

Degradation Mechanisms of Poly(ethylene Terephthalate) Tire Yarn

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SYNOPSIS

In order to clarify the fatigue mechanism of PET tire cords in rubber focusing on chemical degradation, hydrolysis in saturated steam atmosphere, ammonolysis in ammonia gas, and the degradation of the cords embedded in rubber have been studied at high temperature conditions. It was found that the strength loss of polyester tire cords in rubber has linear correlation with the amount of chemically induced chain scissions mainly caused by hydrolysis catalyzed by amines.

INTRODUCTION

The deterioration of poly(ethylene-terephthalate) (PET) tire cords has been examined by many researchers.¹⁻⁸ The deterioration mechanisms can be classified in two categories. One is due to structural deterioration such as occurrence of kink bands or fibrillations⁸ and the other is due to chemical degradation, generally from hydrolysis or aminolysis.¹⁻⁷

In previous papers⁹⁻¹¹ we reported that the fatigue of PET tire cord is not due primarily to structural deterioration but to chemical degradation caused by hydrolysis with amine catalysts. The synergism of amine and water on the chemical degradation of polyester tire cord in rubber has been reported.^{4,5} However, inherently the amines cannot easily penetrate into polyester because of the low dielectric constant of PET. The actual role of amines in the chemical degradation of PET is still obscure.

In this report, we discuss the fatigue of PET tire cord focusing on the mechanisms of chemical degradation.

EXPERIMENTAL

The hydrolysis reaction in saturated steam atmosphere, ammonolysis in ammonia gas, and the deg-

radation in rubber have been studied at high temperature as model tests of chemical degradation of PET tire cords. The greige (uncoated) cords tested in this study are characterized in Tables I and II. The greige cord of sample 12 was heat-treated with Vulcabond E (product of ICI) which is an adhesive for polyester tire cords in the dipping process. The dipping process has been described in another study.¹⁰ The dipped cords, which were used for the test of degradation in rubber, are also characterized in Table III.

Tensile tests were performed using an Instron tensile tester according to the methods of JIS-L-1017. Intrinsic viscosities of these samples were measured with the Ostwald's viscometer in phenol/tetrachloroethane (60/40) at 25°C using the following equation

$$IV \text{ (dL/g)} = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 C} \quad (1)$$

Carboxyl ends were measured by neutralization titration as follows: the samples were dissolved in boiling benzyl alcohol and diluted with chloroform. Then the solution was titrated with sodium hydroxide. Benzyl alcohol treated in the same manner was also titrated as a blank.

The hydrolysis test of greige cord samples was performed with saturated steam at 130 and 150°C in the autoclave under the fixed length condition. The treatment time was from 7 to 72 h.

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Table I Greige Cord Properties

Sample no.	1	2	3	4	5	6	7
Manufacturer	A	A	A	A	C	C	D
Filament no.	190	190	240	240	192	480	192
Construction	1000/2	1000/2	1000/2	1000/2	1000/2	1000/2	1000/2
Twist cable (<i>t</i> /10 cm)	49	49	49	49	49	49	49
Ply (<i>t</i> /10 cm)	49	49	49	49	49	49	49
Tensile strength (kg)	15.5	15.7	14.9	14.6	15.5	14.8	13.9
Elong. at 4.5 kg (%)	5.7	5.8	6.2	6.1	5.1	6.3	6.4
Elong. at break (%)	17.2	17.6	16.1	15.1	15	15.8	17.1
Limiting viscosity number (dL/g)	0.88	0.88	0.86	0.85	0.87	0.88	0.86
Carboxyl ends (mEq/kg)	7	18	20	10	9	28	30

The ammonolysis test of greige cord samples was performed with ammonia gas at 130, 150, and 170°C in the reaction vessel also under the fixed length condition. The gas flow rate of ammonia into the vessel was 30 cc/min and the treatment time was from 1 to 7 h.

Heat-aged, in-rubber tests of dipped cords were performed with rubber at 170°C in the vulcanization mold under a tension of 1 kg/cord. The elapsed time of treatment was from 1 to 5 h. The sample cords treated in rubber were removed from rubber after 48 h immersion in gasoline. After air drying, the cords were used for the tensile test. For chemical characterization of sample cords degraded in rubber, the air-dried cords were chopped and dissolved in a mixture of methylenechloride and trichloroacetic acid (ratio = 1.7 : 1). The solution was filtered with diatomaceous earth then was poured into water to precipitate PET pure powder. The powder PET was filtered, washed, and dried. The carboxyl ends and IV were measured for the pure PET powder.

Calculation of percent broken bonds of ester

bonds (% BB) was determined by the following equation

$$\% \text{ BB} (\%) = 0.245 (IVf_f^{-1.47} - IVf_i^{-1.47}) \quad (2)$$

where IVf_i is IV before degradation and IVf_f is IV after degradation. The total ester bonds is assumed as $10,380 \text{ eq}/10^6 \text{ g}$.¹³ The Moore's relation between IV and number average molecular weight (M_n) was adopted in this study as follows¹²:

$$IV_{\text{phenol/tetrachloroethane}=60/40} = 7.50 \times 10^{-4} M_n^{0.68} \quad (3)$$

RESULTS AND DISCUSSION

Hydrolysis

The relations of strength retention, % BB, and increased carboxyl ends vs. elapsed time of hydrolysis reaction at 130°C are shown in Figure 1. With increasing time, strength retention decreases and % BB and carboxyl ends increase. With the increase

Table II Greige Cord Properties

Sample no.	8	9	10	11	12
Manufacturer	A	A	A	A	A
Filament no.	190	380	190	380	190
Construction	1500/2	1500/2	1500/2	1500/2	1500/2
Twist cable (<i>t</i> /10 cm)	40	40	40	40	40
Ply (<i>t</i> /10 cm)	40	40	40	40	40
Tensile strength (kg)	24.3	22.4	23.4	21.6	24.5
Elong. at 6.8 kg (%)	7.1	7.4	6.7	7	7.1
Elong. at break (%)	20.7	18.4	17.3	19.2	19.7
Limiting viscosity number (dL/g)	0.9	0.903	0.87	0.89	0.9
Carboxyl ends (mEq/kg)	18	18	11	11	18
Hot air shrink at 150°C (%)	13.3	10.1	14.1	9.3	13.5

Table III Dipped Cord Properties

Sample no.	8
Manufacturer	A
Filament no.	190
Construction	1500/2
Twist cable ($t/10$ cm)	40
Ply ($t/10$ cm)	40
Tensile strength (kg)	22.3
Elong. at 6.8 kg (%)	4.3
Elong. at break (%)	16.1
Limiting viscosity number (dL/g)	0.9
Carboxyl ends (mEq/kg)	18
Hot air shrink at 150°C (%)	6
H/Adhesion (kg/cm)	13.5
Dip pick up (%)	5.5

of carboxyl ends, the reaction velocity of hydrolysis increases. It is obvious that the carboxyl ends act as catalyst for this reaction. The reaction velocity was expressed by Zimmermann as follows¹³

$$kt = \frac{1}{10380(1 - X_c) + C_i} \times \ln \frac{10380(1 - X_c)(C_i + \Delta[\text{COOH}])}{C_i\{10380(1 - X_c) - \Delta[\text{COOH}]\}} \quad (4)$$

where C_i are initial carboxyl ends (eq/10⁶ g), $\Delta[\text{COOH}]$ represents increased carboxyl ends, X_c is crystallinity (%), and t is elapsed time (h).

One can assume that the increased in carboxyl ends is negligibly small as compared with total ester

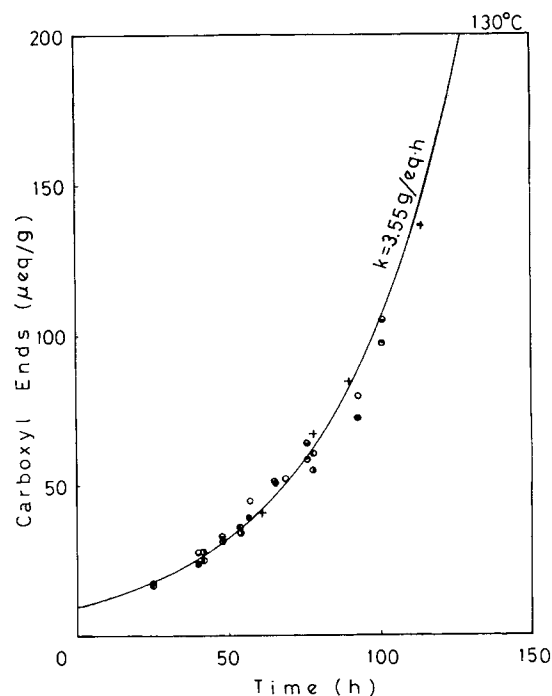


Figure 2 Relation between carboxyl ends and time of reaction at 130°C (—) calculated line by eq. (5); (○) sample 2; (◐) sample 3; (●) sample 4; and (+) sample 6.

bonds (10,380 eq/10⁶ g) in this study. Therefore eq. (4) can be modified to the following expression

$$kt = \frac{1}{10380(1 - X_c)} \ln \left(1 + \frac{\Delta[\text{COOH}]}{C_i} \right) \quad (5)$$

The reaction velocity at 150°C is 14.1 g/eq/h,

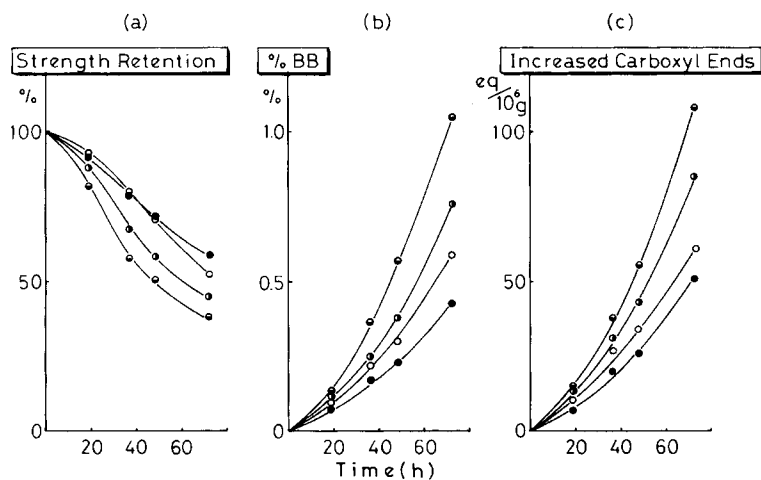


Figure 1 Relations of strength retention (a), % BB (b), and increased carboxyl ends (c) vs. elapsed time of hydrolysis reaction at 130°C. (○) sample 2; (◐) sample 3; (●) sample 4; and (◑) sample 6.

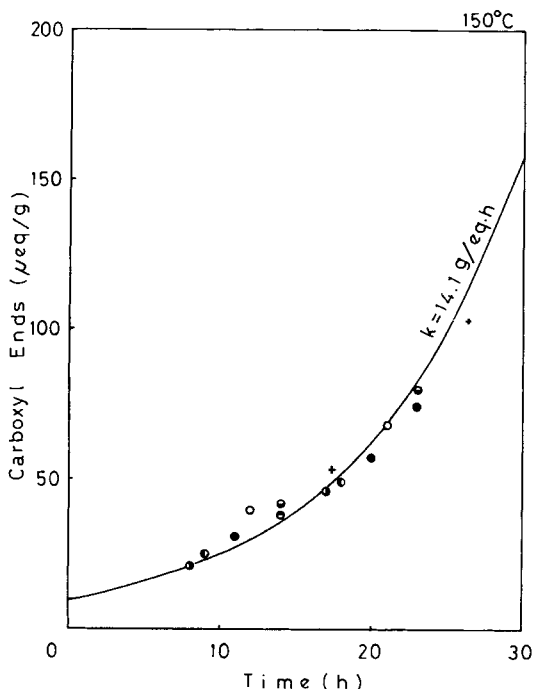


Figure 3 Relation between carboxyl ends and time of reaction at 150°C (—) calculated line by eq. (5); (○ ●) sample 2; (⊖ ⊕) sample 3; (⊙ ⊚) sample 4; and (+) sample 6.

and at 130°C is 3.55 g/eq/h. The activation energy of hydrolysis was determined by an Arrhenius plot as 23.6 kcal/mol which agrees well with others.¹⁴

The calculated relations between carboxyl ends and elapsed time according to eq. 5 are shown in Figures 2 and 3 by the solid line. In each case carboxyl end content is 10 eq/10⁶ g and the reaction velocity constants are 3.55 g/eq/h (130°C) and 14.1

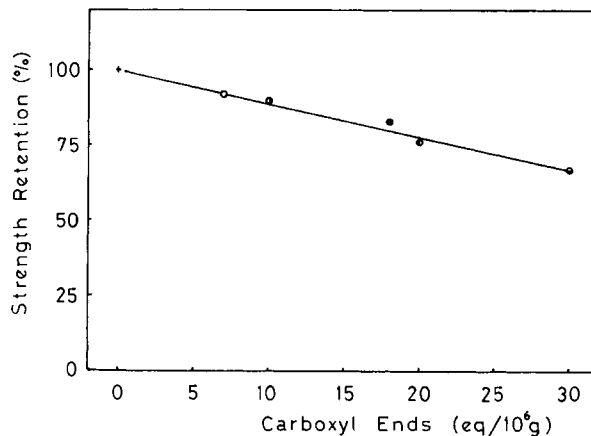


Figure 5 Relation of strength retention and initial carboxyl ends on ammonolysis reaction for 3 h at 135°C (+) monofilament containing no carboxyl ends; (○) sample 1; (●) sample 2; (●) sample 5; (⊙) sample 6; and (⊖) sample 7.

g/eq/h (150°C), respectively. The observed values for which elapsed times were adjusted for the initial carboxyl ends agree well with the theoretical values as shown in Figure 2. Therefore, eq. (4) is widely applicable for the hydrolysis reaction, and % BB is expressed by the following equation

$$\% \text{ BB} = 0.00963 \frac{10380 \times C_i \times (E - 1)}{10380 + E \times C_i} \quad (6)$$

$$E = \exp[\exp(-11800/T + 16.5)t(10380 + C_i)] \quad (7)$$

where C_i is initial carboxyl ends (eq/10⁶ g), T is temperature (K), and t is elapsed time (h).

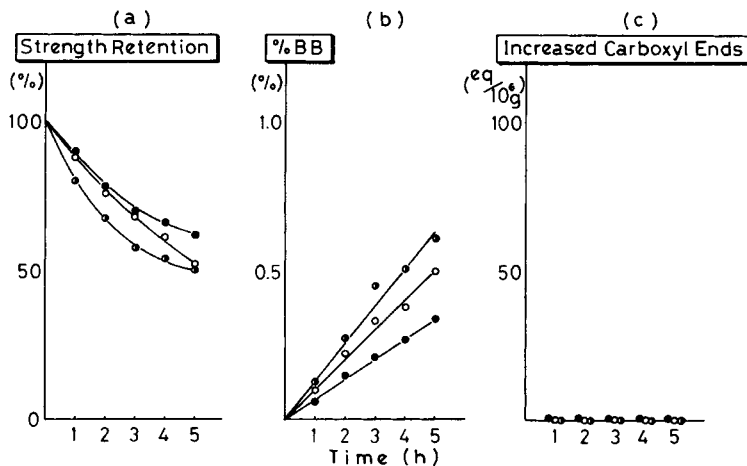


Figure 4 Relations of strength retention (a) % BB (b), and increased carboxyl ends (c) vs. elapsed time of hydrolysis reaction at 150°C. (○) sample 2; (⊙) sample 3; and (●) sample 4.

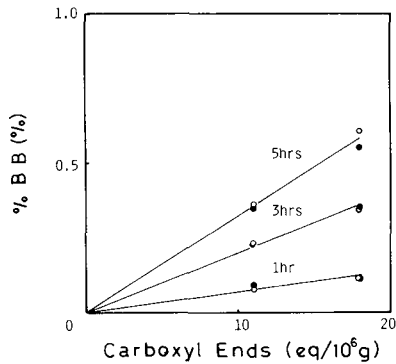
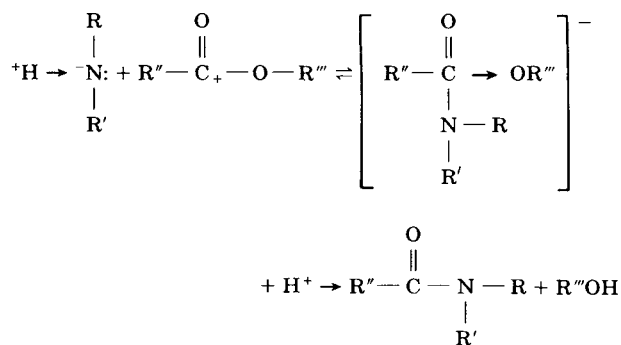


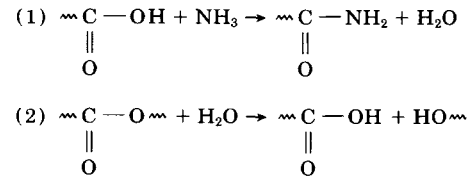
Figure 6 Relation between carboxyl ends and % BB at 150°C. (○) samples 8 and 10; and (●) samples 9 and 11.

Ammonolysis

Figure 4 shows the relation of strength retention, % BB, and increased carboxyl ends vs. elapsed time for the ammonolysis reaction at 150°C. With increasing time, strength decreases, % BB increases linearly, but carboxyl ends do not increase at all. % BB has linear correlation with the carboxyl ends as shown in Figure 6. A conventional explanation concerning the mechanism of aminolysis, which also is applicable for ammonolysis, is as follows¹⁵



This mechanism, however, can not explain the dependency of carboxyl ends on ammonolysis. Therefore, it is deduced that the ammonolysis reaction consists of a two-step reaction, i.e., production of a water molecule by the neutralization reaction of free carboxyl group with ammonia, and formation of a carboxyl end group from the hydrolytic scission reaction of an ester linkage by the newly formed water molecule catalyzed by ammonia as the base catalyst according to the following scheme:



The increase of carboxyl ends was reported even in the case of aminolysis of PET in aqueous solution.^{16,17} Considering these results, one cannot understand the aminolysis of PET according to Arnett's explanation.¹⁵

Figure 7 shows the relation between % BB and elapsed time at various temperatures. From these results, the activation energy of ammonolysis was determined as 12.5 kcal/mol which is almost half that of hydrolysis. One can understand that the existence of ammonia (amine) which acts as catalyst reduces the activation energy of hydrolysis in step 2. As a result, % BB can be expressed by the following equation

$$\% \text{ BB} = 1.91 \times 10^4 \exp(-6.31 \times 10^3/T) \cdot C_i \cdot t \quad (8)$$

where T is the reaction temperature (K), C_i represents carboxyl ends (eq/10⁶ g), and t is elapsed time (h).

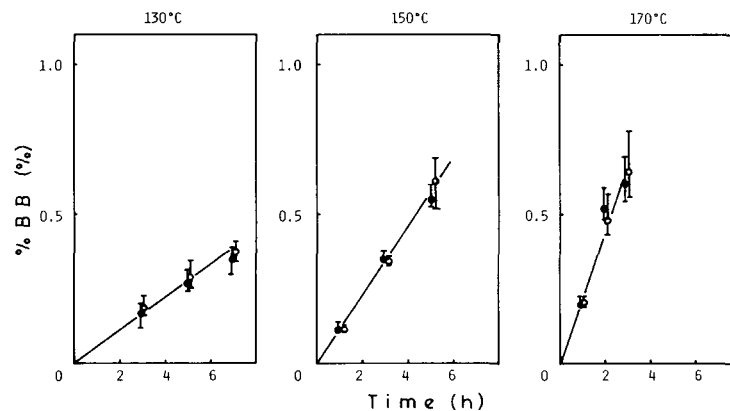


Figure 7 Relation between time elapsed and % BB at various temperatures. (○) sample 8; and (●) sample 9.

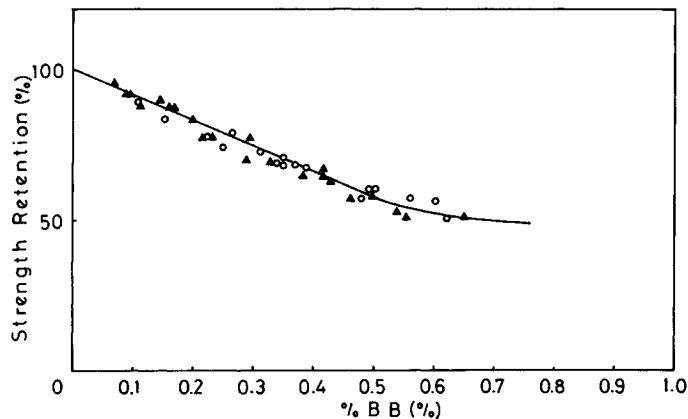


Figure 8 Relation between % BB and strength retention. (○) hydrolysis; and (▲) ammonolysis.

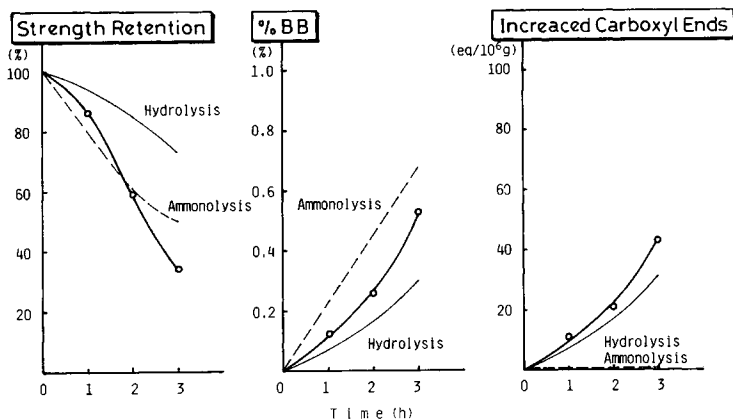


Figure 9 Relations of strength retention (a), % BB (b), and increased carboxyl ends (c) versus elapsed time of vulcanization at 170°C for PET tire cords embedded in rubber. (—) hydrolysis at 170°C; (---) ammonolysis at 170°C; and (—○—) vulcanization at 170°C.

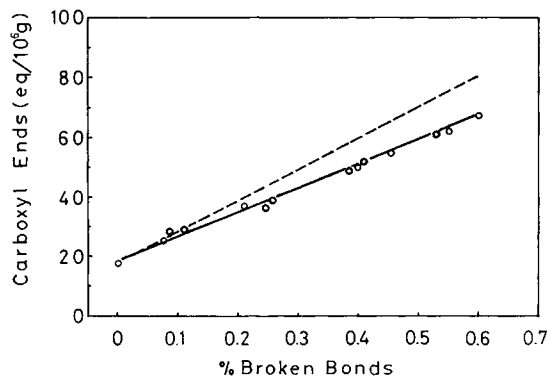


Figure 10 Relation between % BB and carboxyl ends of sample 12 embedded in rubber after vulcanization for different times at 170°C.

Chemical Degradation and Mechanical Properties

Many reports concerned with fatigue of tire cord discuss the relation between strength retention and elapse of time or cycles of strain.^{2,3} In order to clarify the mechanism of fatigue, one should consider chemical degradation such as chain scission. In the case of static degradation mentioned above, the strength retention has a linear correlation with % BB until decreasing to 50% as shown in Figure 8. Below 50% of strength retention, strength loss levels off despite continuing chain scission. As the degradation proceeds to such levels, the probability of chain scission of molecules which do not affect the strength of fibers increases.

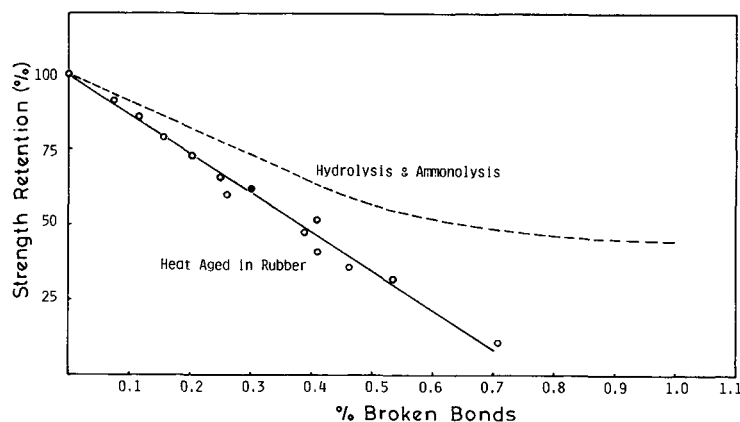


Figure 11 Relation between % BB and strength retention of PET tire cords. (---) hydrolysis and ammonolysis; (○) sample 12 embedded in rubber after vulcanization at 170°C; and (●) PET tire cord embedded in bias tire after running (obtained by Takayama²⁰).

In-Rubber Degradation

A significant decrease in strength observed for PET tire cords embedded in rubber has been reported in terms of hydrolysis and aminolysis.⁴⁻⁷ The tire cord, however, embedded in rubber can not be easily extracted from rubber so the actual degradation of PET in rubber is still indeterminate. In order to clarify this phenomenon, the PET degraded in rubber was dissolved and recovered from composites for measurements in terms of IV and carboxyl ends. As shown in Figure 9, the characteristics of degradation in rubber are very similar to hydrolysis degradation. With increasing time, strength retention decreases, % BB increases, and carboxyl ends increase. The increase of carboxyl ends in particular can not be explained by Arnett's schema. The thin solid lines in Figure 8 show the case of hydrolysis calculated by eq. (6) and the thin broken lines show the case of ammonolysis calculated by eq. (8) at 170°C. Usually, rubber stock contains 0.1–0.5 wt % of moisture and the rubber stock used in this study has about 0.2 wt % of moisture before vulcanization. This amount of moisture can cause 110 eq/10⁶ g of broken bonds of ester linkage. It should be noted that the % BB for the heat aged in-rubber test is greater than for the hydrolysis in saturated steam despite the limitation in moisture amount. Therefore, amines are presumed to act as base catalysts for hydrolysis in rubber.

The relation between carboxyl ends and % BB is shown in Figure 10. The broken line shows the case of 100% hydrolysis. Results show that 80% of degradation in rubber is due to hydrolysis with the remainder due to aminolysis. This rate is affected to some extent by differences in rubber stock.¹⁸

Figure 11 shows the relation between % BB and strength retention. The open circles show the results from static degradation in rubber. It should be noted that the solid circle in Figure 11, which shows the actual degradation result of polyester cord on the shoulder of a 7.00-13-6PR bias tire, after running on an indoor tire test dynamometer with a test wheel drum,¹⁹ fell on the same line of static degradation in rubber.²⁰ According to these results, we can conclude that the strength retention of PET tire cords in rubber is strictly controlled by the rate of chain scission of PET fibers.

CONCLUSION

Chemical degradation of PET tire cords has been studied in terms of hydrolysis and aminolysis. In the case of thermal degradation of polyester in rubber, it was found that polyester degradation was caused by chemically induced chain scission such as hydrolysis catalyzed by amines.

According to the results of this paper, fatigue degradation of polyester tire cord in tire will also be caused by amine catalyzed hydrolysis. In order to confirm such results, further evidence of hydrolytic fatigue in tires, such as samples from fatigue tests, are needed.

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