Macromol. Symp. **2007**, 254, 267–273 DOI: 10.1002/masy.200750840

ABS-Modified Epoxy Resins – Curing Kinetics, Polymerization Induced Phase Separation, and Resulting Morphologies

*Yvonne Müller, Liane Häußler, Jürgen Pionteck**

Summary: A commercial diglycidylether of bisphenol A (DGEBA) was modified with an acrylonitrile-butadiene-styrene-copolymer (ABS) and cured with the diamine hardener 4,4′-diaminodiphenylsulfone (DDS). The curing kinetics was followed by DSC- and PVT-measurements. The polymerization induced phase separation (PIPS) was studied using light microscopy and electron microscopy. While the cloud point analyzed by light microscopy is independent of the ABS content, the curing is accelerated by the presence of ABS. The non-linear dependency of the curing rate on the ABS content must have its origin in the different morphologies developed due to PIPS.

Keywords: ABS; curing kinetics; epoxy; morphology; phase separation

Introduction

Epoxy resins display an important role among thermosetting materials. One drawback is their brittleness which can be avoided by adding a suitable modifier, like rubbers or other impact resistant products. The corresponding blends exhibit a higher toughness which leads to a broader range of applications. Also rather tough thermoplastics like polystyrene or poly(styrene-co-acrylonitrile) are suitable for toughening epoxy thermosets.[1–4] When curing a homogeneous mixture of epoxy resin, hardener, and thermoplastic modifier, the polymerization induced phase separation (PIPS) leads to different morphologies dependent on the content of the added modifier. The phase separation can occur via two different mechanisms. The "Nucleation and Growth" mechanism (NG) is characterized by the formation of spherical particles at the beginning of the separation process that grow as a result of ongoing diffusion controlled phase separation and of coalescence. In contrast, in the case of spinodal decomposition (SD) a co-continuous or interpenetrating structure is initially formed. The present study deals with the analysis of the PIPS mechanism and it's kinetics in epoxy resins modified with acrylonitrile-butadiene - styrene-copolymer (ABS). The influence of the ABS on the curing kinetics was analyzed by DSC- and PVT- (Pressure-Volume-Temperature) measurements. Light microscopy and electron microscopy investigations served to characterize the phase separation mechanism and kinetics as well as the final morphology.

Experimental Part

Materials

The epoxy resin used was a commercial diglycidylether of bisphenol A (DGEBA), LY 556 (Bodo Möller Chemie GmbH, Offenbach, Germany) with a weight per epoxy equivalent of 188.7 g/eq, which was dried under vacuum prior to use. The acrylonitrile-butadiene - styrene-copolymer (ABS 34537 NAT, $T_g = 106.5\,^{\circ}C$, Dow Europe GmbH, Horgen, Switzerland) consists of a styrene-acrylonitrile matrix (SAN) with dispersed butadiene rubber particles

---

Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany
Fax: (49) 351 4658565
E-mail: pionteck@ipfdd.de

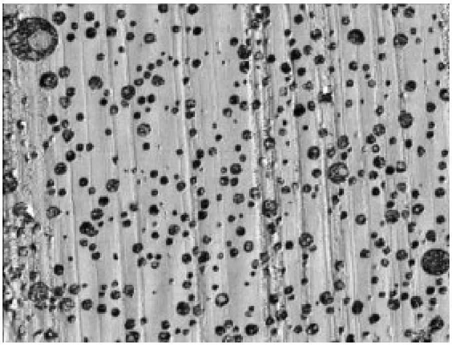


Figure 1.
AFM-image of ABS (phase contrast, frame size 80 × 100 μm).

(0.4–2.2 μm, Figure 1). Some of the rubber particles contain tiny inclusions of SAN. As hardener 4,4′-diaminodiphenylsulfone (DDS, Sigma Aldrich, Seelze, Germany) was used. For blend preparation, ABS was dissolved in the epoxy oligomer at a temperature of 180 °C. Afterwards the hardener was added at 130 °C with an epoxy:amine ratio of 2:1. Blends with ABS contents of 5, 10, 15, and 20 wt% were prepared. The curing was carried out over a period of 6 hours at 160 °C, 180 °C, and 200 °C, for 2 hours at each temperature.[2]

Instrumentation

A DSC (Q1000, TA Instruments) was used for dynamic cure experiments in the temperature range of −60 to 300 °C with a heating rate of 10 K/min. A cooling (with −10 K/min) run and a second heating run were performed to analyze the completeness of the curing. The same conditions were used to analyze the development of the glass transition temperatures (T_g's) during the curing process. PVT experiments were carried out by means of a fully automated GNOMIX high-pressure mercury dilatometer.[5] Below 200 °C the absolute accuracy of the instrument is of 0.002 $cm^3\ g^{-1}$. However, changes in the specific volume V_{sp} as small as 0.0002 $cm^3\ g^{-1}$ can be resolved reliably. The crosslinking reaction was characterized in the so-called data acquisition mode (DAQ) at 10 MPa and 157 °C by following the volume shrinkage of the samples with proceeding time. Light microscopy images were recorded on a Jenapol microscope (Carl Zeiss Jena, camera: TK-1280 E). For this, a film of 100–200 μm was generated between two glass slides and heated up to 220 °C with a rate of 10 K/min in the hot stage THMA 600 (Linkam). The final morphology was analyzed with a scanning electron microscope XL 30 ESEM-FEG (Philips) on cut surfaces, etched with oxygen plasma, and sputtered with gold.

Results and Discussion

DSC

Annealing for 2 hours at 160 °C, 2 hours at 180 °C, and 2 hours at 200 °C is recommended for the complete cure of this epoxy system.[2] To analyze the curing kinetics, the annealing performed in an oven was stopped at defined times and the samples were quenched for thermal analysis. Dynamic heating up to 300 °C was not sufficient for a complete curing of the non-cured sample as well as for the samples cured at different times. Since decomposition starts at temperatures higher than 300 °C, the heat of reaction could not be used for analyzing the curing kinetics as done in literature.[6] Therefore, the glass transition temperature (T_g) of the epoxy phase was used to describe the curing state of the blends (Figure 2). The blend with an ABS-content of 20 wt% exhibits the highest glass transition temperature at each curing state, whereas the neat epoxy resin shows the lowest T_g. These differences are clearly obvious up to a curing time of three hours. After a curing time of 6 hours glass transition temperatures of about 200 °C are determined for all samples independent of the ABS-content. Figure 3 illustrates the kinetics of the crosslinking reaction assuming a linear correlation between T_g and conversion, where the initial T_g is equal to 0% conversion and the final glass transition temperature corresponds to a complete network formation. According to this, the blend with 20 wt% ABS exhibits the fastest

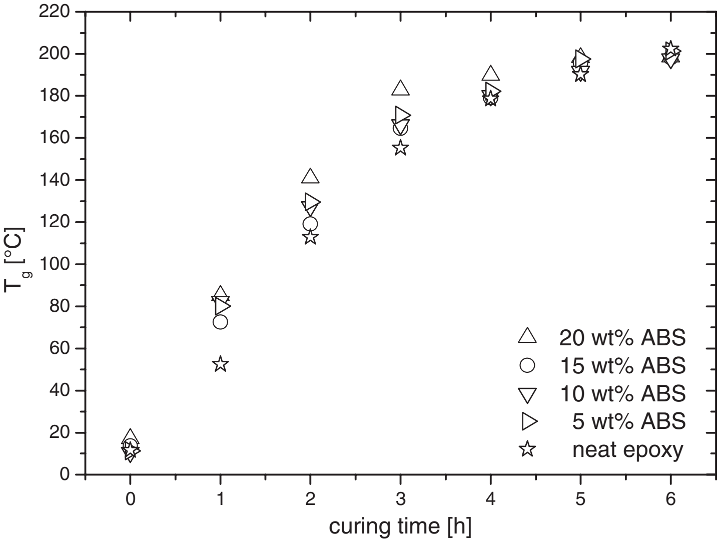


Figure 2.
Development of the glass transition temperature T_g of the epoxy phase with curing time.

curing kinetics. Here, we like to note that "complete curing" in the sense of complete conversion of all epoxy and amino groups can hardly be reached. Due to the increasing T_g with curing time the vitrification hinders the accessibility of the reactive partners. Complete curing in this context means that further annealing does not result in an increased network density.

The glass transition temperature of the SAN-phase was also studied. For all samples the T_g increases with curing time, which demonstrates the progress in phase separation. After 2 hours the T_g of the SAN

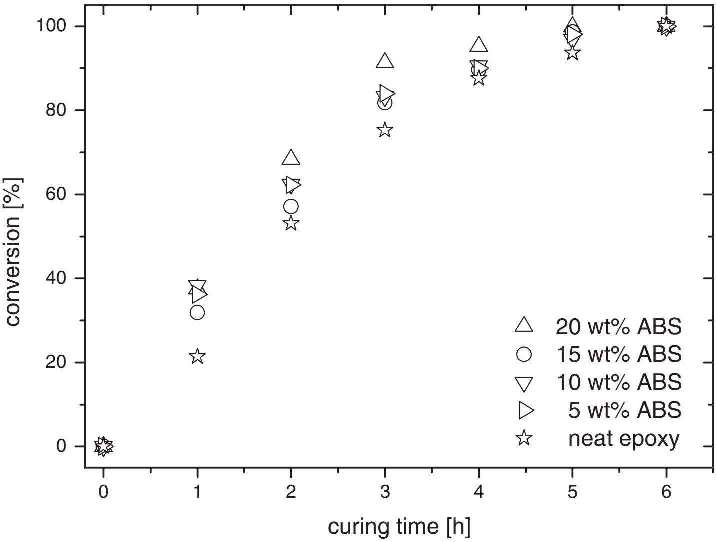


Figure 3.
Conversion versus curing time calculated from the changes in T_g.

phase was about 93 °C, after 6 hours at about 105 °C (±4 K). No significant dependence upon the ABS content could be observed. After an annealing time of 1 hour only the blend with 20 wt% ABS shows a glass transition of the SAN phase. For all the other samples the amount of SAN-rich domains is too small to be detected by DSC after annealing at 160 °C for 1 hour. During the DSC run the curing continues and in the second heating the T_g of the SAN phase is about that of the pure ABS (106.5 ± 2 °C).

PVT- (Pressure-Volume-Temperature) Measurements

The crosslinking of the diglycidylether results in a volume shrinkage, which can be followed by PVT-measurements. A temperature of 157 °C and a pressure of 10 MPa were applied over a period of 13 hours. After an annealing time of 4 hours the specific volume has reached a constant value for each blend, whereby the absolute value increases with increasing ABS-content (Figure 4). Figure 5 illustrates the conversion versus curing time assuming a linear relation between network formation and volume shrinkage, where the initial specific volume of mixing is equal to 0% conversion and the final volume represents a complete crosslinking reaction. Also by this method, the blend with the highest modifier content exhibits the fastest curing kinetics. However, the curing kinetics of the blends with lower ABS contents seems to be similar to that of the neat epoxy resin.

Light Microscopy

The phase separation mechanism was observed via optical microscopy. Due to the insolubility of the butadiene rubber in the epoxy resin, the uncured samples are already cloudy, but the beginning growth of domains is visible. Table 1 represents the temperatures of beginning demixing during heating the samples by a hot stage with 10 K/min, showing that the beginning phase separation is independent of the thermoplastic content of the epoxy blend. The faster curing kinetics of the sample containing 20 wt% ABS results in an enhanced increase of viscosity, which leads to a soft delay in the phase separation kinetics.

In all cases PIPS occurs via the ‘‘Nucleation and Growth’’ mechanism (Figure 6). For the blend with 5 wt% ABS the epoxy phase forms the matrix, for the blends with 15 and 20 wt% modifier the SAN phase of

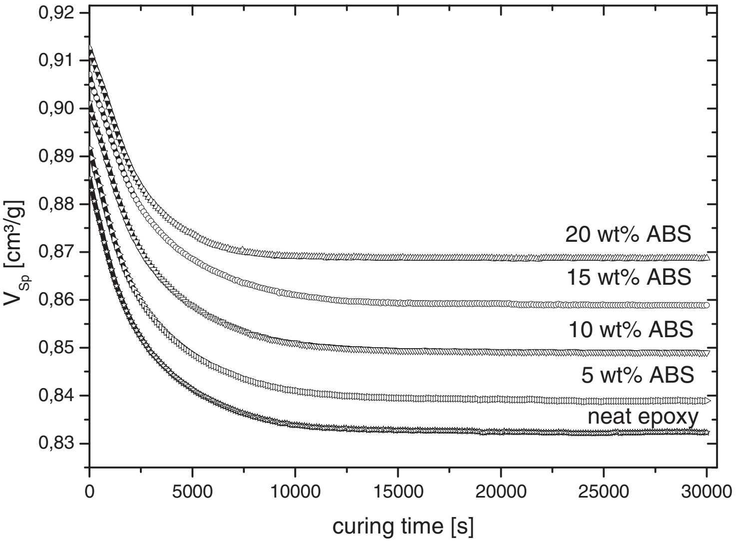


Figure 4.
Decrease of the specific volume (V_{sp}) of epoxy/ABS blends during curing at 157 °C at 10 MPa.

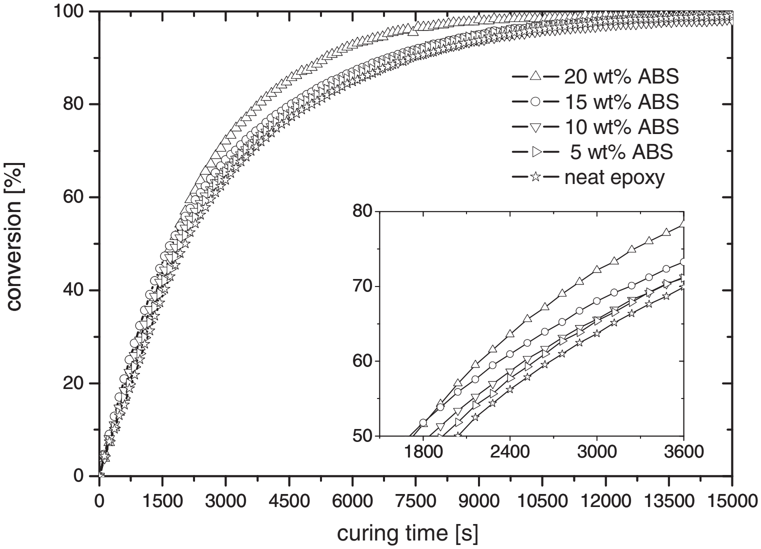


Figure 5.
Conversion of the crosslinking reaction calculated from the volume shrinkage.

the added ABS represents the matrix from the beginning of the phase separation. Only for the blend containing 10 wt% ABS the particle-matrix structure typical for binodal decomposition (NG-mechanism) is not clearly visible since this concentration is near to the phase inversion concentration. In late stages of phase separation a double phase separated structure will be formed (see below). The dispersed particles grow with annealing time due to the ongoing phase separation and coalescence until the increase of viscosity constricts these processes. The butadiene-rubber phase is not distinguishable by this method.

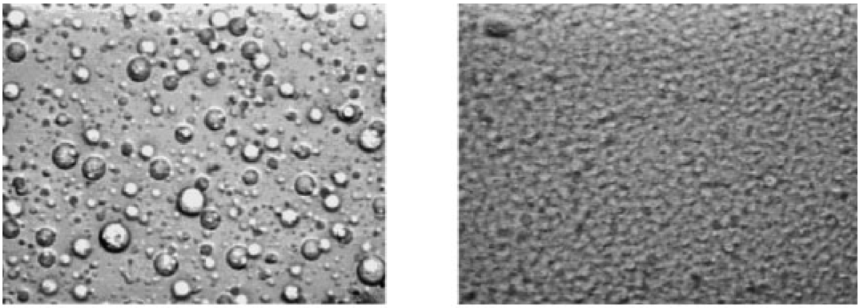
Scanning Electron Microscopy (SEM)

The phase morphology was analyzed via scanning electron microscopy. The completely cured samples were cut to obtain flat surfaces and treated with oxygen plasma (60 s). After etching, the epoxy phase remains smooth, the SAN phase shows some roughness, and the butadiene rubber phase is etched out (Figure 7).

For the sample containing 5 wt% ABS the thermoplastic modifier appears as spherical particles in the size up to 1.3 μm in average. (Note: The rough, porous structure of the epoxy matrix in this sample is an artefact from the cutting procedure and is not related to dispersed rubber particles). At 10 wt% ABS content a double phase separation occurred during curing. An epoxy matrix is formed containing huge domains in the size of some hundred μm, which consists of an ABS matrix containing epoxy spheres in the size of up to 12 μm, and large domains of pure epoxy resin. At higher ABS concentrations the ABS forms the matrix and the hardened epoxy phase exists as deformed spherical particles. Interestingly, the size of the epoxy particles with up to 50 μm is much larger in the sample containing 15 wt% ABS compared to the maximum particle size of 20 μm obvious for the blend with 20 wt% of modifier. Due to the faster curing

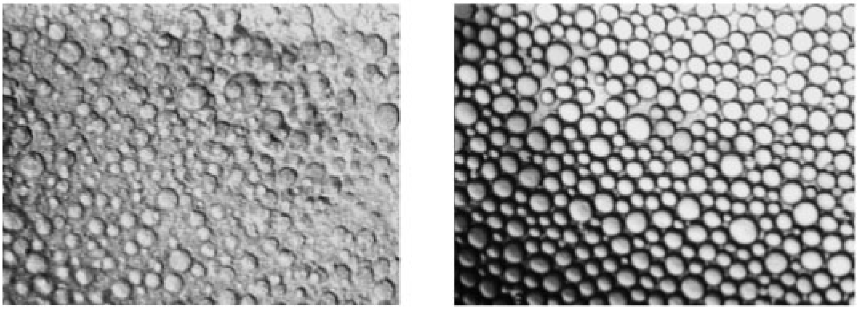
Table 1.
Temperatures of demixing against the ABS-content.

wt% ABS	temperature of demixing [°C]
5	209
10	208
15	211
20	213



5 wt% ABS

10 wt% ABS



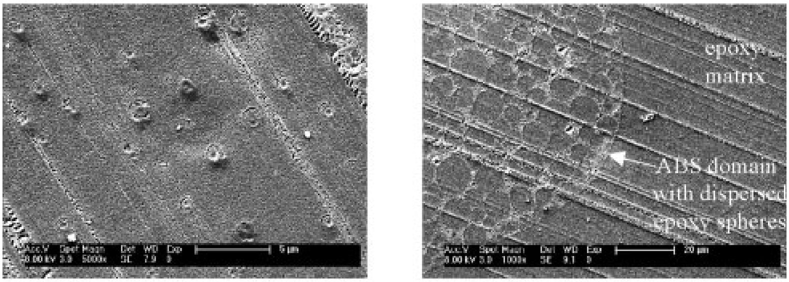
15 wt% ABS

20 wt% ABS

Figure 6.
Light microscopy images taken at early stages of phase separation (frame size 75 μm × 100 μm).

5 wt% ABS

10 wt% ABS

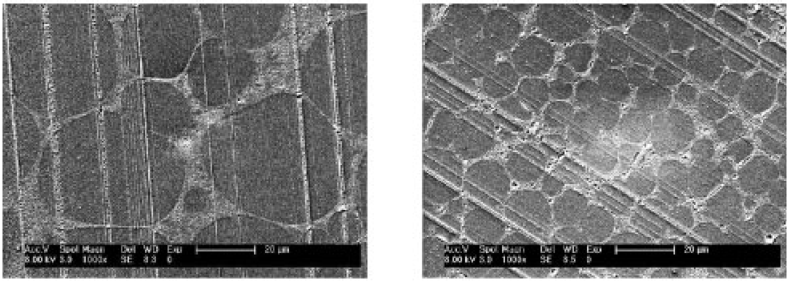


bar = 5 μm

bar = 20 μm

15 wt% ABS

20 wt% ABS



bar = 20 μm

bar = 20 μm

Figure 7.
SEM-images of the cured epoxy blends, etched with oxygen plasma.

kinetics, which goes along with an enhanced increase in viscosity and glass transition temperature the particle growth due to coalescence stops earlier in this sample.

Conclusion

Following the glass transition temperature of the epoxy-phase with increasing annealing time, the epoxy blend with 20 wt% ABS exhibits the fastest curing kinetics. The PVT-measurements confirm this result despite different reaction conditions (temperature: 157 °C, pressure: 10 MPa). The reason for the increase in curing rate is not clear yet. When preparing the epoxy – ABS mixtures, the viscosity of the uncured sample increases with increasing ABS content whereas the concentration of reactive groups is reduced. Both effects would lower the curing rate. Therefore we assume a catalytic activity of the ABS, but also the type of morphology, which develops during annealing may have an effect on the curing rate. Though the curing kinetics is changed by the presence of ABS the phase separation kinetics was found to be nearly independent of the modifier content. The polymerization induced phase separation occurs via the ''Nucleation and Growth'' mechanism. Dispersed ABS particles in an epoxy matrix are observed at a concentration of 5 wt% ABS. At 10 wt% ABS content a co-continuous-like superstructures develops with time, which decomposes during annealing in a double phase separated structure consisting of pure epoxy domains and domains based on ABS-matrix with embedded epoxy spheres. At higher ABS contents a complete phase inversion results in large epoxy particles dispersed in the ABS matrix.

Acknowledgements: We are grateful to S. Thomas, Kottayam, for his valuable advices and A. Janke, Dresden, for the AFM image of ABS. We also thank H. Kunath, Dresden, for the performance of the PVT-measurements and his general technical assistance.

[1] C.B. Bucknall, T. Yoshi, *Br. Polym. J.* **1978**, *10*, 53.
[2] R. Thomas, J. Abraham, P.S. Thomas, S. Thomas, *J. Polym. Sci., Polym. Phys.* **2004**, *42*, 2531.
[3] B.B. Johnsen, A.J. Kinloch, A.C. Taylor, *Polymer* **2005**, *18*, 7352.
[4] J. Lopez, I. Lopez-Bueno, P. Nogueira, C. Ramirez, M.J. Abad, L. Barral, J. Cano, *Polymer* **2001**, *42*, 1669.
[5] P. Zoller, C.J. Walsh, *Standard Pressure-Volume-Temperature Data for Polymers*, Technomic Publ. Co., inc., Lancaster, Basel 1995.
[6] L. Barral, J. Cano, J. Lopez, I. Lopez-Bueno, P. Nogueira, M.J. Abad, C. Ramirez, *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 351.