

Spectroscopic, Thermal, and Mechanical Characterization of Carboxyl-Terminated Polybutadiene-Based Carbon Black-Filled Networks

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ABSTRACT: Carbon black-filled and unfilled carboxyl-terminated polybutadiene (CTPB) networks were prepared by using two types of reactive systems at different reactive group ratios to be applied to the solid propellant motor case as a liner. For the preparation of CTPB networks, tris(2-methyl-1 aziridinyl)phosphine oxide (MAPO) and a mixture of liquid bisphenol A-epichlorohydrin (Epikote-828) and MAPO were used as two different reactive systems. The chemistry and thermal stability of the CTPB networks were followed by Fourier transform infrared spectroscopy (FTIR) and thermogravimetry (TG) techniques, whereas mechanical and adhesive properties were tested by tensile measurements. The mixed reactive system caused a modification in the ultimate tensile stress and elongation-at-break properties, adhesive properties, and thermal stability of the CTPB networks. It was understood that this modification was due to the inter- and intramolecular bridge formation via the end-linking reaction of Epikote-828 with amine groups of the former network chains. The combination of MAPO with Epikote-828 also imparted better peel and lap-shear strength properties to the CTPB elastomers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 355–366, 1997

Key words: carboxyl-terminated polybutadiene; CTPB; liner; CTPB network

INTRODUCTION

In rocket-propellant technology, polybutadiene-based liquid prepolymers such as carboxyl-terminated polybutadiene (CTPB), hydroxyl-terminated polybutadiene (HTPB), and polybutadiene-acrylonitrile-acrylic acid (PBAN) terpolymers have been widely used as polymeric binders. These are low molecular liquid rubbers having terminal allylic carboxyl or hydroxyl groups. For the propellant for-

mulation, a functionally terminated polybutadiene is end-linked with a suitable functionally active reactant to impart physical integrity and to hold the solid particulate oxidizer and other additives. The reactant for the end-linking of these functionally terminated prepolymers are commercially available compounds having the desired degree of reactivity against to the functional group of the prepolymer for the purpose of a state-of-the-art propellant system. Therefore, hydroxyl-terminated polymers such as HTPB can be end-linked with di- or polyfunctional isocyanates. In the same manner, carboxyl-terminated polymers such as CTPB and PBAN are end-linked with aziridinyl or epoxy-type reactants. CTPB is a well-known polybutadiene-based polymeric binder for composite solid propellants. CTPB

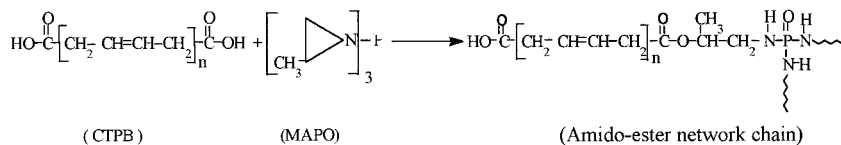
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Scheme I

is a low molecular weight liquid prepolymer ($\bar{M}_n \cong 3500$ g/mol) having terminal carboxyl groups. The network-forming reaction of CTPB is carried out through the end-linking process via its carboxyl end groups. Multifunctional aziridines such as tris(2-methyl aziridines)phosphine oxide (MAPO), the ethylaziridine adduct of sebacic acid (BISA), the butyleneimine adduct of trimesic acid (BITA), and their combinations have been widely used for the end-linking of the CTPB prepolymer.^{1,2} The end-linking process of CTPB with MAPO can be represented as in Scheme I.

The amido-ester network structure is obtained as a result of this reaction, and for a network formation, this reaction is carried out at 65°C for 7 days.¹ However, in the case of using no reaction catalyst, unreacted aziridine groups of MAPO are subjected to homopolymerization and rearrangement to the oxazoline structure. This phenomenon strongly affects the reactive group balance of the reaction mixture.^{1,2} Another problem associated with using only MAPO as a reactive system in the end-linking of CTPB chains is, in particular, that during the course of storage CTPB networks have a tendency to lose some of their original physicochemical properties. Previous studies showed that the softening was caused by an internal rearrangement of the network chain which arose from the breakage of P—N bonds and resulted in a reduced junction point density of the CTPB networks.¹⁻³ The practical solution to this problem was to use a mixed reactive system. Therefore, in the previous works, to eliminate the aforementioned softening problem of the MAPO-reacted CTPB systems, different combinations of MAPO with other types of aziridines (i.e., BISA, BITA) or epoxides as a mixed reactive system were used for the end-linking of CTPB chains.^{2,4}

The network chain forming in the end-linking reaction of CTPB chains with MAPO has the amido-ester structure. The amine groups of this amido-ester structure cause an autocatalytic ring-opening reaction of the oxirane end groups of the epoxides in the presence of CTPB.^{5,6} The reaction mechanism can be shown as in Scheme II.⁷

According to this mechanism, the amine groups being in the network chain show the proton-donor effect and this phenomenon accelerates the reaction by hydrogen bonding to weaken the bond strength of the oxirane ring and the result is the catalytic ring-opening reaction.⁸ In this work, this catalytic reaction of oxirane end groups of Epikote-828 is proposed to cause intra- and intermolecular crosslinking with the amido-ester-type network chain via end-linking of Epikote-828. This inter- and intramolecular crosslinking can be designed as in Scheme III.

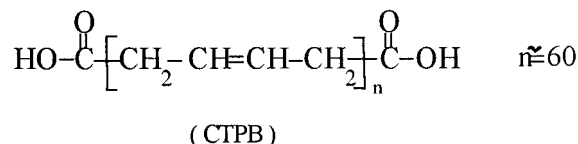
On the other hand, it was previously reported that oxirane end groups of Epikote-828 can easily react with low molecular carboxylic acids and the reaction product has the both ether and ester linkage.⁸ In this case, the conversion of oxirane groups was about 90%. Although the reactivity of CTPB is higher to MAPO than that of Epikote-828, some Epikote-828 molecules may react with CTPB chains and this may cause chain extension.^{9,10} Therefore, the primary objective of this study was to characterize the network-forming reaction of CTPB and, second, to compare the effect of the two types of reactive systems and their reactive group ratios on the thermal and mechanical properties of filled and unfilled CTPB networks by undertaking the spectroscopic, thermal, and mechanical measurements.

EXPERIMENTAL

Materials and Characterization

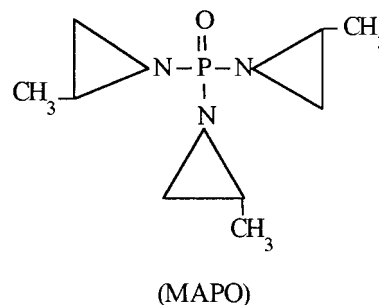
Carboxyl-terminated polybutadiene (CTPB) was purchased from Thiokol Chemical Corp. under the trade name of HC-434. The number-average molecular weight (\bar{M}_n) of CTPB was determined as 3500 g/mol by vapor-phase osmometry (VPO) using benzyl (MW = 210.23 g/mol) as the calibration standard. The carboxyl content of CTPB was determined as 0.45 meq/g by titration with 0.1N potassium hydroxide (KOH) in ethanol using a

thymol blue indicator.¹¹ The molecular structure of CTPB is the following:



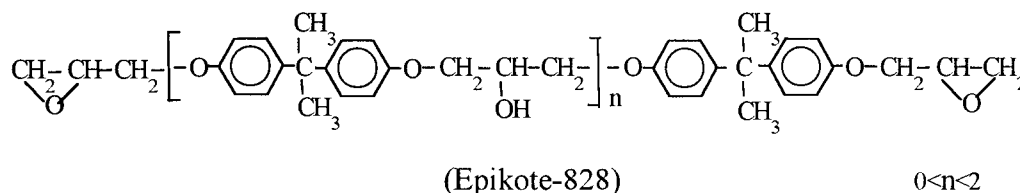
In the IR spectrum of the CTPB prepolymer, the C=O stretching of the carboxylic acid groups of CTPB appears at 1713 cm^{-1} and the peak observed at 1639 cm^{-1} is due to the C=C unsaturated bonds of CTPB. Moreover, the peaks observed at 966 , 911 , and 725 cm^{-1} are assigned to the CH=CH bending (*trans*), =CH₂ (vinyl), and CH=CH (*cis*) groups of CTPB, respectively.

Tris(2-methyl-1-aziridinyl)phosphine oxide (MAPO) was purchased from Arsynco Inc. as better than 98% purity and used as received. The equivalent weight of MAPO was 75.2 g/eq. The molecular structure of MAPO is as follows:



In the infrared spectrum of MAPO, the characteristic absorption band of active aziridin groups are observed at 1401 , 1250 , and 1042 cm^{-1} . As the end-linking reaction proceeds, the intensities of these bands decrease.

Liquid bisphenol A-epichlorohydrin epoxide resin was supplied by the Shell Chemical Co. under the trade name of Epikote-828. It was used as received. It has a molecular weight of 380 g/mol and its equivalent weight and functionality are 187 g/eq and 2.03, respectively. It has the viscosity of 1.25×10^4 cps (at 25°C) as determined by a Brookfield-type viscometer. The molecular structure of Epikote-828 can be represented as follows:



where $n = 0.5$ for a standard commercial resin. In the infrared spectrum of Epikote-828, the characteristic bands observed at 915 and 830 cm^{-1} are due to oxirane groups of this compound.¹²

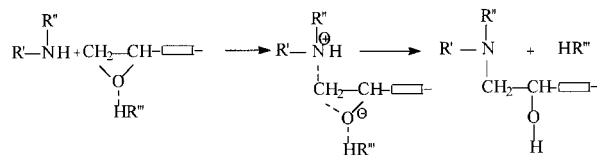
Printex-U-type carbon black was used as a filler for the purpose of improving the mechanical and thermal properties of the networks. The related specifications are as follows:

- Aggregate size = below 825 mesh, 44 microns
- Surface area = $110 \pm 5 \text{ m}^2/\text{g}$
- Carbon (as dust) = 98%
- Acidity (pH) = 4 ± 0.2

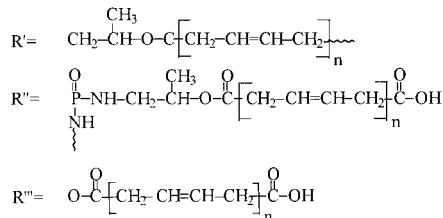
Instrumentation

TGA measurements were carried out using a DuPont 1090 thermal analyzer with a TGA 951 mod-

ule. In the DSC measurements, a Mettler TA 3000 system was used. All TGA and DSC measurements were carried out under a nitrogen atmosphere and at a heating rate of $20^\circ\text{C}/\text{min}$. IR spectra of the samples were obtained using a Nicolet 20 SXB Model FTIR spectrometer. The ultimate tensile stress and elongation-at-break values of the CTPB networks were determined by using an Instron tensile tester (Model 1185) with a Hewlett-Packard 85 computer at a crosshead speed of $50 \text{ mm}/\text{min}$ in accordance with ASTM D-412-68. Shear tests were performed according to ASTM D 1002 at a crosshead speed of $1 \text{ mm}/\text{min}$ and the peel resistance of the samples were measured in accordance with ASTM D 1876-72 at the crosshead speed of $200 \text{ mm}/\text{min}$. The number-average molecular weight (\bar{M}_n) of CTPB was determined in THF at 45°C using a Knauer-type vapor-phase osmometer. A Brookfield-type viscometer was



Where



Scheme II

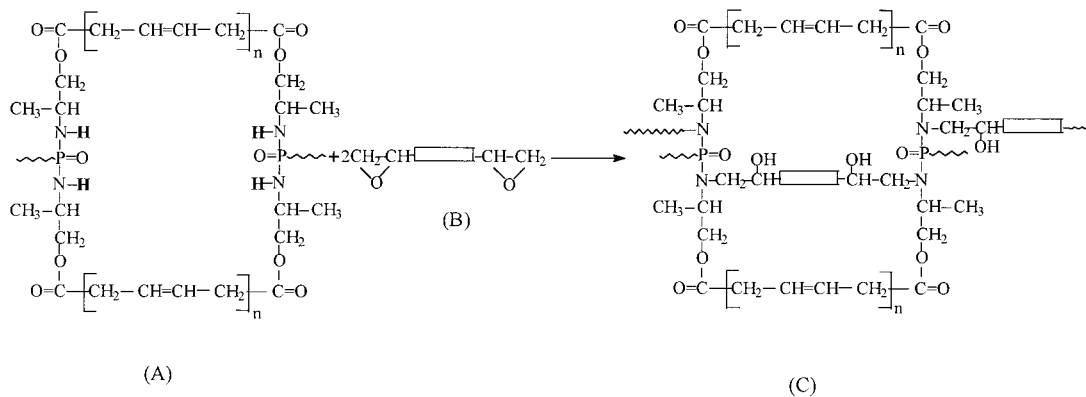
used for viscosity measurements at 20 rpm and with a no. 7 spindle at room temperature.

Preparation of CTPB Elastomers

CTPB networks were prepared by an end-linking process of CTPB chains via their terminal COOH groups. For optimization, to observe the effect of the change in the MAPO/CTPB reactive group ratio on the tensile stress-strain properties of CTPB networks, a series of unfilled CTPB net-

works were prepared by MAPO with various reactive group ratios.

To observe the effect of carbon black and the type of reactive systems on thermal, tensile stress-strain, and adhesive properties, various CTPB networks having different reactive group ratios were prepared by a mixed reactive system and MAPO. The composition of these networks are listed in Table I. In this table, compositions containing the mixture of MAPO and Epikote-828 as the reactive system are referred to as STE (run nos. 1-4 in Table I). For comparison of the aforementioned properties of the STE-type networks,



A= Amido ester network chain forming in the end-linking reaction of CTPB with MAPO

B=Epikote-828

C=Inter- and intra-molecular linked network chains

Scheme III

Table I Compositions of CTPB Networks

Run No.	Composition Name	MAPO/CTPB Reactive Group Ratio	(MAPO + Epikote-828)/CTPB Reactive Group Ratio	CTPB (Wt %)	MAPO (Wt %)	Epikote-828 (Wt %)	Printex-U Carbon Black (Wt %)
1	STE-1.60	1.15	1.60	83.15	3.25	2.80	10.42
2	STE-1.86	1.35	1.86	82.60	3.75	3.23	10.42
3	STE-2.22	1.60	2.22	81.37	4.41	3.80	10.42
4	STE-2.50	1.80	2.50	80.44	4.91	4.23	10.42
5	ST-2.22	2.22	—	83.32	6.26	—	10.42

a CTPB network was prepared by using MAPO as the reactive system with the composition containing an MAPO/CTPB ratio of 2.22. The composition of this network is referred to as ST-2.22 (run no. 5 in Table I). In all compositions shown in Table I, the reactive group ratio of MAPO/Epikote-828 and the percentage of Printex-U were fixed as 3 and 10.42, respectively. To examine these ST-2.22 and STE series of compositions, spectroscopic, thermal, and mechanical characterization were achieved. FTIR analysis was also paralleled to the other techniques mentioned above.

To prepare the CTPB networks using the mixed reactive system (MAPO + Epikote-828), the CTPB prepolymer was first degassed by continuous mixing for 10 min under a 200 mmHg vacuum at 65°C and carbon black (Printex-U) was added and mixed for additional 10 min. After addition of a carefully weighed Epikote-828 and mixing for 15 min under the same conditions, a required amount of MAPO was added and mixed for 3 min. A viscose liquid mixture was cast into Teflon-coated molds to get a film of 2 mm thickness. The molds were kept in an oven under nitrogen atmosphere at 65°C for 7 days. The network-forming reaction was followed by observing the changes in the ultimate tensile stress and elongation-at-break values of test specimens. The preparation of unfilled and MAPO-reacted systems were per-

formed without Epikote-828 and carbon black; the preparation of the ST-2.22-type composition was performed without Epikote-828 by a procedure similar to that described above.

RESULTS AND DISCUSSION

FTIR Assignment of End-linking Reactions

For the FTIR assignment of end-linking reactions, a drop of the reactant mixture was pasted between two sodium chloride plates as a thin film and stored in an oven at 65°C and FTIR spectra were taken at different time intervals. To observe the reactions between the reactive groups of CTPB, MAPO, and Epikote-828 (carboxyl bands of CTPB, aziridine bands of MAPO, and oxirane ring bands of Epikote-828), the changes in the intensities of these reactive groups were determined from the spectral differences.

The end-linking reaction of CTPB with MAPO was observed from the change of the characteristic peak intensities of these compounds. The unchanged —C=C— band of CTPB at 1639 cm^{-1} was taken as an internal standard. As shown in Figure 1, as the reaction proceeds, the peak intensities at 1401 , 1251 , and 1042 cm^{-1} which are due to the aziridine ring of MAPO showed a rapid decrease. After 24 h, these peaks disappeared

Table II T-peel and Shear Strength of ST- and STE-type Elastomers on the Steel Surface

Run No. in Table I	Composition Name	T-Peel Strength (Nt/mm)		Maximum Shear Strength
		$t = 1$ day	$t = 7$ days	
3	STE-2.22	2.5	3.7	2.94
5	ST-2.22	2.0	2.7	2.55

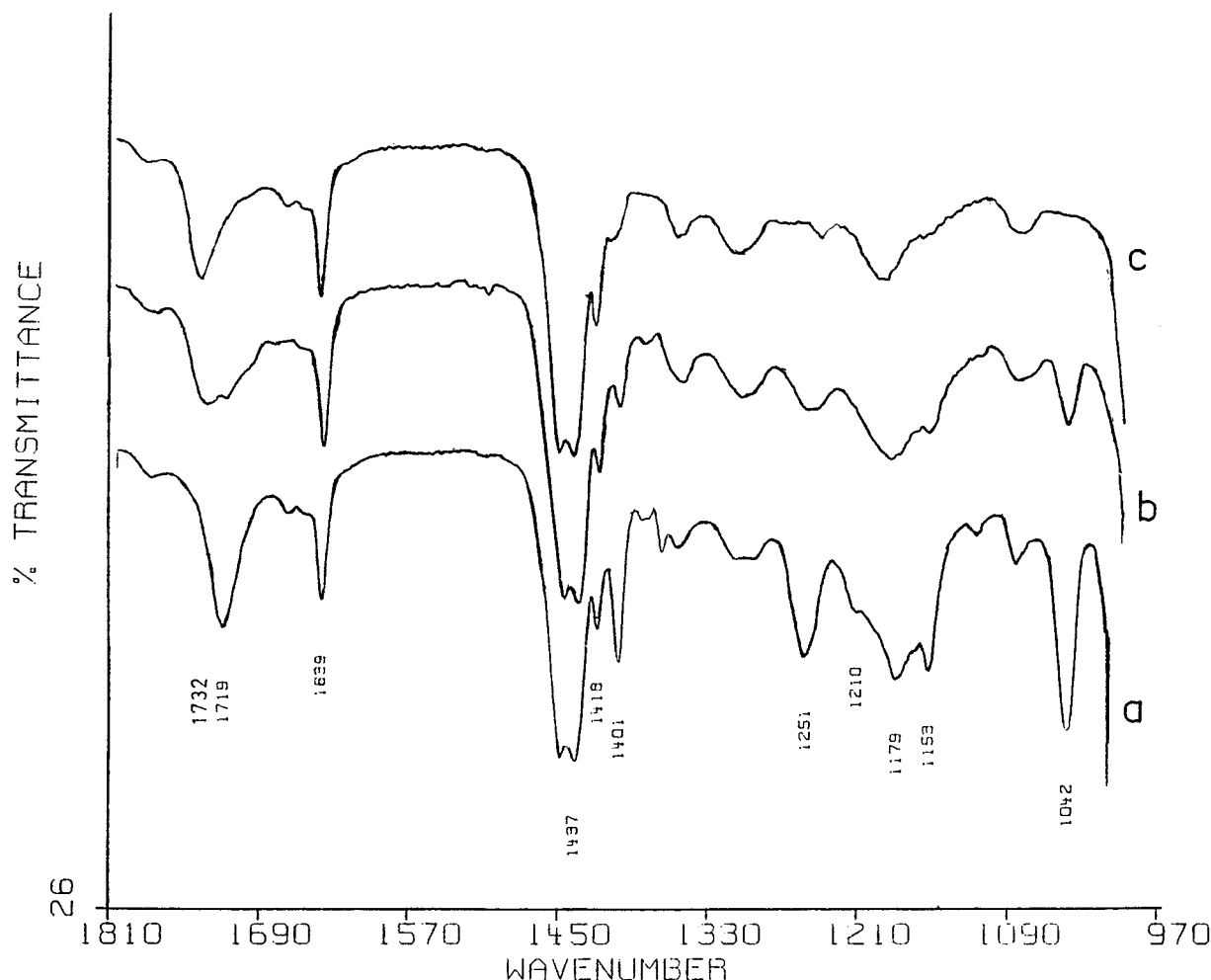


Figure 1 Determination of the end-linking reaction of CTPB with MAPO by FTIR ($1810\text{--}970\text{ cm}^{-1}$): (a) $t = 0$; (b) $t = 2\text{ h}$; (c) $t = 24\text{ h}$.

completely. The intensity of the peak at 1719 cm^{-1} which was due to —C=O groups of the terminal carboxylic acid groups of CTPB dramatically decreased as the network-forming reaction proceeded. In the meantime, a new peak appeared at 1732 cm^{-1} which was due to —C=O groups of the amido-ester-type structure of the network chains.

The reaction between CTPB and Epikote-828 was also investigated by the same method. It was observed in Figure 2 that there was an increase in the OH group intensities at 3500 cm^{-1} which was due to —OH groups forming in the course of the chain-extension reaction. In Figure 3, the —C=O peak of terminal carboxylic acid groups of CTPB at 1712 cm^{-1} was shifted to 1739 cm^{-1} , which was due to the ester network structure formed as a result of the reaction between CTPB

and Epikote-828. After a certain number of carboxylic acid groups were reacted, only a small shoulder was remained at 1712 cm^{-1} .

The reactivity of the oxirane ring was previously investigated.¹ It was pointed out that the oxirane ring is less reactive toward the aziridine ring than are carboxylic acid groups. This finding was confirmed by observing the interaction of the mixed reactive system, namely, the MAPO + Epikote-828 mixture, using FTIR spectroscopy.

Thermal Characterization of Networks

As the first step to characterize the thermal decomposition behavior of carbon black-filled ST- and STE-type CTPB networks first, DSC and TGA thermograms of the CTPB prepolymer were recorded. In the DSC thermogram of CTPB (Fig.

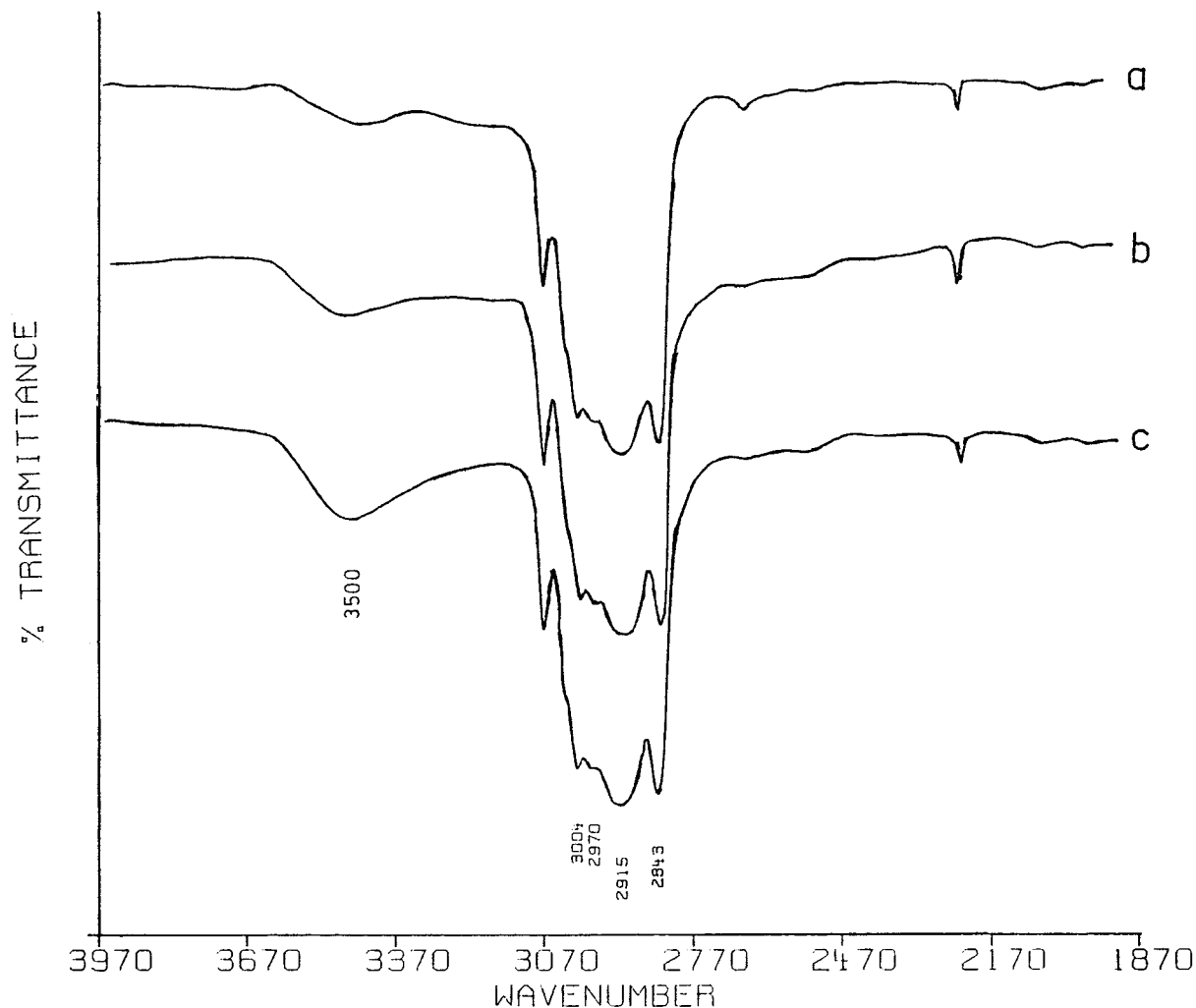


Figure 2 Determination of the end-linking reaction of CTPB with Epikote-828 by FTIR (3970–1870 cm^{-1}): (a) $t = 0$; (b) $t = 4$ h; (c) $t = 24$ h.

4), an initial exothermic peak was observed at around 375°C which was due to the exothermic cyclization and thermal crosslinking process of CTPB chains. The endothermic peak observed at around 475°C was due to the thermal decomposition of CTPB.^{13–15} In the TG and the derivative TG thermograms of CTPB (Fig. 5), two characteristic weight loss steps were easily observed. The first weight loss step coincides with the initial exothermic peak in the DSC thermogram of CTPB which was observed at around 375°C. As was explained by different authors, in the course of the first step weight loss process, lower molecular weight hydrocarbons, such as 1,3-butadiene (C_4H_6) and 4 vinyl cyclohexane (C_8H_{12}), were released.^{13,14} The second and the main weight loss process of CTPB which was due to the endothermic decomposition

of thermally crosslinked residue formed in the first step.

A thermal analysis technique was also employed to observe the effect of the end-linking process and filling with carbon black on the thermal decomposition behavior of CTPB networks. The dynamic weight-loss curves of unfilled and filled CTPB networks having the same reactive group ratio with the STE-2.22 composition are shown in Figure 6(a) and (b), respectively. The weight-loss curve of carbon black-filled CTPB network shifted to even higher temperatures than that of unfilled STE-2.22-type networks [Fig. 6(a) and (b)]. The maximum weight-loss rate temperature of unfilled CTPB networks was observed at 474°C, while for the filled network, this temperature was observed at 503°C. These results showed that the

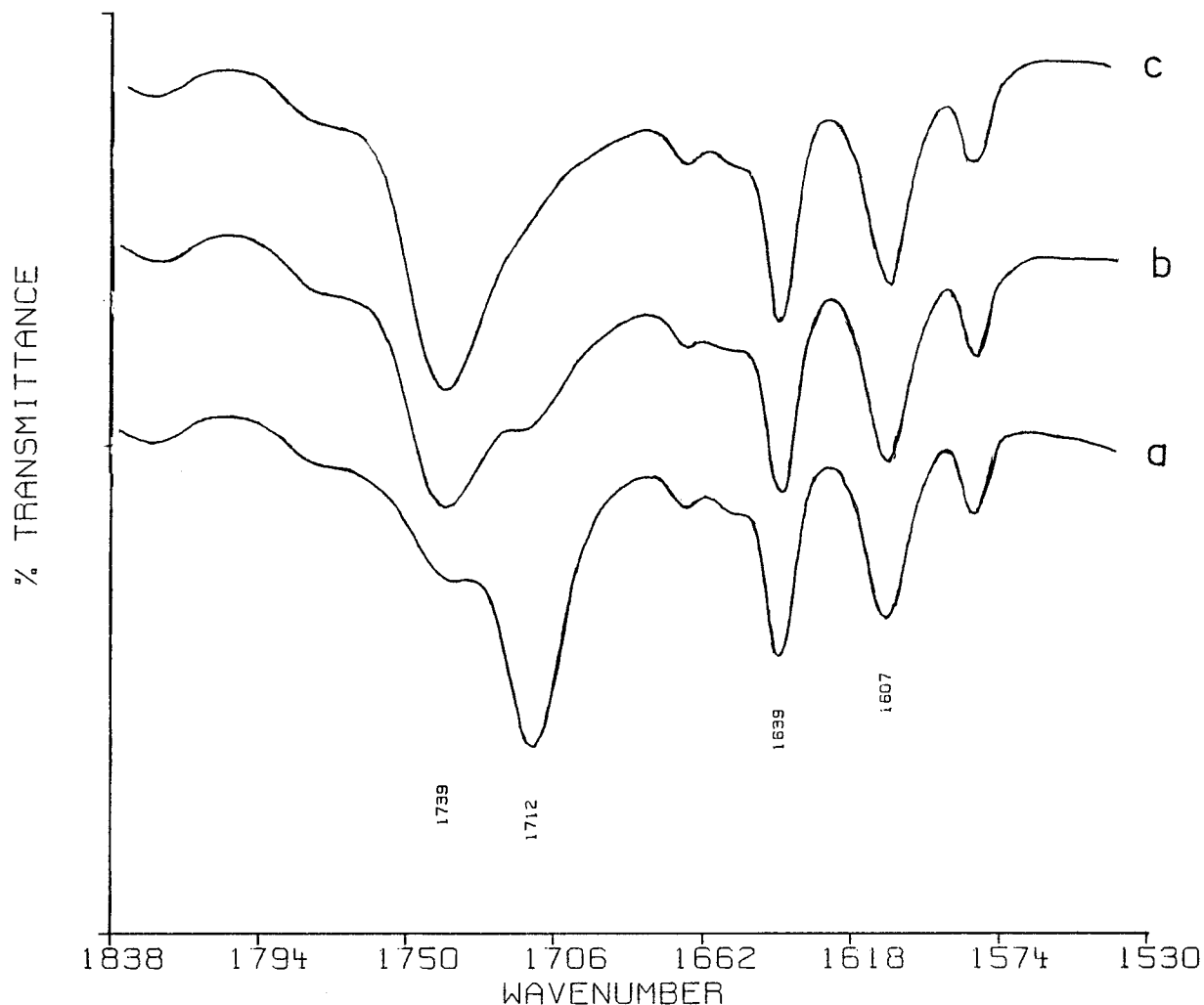


Figure 3 Determination of the end-linking reaction of CTPB with Epikote-828 by FTIR (1838–1530 cm^{-1}): (a) $t = 0$; (b) $t = 4$ h; (c) $t = 24$ h.

Printex-U-type carbon black imparts an additional thermal stability over the CTPB networks.

Furthermore, to elucidate the effect of the mixed reactive system on the thermal decomposition behavior of CTPB networks, we can compare the TG curve of filled STE-2.22- and ST-2.22-type CTPB networks [Fig. 6(b) and (c), respectively]. As seen from these TG curves, the maximum weight-loss rate temperature of STE-2.22 [503°C, Fig. 6(b)] is higher than that of the ST-2.22-type CTPB network [493°C, Fig. 6(c)]. This difference is obviously due to the inter- and intramolecular linking of the MAPO-reacted CTPB network with Epikote-828 as shown in Scheme III. These results are supported by the mechanical characterization of the ST- and STE-type CTPB networks.

Mechanical Characterization of the Networks

The mechanical properties of the ST- and STE-type CTPB elastomers were studied using an Instron tensile tester. For the purpose of the mechanical optimization of MAPO-reacted CTPB elastomer, unfilled networks having different MAPO/CTPB reactive group ratios were prepared and mechanically tested. As can be seen from Figure 7, as the reactive group ratio increased, the ultimate tensile stress values of CTPB elastomers increased and their elongation values decreased up to the MAPO/CTPB reactive group ratio values of 1.15. The maximum ultimate stress and the minimum elongation-at-break values were observed at a 1.15 reactive group ratio. This can

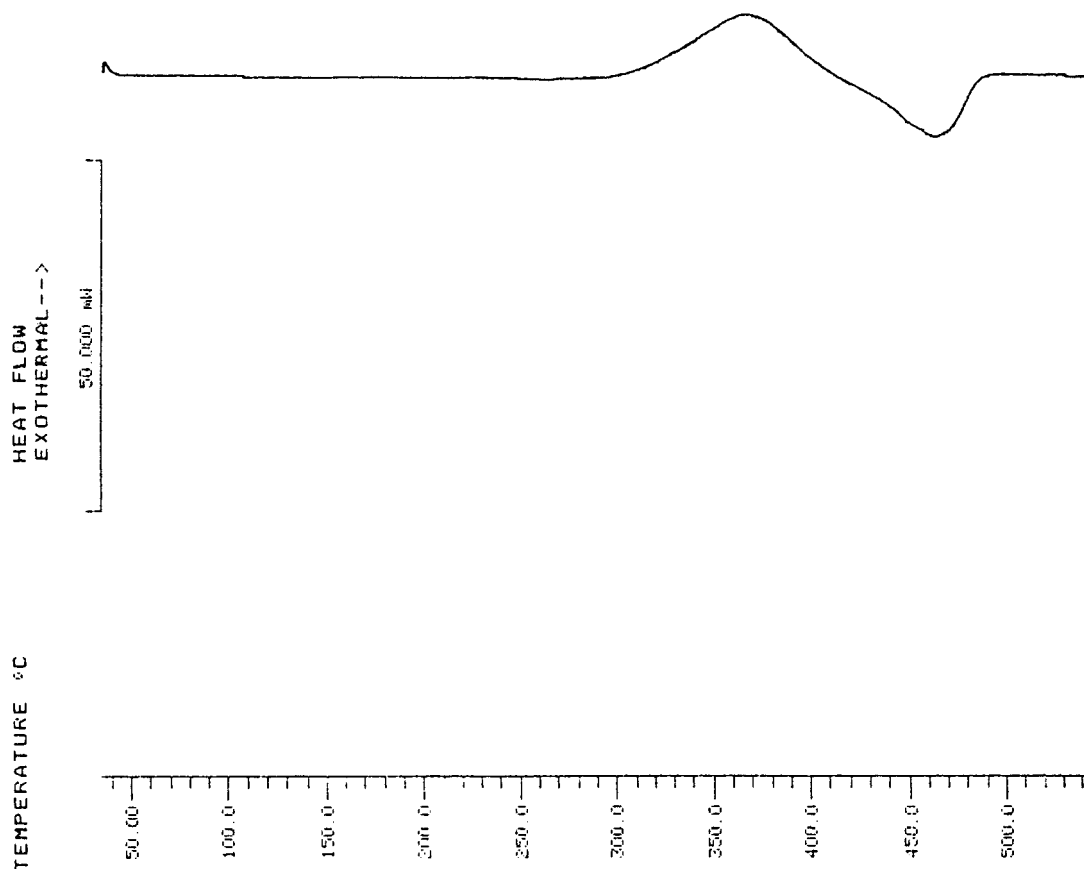


Figure 4 DSC curve of the CTPB prepolymer.

be interpreted as that, at this ratio, nearly all —COOH groups of CTPB reacted with aziridin groups of MAPO. Above the reactive group ratio of 1.15, ultimate tensile stress values decreased with increasing of elongation values of CTPB elastomers. This phenomenon was most probably due to the homopolymerization of unreacted MAPO that exists in a considerable amount over the MAPO/CTPB reactive group ratio of 1.15 which causes the observed change in the mechanical properties.^{1,16} It was clearly observed from these results that the optimum mechanical properties could be achieved at around an MAPO/CTPB reactive group ratio of 1.15.

Mechanical tests were also employed to characterize the extent of the end-linking reaction of both ST- and STE-type carbon black-filled networks and to elucidate the effect of the mixed reactive system (a mixture of MAPO and Epikote-828) on the ultimate tensile stress and elongation-at-break values of CTPB elastomers. For this purpose, test samples reacted at 65°C for different

time intervals were prepared and their tensile tests were performed.

Figures 8 and 9 show the changes in the ultimate tensile stress and elongation-at-break values of ST- and STE-type networks as a function of reaction time. It was clearly observed from Figure 8 that in all compositions the maximum ultimate tensile stress values were attained within 5 days. This result can be taken as a proof of the completion of the end-linking reaction of CTPB chains to a great extent within 5 days.

Another optimization procedure was applied for the use of a mixed curing agent system (i.e., a mixture of MAPO and Epikote-828). In the preparation of CTPB elastomers, the main advantage of using a mixed reactive system is to compensate for the homopolymerization of excess MAPO. From Figures 8 and 9, the changes in the ultimate tensile stress and elongation-at-break values of the ST-2.22- and STE-type networks prepared at different reactive group ratios as a function of the reaction time can be observed. In

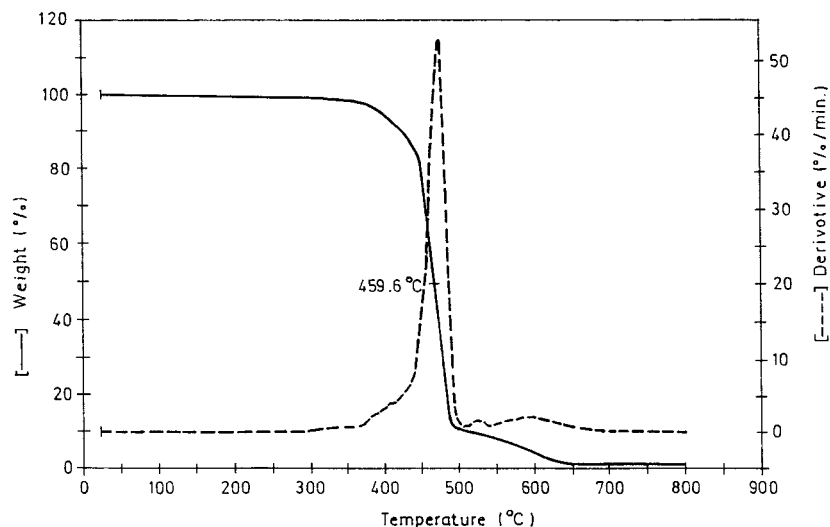


Figure 5 Dynamic TG and DTG thermograms of the CTPB prepolymer.

Figure 8, curve d belongs to STE-2.22-type network and this has a maximum stress value of 1.18 MPa, which is higher than that of the maximum stress value of the composition corresponding the same reactive group ratio in the ST-type composition (curve a, 0.98 MPa for ST-2.22). This result is because in the ST-2.22-type network a stoichiometrically twofold excess of MAPO was used; some part of the MAPO was reacted with all COOH groups of CTPB. The remaining part of the MAPO underwent homopolymerization and other side reactions; this resulted in a less homogeneous elastomeric system. As a result, a lowering in the mechanical properties was observed. The upper-

most curve belongs to the STE-2.50-type composition which has the maximum stress values of 1.37 MPa. In contrast to the unfilled and MAPO reacted elastomers (see Fig. 7), in the STE-type elastomers, over the MAPO/CTPB reactive group ratio of 1.15, the ultimate tensile stress values increased as the reactive group ratio increased. This tendency was also observed in the elongation-at-break values of the STE system (in Fig. 9). The maximum ultimate tensile stress and elongation-at-break values were obtained for the STE-2.50-type composition as 1.37 MPa and 470%, respectively.

Introduction of the higher thermal stability,

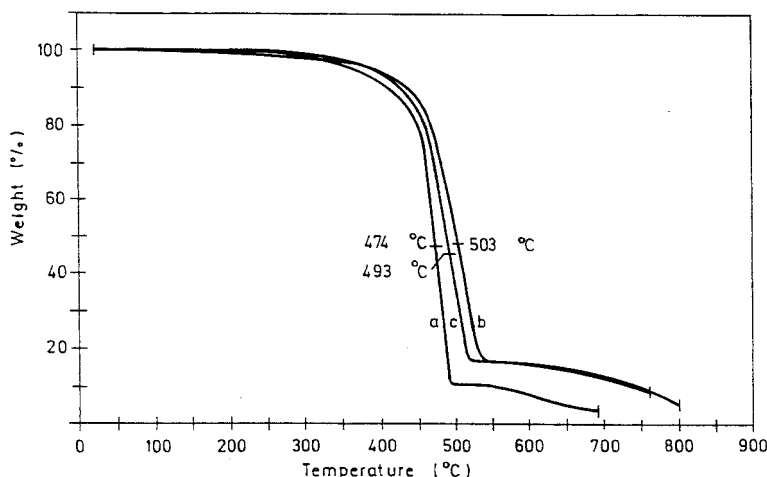


Figure 6 Dynamic TG curves of the CTPB networks: (a) unfilled STE-2.22-type network; (b) filled STE-2.22-type network; (c) filled ST-2.22-type network.

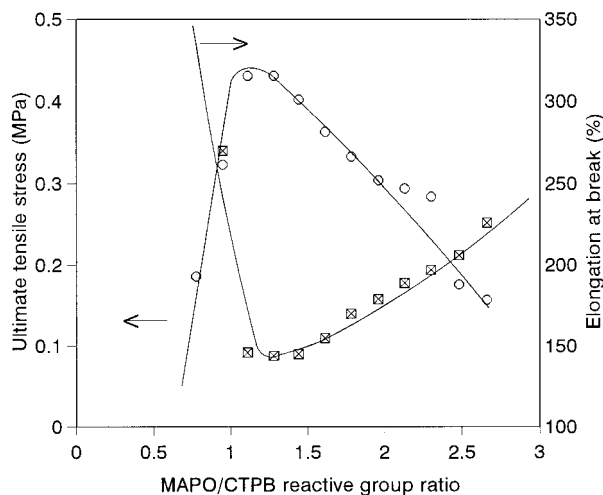


Figure 7 Ultimate tensile stress and elongation-at-break values of unfilled CTPB networks as a function of MAPO/CTPB reactive group ratio.

high ultimate tensile stress, and elongation-at-break values of the STE-2.22-type network as compared to the ST-2.22-type network were achieved by the inter- as well as intramolecular bridges among the amido-ester network chains. These bridges were accomplished by the reaction of N—H groups of amido-ester network chains with oxirane rings of Epikote-828. Taking these findings into consideration, we propose the reaction mechanism shown in Scheme III as a possible route to these formations.

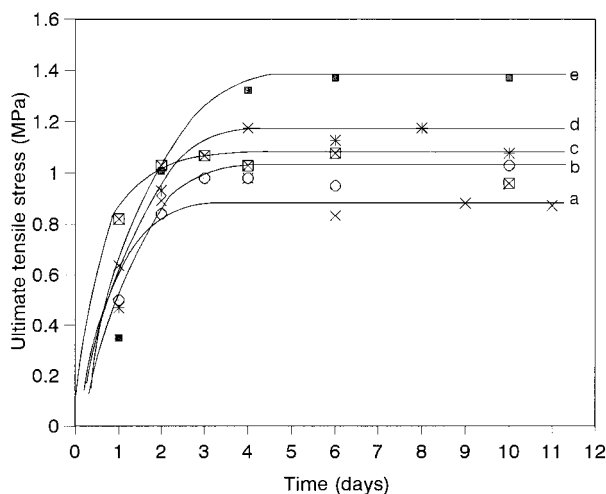


Figure 8 Ultimate tensile stress values of ST- and STE-type networks as a function of reaction time: (a) ST-2.22; (b) STE-1.6; (c) STE-1.86; (d) STE-2.22; (e) STE-2.5.

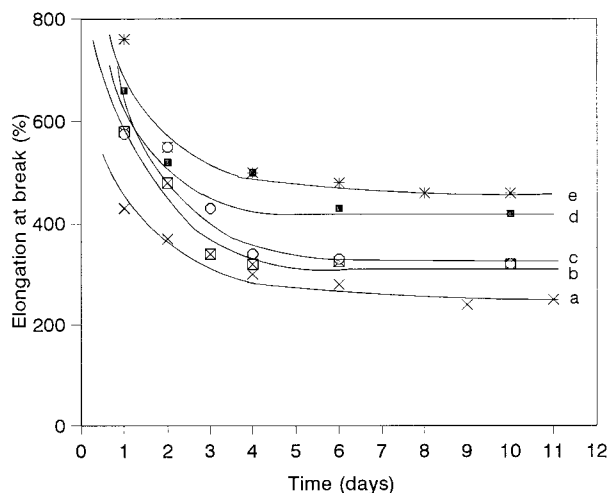


Figure 9 Elongation-at-break values of ST-2.22- and STE-type networks as a function of reaction time: (a) ST-2.22; (b) STE-1.6; (c) STE-1.86; (d) STE-2.22; (e) STE-2.5.

Epikote-828 is a difunctional reactive compound and the STE-type networks showed not only have higher ultimate stress values [compare Fig. 8(a) and (d)], but also showed higher elongation values as compared with the corresponding ST-type elastomer [Fig. 9(a) and (d)]. This was probably due to the flexible —O— bonds of Epikote-828 which improve further the elongation values of the elastomers. In the STE-2.22 composition, in the course of the network-forming process, the insertion of flexible —O— bonds of Epikote-828 into the network structure caused to an increase in network elasticity. That is the reason for the simultaneous increase in both ultimate tensile stress and elongation-at-break values of the STE-type compositions.

The use of Epikote-828 also improved the adhesive strength further, since —O— bonds enable the structure to be more flexible. It was reported that⁶ peel strength is directly proportional and related to the flexibility of the adhesive. Therefore, the improvement in flexibility and formation of polar —OH groups in the course of the network-forming reaction (see Scheme III) also modified the peel and shear strengths of the STE-type elastomers. The peel and shear strength results of ST-2.22- and STE-2.22-type elastomers are listed in Table II.

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