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Notes

Shear-Induced Homogenization during Cure of Thermoset/Rubber Blends

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Introduction

A large body of experimental data indicates that application of shear forces to a mixture of liquids affects the thermodynamic miscibility of the constituents.[1-11] This effect was first reported by Silberberg and Kuhn[1] in a solution of polystyrene and ethylcellulose in benzene. Later, similar effects have been observed both in polymer solutions[2-4,7-9] and polymer blends.[5,6,10,11] Despite attempts to explain these phenomena theoretically,[12-15] the physical mechanism of this effect is not yet resolved. Usually, but not always,[4,12] shear improves the miscibility. In practice, this implies that a system that is not fully miscible but close to the binodal in the phase diagram can be "homogenized" by applying shear. Since there is currently no irrefutable evidence that the effect is strictly thermodynamic, the term "shear induced homogenization" (SIH) was chosen, following Hashimoto.[7,8,10,11]

All reported SIH phenomena have been observed in nonreacting systems. It is therefore interesting to study the possible occurrence of SIH in blends where one of the components is a reacting thermoset because phase separation in such systems can occur at a fixed temperature and pressure, as a function of time, i.e., extent of the reaction, and the morphology in a thermoset system becomes fixed when passing the gelation point.

The experimental system is a typical rubber toughened epoxy resin formulation used in industrial applications where an increased fracture toughness is desired. The rubber is initially miscible with the resin/curing agent mixture. When the cure reaction proceeds, the molecular weight of the resin molecules increases, and, at a certain stage, the system is no longer fully miscible. The rubber demixes in the form of small spherical domains. Such systems have a significantly higher fracture toughness than that of the neat matrix.[16]

Experimental Section

The epoxy resin was Epikote 828 from Shell Chemicals, which was cured with an isophoronediamine (IPD) curing agent. The rubbers were carboxyl-terminated copolymers of acrylonitrile and butadiene (CTBN) with a molecular weight of 3200, purchased from B.F. Goodrich. The resin and curing agent were mixed in a stoichiometric ratio of 0.5 mol of IPD/mol of Epikote 828. The experimental systems contained 10% (by weight) CTBN rubber with 17% or 10% acrylonitrile (AN) content. Glass transition temperatures were measured by dynamic mechanical analysis with a Du Pont 983 DMA. Phase contrast optical micrographs were taken with a Reichert Polyvar optical microscope.

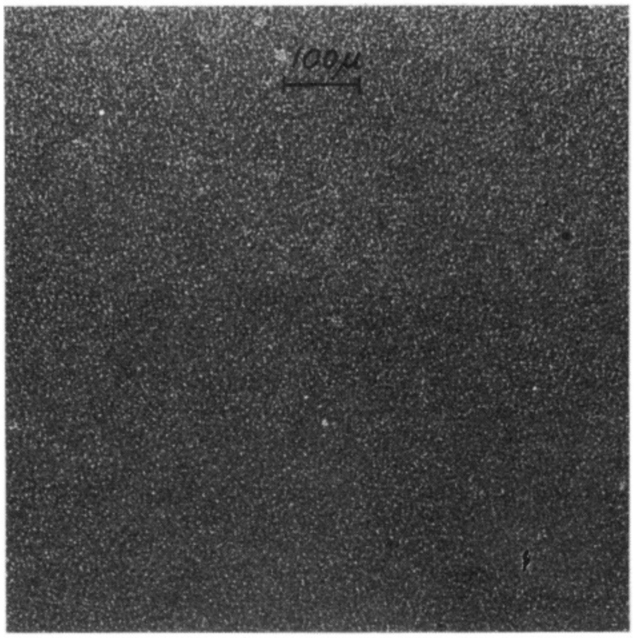

Figure 1. Phase contrast optical micrograph of the phase-separated morphology of a system that was cured under quiescent conditions.

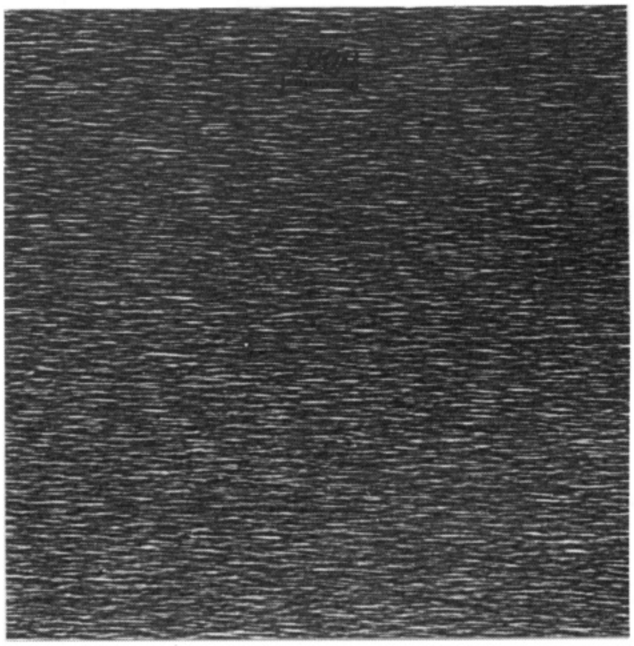

Figure 2. Phase contrast optical micrograph of a moderately sheared sample.

Results and Discussion

Samples were prepared by placing a drop of the above Epikote 828/IPD/CTBN (17% AN) formulation between microscope glass slides. The slides were placed on a hot plate (60–80 °C) to start the curing reaction. Initially the sample was optically clear, but after a certain time the sample became opaque by the phase separation of the rubber. Figure 1 shows a phase contrast optical micrograph of the morphology obtained. At this stage, the resin is still in a liquid state with a relatively low viscosity. Applying shear to the sample (by moving the upper slide relative to the lower) only slightly affects the morphology.

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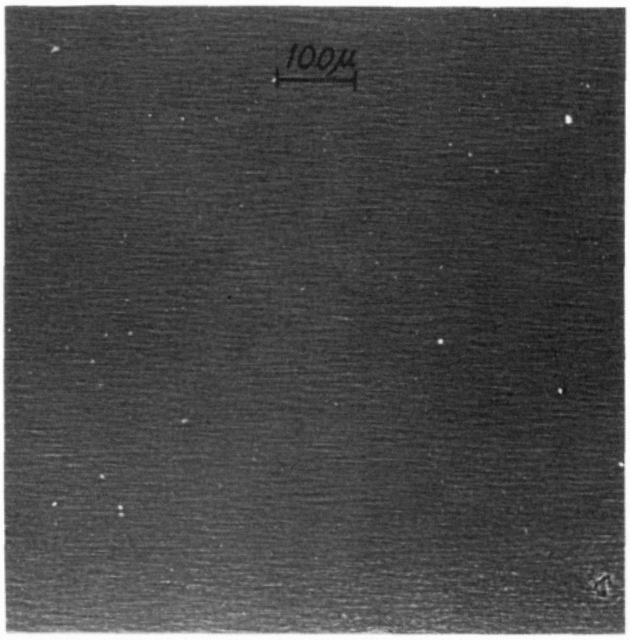

Figure 3. Phase contrast optical micrograph of a strongly sheared sample.

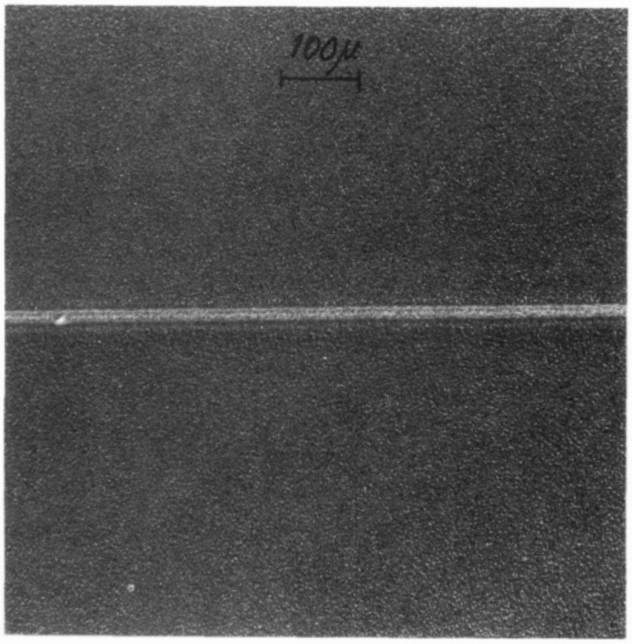

Figure 4. Phase contrast optical micrograph of a glass fiber in a matrix that was cured under quiescent conditions.

However, when shear is applied just prior to gelation, when the viscosity of the resin is increasing strongly, the morphology appeared to be very sensitive to shear. Figures 2 and 3 show phase contrast optical micrographs of respectively a slightly (≈ 10 s^{-1}) and a more strongly (≈ 50 s^{-1}) sheared sample. Figure 2 shows elongated rubber domains in the direction of the applied shear, while, in figure 3, the contrast between the rubber domains and the matrix is disappearing, indicating homogenization of the sample.

Small-angle laser light scattering experiments with the above type of samples gave the following results:

(1) Nonsheared samples gave a circular symmetric pattern around the incident beam, indicating the presence of spherical particles.

(2) Lightly sheared samples produce a streak pattern, perpendicular to the shear direction, indicating oriented structures (in the direction of the shear).

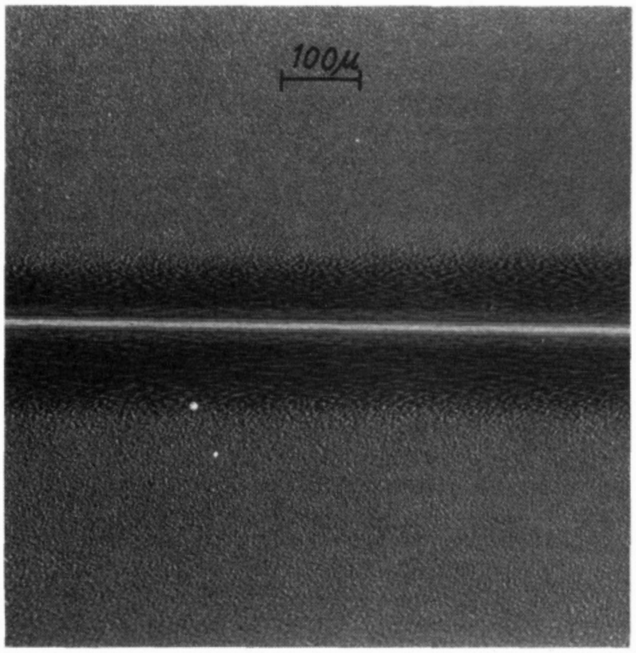

Figure 5. Phase contrast optical micrograph of the phase-separated matrix with a glass fiber that was pulled through the matrix just prior to gelation.

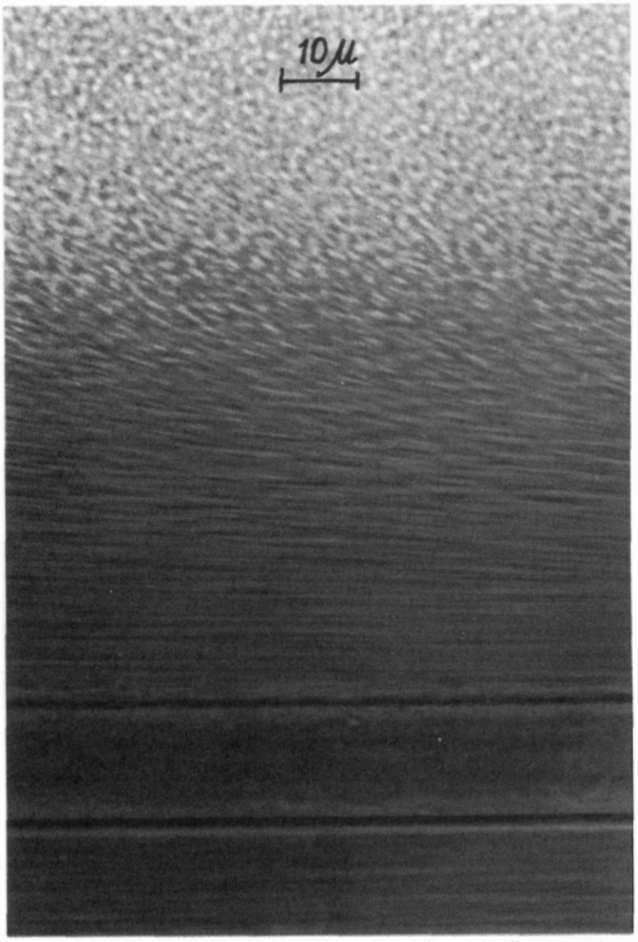

Figure 6. Phase contrast optical micrograph (with oil immersion) of the same sample as shown in Figure 5 at a higher magnification.

(3) Strongly sheared samples showed no scattered light, which indicates the presence of a homogeneous material.

These observations are in line with the small-angle light scattering experiments of Hashimoto et al.[8,10]

Contrary to 17% AN content rubber, the 10% AN containing rubber does not dissolve in the epoxy/IPD mixture at room temperature but only at an elevated temperature. However, experiments with the latter gave similar results. This shows that the physical mechanism of SIH does not depend strongly on details of the chemical composition.

The practical importance of the SIH effect in these systems is shown by the following experiments. During compression molding of a glass fiber reinforced composite with the above resin system, we made the following observations with the 17% AN/CTBN rubber:

(1) Resin inside the composite remained transparent contrary to expelled resin which had the usual opaque appearance.

(2) Confocal laser scanning microscopy showed a two-phase structure in the expelled resin and a homogeneous phase in the composite resin.

(3) The glass–rubber transition temperature (T_g) of the matrix material (no reinforcement, cured under quiescent conditions) dropped by 10 °C due to the addition of the toughening rubber while the T_g of the compression-molded composite dropped by 30 °C in the toughened samples.

These observations strongly suggest that inside the composite the rubber was dissolved in the matrix. In the compression-molding process, excess resin is expelled from the mold, just prior to gelation of the resin matrix. During this process, the resin flows through the densely packed fiber package where it will experience considerable shear forces. The occurrence of SIH phenomena leads to a redissolution of the rubber. When the system passes its gelation point, which, by the nature of the compression-molding process, happens immediately after the matrix experienced the high shear forces, this morphology is fixed. Macroscopic phase separation cannot occur again after the cessation of the shear. This has important consequences for the properties of the final product.

Shear-induced homogenization phenomena around a glass fiber can be demonstrated by pulling an embedded fiber through the phase-separated resin. Figure 4 shows a glass fiber in a matrix that was allowed to cure under quiescent conditions. Figure 5 shows the morphology that is observed when the fiber is slightly pulled (≈5 mm/s) just prior to gelation. Figure 6 shows the sample at a higher magnification. The isotropic, elongated, and homogenized morphologies can be clearly observed in the shear band around the fiber.

The rheology of a curing rubber modified epoxy system changes rather drastically with time. This makes it difficult to execute experiments under fully controlled shear conditions. In fact, by the very nature of this system, equilibrium measurements are impossible. A full quantitative analysis of the SIH phenomena was therefore, at this stage, not attempted.

Conclusion

The above observations offer experimental evidence for the occurrence of shear-induced homogenization phenomena in curing rubber modified epoxy resin systems. The sensitivity to shear of the phase-separated morphology was largest just prior to gelation. These observations are of considerable practical and scientific interest, particularly as the shear-induced morphology is kinetically fixed when the system passes its gelation point.

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Registry No. IPD, 2855-13-2; IPD–Epikote 828 (copolymer), 38294-64-3; Epikote 828, 25068-38-6.