

DTA Studies on the Thermal Oxidation and Crosslinking Reactions of Carboxyl-Terminated Polybutadiene

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Synopsis

Studies on the thermal oxidation of carboxyl-terminated polybutadiene in the presence of antioxidants have been carried out by dynamic DTA. Bis-thioacetylacetonato nickel(II) compounds are found to be effective in inhibiting the air oxidation reaction in the polymer. The crosslinking reaction of the polymer through the double bonds present in the polymer molecule is desensitized by the antioxidants and the effect is more with *N*-phenyl-1-naphthylamine. An exothermic peak formed at 270°C in the presence of tris(2-methylaziridinyl-1)phosphine oxide has been identified as the curing reaction. The infrared spectra of CTPB in the presence of MAPO at various temperatures confirm the various stages of reaction.

INTRODUCTION

Considerable information on the DTA studies of the thermal oxidation of polymers in the presence of antioxidants¹⁻⁴ and of the reactions of epoxy resins with a variety of hardeners⁵⁻⁸ is available in the literature. In isothermal DTA, the induction period is the indication of the inhibiting ability of the antioxidants,⁹ whereas in a dynamic DTA the same information could be obtained from the desensitization of the corresponding peak. Similarly, appearance of an exotherm in DTA in the presence of hardeners indicates a crosslinking reaction.¹⁰ Pure polybutadiene undergoes crosslinking at a higher temperature through the unsaturated centers present in the polymer chain. Carboxyl-terminated polybutadiene, a well-known binder for the composite solid propellants, reacts with MAPO through the carboxyl groups. This reaction has been studied by chemical methods. The extent of disappearance of carboxyl group¹¹ is the indication of the reaction with MAPO. A literature survey revealed that DTA studies on resin-hardener reaction have been carried out on epoxy resins.⁵⁻⁸ In the present investigation, we wish to examine whether the DTA technique could be used to study the CTPB-MAPO curing reaction or not.

For the oxidative stability of the binder, antioxidants are added soon after the resin is synthesized. These antioxidants are sometimes various metal complexes, amine, and phenolic compounds. These compounds may interfere during the curing process but nothing is known about such reactions. Recently we have shown that bis-thioacetylacetonato compounds are good antioxidants for polyolefins.^{9,12} It was also observed that *N*-phenyl-1-naphthylamine is a poorer antioxidant compared to bis-thioacetylacetonato nickel(II) compounds. In the

TABLE I
The DTA Peak Temperature of Neat CTPB and CTPB + MAPO in the Presence of Antioxidants

No.	CTPB + additive	Atmosphere	Temperature (°C)		
			Peak I	Peak II	Peak III
1.	—	N ₂	—	—	342 ± 1.0
2.	—	Air	187 ± 0.5	—	348 ± 1.0
3.	Bis(monothioacetyl-acetonato) nickel(II)	Air	212 ± 0.5	—	353 ± 1.5
4.	Monothioacetylacetonato dithioacetylacetonato nickel(II)	Air	213 ± 0.5	—	353 ± 1.0
5.	Bis(dithioacetyl-acetonato) nickel(II)	Air	222 ± 1.0	—	353 ± 1.0
6.	<i>N</i> -phenyl-1-naphthylamine	Air	210 ± 0.5	—	358 ± 1.5
7.	CTPB + MAPO + bis-(dithioacetylacetonato) nickel(II)	N ₂	—	271 ± 1.0	355 ± 1.0
8.	CTPB + MAPO + <i>N</i> -phenyl-1-naphthylamine	N ₂	—	273 ± 1.0	359 ± 1.5

present investigation, we wish to investigate how these complexes as well as *N*-phenyl-1-naphthylamine affect the CTPB-MAPO curing reactions. It may be pointed out that it is desirable that these antioxidants should either not affect the curing reaction or show only a minimal effect.

EXPERIMENTAL

Bis(monothioacetylacetonato) nickel(II), monothioacetylacetonato dithioacetylacetonato nickel(II), and bis(dithioacetylacetonato) nickel(II) compounds were prepared from nickel(II) chloride and acetylacetone by the method of Ouchi et al.¹³ Carboxyl-terminated polybutadiene (Butarez, Phillips) was dissolved in benzene and precipitated by methanol followed by drying in vacuum. Tris(2-methylaziridinyl-1) phosphine oxide (MAPO) (supplied by Phillips) was used without further purification. All the samples containing antioxidants (9.4×10^{-6} mol antioxidant/g sample) were thoroughly mixed before use. CTPB and a calculated amount of MAPO were taken together and used for DTA studies.

The dynamic DTA studies were done in a Stanton Redcroft Low Temperature DTA Model No. 671 at a heating rate of 10°C/min. Infrared spectra were taken in a Perkin-Elmer infrared spectrometer Model 537.

RESULTS AND DISCUSSION

The DTAs of CTPB in N₂ and in air atmospheres are shown in Figure 1. The temperatures at which the exotherm occurs in the presence of antioxidants are given in Table I. In Figure 1, an exotherm appears at 187°C in static air (b) which

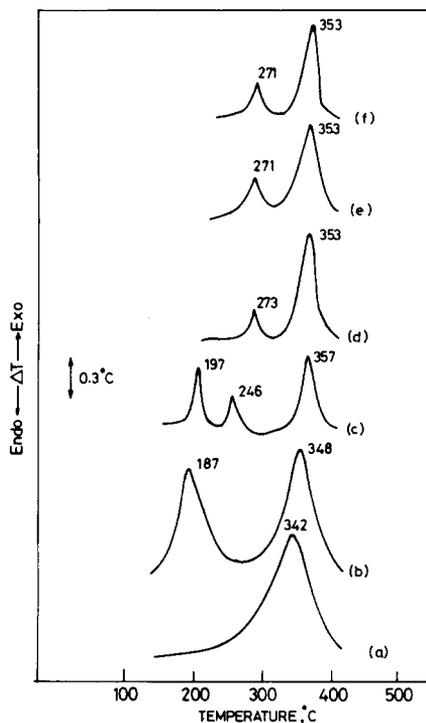


Fig. 1. DTA curves of CTPB with and without MAPO. (a) CTPB (N_2), (b) CTPB (air), (c) CTPB + MAPO (air), (d) CTPB + MAPO (N_2), (e) CTPB + MAPO + *N*-phenyl-1-naphthylamine (air), (f) CTPB + MAPO + bis(dithioacetylacetonato) nickel(II) (air).

is absent in N_2 atmosphere (a). This exotherm is due to the thermal oxidation of CTPB which shifts to a higher temperature in the presence of antioxidants (Table I). The shift to higher temperatures is a measure of the inhibiting ability of the antioxidants. From Table I it is seen that nickel(II) compounds inhibit the oxidation reaction more than *N*-phenyl-1-naphthylamine. The inhibiting ability of nickel compounds is as follows: bis(dithioacetylacetonato) nickel(II) > monothioacetylacetonato dithioacetylacetonato nickel(II) > bis(monothioacetylacetonato) nickel(II).

Figure 1 also shows the DTAs of CTPB + MAPO in (i) static air (c), (ii) in nitrogen atmosphere (d), and (iii) with antioxidants in air (e, f). The additional exothermic peak in (c) is due to the oxidation of polymer. This peak shifts to a higher temperature with CTPB + antioxidant and is absent in the case of CTPB + MAPO + antioxidants. The disappearance of the peak in the latter combinations shows that MAPO, which is a crosslinking agent, also acts as an antioxidant and a combined antioxidant effect in conjunction with the added antioxidant results in a "synergistic effect." As a result of this, the peak in CTPB + MAPO + antioxidants disappears. That the MAPO acts as antioxidant was confirmed from DTA in Figure 2. Figure 2 shows that an increase in the concentration of MAPO leads to a decrease in the intensity of the peak at 190°C , which is for the oxidation of CTPB as mentioned earlier. This suggests that MAPO possesses antioxidation property. One can also see that intensity of peak

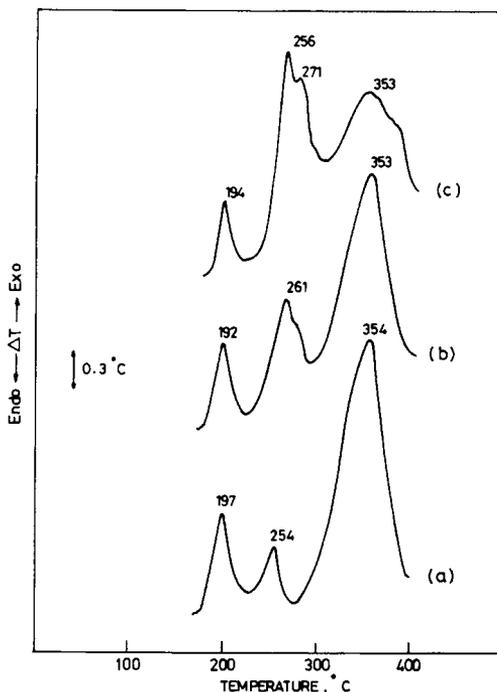


Fig. 2. DTAs of CTPB with different amounts of MAPO in air. (a) MAPO (5%), (b) MAPO (10%), (c) MAPO (40%).

at 250–270°C increases with the MAPO concentration which is due to the greater extent of crosslinking.

The exothermic peak at 250 to 273°C is attributed to the curing reaction of CTPB with MAPO. This is confirmed from the IR spectra (Fig. 3) of the CTPB, cured at 280°C.

Figure 3 shows that C=O stretch at 1700 cm^{-1} for CTPB shifts to a higher region (1730 cm^{-1}). Also, a new peak at 3300 cm^{-1} indicates N–H stretching. The curing process is not affected by the addition of antioxidant (Table I).

All the DTAs in Figures 1 and 2 show an exotherm above 350°C which is due to the thermal crosslinking reactions in CTPB through the double bonds present in the polymer chain. The IR spectra (Fig. 3) of CTPB + MAPO heated to 360°C confirm this by showing a tremendous decrease in the intensity of peaks at 3030 cm^{-1} (olefinic C–H stretch), 1630 cm^{-1} (C=C stretch), 670 and 730 cm^{-1} (olefinic C–H out of plane bending). These indicate the absence of a major portion of the double bonds in the polymer chain.

Coffman¹⁴ in his studies on butadiene rubber observed exothermic crosslinking after several days of heating at 255°C. Brazier and Schwartz¹⁵ in their degradation studies of polybutadiene observed an exothermic reaction which they attributed to the cyclization and crosslinking. Although there is a decrease in the intensity of the peak corresponding to the double bonds and the substituents attached to the double-bonded carbon, there still is an indication of the presence of double bonds. The mechanism proposed^{16–18} for the crosslinking reaction of rubbery polybutadiene involves the production of free radical fragments by

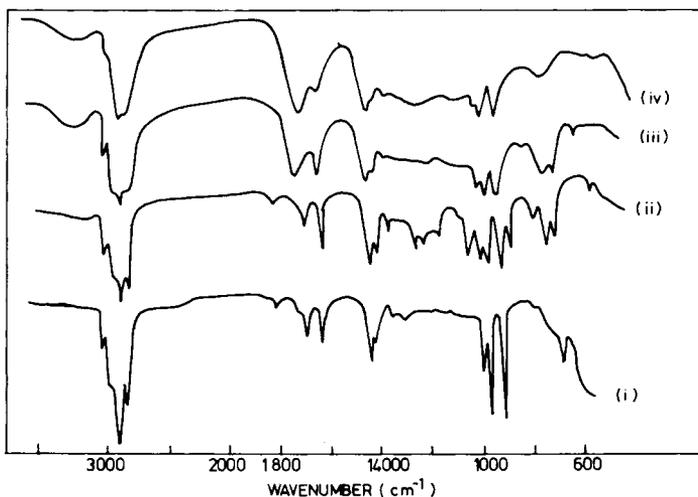
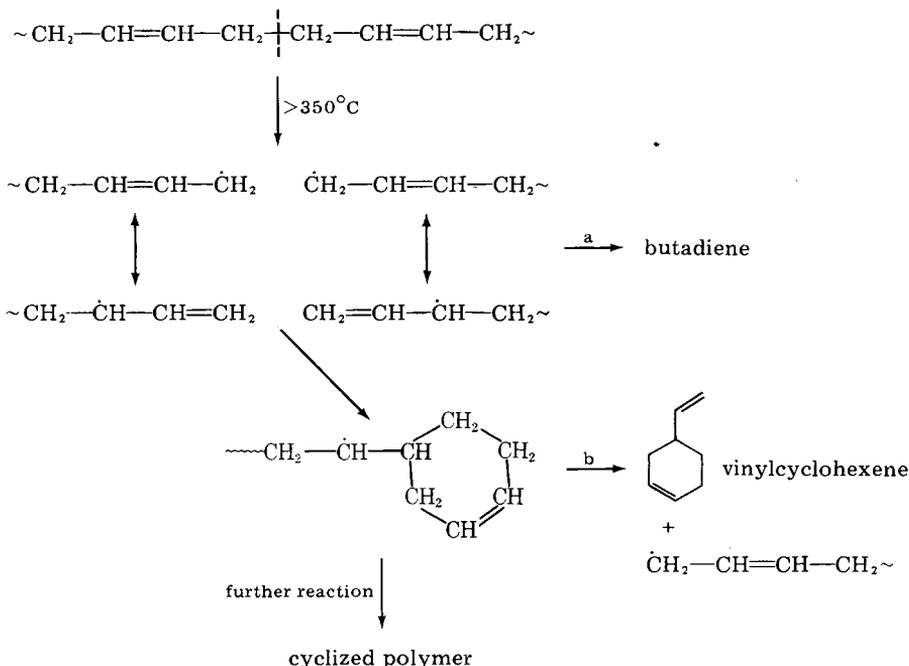


Fig. 3. Infrared spectra of CTPB with MAPO at different temperatures. (i) CTPB at 25°C, (ii) CTPB with MAPO at 200°C, (iii) CTPB with MAPO at 280°C, (iv) CTPB with MAPO at 360°C.

the homolytic cleavage of C-C σ -bonds. This results in the cyclized polybutadiene via the formation of new σ -bonds from the π -bonds present in the fragments as shown below.



The weight loss of the polymer samples in nitrogen atmosphere at 360°C was found to be negligible (<5 wt %) and so the secondary reactions (a) and (b) are considered insignificant. Therefore the only major reaction occurring in the polymer is the formation of cyclized polybutadiene. The exotherm corre-

sponding to the crosslinking reaction shifts to higher temperature in the presence of antioxidants (Table I). This shift is more pronounced with *N*-phenyl-1-naphthylamine. This effect is expected on the basis that the aryl amino compounds are chain-breaking antioxidants² which can inhibit the propagation of any free radical reaction. The crosslinking reaction follows a free radical mechanism which can be inhibited considerably by *N*-phenyl-1-naphthylamine. It has been observed¹⁹ that amino compounds are the most effective in preventing crosslinking reactions. Thio-organic compounds of nickel(II), a well-known peroxide-decomposing antioxidant,^{20,21} inhibit the crosslinking reaction to a lesser extent.

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