

Reinforcement Mechanism of Polyester-Fiber-Reinforced Rubber—A Model Study

GI XUE, JACK L. KOENIG, DONALD D. WHEELER,* and HATSUO ISHIDA, *Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

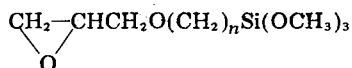
Synopsis

The reinforcement mechanism of polyester tire cord was studied by Fourier-transform infrared spectroscopy using various model compounds. Three model compounds representing the main chain of polyester and the terminal groups, namely carboxylic acid and hydroxyl groups, were used. Chemical reactions between these polyester models and an epoxy functional silane coupling agent were studied qualitatively as well as quantitatively. Among the many possible reactions, the reaction between the carboxylic acid and epoxy group was found to proceed readily. Kinetic studies of the major reactions also show quantitative differences in their activation energies as well as the rate constants. Based on the quantitative studies, we have estimated the expected rate of interfacial reaction at the heat treating temperature of polyester tire cord.

INTRODUCTION

The reinforcement mechanism of fiberglass reinforced plastics has been the subject of investigation for many years. The studies of the nature of the glass fiber-polymer interface provided fundamental scientific information.¹⁻³ Progress in elucidation of the molecular structure of the complex interface has been noteworthy.

In the case of silane-finished polyester-fiber-reinforced rubber, both the fiber and the matrix are organic compounds. The molecular structure of the interface is expected to be different from that of glass fiber-resin matrix interface. The treatment of organic fibers with silane coupling agents has proven effective in increasing the retention of strength of composite materials. Fusco found that a vinyl-containing silane would greatly increase the modulus and tensile strength of ethylene-propylene elastomers.⁴ Ragep et al.⁵ reported that polyglycidyl ethers would increase the adhesion of the polyester fiber and rubber matrix. Further study⁶ showed that the poly(ethylene terephthalate) (PET) fiber could be finished by the epoxy silane having the chemical formula



where $n = 2-5$, among which γ -glycidoxypropyltrimethoxysilane (γ -GPS) is the typical one. This technique could avoid some processing problems and eliminate the need for the isocyanate dip in the time of processing. Although much work has been done on the modification of adhesion of organic fiber to rubber, none has shown the chemical structure of the interface.

* Fibers and Plastics Company, Allied Corporation, Richmond, Virginia 23201.

Ranney and Pagano studied the significance of the functionality of the silane coupling agent in the modification of the filler-rubber composites by the measurement of their tensile strengths.⁷ They pointed out that the actual interaction of silane in elastomer formulation is very complex and has not been established. The investigation of the nature of the organic fiber/matrix interface on the molecular level is a new subject in the studies of composite materials. At present, no theory provides a satisfactory explanation of the adhesion-promoting action at the interface.

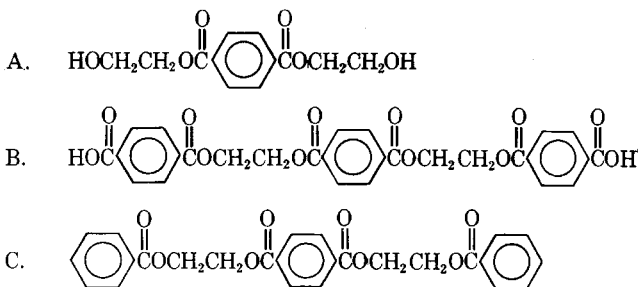
It is our interest to investigate the molecular structure of the PET tire cord/rubber matrix interface by means of Fourier transform infrared and Raman spectroscopy. Emphasis is placed on the determination of the type and number of chemical bonds formed at the PET fiber/silane interface and at the silane/overcoating layer interface. It is possible that the terminal OH or COOH groups of PET on the fiber surface chemically react with the epoxy group of the silane. Model compounds have been used in order to simplify the study.

Reported in this paper are the syntheses of the PET model compounds with various terminal groups and reactions between the PET model compounds and γ -GPS. The kinetics of the various reactions have been studied in an attempt to determine quantitatively which process predominates the interfacial reactions of the composite.

EXPERIMENTAL

Synthesis of Model Compounds

Three model compounds of PET were synthesized for studying possible chemical reactions between PET fiber and silane coupling agent, and these are shown below as compounds A, B, and C.



The compounds A and B model the terminal groups of polyester used for a tire cord and the compound C represents the main chain of polyester without influence of chemically reactive terminal groups.

Compound A was synthesized and supplied by Allied Corporation. Compound B was prepared by acylation of compound A with terephthaloyl chloride. Compound A (2.54 g, 0.10 mol) was slowly added (with stirring) to terephthaloyl chloride (20.3 g, 1.00 mol) dissolved in toluene. The mixture was kept boiling after the reaction had subsided; the excess terephthaloyl chloride was evaporated under vacuum at 0.1 mm Hg and 110°C. The residue was dissolved in a mixture

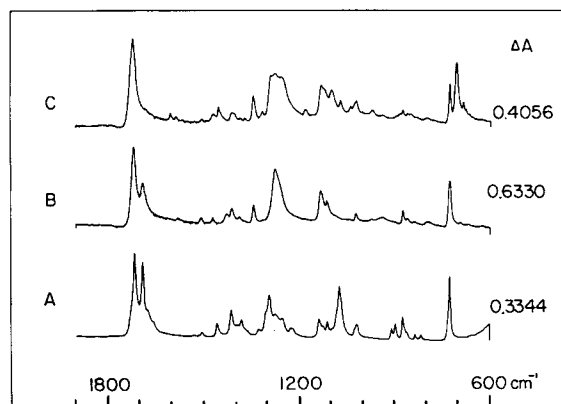
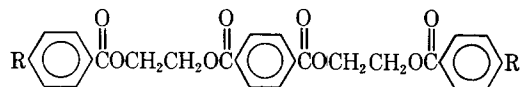


Fig. 1. Infrared spectra of three model compounds of PET: (A) the model compound A with OH terminal group; (B) the model compound B with COOH terminal group; (C) the model compound C without active terminal group.

of 30.0 g of THF, 20.0 g of H₂O, and 0.5 g of Na₂CO₃. Acetic acid was added to the solution until it became acidic. The precipitate formed is mainly model compound B with a small amount of terephthalic acid. The precipitate was filtered and recrystallized five times from a solution of 30 g of THF and 6 g of H₂O. The pure compound B was obtained, which had a mp of 274–277°C. A British patent reported that the same dicarboxylic acid was prepared by oxidizing the R groups in the following formula to carboxylic acid:

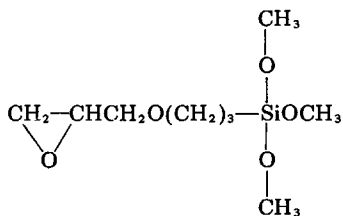


Repeated recrystallization from the mixture of esters gave a product of mp 270–277°C.^{8,9}

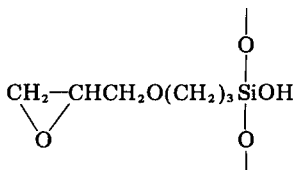
Compound C was prepared by the acylation of compound A with benzoyl chloride. Compound A (3 g) was slowly added to a solution of 4 mL of benzoyl chloride in 15 mL of anhydrous pyridine with stirring. After the initial reaction had subsided, the mixture was warmed up for 1 min and poured, with vigorous stirring, into 100 mL of water. The precipitate was allowed to settle, and the supernatant liquid was decanted. The residue was dissolved in acetone. A solution with 5% Na₂CO₃ was added. The precipitate was removed by filtration and dissolved in acetone retreated by Na₂CO₃ solution. The initial product was recrystallized from acetone. Compound C with mp 102–105°C was obtained. The infrared spectra from 600 cm⁻¹ to 1900 cm⁻¹ of model compounds A, B, and C are shown in Figure 1.

Sample Preparation for Spectroscopic Measurements

Using model compounds A, B, and C, several possible reactions between the functional groups of PET and a coupling agent can be studied. The coupling agent, γ -glycidoxypropyltrimethoxysilane, was used; the chemical structure is shown below:



The spectrum of the epoxy silane from 600 cm^{-1} to 1900 cm^{-1} is shown as spectrum A in Figure 2. After hydrolyzing in water, the silane hydrolyzate contains a silanol group:



The spectrum of the silane hydrolyzate is shown as spectrum B in Figure 2. The structure of the reactants and products were observed by Fourier-transform infrared spectroscopy (FT-IR). The several possible combinations of reactants were set as six different systems. IR samples were withdrawn from the reaction vessels before and after the reaction for each system. The samples were first dissolved in dimethyl acetamide, placed on the surface of KBr plates, and then the solvent was evaporated under vacuum at room temperature.

In order to compare the relative rates of reactions, four of these main systems were chosen, and the kinetics of the reactions were studied. The intensities of some specific bands in the infrared spectra were measured in order to determine the concentration of the reactants at various reaction times, or the chemical titration method was used.

A Fourier transform infrared spectrophotometer (Digilab FTS-14) was used at a resolution of 2 cm^{-1} with coaddition of 200 scans. The spectra are shown in absorbance mode. The difference between the maximum and minimum absorbance is designated as ΔA and shown in absorbance units.

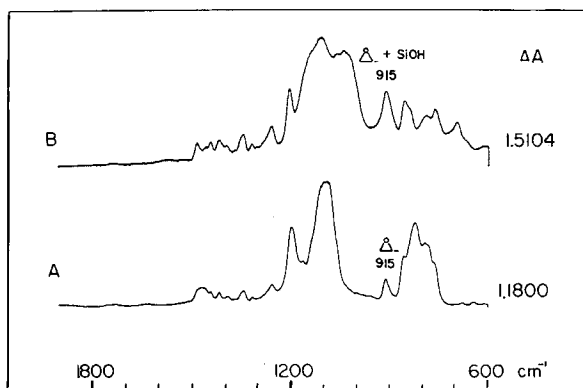


Fig. 2. Infrared spectra of the silane coupling agent: (A) γ -glycidoxypropyltrimethoxysilane; (B) the silane hydrolyzate.

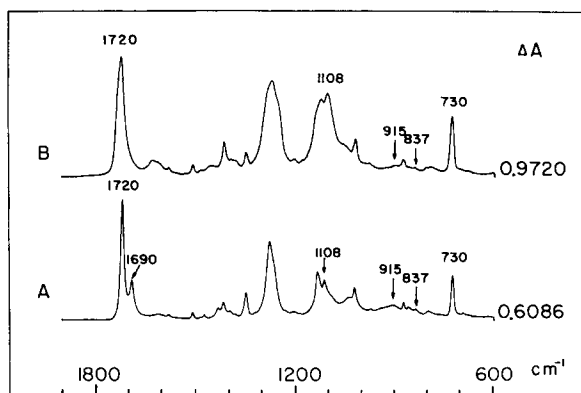


Fig. 3. Infrared spectra of system 1: (A) the mixture of model compound B with COOH terminal group and γ -glycidoxypropyltrimethoxysilane before reaction; (B) the reaction products.

RESULTS

Observation of Various Reactions

System 1: The Carboxylic Acid-Terminated Model Compound B and the Epoxy Silane

The spectrum of the initial mixture of model compound B and the epoxy silane is designated as the spectrum A in Figure 3. Spectrum B is obtained from the reaction products. After the reaction at 100°C for 0.5 h, there was a decrease in the intensity of the bands at 915 cm^{-1} and 837 cm^{-1} , which are assigned to the terminal epoxy ring. The intensity of the C—O—C antisymmetric stretching mode in the aryl ester at 1108 cm^{-1} increased. In spectrum A, there are two carbonyl modes due to the ester and carboxylic acid. The band at 1720 cm^{-1} is assigned to the carbonyl in the ester group; the band at 1690 cm^{-1} is assigned to the carbonyl in the carboxylic acid group. After reaction, the band at 1690 cm^{-1} almost disappeared, and the intensity of the 1720 cm^{-1} band relative to

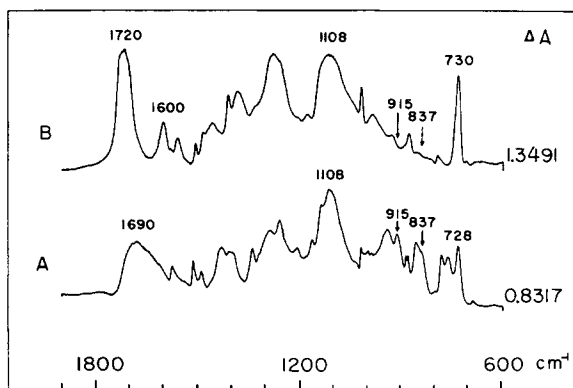


Fig. 4. Infrared spectra of system 2: (A) the mixture of terephthalic acid and 1,4-butanediol diglycidyl ether before reaction; (B) the reaction products.

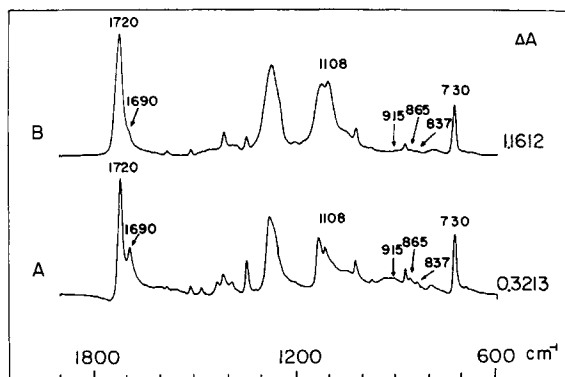
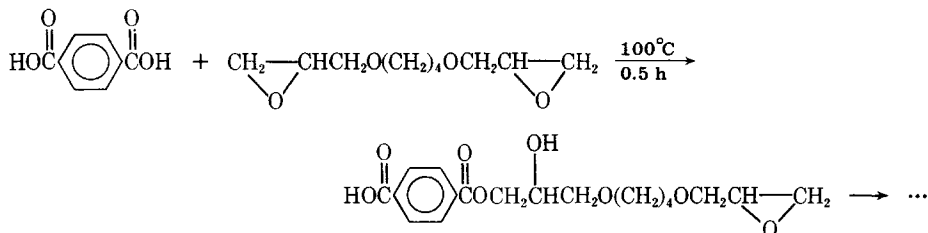


Fig. 5. Infrared spectra of system 3: (A) the mixture before reaction of the silane hydrolyzate and model compound B with COOH terminal group; (B) the reaction products.

the benzene ring mode at 730 cm^{-1} increased. Accordingly, the reaction between the carboxylic acid and the epoxy group is confirmed.

System 2: Terephthalic Acid and 1,4-Butanediol Diglycidyl Ether

This system was chosen to study the chemical reactions without being influenced by the silanol groups. In Figure 4, the spectra obtained for the reaction between the carboxylic acid and the epoxy group are shown. The spectrum of the initial reactants mixture is designated as spectrum A, and that of the reaction products is designated as spectrum B. In spectrum B the disappearance of the band at 915 cm^{-1} confirmed the ring opening of the epoxy group. The carbonyl band at 1690 cm^{-1} in spectrum A disappeared, and a band at 1720 cm^{-1} appeared in spectrum B indicating the esterification of the carboxylic acid group. Thus the following reaction is occurring:



The new band at 1600 cm^{-1} appears in spectrum B which is assigned to the ring stretching mode of the benzene ring. Terephthalic acid has a D_{2h} symmetry, and the ring stretching at 1600 cm^{-1} is inactive in the infrared spectrum. After the reaction, the D_{2h} symmetry is lost causing the appearance of the C=C stretching mode of the benzene ring.

System 3: The Carboxylic Acid-Terminated Model Compound B and the Hydrolyzate of the Epoxy Silane

In Figure 5 the spectra A and B were obtained from the reactants and the reaction products, after 0.5 h at 100°C , respectively. The spectrum B shows the intensity decrease of the epoxy bands at 915 cm^{-1} and 837 cm^{-1} and of the car-

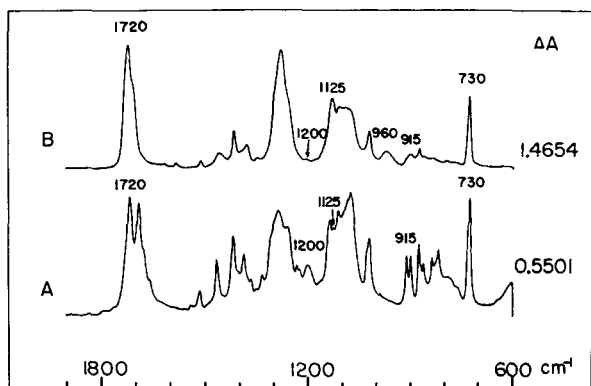
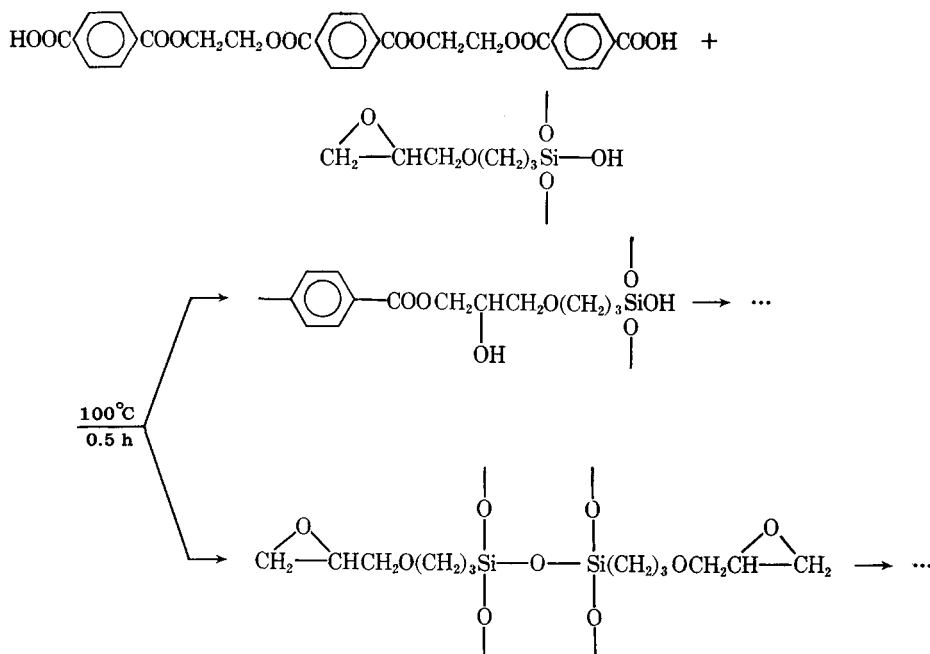


Fig. 6. Infrared spectra of system 4: (A) the mixture of model compound A with OH terminal group and γ -glycidoxypropyltrimethoxysilane before reaction; (B) the reaction products.

boxylic acid at 1690 cm^{-1} . It shows the intensity increase of C—O—C asymmetric stretching mode in the aryl ester at 1108 cm^{-1} . All of these observations confirm the reaction between the carboxylic acid and the epoxy groups. No evidence was obtained concerning the formation of the terephthalate ester group between the carboxylic acid and the silanol groups. The number of silanol groups, which give rise to a band at 865 cm^{-1} , decreased due to the condensation reaction to form siloxane groups. Thus,



System 4: The Hydroxyl-Terminated Model Compound A and the Epoxy Silane

In Figure 6 the spectrum of the initial physical mixture of crystalline model compound A and γ -glycidoxypropyltrimethoxysilane is designated as spectrum

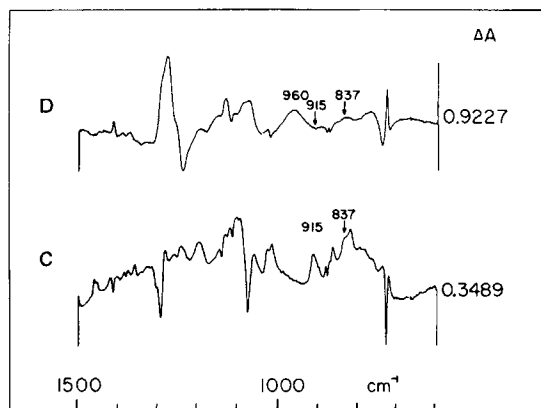
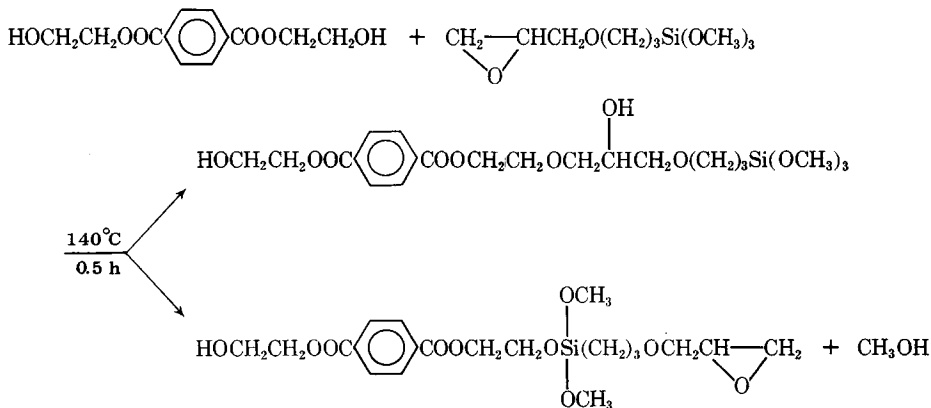


Fig. 7. Infrared spectra of system 4: (C) the difference spectrum between the spectrum A in Figure 6 and the spectrum of crystalline model compound A; (D) the difference spectrum between the spectrum B in Figure 6 and the spectrum of amorphous model compound A.

A, whereas spectrum B is the mixture of the reaction products after 0.5 h at 140°C . Spectrum B shows a new band at 960 cm^{-1} , which is assigned to the C—C—O—Si stretching mode.¹⁰ The intensity of the methoxy band at 1200 cm^{-1} decreased after reaction. The band of CH out-of-plane bending mode at 730 cm^{-1} was used as the internal thickness band. The C=O mode shows a doublet at 1720 cm^{-1} and 1690 cm^{-1} due to crystal field splitting. The mixture became homogeneous after the reaction, and the carbonyl band became a singlet at 1720 cm^{-1} . Since the band of the epoxy group at 915 cm^{-1} overlaps with other bands of the model compound A, digital subtraction is necessary to observe the relative change of the 915 cm^{-1} band. Shown as spectrum C in Figure 7 is the difference spectrum between the spectrum A in Figure 6 and the spectrum of pure model compound in the crystalline state. Spectrum D is the difference spectrum between the spectrum B in Figure 6 and the spectrum of the model compound A in the amorphous state. Judging from the decrease of the epoxy band at 915 cm^{-1} and the increase of the 960 cm^{-1} band due to the C—C—O—Si group, two reactions are simultaneously occurring:



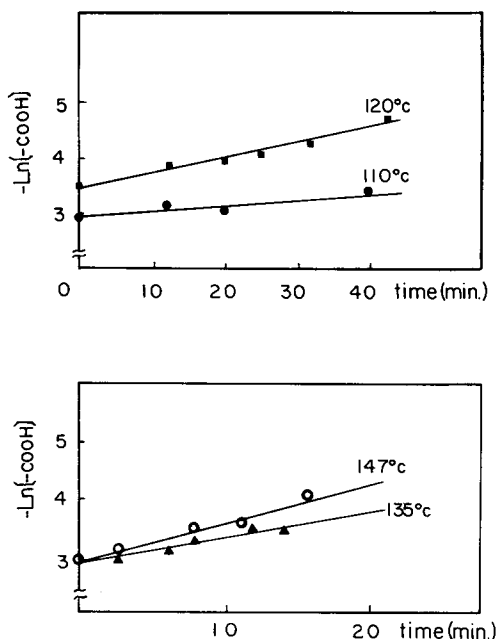


Fig. 10. Plot of $-\ln[-\text{COOH}]$ vs. time for reaction between $[-\text{COOH}]$ group and $[\dot{\Delta}_-]$ group.

$$-\frac{\partial[-\text{COOH}]}{\partial t} = k_2[\dot{\Delta}_-][-\text{COOH}]$$

and since $[\dot{\Delta}_-]_0 \gg [-\text{COOH}]_0$ we can approximate $[\dot{\Delta}_-] \approx [\dot{\Delta}_-]_0$ yielding

$$-\frac{\partial[-\text{COOH}]}{\partial t} = k_2[\dot{\Delta}_-][-\text{COOH}] = k_1[-\text{COOH}]$$

where $[\dot{\Delta}_-]_0$ is the initial concentration of the epoxy group, $[\dot{\Delta}_-]$ is the concentration of the epoxy group during reaction, $[-\text{COOH}]_0$ is the initial concentration of the carboxylic acid group, $[-\text{COOH}]$ is the concentration of the carboxylic acid group during the reaction, and k_1 and k_2 are the first-order and second-order reaction rate constants, respectively. Under the above conditions, the kinetic equation changes to first order:

$$-\ln[-\text{COOH}] = k_1t + c, \quad \text{where } k_1 = k_2[\dot{\Delta}_-]_0$$

Thus plotting $-\ln[-\text{COOH}]$ vs. time t , straight lines for the various reaction

TABLE I
Rate Constants for the Reaction of Model Compound B and 1,4-Butanediol Diglycidyl Ether at Different Temperatures

	Temperature (°C)				
	110	120	135	140	147
Rate constant (mol/L) ⁻¹ · min ⁻¹	3.3 × 10 ⁻²	4.9 × 10 ⁻²	8.1 × 10 ⁻²	9.2 × 10 ⁻²	9.5 × 10 ⁻²

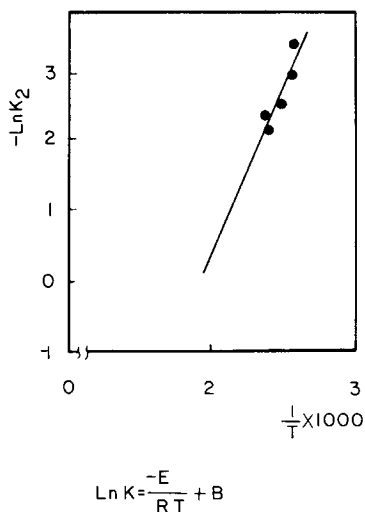


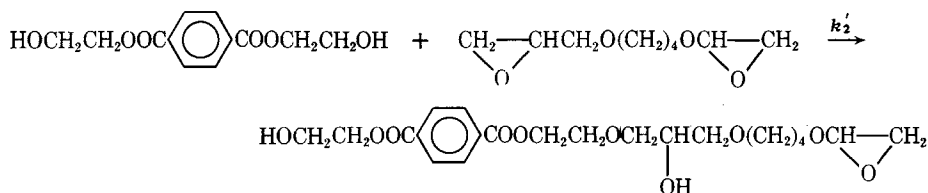
Fig. 11. The Arrhenius plot of $-\ln k_2$ vs. $1/T$ for the reaction between $[-\text{COOH}]$ group and $[\Delta]$ group.

temperatures were obtained, as shown in Figure 10. From the slope, k_1 can be calculated and, then, the second-order constants k_2 , as shown in Table I.

Figure 11 shows the Arrhenius plot from which the activation energy was calculated to be 10.7 kcal/mol. The rate constant at the application temperature 250°C could be estimated, assuming that the same reaction mechanism holds up to 250°C.

We determined the reaction rate constant between the hydroxyl group and the epoxy group using the model compound A and 1,4-butanediol diglycidyl ether.

The main reaction taking place between the terminal hydroxyl group and epoxy is



It is a second-order reaction whose rate constant is designated as k'_2 . The product contains a secondary hydroxyl group which may further react with the epoxy group. Due to steric effects, the secondary hydroxyl group is expected to have lower reactivity than the primary one. Since the concentration of the secondary hydroxyl group is low initially, only the primary reaction was considered. The reaction rate in terms of the concentration of the epoxy group is

$$-\frac{\partial[\Delta_-]}{\partial t} = k'_2[\text{OH}][\Delta_-]$$

The initial concentration of the hydroxyl group was the same as the epoxy group. At low conversions, they are considered to be approximately equal, thus

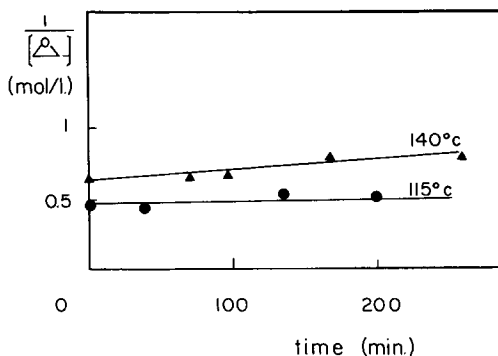


Fig. 12. Plot of $1/[\Delta_-]$ vs. time for reaction between $[-OH]$ group and $[\Delta_-]$ group.

$$[\Delta_-] = [OH] \quad \text{and} \quad -\frac{\partial[\Delta_-]}{\partial t} = k'_2[OH][\Delta_-]$$

Integrating yields $= k'_2[\Delta_-]^2$,

$$1/[\Delta_-] = k'_2t + C$$

Therefore, plotting $1/[\Delta_-]$ versus time t , straight lines for various reaction temperatures were obtained as shown in Figure 12. From the slope of the lines, the rate constants were obtained:

at 150°C $k'_2 = 9.4 \times 10^{-4} \text{ (mol/L)}^{-1} \cdot \text{min}^{-1}$

at 140°C $k'_2 = 5.6 \times 10^{-4} \text{ (mol/L)}^{-1} \cdot \text{min}^{-1}$

at 115°C $k'_2 = 1.3 \times 10^{-4} \text{ (mol/L)}^{-1} \cdot \text{min}^{-1}$

From the Arrhenius equation $k = Ae^{-E/RT}$, the activation energy was calculated as 18.6 kcal/mol. Table II shows the kinetic results and prediction of rates at the application temperatures used in tire cord heat treating.

In addition, the rate constants of the reactions between the $-COOH$ or $-OH$ and the

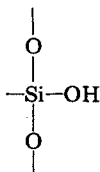


TABLE II
The Prediction from the Kinetic Study

System	Activation energy (kcal/mol)	Half-life of $-OH$ or $-COOH$ group at 250°C (s)	90% conversion time of $-OH$ or $-COOH$ at 250°C (s)
$-OH$ group and 1,4-butane-diglycidyl ether	18.6	481	1525
$-COOH$ group and 1,4-butane-diglycidyl ether	10.7	14	46

were studied, and the rate constants were found to be much smaller than that of the reaction between the —OH group and the epoxy group.

CONCLUSION

Based on the above findings, one can conclude that the studies using model compounds are useful in characterizing the reactions at the tire cord/rubber interface. The carboxylic acid and the hydroxyl end groups of PET can react with the epoxy group, and the hydroxyl group can react with the silanol. At the interface, the silane hydrolyzate may condense to form siloxane. Through kinetic studies, we found that the reaction rate of the terminal carboxylic acid with the epoxy group is much faster than the other reactions except for silanol selfcondensation, and we estimated the curing time at the application temperature to be less than 1 min.

It is also expected that increasing the number of carboxylic acid groups of PET fibers and the epoxy silane concentration will increase the number of chemical bonds at the interface.

The authors gratefully acknowledge the financial support from The Fibers and Plastics Company of Allied Corporation.

References

1. H. Ishida and J. L. Koenig, *Polym. Eng. Sci.*, **18**, 128 (1978).
2. R. T. Schwartz and H. S. Schwartz, *Fundamental Aspects of Fiber Reinforced Plastic Composites*, Wiley-Interscience, New York, 1968.
3. H. Ishida and J. L. Koenig, *Polym. Sci. Phys.*, **17**, 615 (1979).
4. J. V. Fusco, *Rubber World*, **48**, 147 (1966).
5. G. K. Rager and N. C. Duram, U.S. Pat. 3,729,336 (1973).
6. R. M. Marshal and K. L. Dardoutas, U.S. Pat. 3,730,892 (1973).
7. M. W. Ranney and C. A. Pagano, *Rubber Chem. Technol.*, **44**, 1080 (1971).
8. Imperial Chemical Industries Ltd., Br. Pat. 744,180 (1962).
9. J. E. McIntyre, Br. Pat. 978,660 (1962).
10. A. Lee Smith, *Analysis of Silicones*, Wiley-Interscience, New York, 1974, Chap. 10, p. 271.

Received January 18, 1983

Accepted March 3, 1983