

Synthesis, Characterization, and Properties of Reactive Liquid Rubbers Based on Butadiene–Acrylonitrile Copolymers

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SYNOPSIS

Reactive liquid polymers (RLP), carboxyl-terminated butadiene–acrylonitrile copolymers (CTBN), epoxy-terminated butadiene–acrylonitrile copolymers (ETBN), amine-terminated butadiene–acrylonitrile copolymers (ATBN) of different molecular weights (from 2200 to 6500 g/mol), and a nonfunctional butadiene–acrylonitrile copolymer were synthesized and characterized. Selection of end groups of RLPs and the synthesis were discussed. Phase behaviors of CTBN, ETBN, and NFBN in the RLP/DGEBA system were investigated regarding to the molecular weight, molecular weight distribution, chain composition, and end groups with a light transmission method. These experimentally determined phase behaviors will be related to those of the RLPs in the systems to be modified. The effect of molecular weight of RLP on the viscosity was also studied. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Brittle polymers can be best toughened by a second phase dispersed in the matrix in the form of particles of μm order^{1,2} without significant loss in the other properties. To introduce the second phase, two kinds of additives can be independently used: soluble or preformed additives. The soluble additives dominate in the applications by their low viscosity, versatility, and facility of adjusting the morphologies. In the soluble additive method, the additive is dissolved in the reactive monomers and phase separates due to a change in entropy originated from the increase of reactants' molecular weight to form the desired morphology during the curing.

HycarTM reactive liquid butadiene–acrylonitrile copolymers are the oldest and still the most widely used low-viscosity soluble additives. A vast amount of work has been done with these Hycar reactive liquid polymers (RLP) to optimize many relevant parameters, such as solubility parameters and func-

tionality, and to clarify the relationships between morphology and mechanical properties of modified thermosets, the toughening mechanism, and the phase separation processes. Some reviews are given in Refs. 1–10.

Different studies have been conducted in our laboratories to obtain further understanding of the process of rubber domain formation. Several reactive liquid rubbers based on butadiene–acrylonitrile copolymers of different molecular weight and different end groups were used and their miscibility¹¹ with DGEBA were discussed.

Miscibility can be estimated, as done in the most articles concerning soluble additives, by the solubility parameter calculation.¹² Mülhaupt² recently suggested a criterion of solubility parameters that

$$0.4 < |\delta_{\text{monomers}} - \delta_{\text{additive}}| < 1.2 \text{ MPa}^{1/2} \quad (1)$$

But the solubility parameter approach intrinsically has an error¹³ of approximately $\pm 0.4 \text{ MPa}^{1/2}$ and considers only the excess free-energy factor. The reaction-induced phase separation, in which small molecular weight polymers are always involved, originates directly from the entropic factor. A com-

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plete thermodynamic description is given by the Gibbs equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (2)$$

This equation considers both excess free energy, ΔH_m , and combinatorial, ΔS_m , terms. Experimentally, this description is based on measurable phase diagrams. This approach gives a complete and quantitative method to describe and compare the additive phase behaviors. In a few works,^{11,14-18} this approach has been used to describe the additive miscibility.

The adhesion between phases should be important and it is considered to be related to the reactivity of the additive. Therefore, carboxyl-terminated butadiene-acrylonitrile (CTBN) liquid rubbers that are directly obtained from free-radical synthesis are often converted into adducts with functions other than carboxyl, e.g., epoxy (ETBN)¹⁹ or amine (ATBN).²⁰

In this present work, CTBN additives with 18% acrylonitrile (AN) and with different molecular weight (MW) were synthesized and characterized. The phase diagram method is used to describe the

miscibility of butadiene-acrylonitrile (BD-AN)-type additives with epoxy prepolymers. Influence of molecular weight, the entropic factor, on the miscibility is investigated. Results on miscibility-structure relationships, such as molecular weight, AN content, end groups, and block units, are surveyed and discussed. The viscosity-structure relationship is also discussed. The choice of the additive reactivity and the synthesis and characterization of ATBN and ETBN adducts from the CTBNs are discussed. This study offers information for optimization of these kinds of rubbers to adapt to different thermoset systems.

EXPERIMENTAL

Materials

Figure 1 shows the structural formulas of the epoxy and the RLPs. The epoxy- and amine-terminated butadiene-acrylonitrile random copolymers (ETBN and ATBN) additives were synthesized from the corresponding carboxyl-terminated butadiene-acrylonitrile random copolymers: CTBN-8L ($\bar{M}_n = 2030$), CTBN-8 ($\bar{M}_n = 3600$), and CTBN-8H

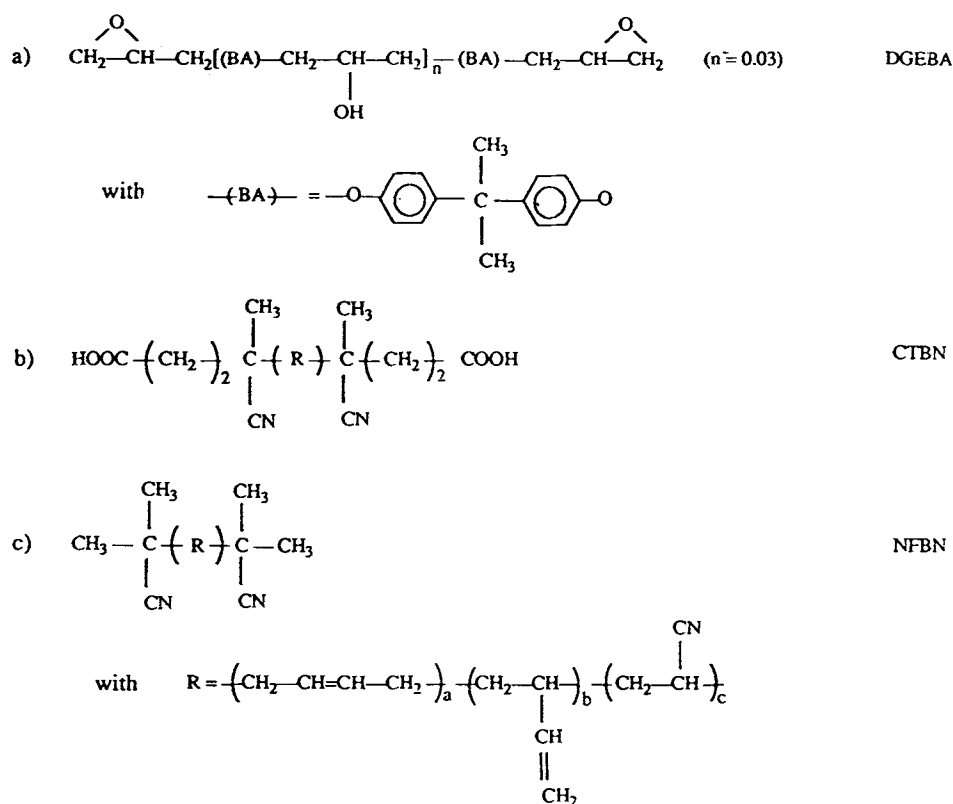


Figure 1 Structures of CTBNs, NFBN, and DGEBA.

($\overline{M}_n = 6050$). CTBN-8 is the standard commercial product, Hycar 1300 \times 8 (BFGoodrich). 8L means a low molecular weight rubber, and 8H, a high molecular weight rubber. The synthesis and characteristics of these materials will be discussed later in detail. ETBNs and ATBNs are designated like the corresponding CTBNs.

The DGEBA-based epoxy was DER 332 (DOW), with an equivalent weight of epoxy groups equal to 174.3 g/equiv as determined by acid titration, with $\overline{n} = 0.03$. The diamine used for the reactive system was 3,3'-dimethyl 4,4'-diamino dicyclohexyl methane (3DCM, Laromin C260, BASF). The amino content, determined by a potentiometric titration, agreed with the theoretical value within the experimental error.

Techniques

A Waters apparatus with a refractive index detector and tetrahydrofuran (THF) as elution solvent was used for size exclusion chromatography (SEC) measurements. A Mettler TA3000 was used to measure the glass transition temperature, T_g , of different samples at a 10°C/min heating rate, under argon. The T_g was always taken as the onset value. The viscosity was measured with a coaxial-cylinder viscometer (Contraves-Rheomat 115) with shear rates of 100 s⁻¹ or from 10 to 0.065 s⁻¹. A Nicolet MXI (FTIR) was used to obtain the IR spectra with KBr plates. The high-resolution ¹H-NMR spectra was recorded in a Bruker AM400 at 80°C with deuter-

ated DMF as solvent and tetramethylsilane as the internal reference.

Cloud-point curves (CPC) were obtained with a self-made device¹¹ as follows: mixtures of epoxy monomer with rubbers (pure CTBN or adducts) were prepared by mixing both components in the desired mass fractions, for about 10 min, at convenient temperatures to attain the homogeneous region (as judged by the transparency of the mixture). The determination of a particular cloud point (CP) was made by heating the sample to a temperature located at some 20°C higher than the CP, keeping it constant for 5–10 min, and decreasing it with a cooling rate in the order of 1°C/min. It was also verified that experimental values were in agreement with those obtained by heating at a rate of 0.2°C/min. Higher heating rates shifted CP to higher temperatures ($\Delta T = 2\text{--}3^\circ\text{C}$ for a 5°C/min heating rate).

RESULTS AND DISCUSSION

Synthesis and Characterization of Carboxyl-terminated Butadiene Acrylonitrile Random Copolymers (CTBN)

CTBNs are obtained through a free-radical copolymerization^{21,22} of BD and AN with 4,4'-azobis(4-cyanopentanoic acid) (ACVA) as initiator and an appropriate solvent. Since in the radical BD and AN copolymerization the termination is mainly through coupling and as each initiator segment de-

Table I Characteristics and Physical Properties of CTBNs and NFBN

Characteristics	CTBN 8L	CTBN 8	CTBN 8H	NFBN
Molecular weight (g/mol)				
\overline{M}_n	2030	3600	6,050	2770
\overline{M}_w	3610	6660	15,800	5310
$\overline{M}_w/\overline{M}_n$	1.78	1.85	2.61	1.92
Functionality				
$\overline{E}_{\text{phr}}$	0.079	0.053	0.026	—
\overline{f}_n	1.60	1.91	1.57	—
Composition				
% N	4.77	4.86	4.60	4.65
% AN	18.1	18.4	17.4	17.6
T_g (°C)	-57	-60	-60	—
Viscosity				
η (Pa-s), 27°C	65	260	1,390	37
$E_{(n)}$ (kJ/mol)	60.3	55.1	52.1	—
Surface tension				
γ (mN/m)	—	35.1	—	—
$d\gamma/dT$ (mN m ⁻¹ /°C)	—	0.06	—	—

rived from ACVA possesses one carboxyl group, the resulting CTBN copolymers have a mean carboxyl functionality close to 2. The copolymer structure is controlled by the initial $[BD]/[AN]$ ratio, and the molecular weight, by maintaining a constant $[\text{monomer}]_0/[\text{initiator}]_0$ ratio throughout the polymerization.

Three CTBNs with different molecular weights have been synthesized for this study. All other RLPs with functional end groups different from carboxyl were derived from the CTBNs. For a comparison, a nonfunctional butadiene-acrylonitrile copolymer, NFBN, was synthesized in a similar way with CTBN but with azobisisobutyronitrile (AIBN) as the initiator instead of ACVA. The structures are shown in Figure 1.

The BD units in the random copolymer of BD-AN were determined by $^1\text{H-NMR}$ to be 81.2% 1,4- and 18.8% 1,2-, remaining unchanged with the molecular weight. Since the reactivity ratios $r_{BD} = 0.35$ and $r_{AN} = 0.05$,¹² it can be inferred that the AN sequence is one.

The nitrile groups are polar units compared to the nonpolar BD units. Nitrile groups are introduced from the AN and also from the initiator residue at the ends of molecules (Fig. 1). The polarity of the backbone can be better expressed by the nitrogen content (%N) determined by elemental analysis (Table I) if the nitrile groups from the AN monomer and from the initiator have the same contribution to the polarity. An increase in AN units results in more polarity and intra- and interchain interactions—consequently, a higher viscosity and a better miscibility with a polar liquid like DGEBA.

The molecular weight (MW) and molecular weight distribution (MWD) of the CTBNs and NFBN were determined with SEC by assuming that

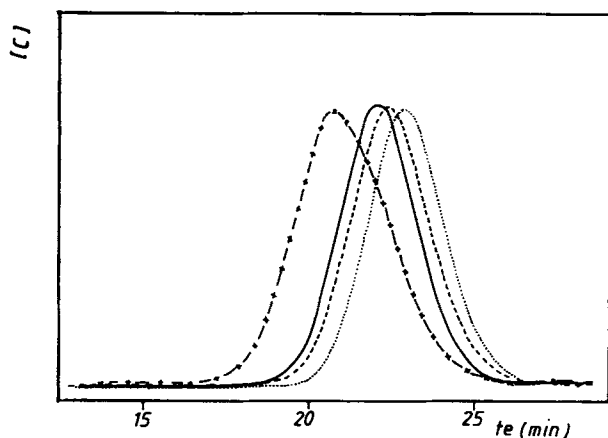


Figure 2 SEC traces for CTBNs and NFBN.

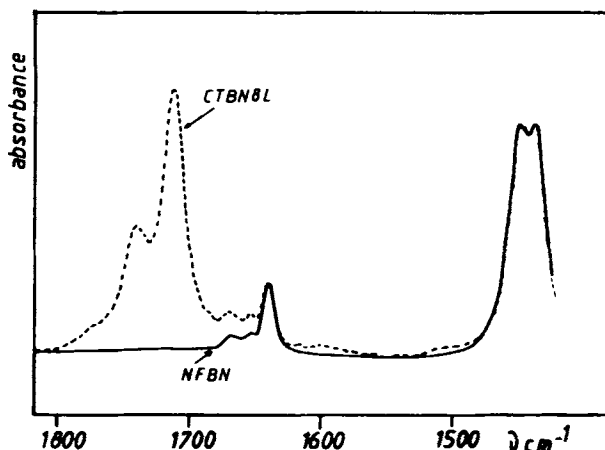


Figure 3 IR spectra of CTBN 8L and NFBN.

the ratio between the average molecular weight expressed in polystyrene standard and the real average molecular weight is the same for all these CTBNs. The ratio for CTBN 8 is 2.47. The number-average molecular weight, \overline{M}_n , of CTBN 8 is measured to be 3600 (g/mol) by the osmometric method according to BFGoodrich. The results are listed in Table I. The SEC traces for the CTBNs are shown in Figure 2.

The average functionality, \overline{F}_n , of CTBN can be determined with the equation

$$\overline{F}_n = \overline{M}_n \times \frac{E_{\text{phr}}}{100} \quad (3)$$

where E_{phr} is the moles of functional groups in a 100 g sample. E_{phr} in CTBN was measured by chemical titration. The results show that they are closed to but lower than 2.

The carboxyl groups^{23,24} of CTBNs have a strong absorption at 1704 and 1740 cm^{-1} in the infrared (Fig. 3). The absorption at 1740 cm^{-1} is due to the associated carboxyl groups. About 20% of the carboxyl groups are associated. As expected, NFBN has no absorption in the range of 1700–1750 cm^{-1} (Fig. 3). The association of carboxyl groups in bulk CTBNs may also have an influence on the viscosity²⁵ and even on the miscibility if this association still exists in the blend.

Viscosity is an important parameter in industry. Increase in either molecular weight or % AN leads to an increase in the viscosity of RLPs. At the molecular weight range of 2000–6000 and at the % AN range of 0–26% wt, the viscosity is more significantly affected by the molecular weight than by the % AN

(Fig. 4). As mentioned above, the end groups can have an influence on the viscosity. For example, NFBN has a higher \overline{M}_n but a lower viscosity than those of CTBN 8L (Table I). At 50°C, CTBN 8 has a Newtonian behavior when the shear rate is less than 70 s⁻¹.

The initial viscosity of reactive systems (epoxy and hardener) modified with these RLPs is directly related to that of the bulk RLPs. For example, in an epoxy diamine system with 15% wt of rubber and the initial viscosity of the system at 50°C, η_0 , increases with the viscosity of bulk CTBN additive (Fig. 5).

Finally, surface tension (γ) of CTBN 8 was measured with the plate method^{26,27} (Table I). γ is considered to play a role during the phase separation process and to have an influence on the morphology.²⁸

Synthesis and Characterization of Adduct from CTBNs

The reactive groups of liquid polymers are believed to be important for the final properties of the modified thermoset. Careful consideration in choosing the reactivity of an additive should be given. Generally, the reactivity of RLPs should be chosen based on the coreactants of the system to be modified. Therefore, other RLPs adducts based on CTBNs are synthesized, generally through a classical step-growth reaction with a difunctional agent, X_2 . By using reactive molecules with different moieties (e.g., hydroxyl, amine, epoxy, isocyanate), different functionality (2 or higher), different molecular weight, and different stoichiometric ratios, the adduct structure can be tailored to have different functions and different segmented copolymer lengths.²¹

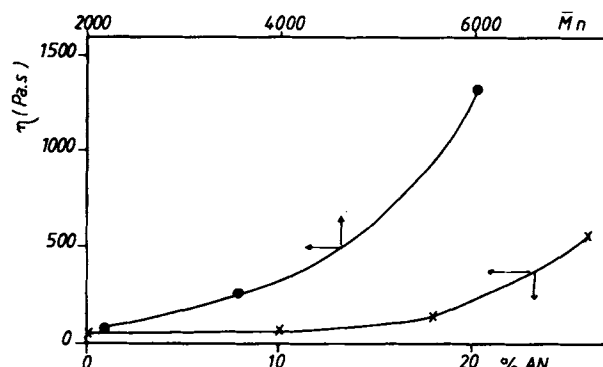


Figure 4 Influences of molecular weight and AN content on the viscosity of CTBN. Shear rate: 2 s⁻¹.

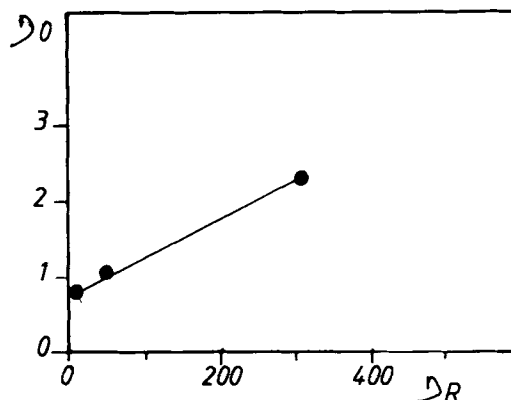


Figure 5 Initial viscosity of the DGEBA/3 DCM, with 15% wt rubber at 50°C vs. rubber viscosity at the same temperature.

If one hopes to avoid chain extension (segmented copolymers) and, therefore, a high viscosity, a large molar excess of the reactive molecules, X_2 , should be used. Typically, the excess unreacted agent X_2 is not separated from the RLP adduct. If the reactive molecule X_2 is different from any of the monomers in the system to be modified, the introduction of the new molecules, X_2 , in excess may have an influence on the formation of networks (final structure, T_g , etc.). For this reason, X_2 should be selected to be one of the monomers of the system to be modified. In this case, the reactivity of the adduct is quite the same as that of one of the monomers.

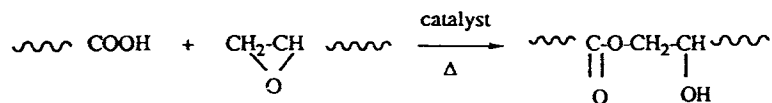
Furthermore, particular properties can be given to the RLP by synthesis of adducts through reaction of CTBNs with some special agent. For example, addition of a surface active agent like siloxane to CTBN can change the surface properties of the RLP.

In some cases, chain extension of the additive molecules and synthesis of a segmented copolymer is needed and realized through the reaction between CTBN and the difunctional agent, X_2 , at a high ratio of RLP to X_2 . The chain extension, the adduct molecular weight, molecular weight distribution, and the unreacted difunctional agent can be statistically calculated.

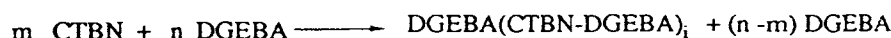
For the reactions involving CTBN, the conversion of carboxyl groups of CTBN can be easily followed by the disappearance of the absorption at 1704 cm⁻¹ in the infrared (Fig. 3). We are now going to discuss here two typical adducts derived from CTBN: ETBN and ATBN.

ETBNs used in this study were prepared by reacting the carboxyl groups of the CTBN with a large excess of DGEBA ($\bar{n} = 0.03$ or $\bar{n} = 0.15$)^{29,30} (Fig. 6), in the presence of triphenylphosphine (TPP) as

1) carboxyl-epoxy reaction:



2) step-growth copolymerization of CTBN and DGEBA:



$m \ll n$ and i is used as degree of chain extension

Figure 6 Carboxyl-epoxy reaction and step-growth copolymerization of CTBN and DGEBA.

catalyst at 85°C. The conversion was followed by either chemical titration or infrared absorption of carboxyl groups. This reaction goes to near 100% completion. Some side reactions can occur at the stoichiometric ratio = 1 and at high temperature.²⁹

An example of chain extension is the synthesis of ETBN44 (Hycar 1300 × 44 reactive liquid polymer). This is a segmented copolymer of CTBN 8 and DGEBA ($\bar{n} = 0.15$) prepared with a ratio of carboxyl to epoxy of $c/e = 0.5$. At such a high c/e ratio, the chain extension is very significant ($\bar{i} = 2$, Fig. 6) and the viscosity increases dramatically. In our study, ETBN 8L, ETBN 8, and ETBN 8H were synthesized with a very low c/e ratio of 0.06 to prevent chain extension. These ETBNs are composed mainly of triblocks ($i = 1$) and with a slight chain

extension ($\bar{i} \approx 1.06$). The measured and statistically calculated results are shown in Table II for the ETBNs. The SEC traces for the ETBNs are not given here but they are very closed to that of the mother CTBN.

Compared with ETBNs, the reactivity of ATBNs^{20,31} can be adjusted in a wide range because the reactivity of amines can be very different from one to another while the reactivity of epoxide is almost the same. Commercialized ATBN examples are Hycar 1300 X16, X21 and X42. Hycar 1300X16 and X21 RLP are adducts from the CTBNs: Hycar 1300X8 or 1300X31 and *N*-aminoethylpiperazine (AEP). Hycar 1300 × 42 RLP is an adduct from Hycar 1300 × 8 reactive liquid polymer and 2-methyl pentamethylene diamine (MPMD). Other adducts

Table II Characteristics of ETBNs

Rubbers	c/e^a	\bar{i}^c	\bar{M}_n^c	Free DGEBA % ^{b,c} Calculated	Free DGEBA % ^{b,d} Measured
ETBN 8L	0.059	0.06	2870	62.0	61.3
ETBN 8	0.068	0.05	4470	49.8	49.1
ETBN 8H	0.052	0.04	7030	41.9	39.2
ETBN 44	0.5	2.0	7400	4.4	3.5

^a Ratio carboxyl to epoxy in the synthesis of adducts.

^b Free DGEBA wt % to total weight after the reaction.

^c Statistically calculated values assuming 10% of CTBN molecules has no reactivity and 90% are difunctional.

^d Measured by SEC.

are reported in the literature based on different diamines, such as Jeffamine D230, decanediamine, ethylenediamine, and aromatic diamines (Table III).

The reaction between CTBN and diamine is carried out at 130°C until all carboxyl groups have reacted. Again, to avoid the chain extension and high viscosity, a ratio of carboxyl to primary amino hydrogen of $c/a \approx 0.16$ was used. The SEC chromatograms for the ATBNs are not given here but they are very closed to that of the mother CTBN.

Due to the high polarity of amine, the viscosity of ATBNs are higher than the corresponding CTBNs, even though an excess of amine is used and the unreacted amine remains. For the same reason, their high polarity, ATBN molecules based on aliphatic or cycloaliphatic diamines interact with the polystyrene columns used in SEC and give false elution curves with a long tail at small molecule range, and so cannot be characterized with this technique.

New ATBNs are prepared from CTBNs and

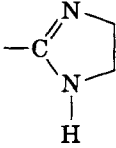
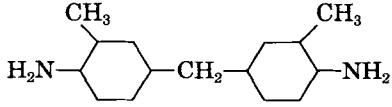
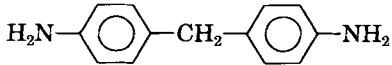
3,3'-dimethyl 4,4'-diamino dicyclohexyl methane (3DCM), which is the hardener in the epoxy system used for our next study. Since the ATBN chain ends have the same structure as that of the diamine cure agent of the epoxy system, no new amine is introduced into the system. The ATBNs and the ETBNs have exactly the same main chain; the difference between the ATBN and ETBN systems can be attributed uniquely to the difference in their end groups.

Miscibility of RLPs with DGEBA

The Solubility Parameter Approach

The initial miscibility of an additive can be approximated by the solubility parameter method. Figure 7 offers an example how to match the miscibilities of a system and an additive by this approach. It locates DGEBA, two diamines, three commercial RLPs, and a high T_g thermoplastic soluble additive

Table III Different Possibilities of ATBNs

Diamines	Formulas	Chain Ends
Aminoethyl piperazine (AEP)	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{N}-\text{H}$	$\begin{array}{c} \diagup \\ \text{N}-\text{H} \\ \diagdown \end{array}$ but also tertiary amine
2-Methyl pentamethylene diamine (MPMD)	$\text{H}_2\text{N}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-(\text{CH}_2)_3-\text{NH}_2$	$-\text{NH}_2$
Ethylene diamine (EDA)	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$	$-\text{NH}_2$ and 
Jeffamine [poly(propylene oxide)]	$\text{H}_2\text{N}-(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{O})_x-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{NH}_2$	$-\text{NH}_2$
3,3-Diaminodipropyl ether	$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_3-\text{NH}_2$	$-\text{NH}_2$
3,3'-Dimethyl 4,4'-diamino dicyclohexyl methane (3DCM)		$-\text{NH}_2$
Methylene dianiline (MDA)		$-\text{Ar}-\text{NH}_2$

in the solubility parameters (δ) axis. 4,4'-Diaminodiphenyl sulfone (DDS) is an aromatic diamine. The systems based on DGEBA/3DCM and on DGEBA/DDS have very different solubility parameters. For example, for DGEBA-3DCM at $a/e = 1$ with CTBN 8, $\Delta\delta = 2.5 \text{ MPa}^{1/2}$; for DGEBA-DDS at $a/e = 1$ with CTBN 8, $\Delta\delta = 3.4$; and with CTBN 13, $\Delta\delta = 2.6 \text{ MPa}^{1/2}$. In practice, it is experimentally very difficult to modify the DGEBA-DDS network with CTBN 8. The DGEBA-3DCM and -DDS are modified with CTBN 8 and CTBN 13, respectively.

The Thermodynamic Approaches

The Gibbs free energy associated with a mixing of component E (epoxy prepolymer) of molar volume V_E with component R (rubber) of molar volume V_R expressed per unit volume of mixture is theoretically calculated by

$$\Delta G^V = RT [(\phi_E/V_E) \ln \phi_E + (\phi_R/V_R) \ln \phi_R + \chi \phi_E \cdot \phi_R] \quad (4)$$

at the critical point where the binodal and spinodal curves meet:

$$\partial^2 \Delta G_m / \partial \phi^2 = \frac{\partial^3 \Delta G_m}{\partial \phi^3} = 0 \quad (5)$$

we have

$$\phi^c = V_E^{1/2} / (V_E^{1/2} + V_R^{1/2}) \quad (6)$$

where ϕ_R , ϕ_E are the corresponding volume fractions, and χ , the polymer-polymer interaction parameter. By calculating the composition of the critical point from the equation, the critical temperature T_c may be obtained from the CPC. In the phase diagram approach, comparison of miscibility between samples is difficult due to the different shape of the curves. But in this study, as will be seen, all the cloud-point curves (CPC) have a similar form. This allows us to take the maximum temperature of CPC (T_{\max}) as one indicator of miscibility. Another characteristic point in CPC is the critical point.^{32,33} Experimental evaluations of T_{\max} and T_c allow one to make comparison between samples.

We intend to study the phase behavior of a soluble additive in a nonreactive system to simulate that in a reactive system. This may give a precise method of miscibility evaluation of an additive. In the case of the DGEBA-CTBN system, an SEC analysis confirms that there was no reaction during the measurement.

Molecular Weight of RLPs

In the thermodynamics of binary or quasi-binary systems, T_c is related to molecular weight:

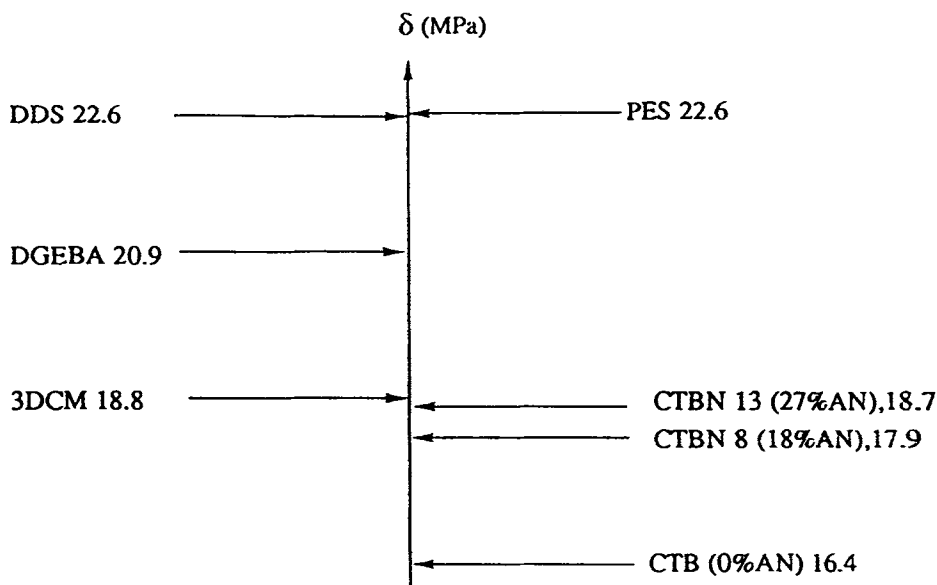


Figure 7 A schematic scale of solubility parameters of epoxy prepolymer, hardeners, and additives.

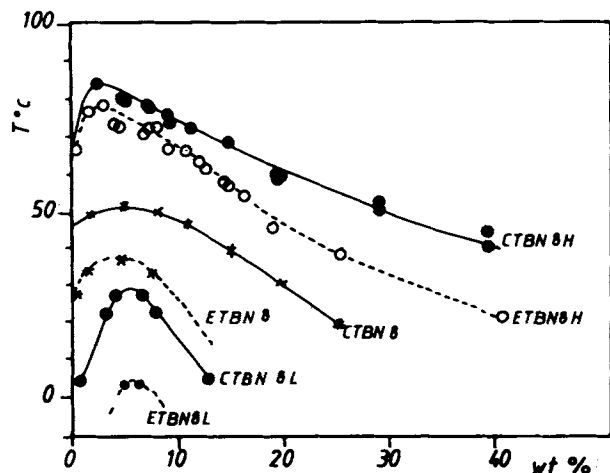


Figure 8 Cloud-point temperature curve of CTBNs and ETBNs.

$$\frac{1}{T_c} = \frac{1}{\theta} \left(1 + \frac{b}{M_w^{1/2}} \right) \quad (7)$$

θ and b are constant for a given DGEBA (solvent)–RLP system. This equation indicates that the reciprocal of the critical temperature (in K) for incipient miscibility should vary linearly with the reciprocal of the square root of the molecular weight in a given polymer solvent system.^{32,37}

The CPC of CTBNs (%AN = 18) with different molecular weights are shown in Figure 8. The increase in molecular weight of rubber leads to a decrease in the miscibility and a CPC of wider coexistent composition span. The T_{max} and T_c values for CTBNs with different molecular weights and %AN are listed in Table IV. For T_c , we have only two experimental results, because CTBN-8L is quite miscible at a high rubber fraction. Even if we have few points, relation (7) seems to be roughly re-

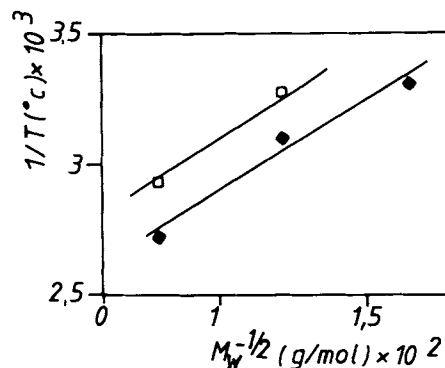


Figure 9 Relation between \overline{M}_w of CTBNs and T_{max} with DGEBA.

spected (Fig. 9). This can be explained by the fact that we have low molecular weight and an effect of carboxyl chain ends is expected to occur. In this range of molecular weight, an estimation effect on both T_{max} and T_c shows that an increase of 100 in \overline{M}_n leads to an augmentation of 1.4°C.

Molecular Weight Distribution of RLPs

In a system with components of disperse molecular weight, the coexistent phase components (composition span) follow neither binodal nor spinodal curves but depend on the initial concentration during the phase separation.^{32,33,35–37} Molecular weight distribution plays a very important role in phase behavior, while, in practice, most polymers are polydisperse.

A blend of 95% b.w. CTBN 8L and only 5% b.w. CTBN 8H has much higher CPC than that of the CTBN 8L with DGEBA (Fig. 10). At low concentration, the CPC of the blend is unclear. This experimental result shows that the CPC is very sensitive to the high molecular weight fraction even with

Table IV Influence of AN % and MW on the Miscibility of RLP with DGEBA: (a) with DGEBA ($\bar{n} = 0.15$); (b) with DGEBA ($\bar{n} = 0.03$)

	RLP	\overline{M}_n (g/mol)	AN %	T_{max} (°C)	T_c (°C)
(a)	CTBN 13	3600	27	Miscible	Miscible
	CTBN 8	3600	18	66	37
	CTBN 15	3600	10	153	—
(b)	CTBN 8L	2030	18	29	< 20
	CTBN 8	3600	18	50	32
	CTBN 8H	6050	18	84	68

a very small amount. The \overline{M}_n and \overline{M}_w of the blend are 2100 and 4400, respectively, and not very different from those of CTBN 8L. We see that neither \overline{M}_n and \overline{M}_w can be directly used to describe this phenomenon. A similar study was reported in a polystyrene-cyclohexane system in which the polystyrene has been prepared anionically with a very narrow molecular weight distribution.³⁶

Acrylonitrile (AN) Content

The polar AN units in RLP can have specific interactions with the polar groups in DGEBA, like hydroxyl or epoxy. An increase in % AN of the additive results in a better miscibility between the RLP and DGEBA monomer.

Verchère et al.¹¹ determined the CPC of RLP of different % AN with DGEBA ($\bar{n} = 0.15$) (Table IV). An estimation was made by assuming a linear relationships between AN content and T_{max} and it shows that an increase of 1% in AN content leads to a decrease of about 10°C in T_{max} .

End Groups

To illustrate the effect of the end groups on the RLP phase behavior, comparison is made between the CPC of CTBNs, ETBN, and NFBN. Such a comparison is based on the fact that CTBNs and the ETBNs have exactly the same backbone (Fig. 11).

The phase behavior of RLP is significantly affected by its end groups as blocks. In the case where the liquid polymer has no polar end group (NFBN), the miscibility is the poorest (10°C higher in T_{max}

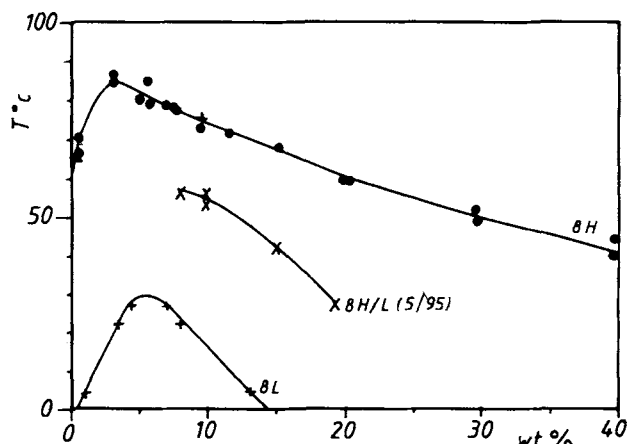


Figure 10 Influence of high molecular weight fraction on the miscibility of the rubber with DGEBA. 8H/8L blend, 5% wt of CTBN 8H and 95% wt of CTBN 8L.

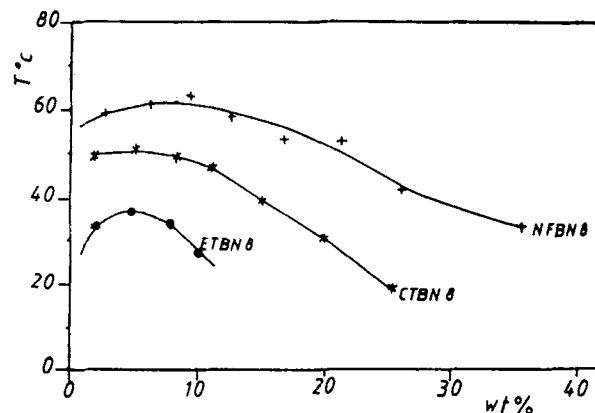


Figure 11 Effect of end groups for CTBN 8 and the adducts/DGEBA ($\bar{n} = 0.03$) on the miscibility.

than that of CTBN 8), even though the molecular weight of NFBN is smaller than that of CTBN 8. On the other hand, ETBN is more miscible than is the corresponding CTBN.

The contribution of the end groups to the miscibility of RLP may be attributed to their weight fraction to the backbone. The end groups play a role of blocks in a triblock copolymer.³⁸ The difference between the T_{max} of CTBN and its ETBN adduct, ΔT_{max} , can be well related to their difference in the end group portion (Fig. 12). The weight portion of end groups in the RLPs are listed in Table V.

Unfortunately, such a comparison cannot be done with ATBNs due to the reactivity of the ATBNs with DGEBA and the presence of an excess of diamine. The miscibility of CTBNs with 3DCM was tested: The three CTBNs with different molecular

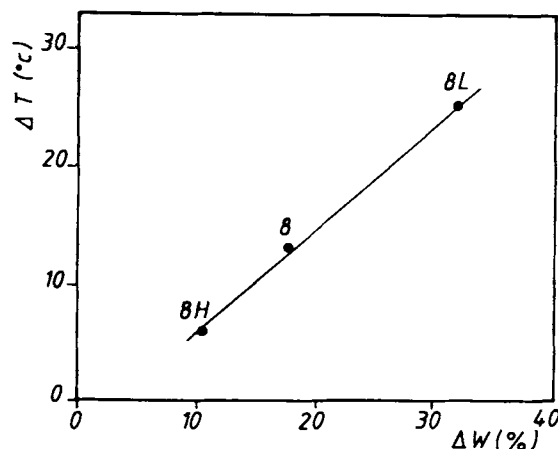


Figure 12 Difference in end group weight portion, ΔW vs. ΔT_{max} between ETBNs and corresponding CTBNs.

Table V End Group Weight Fraction of Some RLPs, Weight Fraction (MW of end group)/(\overline{M}_n of backbone) $\cdot \overline{F}_n$

CTBN-	End Group MW	8L	8	8H
CTBN	45	4.2%	2.3%	1.3%
ETBN	394	36.3%	20.1%	11.9%
ATBN (3DCM)	283	26.1%	14.5%	8.5%

weights are miscible with 3DCM at all concentration at 4°C.

Therefore, we can give a miscibility order for these rubbers of different end groups with DGEBA: ATBN > ETBN > CTBN > NFBN. Koberstein et al.³⁸ found the same order for the polydimethylsiloxane of different end groups with nonfunctional polybutadiene. These three CTBNs are all miscible with the diamine 3DCM at room temperature.

Molecular Weight and Molecular Weight Distribution of DGEBA

The effect of DGEBA's molecular weight and molecular weight distribution on the miscibility of a CTBN 8 with different DGEBA was examined by Verchère et al.¹¹ In the range from 300 to 500 of \overline{M}_n , the effect of \overline{M}_n on T_{max} is estimated to be roughly linear and on the order of 50°C/100 in \overline{M}_n .

It has been seen that the molecular weight of DGEBA, the component of lower molecular weight in the mixture, has a much more important influence on the miscibility than does the \overline{M}_n of CTBN ($\approx 1.4^\circ\text{C}/100$ in \overline{M}_n). It can be explained by the entropic factor in the Flory-Huggins equation. Also, according to Koningsveld,³² the increase of molecular weight of the small molecular weight component, e.g., the solvent, results in a big augmentation in CPC and a wider coexistent composition span.

CONCLUSION

We have studied the synthesis, miscibility, and some other properties of different reactive liquid polymers (RLPs) with different molecular weights and different end groups:

1. The reactive liquid rubbers with the same chain structure but with three different molecular weights (from 2030 to 6050 g/mol) and different end groups were synthesized and characterized. These rubbers as soluble additives are carboxyl-terminated (CTBN),

epoxy-terminated (ETBN), amine-terminated (ATBN), and a nonfunctional (NFBN) butadiene-acrylonitrile (BD-AN) copolymers.

2. The reactivity of RLPs should be chosen based on the coreactants of the system to be modified. The nature of the chemical agent used to change the RLP's end groups through a step polymerization should be considered not to give an unfavorable influence on the system to be modified.
3. The miscibility parameter method is not enough to describe the phase behavior of an RLP. The complete description including both excess free energy and entropic terms through experimental determination of the phase diagram is efficient and sensitive. The phase behavior of an RLP can be simulated in a blend of a rubber and one of the monomers in the system to be modified.
4. Estimations of the influences of several structural parameters on the rubber miscibility with DGEBA have been obtained:
 - (i) An increase of 1% in AN content in a rubber of about a number-average molecular weight of 4000 g/mol leads to a decrease of about 10°C in T_{max} in the cloud-point curve of the rubber with DGEBA.
 - (ii) An increase of 100 g/mol in the number-average molecular weight of CTBN of 18% AN leads to 1.4°C in T_{max} in the cloud-point curve of the rubber with DGEBA.
 - (iii) An increase of 100 g/mol in the number-average molecular weight of DGEBA leads to 50°C in T_{max} in the cloud-point curve of the DGEBA with the rubber with a number-average molecular weight of 3600 g/mol and with 18% AN.
 - (iv) The end groups of the rubbers have also a significant influence on their miscibility with DGEBA. The miscibility order of the rubbers is

ATBN > ETBN > CTBN > NFBN

In the case of ETBN, this influence of end groups is proportional to their weight portion in the molecules.

5. A small amount of molecules of poor miscibility can greatly change the phase behavior of an RLP.
6. A characteristic of monitoring the miscibility of an RLP through changing the molecular weight is that the viscosity of the RLP can be remarkably adjusted.

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