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Reactive Epoxy-CTBN Rubber Blends: Reflection of Changed Curing Mechanism in Cure Shrinkage and Phase Separation Behaviour

Jürgen Pionteck, Yvonne Müller, Liane Häußler*

Summary: During curing of epoxy resins shrinkage occurs, which is caused by the formation of polymeric and crosslinked structures. We analysed this shrinkage for a system consisting of diglycidyl ether of bisphenol-A (DGEBA), diamino diphenyl sulfone (DDS) as hardener, and a reactive or a nonreactive rubber, with or without catalyst. The shrinkage and the phase separation behaviour strongly depend on the composition. The addition of reactive rubber and of the catalyst influences the curing mechanism and reduces the crosslinking density, which is reflected by lowered glass transition temperatures and reduced shrinkage. The reactive rubber is partially incorporated in the crosslinked epoxy phase and vice versa. In this way it is possible not only to modify the morphology-related properties but also to control the degree of the unwanted shrinkage.

Keywords: curing of polymers; epoxy blends; reaction induced phase separation; reactive rubber; shrinkage

Introduction

Epoxy resins display an important role among thermosetting materials.[1] During curing of epoxy resins extensive shrinkage occurs caused by the polymerisation and crosslinking. This shrinkage may cause difficulties during processing, stress induced deformations, failures, etc., all limiting the applicability of epoxides. To reduce the shrinkage fillers or other non-shrinking additives can be added. Interesting is the addition of materials which introduce another functionality to the resin, e.g. rubbers or thermoplastics, both often used to improve the toughness of the in general high strength but brittle materials.[2] The additives change the cure shrinkage during processing following the additivity rule as long as they do not interfere with the curing mechanism and not influence the curing degree of the resins. However, in epoxy oligomer/thermoplastic mixtures having intrinsic 'dynamic asymmetry' between their components quite unusual phase separation was found. As in blends of components with large difference in T_g or molecular weight the slow fluid component cannot catch up with the deformation rate of phase separation and starts to behave like a viscoelastic body. Since viscoelastic effects play a crucial role in this phase separation, it is called "viscoelastic phase separation".[3] This type of phase separation is characterized by unique coarsening behavior like phase inversion and can also cause thermoplastic volume shrinkage.[4]

When reactive or catalytic acting modifiers are added to the epoxy resin, they can influence the curing reactions by changing the stoichiometry or the curing mechanism.[1,5,6,7] So, acidic additives can react with the oxirane rings, basic additives can cause the pronounced formation of linear ether structures, and hydroxyl groups or moisture catalyse the reaction resulting in

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Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany
Fax: (+49) 351 4658393;
E-mail: pionteck@ipfdd.de

changes in the final morphologies developed due to reaction induced phase separation (RIPS).[8]

The principle curing reactions of epoxy-diamine systems are shown in Figure 1.[1] When crosslinking epoxy resins with primary diamines in a first step the amino group adds to an oxirane ring forming a secondary amine and a secondary hydroxyl group (reaction 1, Figure 1). The secondary amine reacts with additional oxirane units under formation of a tertiary amine, again under formation of a secondary hydroxyl group (reaction 2, Figure 1). Both reactions exhibit similar polymerisation rates due to the only small differences in their basicity, so that at the end only tertiary amines exist. The hydroxyl groups are rather stable and do not react with epoxide units under normal conditions but catalyse the oxirane-amine reaction. The catalytic activity of hydroxyl containing substances as alcohols, phenols, carboxylic acids was studied by Shechter[6] who proposed a trimolecular mechanism which included the formation of H-bridges to the oxygen of the oxirane ring.

For complete conversion of one amine group two oxirane rings are necessary. The ether formation according to reaction 3, Figure 1, is practically irrelevant at normal conditions but starts at higher temperatures, caused by catalytic activity of the formed tertiary amines. Narracot[7] suggested an anionic mechanism for this homopolymerisation. The tertiary amine reacts with the oxirane ring under formation of an ammonium zwitterion. The formed oxygen anion reacts with another oxirane ring under formation of the ether bond. The reaction continuous until the tertiary amine eliminates. The addition of alcohol or water accelerates this catalytic polymerisation by the formation of a zwitterion made from the tertiary amine, oxirane ring and the hydroxyl compound forming an H-bond to the oxirane oxygen. In presence of such accelerators the curing can start already at room temperature.

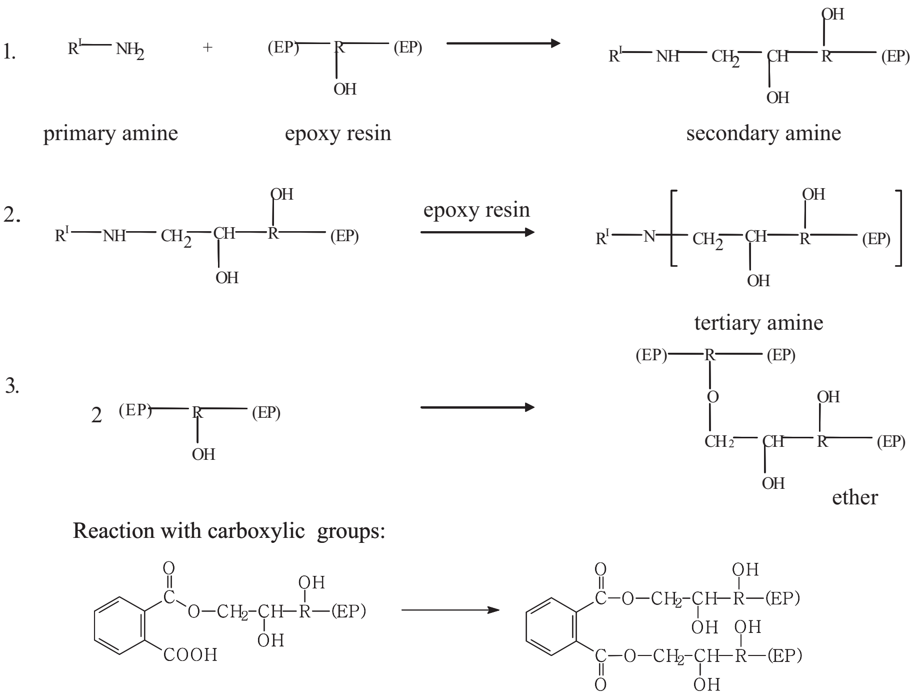


Figure 1.
Crosslinking and polymerisation reactions occurring during curing of epoxides with diamines.

The ether formation effects the stoichiometry of the system and so the properties of the obtained material. In general, due to variation of the amine/oxirane ratio the properties of the cured resins can be controlled. Excess oxirane units improve the water resistance, while excess amine improves the stability against organic solvents. Carboxylic acid groups also can react with the oxirane rings forming ester structures and hydroxyl units (Figure 1).[5]

The toughening of epoxy resins with reactive rubbers is intensively studied in literature.[9–16] Carboxyl-terminated butadiene-co-acrylonitrile rubber (CTBN) was studied as toughener for epoxy resins already in 1970 [9] In a system consisting of DGEBA cured with 2,4,6-tri-dimethylaminoethylphenol CTNB showed the highest efficiency compared to other rubbers. The impact strength was dependent on the crosslinking density of the epoxide, rubber content, the rubber molecular weight, and the particle diameter. The effect of the particle size on the toughening efficiency was intensively studied for reactive rubbers (including CTBN) and core-shell particles by Pearson and Yee.[11] Also in the system DGEBA hardened with DDS best results in toughening with CTBN were reached using DGEBA with higher molecular weights.[10] In dense networks the low plastic deformation caused brittle behaviour. Thomas et al.[16] used CTBN for the modification of DGEBA-nadic methyl anhydride resins catalysed with a triamine. The rubber particle size increased with increasing content due to enhanced coalescence. The chemical incorporation of the reactive rubber into the epoxy network resulted in a reduced glass transition temperature. However, up to 15 wt.% rubber high strength materials were obtained with improved toughness.

In all attempts to improve the material properties, the knowledge about the underlying curing mechanism as well as the curing kinetics is crucial. In this study we analysed epoxy resins based on diglycidyl ether of bisphenol-A (DGEBA) using diamino diphenyl sulfone (DDS) as hardener. The effect of CTBN on the epoxy curing was determined using a non-reactive CTBN-ester as reference. To control the kinetics partially dimethyl benzyl amine (DMBA) was used as catalyst. The focus is laid on the influence of the rubber reactivity and of the catalyst on the shrinkage, which was taken as measure for the polymerisation kinetics, mechanism of network formation, and the resulting morphologies.

Experimental Part

Materials

The epoxy resin used was a commercial diglycidylether of bisphenolA (DGEBA) LY 556 (Ciba Geigy, supplied by Bodo Möller Chemie GmbH, Germany) with a weight per epoxy equivalent of 188.7 g/eq, which was dried under vacuum prior to use. As hardener 4,4′-diaminodiphenylsulfone (DDS, 97%, Fluka) was used. As catalyst the triamine dimethylbenzylamine (DMBA, Aldrich) was used.

Poly(butadiene-co-acrylonitrile) rubber with two terminal carboxyl units (CTBN $M_n = 3500$ g/mol, $T_g = -52\,°C$, molar ratio butadiene/ acrylonitrile = 5: 1, from Aldrich) was used in its reactive form or after conversion with 1-butanole to the diester (CTBN-ester). For the conversion CTBN was dissolved in toluene/1-butanol in a molar ratio COOH: OH = 1: 2 and p-toluenesulphonic acid (1 mol% in regard to CTBN) were added. The solution was boiled under reflux for 5 hours and the formed water was separated by means of a Dean-Stark apparatus. Excess toluene and 1-butanol were removed by distillation, the product was dissolved in chloroform, washed with water, dried, and finally the solvent was removed by distillation. The FTIR/ATR spectra (Bruker Tensor 27 spectrometer with diamond reflection element) of the converted rubber exhibits a strong ν(C=O) signal at 1737 cm^{-1} referring to the ester units compared to the ν(C=O) absorption of the carboxylic acid groups in the non-modified CTBN at

1708 cm^{-1} ($T_g = -48$ °C). The ^{1}H NMR spectrum (Bruker DRX 500 NMR spectrometer, 500.13 MHz, in $CDCl_3$) of the ester shows the expected proton signals of the n-butyl substituent (-$C^{\alpha}H_2$-$C^{\beta}H_2$-$C^{\gamma}H_2$-$C^{\delta}H_3$) at 4.09 ppm (α, t), 1.61 ppm (β, p), 1.35 ppm (γ, p), and 0.94 ppm (δ, t). The β methylene and γ methylene proton signals are superposed by signals of the CTBN, but the α methylene and γ methyl protons give individual signals. The chemical structures of the epoxy-rubber blend components are shown in Figure 2.

All other chemicals and solvents were obtained in laboratory grade and used without purification.

Blend Preparation

First all components were carefully dried to avoid moisture induced side reactions. Then the desired amount of rubber (resulting in 5, 10, 15, or 20 wt.% in the final blend) was dissolved in 100 g DGEBA under stirring in vacuum at elevated temperature. Eventually the hardener DDS (33 g, mol ratio NH_2: oxirane = 1:2) and, if mentioned, the catalyst (1 mol.% in regard to DGEBA) were added and dissolved at 130 °C until a clear solution was achieved. The clear solution was then quenched in liquid nitrogen and stored in a freezer to prevent any curing before the actual measurements started. The shrinkage studies were carried out within the PVT-cell over a period of 13 hours at 157 °C. For DSC analysis curing was performed in an oven at 160 °C, 180 °C, and 200 °C, for 2 hours at each temperature, which was described as optimum for complete conversion.[16]

Measurements

Pressure-Volume-Temperature (PVT) Analysis

Changes in the specific volumes (V_{sp}) were measured using a fully automated GNOMIX high-pressure dilatometer capable of detecting volume changes as small as 0.0002 cm^3/g within an accuracy limit of 0.002 cm^3/g (below 200 °C). The apparatus is described elsewhere.[17] 1.5 g of the non-cured samples were loaded in the measuring cell which then was completely filled

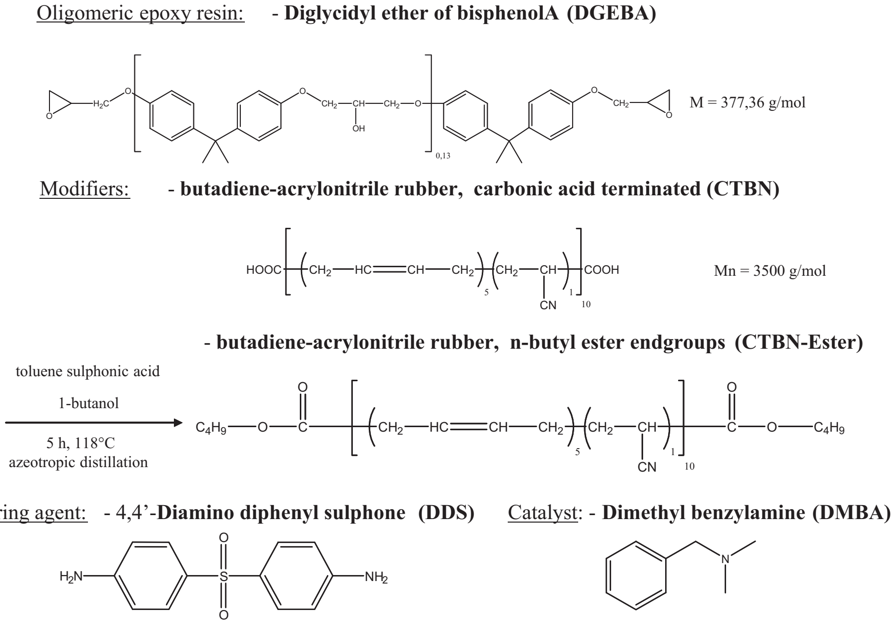


Figure 2.
Chemical structure of the epoxy-rubber blend components.

with mercury ensuring permanent hydrodynamic pressure to the sample. To hinder sticking of the resin to the cell wall the samples were embedded in a nickel foil cup. The apparatus was pressurised to 10 MPa, heated to the desired temperature, and then the changes in specific volume of the sample were recorded over time.

To calculate the theoretical V_{sp}-values of the non-reacted mixtures the specific volume of each component of the blends in dependence on p and T (except the catalyst) was analysed by PVT in the so-called ITS (standard isothermal) mode. In this mode at constant temperature the sample was pressurised from 10 MPa to 200 MPa and the data were collected in steps of 10 MPa. The values for ambient pressure (0.1 MPa) were obtained by extrapolating the V_{sp}-values between 30 MPa and 10 MPa in steps of 1 MPa according to the Tait equation by means of the internal PVT software. After each run the temperature was raised by 5 to 15 K, resulting in a set of PVT-data in the temperature range between room temperature and 220 °C for pressures of 0.1 to 200 MPa. Since the PVT-apparatus measures only the changes in V_{sp} and not the absolute values, for calibration the densities of the components at standard pressure and defined temperature were determined separately by pycnometer measurements.

Differential Scanning Calorimetry (DSC)

A DSC (Q1000, TA Instruments) was used for dynamic curing experiments in the temperature range of -60 to 300 °C with a scan rate of ± 10 K/min under nitrogen atmosphere. A cooling and a second heating run were performed to analyse the completeness of the reaction. The same conditions were used to analyse the development of the glass transition temperatures (T_g) on samples cured in the oven. Samples were taken after each hour. The samples cured within the PVT cell were analysed under the same temperature regime (10 K/min) but in modulated mode (amplitude ± 1 K, period 20 s) to separate glass transition from relaxation phenomenon and other endothermic processes like vaporisation of moisture which overlap the glass transition. The glass transition temperatures were calculated from the reversing heat flow signal using the half step method. It has to be taken into account that there is a difference in the calculated T_g values between total heat flow evaluation and reversing heat flow evaluation that gives values roughly 8 K higher. Slower heating/cooling rates in modulated DSC would reduce this difference but for reason of comparability we decided to use same rates for both DSC methods.

Scanning Electron Microscopy (SEM)

The final morphology of the samples (prepared in the same manner as described above) was analysed with a scanning electron microscope XL 30 ESEM-FEG (Philips) on smoothed cuts. The surface of the cuts was either etched with chloroform for 4 hours to dissolve the rubber phase or etched in oxygen plasma for 60 s resulting in a decomposition of the rubber. All samples were sputtered with gold to hinder electrostatic charging during SEM analyses.

Results and Discussion

PVT

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 (Figure 3, shown are the first 30000 s (ca. 8.3 hours)). In the non-catalysed system after an annealing time of 4 hours the specific volumes have reached constant plateau values except in case of the blend with highest non-reactive rubber content, where after 6 hours a continuous increase in V_{sp} of 0.4% is observed during the next 7 hours. This could be explained by the degradation of the rubber. This is supported by the finding that annealing the pure liquid CTBN-ester for 30 hrs at 190 °C and a pressure of 10 MPa a completely crosslinked elastomer

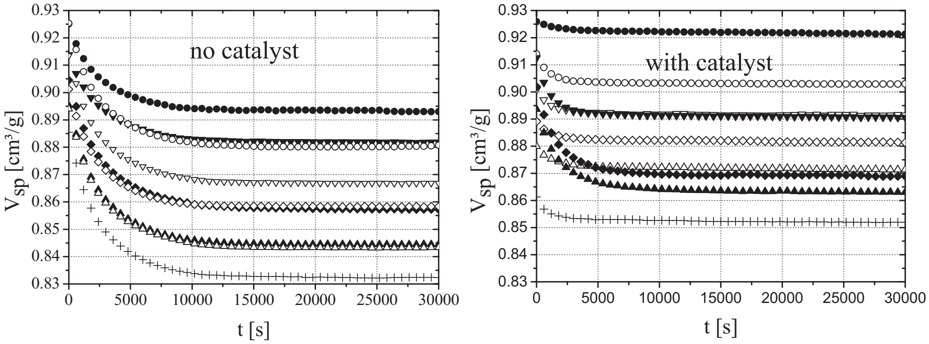


Figure 3.
Influence of the rubber content and rubber reactivity on the shrinkage during curing of DGEBA/DDS without catalyst (left) and with 1 Mol.% DMBA (right). Rubber content: 0 (+), 5 (△), 10 (◇), 15 (▽), and 20 wt.% (○); full symbols CTBN, open symbols: CTBN-ester.

was obtained that exhibits a drastically different IR-spectra compared to that of the starting material (not shown).

The specific volumes increase with increasing rubber content. The mixtures with 5 or 10 wt.% rubber showed a similar shrinkage behaviour for the reactive and non-reactive rubber, however, in case of higher rubber loadings the blends with the reactive CTBN exhibit lower shrinkage than the blends with the nonreactive CTBN-ester. A possible explanation is the increasing content of carboxylic groups, which can catalyse the ether formation (see reaction 3 in Figure 1). The ether formation would reduce the network density, but the degree is rather low so that the T_g is not much influenced (see Table 3 below). The non-reactive CTBN does not influence the crosslinking mechanism and a dense network is formed as in the materials devoid of rubber. Overall we observed a catalytic effect as well of the CTBN as the CTBN-ester; the time for reaching constant Vsp values reduces with rising rubber content.

Complex behaviour is especially observed when comparing the influence of the tertiary amine catalyst DMBA on the curing of the non-reactive and reactive rubber containing systems. First, the curing rate is accelerated, the plateau values are reached faster, and the starting point (the V_{sp}-value at $t = 0$) is in some cases, especially in the samples with the non-reactive and the rubber free sample, decreased, showing that the polymerisation starts already during the mixture preparation and during the heating of the PVT-cell. At low rubber contents the final shrinkage in the CTBN containing systems is more pronounced than in the CTBN-ester systems, with 15 wt.% rubber almost equal shrinkage is observed, and with 20 wt.% the behaviour is inverse with a very small volume shrinkage in case of reactive rubber. This very low shrinkage of the catalyst system containing 20 wt.% CTBN is a strong hint that an incorporation of the CTBN into the network and the oxirane homopolymerisation (which is catalysed by tertiary amines) occur parallel to each other. At lower rubber concentrations the interaction of the catalyst with the reactive rubber sites may form quaternary ammonium salts. This hampers the catalytic activity of the amines and also the reactivity of the carboxylic units to the epoxide, resulting in reduced reaction kinetics similar to that of the non-catalyst system. However, in all compositions the catalysed systems (Figure 3, right image) exhibit lower shrinkage than the non-catalysed (Figure 3, left image) so that we assume in all catalysed systems a partial epoxy hompolymerisation. The changes in the shrinkage behaviour are accompanied with changes in the phase morphology from an epoxy-matrix/rubber particle to a co-continuous-like structure (see below). Such morphological changes can also have an additional strong influence on the shrinkage even in nonreactive systems.[4]

To quantify the shrinkage we calculated the theoretical specific volumes of the noncured mixtures according to the additivity rule, assuming no changes in the component density due to miscibility effects. Deviations of the measured V_{sp}-values at the beginning of the crosslinking at $t = 0\,s$ from the calculated values are hints of the beginning curing reactions already during the mixture preparation and during the heating to the annealing temperature, which was performed with a rate of about 10 K/min. The effect of the small amount of catalyst on the theoretical V_{sp}-values was ignored in this estimation.

Table 1 contains the linear fit values of the specific volumes of each blend component in the interesting temperature range of 20 to 200 °C at a pressure of 10 MPa. Using this data for each temperature and composition the V_{sp} data of the virgin, nonannealed mixtures can be calculated. Table 2 summarises the shrinkage of the different blends. Comparing the relative shrinkage values determined experimentally with those determined by calculating with the theoretical V_{sp} $(t = 0)$ value it becomes obvious that the shrinkage curves shown in Figure 3 present V_{sp} $(t = 0)$ values that are too low in case of the catalysed blends, while the non-catalysed blends show in most cases a rather good agreement between both the calculated and experimental values. This indicates that the assumption of additive behaviour of the specific volume of the mixtures according to their composition is correct and that during the material preparation of non-catalyst systems no or only marginal curing occurs, while in presence of the catalyst up to 2 thirds of the cure shrinkage can occur already during the sample preparation and heating to the cure temperature. Thus, for evaluation of the influence of the reactivity on the overall shrinkage the theoretical values have been used.

Table 1.
Fit-parameters of the T-dependency of the specific volumes of the blend components at 10 MPa.

Material	V_{sp} (in cm^3/g)
DDS	$0.7570 + 3.5525\ E^{-4} * T$ (in °C)
CTBN	$1.0292 + 6.8059\ E^{-4} * T$(in °C)
DGEBA	$0.8443 + 4.8685\ E^{-4} * T$(in °C)
CTBN-Ester	$0.9954 + 7.2485\ E^{-4} * T$(in °C)

Normalising the shrinkage of the blends to the epoxy content (DGEBA + DDS) results in an epoxy phase shrinkage of 5.3 to 6.7% for all samples devoid of catalyst. The pure epoxy resin shrinks roughly 5.8%. In presence of catalyst we observed much lower shrinkage of 1.8 to maximum 5%, in the rubber free system of 3.5%.

In both cases, with or without catalyst, the non-reactive rubber addition results in rather similar shrinkage of the epoxy phase, nearly independent of the rubber content, while in case of reactive rubber lower shrinkage and especially in the catalyst systems a strong dependence of the shrinkage on the rubber content is detected. We like to note here, that the catalysed homopolymerisation of DEGBA in absence of the hardener DDS during an ITS run in the regime heating – cooling in the temperature range between room temperature and 197 °C resulted in a shrinkage of 2.0%.

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.[16] To analyse 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 showed a beginning exothermic curing peak at about 110 °C for all CTBN containing samples, only the catalyst blend containing 20 wt.% started to cure already at about 80 °C. However, the dynamic heating was not sufficient for a complete curing of the noncured sample as well as for the samples cured at different times. Therefore, and

Table 2.
Theoretical and experimental specific volumes of epoxy-CTBN blends in the non-cured and cured state.

Rubber content [wt.%]	V_{sp} (t = 0s) exp. [cm^3/g]	V_{sp} (t = 0s) theor. [cm^3/g]	V_{sp} (final) exp. [cm^3/g]	Δ V_{sp} exp.[a] [cm^3/g]	Δ V_{sp} exp.[b] [%]	Δ V_{sp} theor.[c] [cm^3/g]	Δ V_{sp} theor.[d] [%]	Δ V_{sp} normalised[e] [%]
DEGBA/DDS								
0	0.8854	0.8832	0.8318	−0.0536	6.1	−0.0514	5.8	5.8
DEGBA/DDS + catalyst								
0	0.8613	0.8832	0.8520	−0.0093	1.1	−0.0312	3.5	3.5
DEGBA/DDS + CTBN								
5	0.8953	0.8958	0.8446	−0.0507	5.7	−0.0512	5.7	6.1
10	0.9045	0.9085	0.8570	−0.0475	5.3	−0.0515	5.7	6.5
15	0.9138	0.9211	0.8818	−0.0320	3.5	−0.0393	4.3	5.3
20	0.9251	0.9338	0.8933	−0.0318	3.4	−0.0405	4.3	5.7
DEGBA/DDS + CTBN + catalyst								
5	0.8936	0.8958	0.8629	−0.0307	3.4	−0.0329	3.7	3.9
10	0.9019	0.9085	0.8685	−0.0334	3.7	−0.0400	4.4	5.0
15	0.9125	0.9211	0.8899	−0.0226	2.5	−0.0312	3.4	4.2
20	0.9259	0.9338	0.9207	−0.052	0.6	−0.0131	1.4	1.8
DEGBA/DDS + CTBN-ester								
5	0.8940	0.8945	0.8438	−0.0502	5.6	−0.0507	5.7	6.1
10	0.9012	0.9058	0.8588	−0.0424	4.7	−0.0470	5.2	5.9
15	0.9135	0.9171	0.8669	−0.0466	5.1	−0.0502	5.5	6.7
20	0.9253	0.9284	0.8836	−0.0417	4.5	−0.0448	4.8	6.3
DEGBA/DDS + CTBN-ester + catalyst								
5	0.8800	0.8945	0.8713	−0.0087	1.0	−0.0232	2.6	2.8
10	0.8891	0.9058	0.8813	−0.0078	0.9	−0.0245	2.7	3.1
15	0.9009	0.9171	0.8912	−0.0097	1.1	−0.0259	2.9	3.5
20	0.9140	0.9284	0.9029	−0.0111	1.2	−0.0255	2.7	3.5

[a] = V_{sp} (final) - V_{sp}(t = 0s, exp.); [b] = (-(V_{sp} (final) – V_{sp}(t = 0s, exp.))/ V_{sp} (final))*100%; [c] = V_{sp} (final) - V_{sp}(t = 0s, theor.); [d] = (-(V_{sp} (final) – V_{sp}(t = 0s,theor.))/V_{sp} (final))*100%; [e] = Δ V_{sp} (theor)/(epoxy vol.content).

since decomposition starts at temperatures higher than 300 °C, the heat of reaction could not be used for analysing the curing kinetics as it was done in literature.[18] Thus, the glass transition temperature (T_g) of the epoxy phase was used to describe the curing state of the blends after different times of annealing (Figure 4, 5).

The filled symbols give the glass transition T_g as determined from DSC in the 1st heating run. In the non-catalysed system the T_g increases continuously and is rather independent of the CTBN-content (Figure 4, left image). In the 2nd heating the glass transitions of the less annealed samples are much increased and narrow the values of the samples annealed for 6 hours, showing that during the heating – cooling – heating cycle the curing continuous. The samples annealed for 6 hours showed a maximum increase in T_g of 9 K during the complete DSC run, the sample containing 10 wt.% CTBN even a small reduction of 1.5 K, proving that the chosen annealing regime of 6 hours results in almost complete crosslinked samples. The T_gs of the samples cured without catalyst are rather similar; no significant influence of the rubber content on the network density can be detected. Here we like to note that "complete crosslinking" or "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" in this context means that further annealing does not result in an increased network density. Therefore it is also not possible to create absolute conversion curves, neither from the PVT shrinkage nor from the T_g development, since the parameter of the ideally crosslinked epoxy networks are not known.

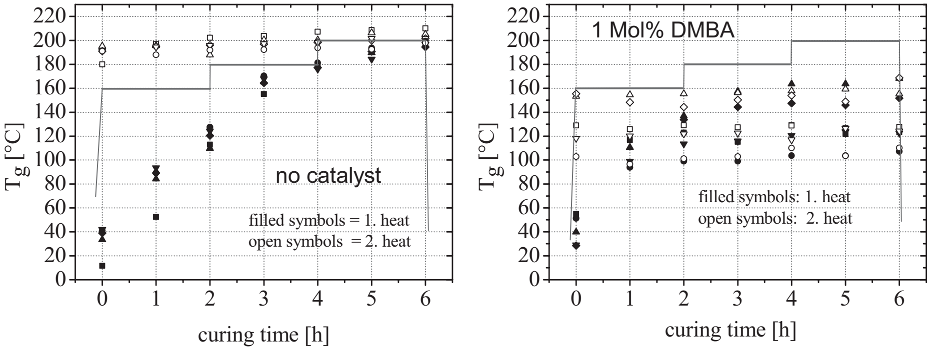


Figure 4.
Development of glass transition of epoxy resin in presence of CTBN during curing in an oven for 2 hrs at 160 °C, 2 hrs at 180 °C, and 2 hrs at 200 °C, respectively (the solid lines indicate the annealing regime): Left: no catalyst; right: with 1 Mol.% DMBA; Rubber content: 0 (□), 5 (△), 10 (◇), 15 (▽), and 20 wt.% (○).

The curing kinetics of the catalysed CTBN-containing system (Figure 4, right image) is strongly dependent on the CTBN content. With 20 wt.% reactive rubber already after 1 h at 160 °C the reaction is almost complete. Further annealing for 5 hours results only in a soft increase in the T_g of 14 K and also the T_gs determined in the second heating run are only slightly higher than that from the first heating run. Also the sample with 15 wt.% CTBN and the rubber-free sample exhibit fast curing kinetics and give only low T_g materials, while the samples with 5 and 10 wt.% CTBN need 3 hrs for curing and give the highest T_gs. This supports our assumption that the catalytic activity of the catalyst is hampered in presence of small amounts of carboxylic groups due to ammonium salt formation. When no carboxylic groups are present the tertiary amine favours the ether formation, and when the carboxylic groups are in excess it catalyses the curing reaction and also the incorporation of the CTBN into the epoxy network is possible, both resulting in reduced network densities.

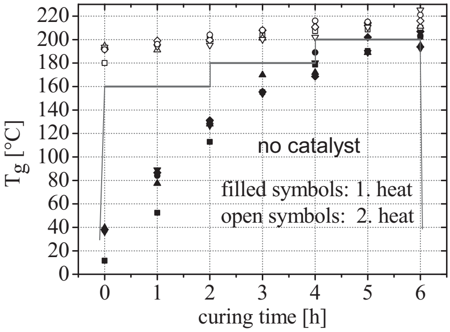


Figure 5.
As in Fig. 4, but with CTBN-Ester, no catalyst.

Non-reactive rubber has only a soft effect on the curing kinetics. As in the reactive rubber system the curing is slightly increased in presence of the rubber and there is almost no influence of the rubber content on the kinetics. Figure 5 shows a continuous increase in T_g with time and after 6 hours almost same T_gs are reached. During the DSC run some post-curing occurs so that the T_gs slightly increase to values higher than in the case of the presence of reactive rubber. CTBN-ester can not be incorporated into the epoxy network so that the network density of the epoxy phase is not affected.

Table 3 summarises the T_g of the samples in the uncured and the cured state, either in the oven or within the PVT cell. The presence of CTBN in the epoxy mixture raises somehow the T_g of the starting mixture. Since CTBN itself has a very low T_g we can explain it just by a certain degree of curing during preparation of the mixture. When comparing the final T_gs we have to consider the different annealing conditions. In the oven we have ambient pressure, in the PVT cell a

Table 3.
Glass transition temperatures of epoxy resins before and after curing.

Sample	T_g [°C] (1st heat)		
	non-annealed	after 6 h annealing in oven[a)]	after 13 h annealing in PVT cell[a)]
pure resin	11.6	202	190
0 wt.% CTBN + cat	55	123	119
5 wt.% CTBN	33	196	187
10 wt.% CTBN	39	194	185
15 wt.% CTBN	42	197	191
20 wt.% CTBN	41	199	187
5 wt.% CTBN + cat	40	168	166
10 wt.% CTBN + cat	29	152	164
15 wt.% CTBN + cat	29	123	125
20 wt.% CTBN + cat	51	107	102
5 wt.% CTBN-ester	40	195	185
10 wt.% CTBN-ester	38	207	188
15 wt.% CTBN-ester	36	193	187
20 wt.% CTBN-ester	37	203	188
5 wt.% CTBN-ester + cat			126
10 wt.% CTBN-ester + cat			127
15 wt.% CTBN-ester + cat			131
20 wt.% CTBN-ester + cat			128

a)Annealing and DSC conditions see experimental.

pressure of 10 MPa, which reduces the free volume and hampers the chain mobility. Even more important, the highest curing temperature in the oven is 200 °C and in the PVT cell 157 °C. When the glass transition rises above these temperatures the chain mobility reduces drastically and the material becomes frozen in few degrees above the curing temperature. This explains also that the T_g of the seemingly completely annealed samples increases further when performing the DSC heating – cooling – heating cycle, where the temperature is raised up to 300 °C. Furthermore, as mentioned in the experimental section, the different modes of DSC runs and T_g determination result in an overestimation of the T_g values of the PVT samples of about 8 K. Furthermore, the scatter in the T_gs of the different series is higher in the samples annealed in the oven, certainly caused by worse temperature control in the oven.

The final T_gs of the blends are slightly lower than in the pure resin, which is caused by the presence of the low T_g-material. The situation is similar for all non-catalysed samples containing reactive CTBN or non-reactive CTBN-ester, where no significant effect of the CTBN reactivity and the rubber content on the T_g is detectable. As already seen in the kinetic study, the final T_gs of the cured samples reflect the interactions of the catalyst resulting in the non-linear dependence of the T_g in dependence on the CTBN-content, as described above. The situation in the catalysed non-reactive rubber containing systems is changed. Even if the kinetics of the catalysed CTBN-ester containing systems has not been studied by DSC, the rather similar T_gs of all samples show that there is no strong interaction between the catalyst and the rubber. The catalyst is very active and the final curing state is reached already after 1 h, as shown above by PVT. Compared to the rubber free epoxide the T_gs are somehow higher, possibly due to slightly reduced ether formation.

Eventually, we like to note that there is a rather good correlation between the shrinkage detected by PVT analysis and the glass transition temperatures detected by DSC (Figure 6).

SEM

The morphologies of the cured epoxy-rubber blends are dependent on the

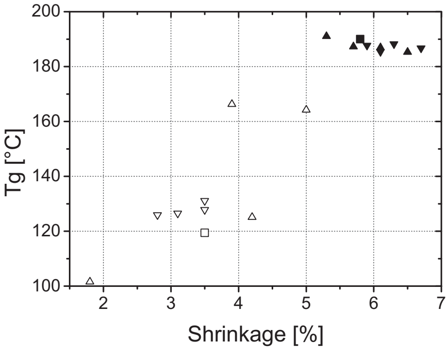


Figure 6.
Correlation between shrinkage and glass transition of samples cured at 157 °C and 10 MPa for 13 hours within the PVT cell. No rubber: □; CTBN: △; CTBN-ester: ▽; filled symbols: no catalyst; open symbols: 1 Mol.% DMBA.

composition, on the rubber reactivity, and on the presence of the catalyst. In all compositions the polymerisation induced phase separation (PIPS) of the non-catalysed blends resulted in particle-matrix morphologies with dispersed rubber particles in the epoxy matrix (Figure 7). The non-reactive CTBN-ester shows the typical blend behaviour of coarser morphologies with higher dispersed phase content, caused by increasing coalescence probability. Contrary to that, the reactive CTBN has smaller particle sizes at higher CTBN concentration. The increasing amount of acidic units accelerates the vitrification so that morphologies become frozen after shorter times hindering further coalescence. However, the CTBN particles are bigger than the CTBN-ester particles. Possibly, the formation of less dense networks due to catalysed ether formation enables larger degrees of coalescence than in the more dense network in the epoxy/CTBN-ester blends.

Drastic changes in the morphology are observed when the polymerisation is catalysed (Figure 8). At low rubber loadings of 5 and 10 wt.% the morphology is similar to the non-catalysed CTBN-ester containing system. As described above, the catalyst interferes with the carboxylic groups so that the whole blend behaves like a non-reactive, non-catalysed system during RIPS. But at higher CTBN concentration most of the rubber phase is incorporated in the epoxy phase and vice-versa and covalently bonded, so that the phase separation stops early without forming pure, etchable rubber particles. The resulting co-continuous-like morphologies consist of phases with different composition. They are not completely extractable and differ only slightly in their solubility or sensitivity to oxygen plasma, so that no holes are formed under the conditions used.

The morphologies of the blends cured in the oven (Figure 8) or in the PVT cell (Figure 9) look very similar. However, there is a strong influence of the curing pressure and temperature on the phase separation. The domain size rises much faster with increasing CTBN content at the higher pressure and lower temperature applied in the PVT cell and the domain sizes of the co-continuous domains at higher rubber loadings are smaller than those of blends cured at ambient pressure and higher temperature.

Finally we like to note that the catalysed curing of the CTBN-ester containing blends results in very large rubber particles of up to 100 μm, and, more importantly, to secondary phase separation. The fast curing kinetics limits the diffusibility of the epoxy component from the rubber and vice versa, so that in a first step primary domains enriched with epoxy and domains enriched with rubber are formed. Since there is no time for the epoxy units captured in the rubber to reach the epoxy-enriched domains, a secondary phase separation starts. Thus, the huge rubber domains contain separated spherical epoxy domains. In the blends with high rubber contents these epoxy spheres are very densely packed filling a large part of the rubber domains (Figure 10). At low rubber contents the effect is also visible but less pronounced.

In the CTBN containing systems the chemical coupling between the components hinders such secondary phase separation. In former studies we observed the second-

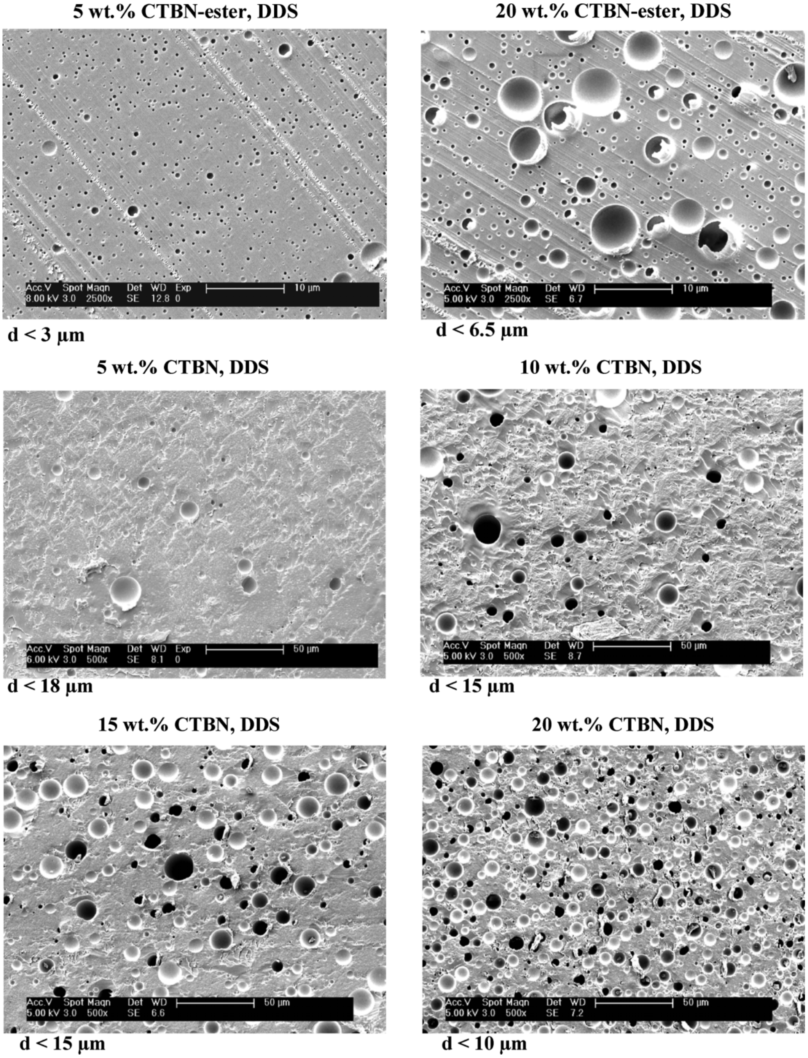
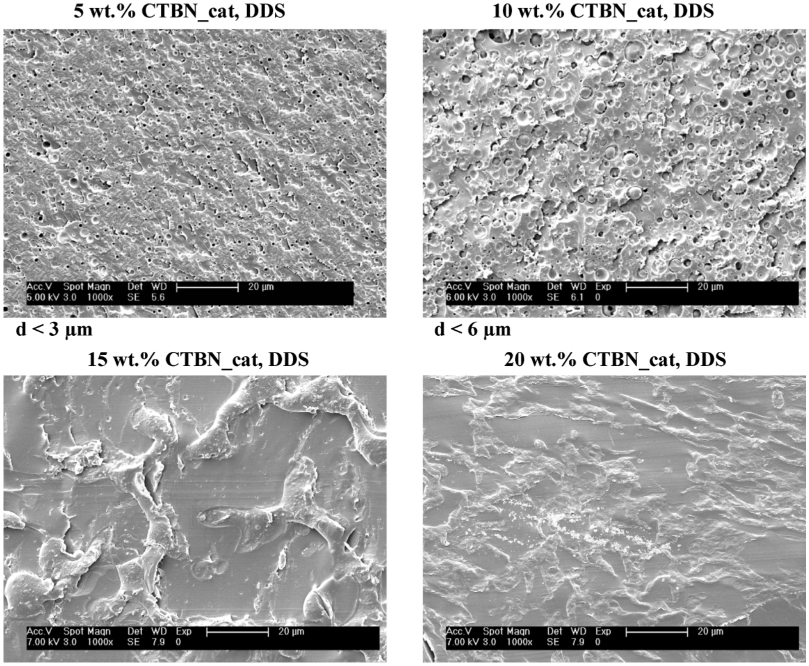


Figure 7.
Morphology of non-catalysed epoxy/CTBN-ester blends (bar = 10 µm) and epoxy/CTBN blends (bar = 50 µm) cured in an oven and etched with chloroform for 4 hours.

ary phase separation on epoxy/DDS blends with poly(styrene-co-acrylonitrile) SAN.[4] In this blends also small SAN domains were detectable in the epoxy-rich phase formed by separation of the SAN from the primary epoxy-rich domains. However, in the CTBN-ester modified blends this kind of secondary phase separation was not detectable. The 20 wt.% CTBN-ester containing system behaves similar like the same epoxy modified with 10 wt.% acrylonitrile-butadiene-styrene copolymer (ABS). At 15 wt.% ABS complete phase inversion occurred.

Conclusion

By means of PVT analyses in combination with DSC studies it is possible to detect differences in the curing mechanism of epoxy/rubber blends, which are caused by


5 wt.% CTBN_cat, DDS

10 wt.% CTBN_cat, DDS

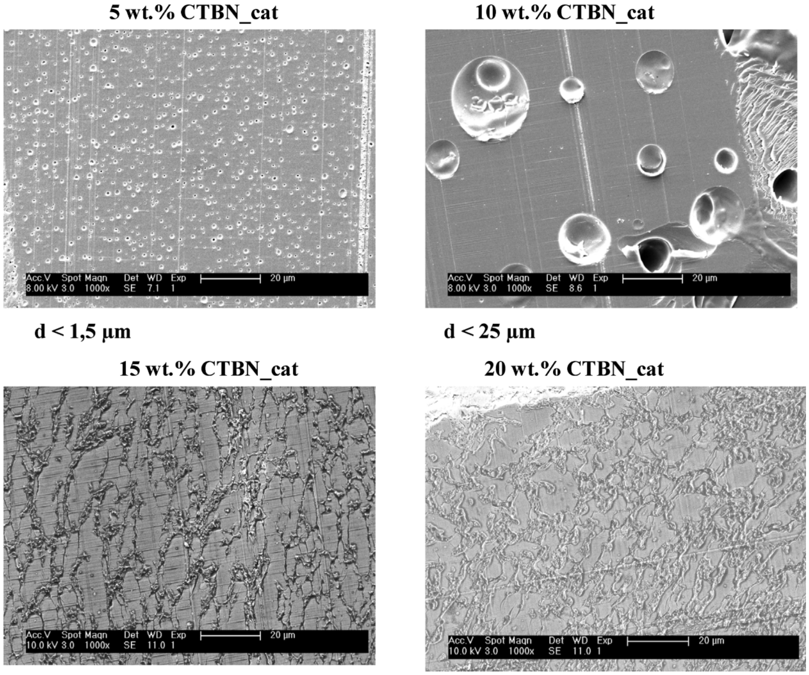
d < 3 µm

d < 6 µm

15 wt.% CTBN_cat, DDS

20 wt.% CTBN_cat, DDS

Figure 8.
Morphology of catalysed epoxy/CTBN blends (bar = 20 µm) cured in an oven and etched in oxygen plasma (5 and 10% CTBN).


5 wt.% CTBN_cat

10 wt.% CTBN_cat

d < 1,5 µm

d < 25 µm

15 wt.% CTBN_cat

20 wt.% CTBN_cat

Figure 9.
Morphology of catalysed epoxy/CTBN blends (bar = 20 µm) cured in the PVT apparatus and etched with xylene.

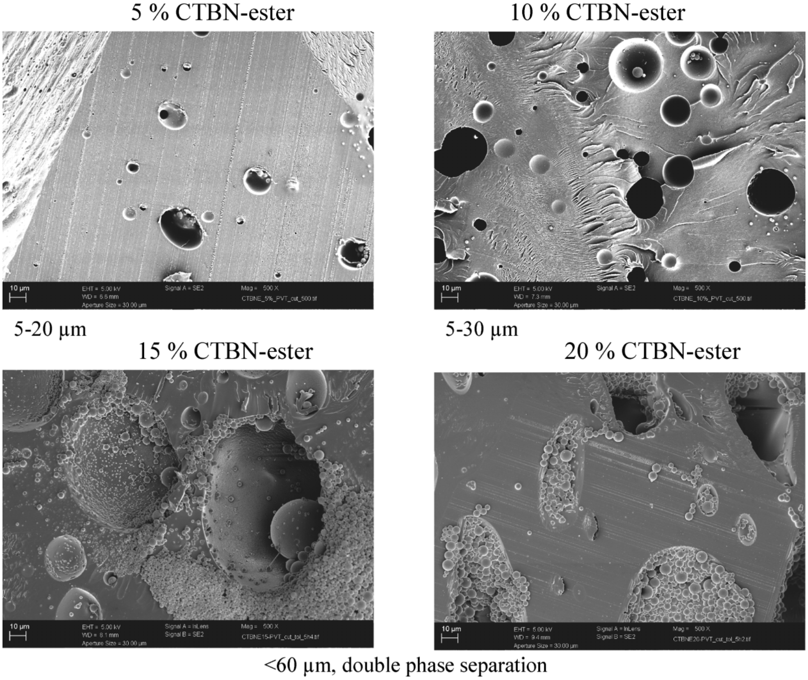


Figure 10.
Morphology of catalysed epoxy/CTBN-ester blends (bar = 10 μm) cured in the PVT apparatus and etched with xylene (images taken with an ULTRA 55 plus, Zeiss, sputtered with platinum).

different reactivities of the rubbers and the presence of catalytic sites and substances. The results of both methods give the same tendency and correlate well with each other.

In the non-catalysed systems the epoxy network structure is not significantly influenced by the rubber reactivity and rubber content. Final shrinkage and T_gs are very similar. However, the carboxylic groups accelerate the kinetics which affects the morphologies formed by reaction induced phase separation. The different sizes of the separated spherical rubber particles influence neither the T_gs nor the epoxy network density but the overall blend density.

Different is the situation in presence of a catalyst. DMBA causes the formation of linear ether structures and thus less dense epoxy networks are formed. However, due to interactions with the carboxylic groups the catalyst activity is hampered in presence of CTBN due to formation of quarternary ammonium salts. If the CTBN is in excess an accelerated polymerisation and increased formation of linear epoxy structures and the incorporation of the rubber phase into the epoxy phase are favoured, which is reflected in reduced shrinkage, lower T_gs, and changed phase morphology of co-continuous structures of phases with different composition. The catalysed curing of the CTBN-ester containing blend results in a fast curing and to a secondary phase separation in the initially formed rubber rich domains.

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