (~ 4.6 J g^{-1} for CO and 3.7 J g^{-1} for ETBN) covering the cloud-point time observed by light transmission (denoted by a circle on each curve). Therefore, these shoulders are ascribed to the heat evolved in the phase separation process. The beginning and end of each shoulder are indicated by dotted lines in the conversion *versus* time curves shown in *Figure 3*. In the case of CO, the onset of phase separation as detected by both light transmission and d.s.c. is practically the same. This means that particles with sizes $> \sim 0.1$ μm are rapidly formed and detected by visible light. However, for the case of ETBN, phase separation begins at a significantly lower conversion than that detected by light transmission. This agrees with the SAXS results reported by Chen[2].

These examples show that d.s.c. may provide useful information related to the conversion range where phase separation takes place. The analysis of morphologies generated under different cure conditions and of the properties of the resulting materials is currently under way.

Conclusions

The phase separation of a modifier (i.e. a rubber) in the course of a thermosetting polymerization is characterized by a simultaneous heat release. D.s.c. may be used to detect the phase separation process in both unreactive and reactive formulations. In the former case the cloud-point curve may be easily obtained; in the latter, the conversion range where phase separation takes place may be estimated. This requires the use of the unmodified system in the reference pan.

References

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