Reaction During Cure of a Blocked Isocyanate–Epoxy Resin Adhesive

ROY E. HARTZ, *Uniroyal, Inc., Fiber and Textile Division, Winnboro, South Carolina 29180*

Synopsis

Model compound reactions of isocyanate sources with alcohols and an epoxy resin indicated that the major reaction product from the phenol-blocked methylenebisphenylene diisocyanate and epoxy resin-based adhesive dip for poly(ethylene terephthalate) cord was a polyurethane. A significant portion of the hydroxyl groups required for the reaction were formed by ring opening of the epoxide groups of the resin. The reaction rate for the unblocking of the isocyanate source was inhibited in the presence of polyester yarn finishes containing sulfated esters of fatty acids. Also, compounds containing carboxylic acid groups and sulfonic acid groups inhibited the unblocking step. Amines and their salts catalyzed the unblocking step. A mechanism for the polyurethane adhesive–polyester bond based upon physical interaction is postulated. The presence of certain nonsulfated ester finishes permitted good wetting of the polyester surface and penetration of the adhesive into the polyester. By contrast, sulfated ester finishes result in poor wetting and penetration by the adhesive on the polyester. The latter finishes resulted in a weak boundary layer between the adhesive and the cord.

INTRODUCTION

The bonding of poly(ethylene terephthalate) cord to a rubber requires application of an intermediate adhesive layer. A number of single-dip and double-dip systems have been reported as adhesives for polyester.[1-5] This paper deals only with the two-dip system developed by Shoaf.[3] This first dip is prepared by mixing a ball-milled phenol-blocked methylenebisphenylene diisocyanate, an epoxy resin, a wetting agent, and water. The second dip consists of a standard resorcinol–formaldehyde–latex (RFL) system.

Yarn suppliers apply a lubricant, called a finish, to their material as a processing aid. One must consider this finish as one of the important elements in the composite structure consisting of fiber–finish–adhesive–rubber. Chemicals used as finishes for man-made fibers include polyglycerol esters, sulfated esters of fatty acids, and alkanolamides.[6]

This paper will elucidate, based upon studies with model compounds, the significant reactions during the cure of the blocked isocyanate–epoxy resin-based dip. The effects of yarn finish on the wettability, compatibility, and penetration of the isocyanate–epoxy system are discusssed. Measurements on the rate of reaction in the presence of various yarn finishes and compounds which contain particular functional groups found in finish compositions are interpreted. Finally, a mechanism based upon physical interaction between the adhesive and the polyester is postulated.

735

EXPERIMENTAL

Materials

Phenol-blocked methylenebisphenylene diisocyanate was received from du Pont. Hereafter, the material will be referred to by its tradename, Hylene MP.

Methylenebis-*p*-phenylene diisocyanate (MDI) was obtained from Upjohn as Isonate 125 MF.

Toluene diisocyanate dimer was received from Mobay Chemical as Desmodur TT. It is referred to henceforth as TDID.

Epon 812, epoxy resin, was obtained from Shell Oil Company.

Ethylene glycol monolaurate and propylene glycol monolaurate were received from Pfautz and Bauer, Inc.

Decyl alcohol was obtained from Fisher Scientific Company.

Equipment and Procedure for Tube Runs

A 1-ft^3 block with holes bored for insertion of glass tubes was used as the heating oven. The block was preheated overnight with a rheostat control to obtain an equilibrium test temperature (by thermometer). Pyrex tubes, 8 in., were charged with the test chemicals. For example, 4.8 g (0.011 mole) Hylene MP and 3.4 g (0.011 mole) Epon 812 were mixed and charged into a tube. The tubes were covered with a rubber stopper with two pieces of glass tubing attached. One piece of tubing was connected to a Dry Ice–acetone-cooled condensation trap. After a 30- to 60-sec purge with argon, the glass tube was inserted into the preheated block with argon purge continued for the time of heating at the designated temperature. At the completion of the desired residence time, the tube was removed from the block, purged 30 sec with argon and the contents of the tube transferred to a beaker for separation and characterization. Reaction products were isolated by filtration, column chromatography, or distillation, based upon the physical state of the resulting mixture.

The same equipment was used for determination of the effect of finish or functional compounds on reaction rates. Tubes were charged with 32 g cyclohexanone solvent, 2.4 g (0.006 mole) Hylene MP (or 1.4 g, 0.006 mole) methylenebis-*p*-phenylene diisocyanate), 1.8 g (0.006 mole) Epon 812, and variable levels of finish or functional compound. After mixing to dissolve the Hylene MP in cyclohexanone, the tubes were inserted into the previously described preheated block (at 150°C). The reaction mixtures were followed until the first indication of cloudiness and formation of precipitate occurred. The solutions had reached temperatures of 125° to 130° by this time. In order to obtain sufficient precipitate for characterization, the heating at the same solution temperature was continued for an additional 15 to 20 min. The tubes were removed from the block and cooled to room temperature (ca. 25°). The solid precipitate was isolated by filtration, dried, and characterized. The cyclohexanone solution was then evaporated to dryness and the residue was isolated. Infrared spectra and melting point confirmed unreacted Epon 812 and Hylene MP as the components of the residues.

Procedure for Cure of Isocyanate–Epoxy Films

In the casting of films of the epoxy and isocyanate source a 3 in. × 8 in. × $1/_8$ in. Pyrex slide coated with a Teflon film to prevent sticking was used. The desired chemicals in equal molar charges were premixed in a beaker and then

poured on the glass plate. The films were cured in a hot air oven (Blue M). After cooling, the films were scraped from the plate and characterized.

Procedure for Finish Effects on Wettability, Compatibility, and Penetration

A 6 in.² piece of poly(ethylene terephthalate) [Mylar] film was mounted in a metal frame to prevent heat shrinkage of the polyester. The surface of the Mylar film was cleaned with a Kimwipe to remove dust particles. A thin layer of finish was applied. The film with finish was heated for 25 sec at 230°C to partially volatilize the finish (analogous to partial vaporization of finish during the drawing processes used by yarn suppliers). The dip, which was applied with an eyedropper, was spread by the use of a glass rod as a draw-down blade and then dried for 60 sec at 230°C. The film was cooled and the adhesive reaction product examined for peelability and penetration into the polyester.

RESULTS AND DISCUSSION

Isocyanate Dimer–Alcohol Model Compound Reactions

The Shell Epon 812 epoxy resin is known to contain hydroxyl and epoxide functional groups. The reaction and kinetics of hydroxyl with isocyanates is well defined[7] and can occur in the absence of catalyst. Reactions of epoxide groups with isocyanates require the presence of catalysts including lithium bromide[8] and tetraalkylammonium salts.[9] The reaction of the hydroxyl group was thus predicted to be most important during a drying and curing operation. Decyl alcohol, ethylene glycol monolaurate, and propylene glycol monolaurate were chosen as model compounds for the hydroxyl functionality.

Initially TDID was chosen as the isocyanate source to avoid potential side reactions of phenol formed by unblocking of the Hylene MP. Infrared analyses confirmed that the major product of the TDID reaction with ethylene glycol monolaurate, propylene glycol monolaurate, and decyl alcohol was the corresponding carbamate. A sharp band at 1700 cm^{-1} for the carbamate was present in all spectra. The carbamate products were very high-melting solids (Table I). In all trials side reactions, which resulted in formation of carbodiimides, ureas, and isocyanurates, were confirmed by infrared (Table II, Fig. 1). The discrepancy between the calculated value for a pure carbamate reaction product and the found value for elemental analysis was explained by the side reaction products.

Fig. 1. Infrared spectrum of TDID- decyl alcohol reaction product. Potassium bromide pellet, 1.6 mg/cm².
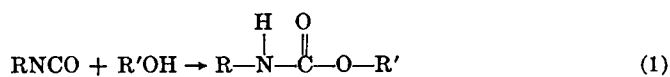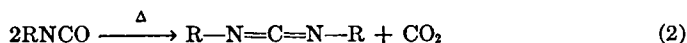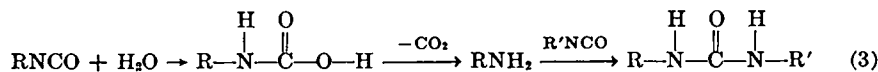
TABLE I
TDID Reactions[a]

Hydroxyl source	OH, mole	TDID, mole	mp, °C	Elemental analysis Calcd.	Found
Decyl alcohol	0.023	0.015	260–265	C, 64.1%	68.8%
				H, 10.4%	7.3%
				N, 9.4%	10.1%
Ethylene glycol monolaurate	0.023	0.015	240–245	C, 66.5%	67.6%
				H, 8.1%	8.7%
				N, 6.7%	6.7%
Propylene glycol monolaurate	0.023	0.015	210–215		

[a] OH = Hydroxyl.

TABLE II
Infrared Bands

Band	Probable band origin
2140 cm^{-1}	carbodiimide
1780 cm^{-1}	uretidenedione C=O stretch
1738 cm^{-1}	ester C=O stretch
1700 cm^{-1}	urethane C=O stretch
1645 cm^{-1}	urea C=O stretch
1534 cm^{-1}	urethane carbamate (amide II band)
1420 cm^{-1}	isocyanurate ring
1400 cm^{-1}	uretidenedione ring
1220 cm^{-1}	urethane stretch of C=O combined with N—H (amide III)

The formation of the carbamate and the side products are illustrated in eqs. (1) through (4), respectively:

Carbamate

$$\text{RNCO} + \text{R'OH} \rightarrow \text{R—}\overset{\text{H}}{\underset{}{\text{N}}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—R'} \tag{1}$$

Carbodiimide

$$2\text{RNCO} \xrightarrow{\Delta} \text{R—N=C=N—R} + \text{CO}_2 \tag{2}$$

Urea

$$\text{RNCO} + \text{H}_2\text{O} \rightarrow \text{R—}\overset{\text{H}}{\text{N}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—H} \xrightarrow{-\text{CO}_2} \text{RNH}_2 \xrightarrow{R'NCO} \text{R—}\overset{\text{H}}{\text{N}}\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—}\overset{\text{H}}{\text{N}}\text{—R'} \tag{3}$$

Isocyanurate

$$3\text{RNCO} \rightarrow \tag{4}$$

TABLE III
Isocyanate-Epoxy Reaction

Run	Isocyanate source	Time,[a] min	Product comments
A	MDI	5	swells in DMF[b] and HFIP[c]
B	MDI	8	insoluble in DMF, charred and brittle
C	MDI	10	insoluble in DMF, charred and brittle
D	Hylene MP	5	soluble in DMF
E	Hylene MP	8	insoluble in DMF
F	Hylene MP	10	insoluble in DMF and HFIP

[a] At 210°C.
[b] N,N-Dimethylformamide.
[c] Hexafluoroisopropanol.

Blocked Isocyanate–Epoxy Resin Cure Reactions

The mixture of Hylene MP and Epon 812 reacted vigorously at 230°C within 5 min with the formation of a rubbery crosslinked polymer which showed initial decomposition at 270°. The simplest structure for the reaction of an isocyanate and a 1,2-epoxide is a 2-oxazolidinone, which does not contain an N–H group, by eq. (5)[10]:

$$R\text{---}N\text{=}C\text{=}O \ + \ \underset{O}{H_2C\text{---}CH_2} \ \longrightarrow \ R\text{---}N \quad (5)$$

However, the infrared spectrum contained a band at 3300 cm^{-1} which indicates the hydrogen-bonded N–H of a carbamate or polyurethane.[11,12] A mechanism will be proposed later in this paper justifying formation of sufficient hydroxyls for polyurethane formation.

An indication of the rate of crosslinking for the epoxy–isocyanate reaction product was obtained from independent film studies (Table III). These studies indicated the initial formation of a soluble, low molecular weight polyurethane. After 5 min of reaction, the polyurethane became an insoluble, crosslinked product. The results, furthermore, indicated that within the normal drying times of the two dips and the cure time for a tire, a highly crosslinked material would be formed from the isocyanate and epoxy resin.

Finish Studies on Wetting and Compatibility

By the use of Mylar film, the effect of yarn finish on wettability, compatibility, and penetration into the polyester by the adhesive layer was determined. In the presence of finishes based upon nonsulfated esters, excellent wetting of the polyester was observed. The cured adhesive product was interdiffused into the Mylar and could not be readily stripped from the Mylar. However, a poor wetting of the polyester surface in the presence of sulfated finishes was noted. The cured polyurethane adhesive product prepared in the presence of sulfated finishes could be manually peeled from the Mylar.

Finish Effects on Epon 812–Hylene MP Cure

A solution-based system was chosen for the reaction of Hylene MP and Epon 812 in the presence of polyester yarn finishes. Solvents allow a more uniform heat transfer and a better method of observation of the reactions. The solvents for Hylene MP are limited in number and none has a boiling point above 160°C. Cyclohexanone and N,N-dimethylformamide are the only solvents whose boiling points are at least 150°. Cyclohexanone was chosen as a solvent for the studies.

In Table IV, an inhibition of the reaction of Hylene MP with Epon 812 is shown in the presence of sulfated esters of fatty acids as judged by the time of appearance of insoluble product and the total yield of insoluble product. The N,N-dimethylformamide- and cyclohexanone-insoluble polyurethane products had infrared spectra similar to Figure 2 and began to decompose with charring above 250° but did not melt by 350°.

The time to cloudiness (Fig. 3) was the first evidence that any reaction occurred in solution. A number of samples were stopped short by rapid cooling prior to the appearance of cloudiness. From Table V, we found that a short heating time at a maximum of 90° does not permit complete dissolving of Hylene MP and subsequently no polymerization. Hylene MP, mp 210°, was recovered in trials 1 and 4 of Table V. However, once the solution temperature reached 115°, unblocking of Hylene MP and polymerization with Epon 812 occurred.

TABLE IV
Isocyanate–Epoxy Reaction with Finish Present

Run no.	Finish class[a]	Finish,[b] g	Time to cloudiness, min	Total time, min	Ppt., g
1	None	—	10	15	1.0
2	NSE	0.04	10	15	1.0
3	NSE	0.08	10	15	1.1
4	SE	0.02	185	205	0.5
5	SE	0.04	195	260	0.6
6	SE	0.08	300	360	0.7

[a] NSE = Nonsulfated ester; SE = sulfated ester.
[b] g of finish per 0.006 mole Hylene MP, 0.006 mole Epon 812, 0.32 mole cyclohexanone.
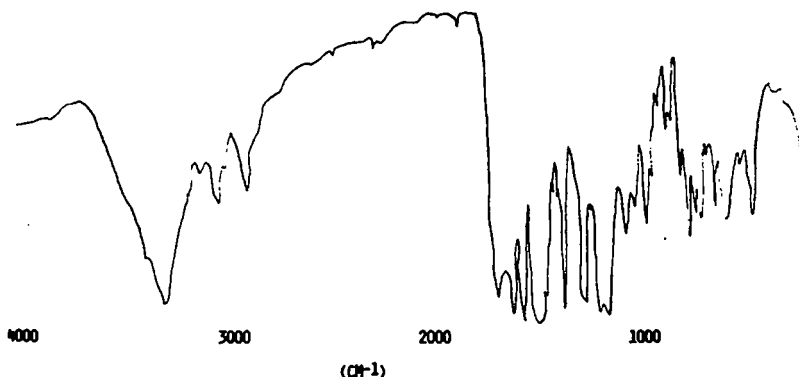

Fig. 2. Infrared spectrum of Hylene MP- Epon 812 reaction product. Potassium bromide pellet, 2 mg/cm².

TABLE V
Shortstopping Trials

Run no.	Finish[a,b]	Time, min	Solution T, °C	Isolated polymer, g
1	None	5	90	—
2	None	10	115	0.5
3	None	15[c]	135	0.7
4	NSE	5	88	—
5	NSE	10	116	0.5
6	NSE	15[c]	140	0.7
7	SE	60	140	0.2
8	SE	120	140	0.3
9	SE	180	140	0.7

[a] 0.04 g NSE finish; 0.02 g SE finish.
[b] g of finish per 0.006 mole Hylene MP, 0.006 mole Epon 812, 0.32 mole cyclohexanone.
[c] At these times, the solutions began to turn cloudy.
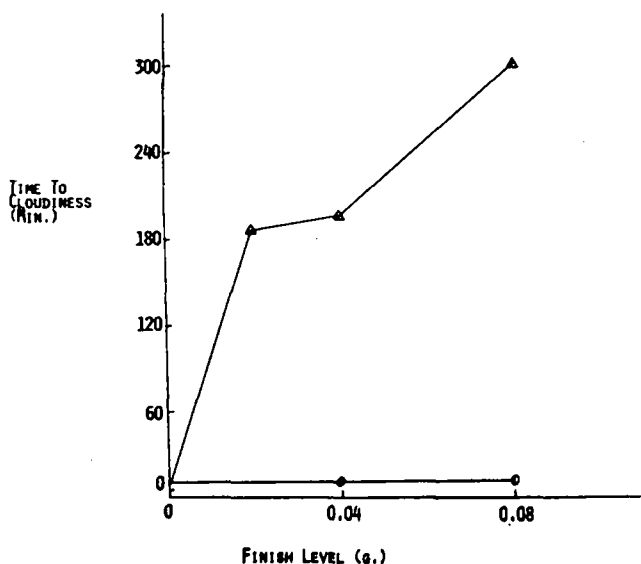
Fig. 3. Effect of finishes on cure of Hylene MP-Epon 812: (△) nonsulfated ester finish; (○) sulfated ester finish; additives g per 0.006 mole Hylene MP and 0.006 mole Epon 812.

Although the sulfated finish retarded the reaction rate, polymer was formed prior to the time of cloudiness. The polymers isolated from short-stopping were low molecular weight materials soluble in N,N-dimethylformamide. The polymers also charred from 250° to 350° with decomposition but no melting.

A limited characterization of the polymers isolated after the time of cloudiness was conducted. Table VI summarizes data for several polymers. The intrinsic viscosity–molecular weight relationship for polyurethanes in N,N-dimethylformamide is discussed to a limited extent in the literature.· Nesterov[13] and Soto[14] have derived equations for MDI-based polyurethanes. Although the comonomer was not Epon 812 in either study, the equations were used for calculations of molecular weight based on the intrinsic viscosities of the soluble fractions. Control trials and the trials with nonsulfated ester finish appeared to yield a

TABLE VI
Polymer Characterization

Sample no.	Finish	IV[a]	M[b]	M[c]	Insolubles, wt-%	%N
1	None	0.43	8,300	26,800	38.8	8.8
2	NSE	0.17	2,370	6,020	49.5	8.7
3	SE	0.14	1,820	4,400	11.8	8.8

[a] In N,N-dimethylformamide (for soluble fraction).
For Soluble Fractions

[b] Nesterov equation: $\eta = 5.4 \times 10^{-4} M^{0.74}$.

[c] Sato equation: $\eta = 7.71 \times 10^{-4} M^{0.62}$.

higher molecular weight soluble fraction and more of an insoluble or gelled fraction than the sulfated ester finishes.

Cure of Hylene MP and Ethylene Glycol

Ethylene glycol was substituted for Epon 812 for the purpose of producing a linear polyurethane. The solutions were heated for 1 hr at 140° and then the cyclohexanone solutions were concentrated. Quantitative recovery of unreacted Hylene MP and ethylene glycol was made. An interpretation of these results will be discussed later.

Finish Effects on Epon 812–MDI Cure

MDI was substituted for Hylene MP for comparison of a free and blocked isocyanate on the cure reaction. Unlike the Hylene MP studies, some of the solutions did not become cloudy, but a rubbery clear polymer would separate from solution. The results in Table VII show no difference in precipitation or rubber formation time with nonsulfated ester and sulfated ester finishes. The polyurethanes isolated were found to char between 250° and 350° with no melting. The polymers were insoluble in N,N-dimethylformamide, which is indicative of high molecular weight branched or gelled materials.

TABLE VII
MDI–Comonomer Reaction with Finish Present

Run	Comonomer[a]	Finish class[b]	Finish,[c] g	Time to cloudiness min	Total time, min	Ppt., g
1	Epon 812	none	0	30	45	1.6
2	Epon 812	NSE	0.04	—	27	0.7
3	Epon 812	SE	0.04	—	27	0.9
4	Ethylene glycol	none	0	—	60	1.8
5	Ethylene glycol	NSE	0.04	—	60	1.8
6	Ethylene glycol	SE	0.04	20	30	0.7[d]

[a] 0.006 mole per 0.006 mole MDI.

[b] NSE = Nonsulfated ester finish; SE = sulfated ester finish.

[c] Per 0.006 mole MDI, 0.006 mole comonomer, 0.32 mole cyclohexanone.

[d] From precipitation during trial plus 1.1 g polymer from cyclohexanone concentration.

Cure of MDI with Ethylene Glycol

Ethylene glycol was substituted for Epon 812 and similarly studied with MDI (Table VII). The linear polymers formed in the absence of finish and in the presence of nonsulfated ester finish began to decompose above 270°. In the presence of the sulfated ester finish, cloudiness occurred after 20 min of reaction. Polymers were isolated in the precipitate and from the concentration of the cyclohexanone solution. Both polymers which began to decompose above 270° were insoluble in hot N,N-dimethylformamide. Since no inhibition of reaction was found for either Epon 812 or ethylene glycol with MDI in the presence of sulfated ester finish, we conclude that the unblocking of the isocyanate source (Hylene MP) is the retarded step.

Functional Compound Studies

Finishes contain a number of functional groups in their compositions. Model compounds were chosen to determine what functional groups retarded the unblocking step (Table VIII). Carboxylic acid groups and sulfonic acid groups were found to retard the rate of reaction (Fig. 4). Amine bases and the in situ salt of 1-pentanesulfonic acid and triethylamine exhibited a catalytic effect on the rate of the unblocking compared to the carboxylic and sulfonic acid groups (Table VIII, Fig. 5).

The catalytic effect of the base and its salt is visualized by eq. (6). The free acid groups cannot act as a proton acceptor because they do not contain a free pair of electrons:

$$R'OH + B: + R—N=C=O \qquad (6)$$
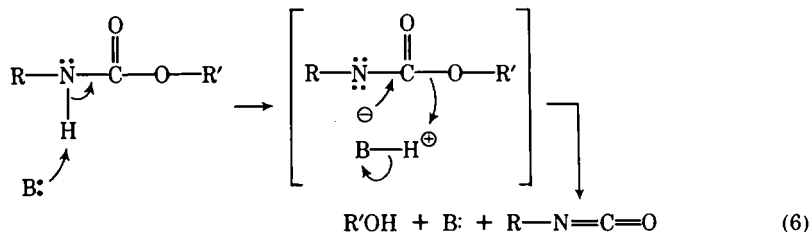
It is our belief that in the absence of catalyst the epoxide ring is acting as a weak base according to eq. (7)[15-19]:

$$R—N=C=O \qquad (7)$$
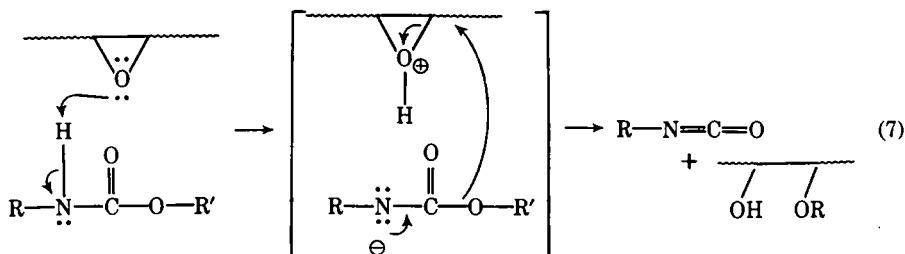
The concerted ring opening of the epoxide ring results in an increase in hydroxyl level for the epoxy resin and enhances potential reactivity with isocyanate to form the polyurethane. When the compounds containing carboxylic acid groups and sulfonic acid groups are added to the system, they compete with the proton of the carbamate for formation of the intermediate oxonium complex. Under the reaction conditions employed, the increased base strength of the epoxy resin

TABLE VIII
Functional Group Effect on Isocyanate-Epoxy Reaction

Run	Additive	Additive,[a] mole	Time to cloudi-ness, min	Total time, min	Polymer product, g
1	None	—	20	30	1.5
2	Stearic acid	7×10^{-5}	22	35	1.0
3	Stearic acid	1.4×10^{-4}	37	60	1.0
4	Stearic acid	1.7×10^{-4}	45	100	0.1
5	1-Pentanesulfonic acid	2.7×10^{-4}	20	30	0.6
6	1-Pentanesulfonic acid	6.7×10^{-4}	15	30	0.7
7	1-Pentanesulfonic acid	13.4×10^{-4}	—	300	0.0
8	Triethylamine	1×10^{-3}	20	30	0.8
9	Triethylamine	2×10^{-3}	15	30	1.4
10	N-Methyldicyclohexylamine	1×10^{-3}	9	20	1.1
11	N-Methyldicyclohexylamine	2×10^{-3}	6	20	1.8
12	Salt[b]	2×10^{-4}	20	30	0.7
13	Salt[b]	4×10^{-4}	18	30	1.4
14	Salt[b]	6.7×10^{-4}	10	30	1.6
15	Salt[b]	13.4×10^{-4}	8	30	1.8

[a] Mole per 0.006 mole Hylene MP, 0.006 mole Epon 812, 0.32 mole cyclohexanone.
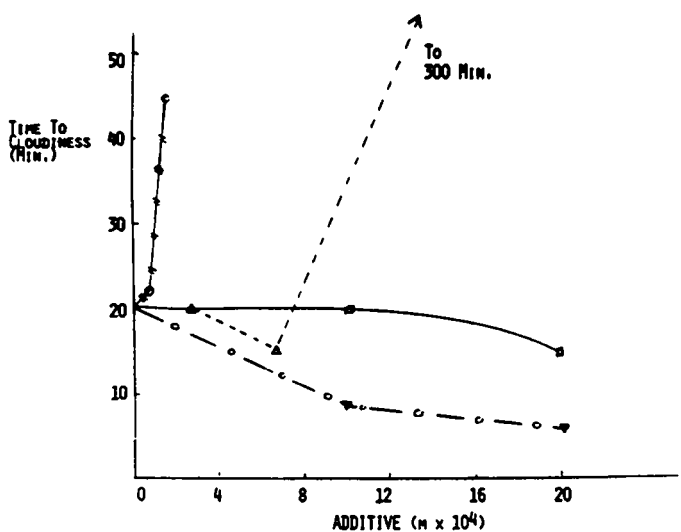[b] In situ salt of triethylamine and 1-pentanesulfonic acid.

Fig. 4. Functional compound studies: (□) triethylamine; (△) 1-pentanesulfonic acid; (#) stearic acid; (○) N-methyldicyclohexylamine; additive, M = mole ($\times 10^4$) per 0.006 mole Hylene MP and 0.006 mole Epon 812.

compared to ethylene glycol is essential to produce free isocyanate from Hylene MP without which no reaction can occur.

CONCLUSIONS

Model compound reactions of isocyanate sources with alcohols and/or Epon 812 showed that the major reaction product from the cure of the Shoaf-developed dip was a polyurethane. The primary source of the hydroxyl group for the
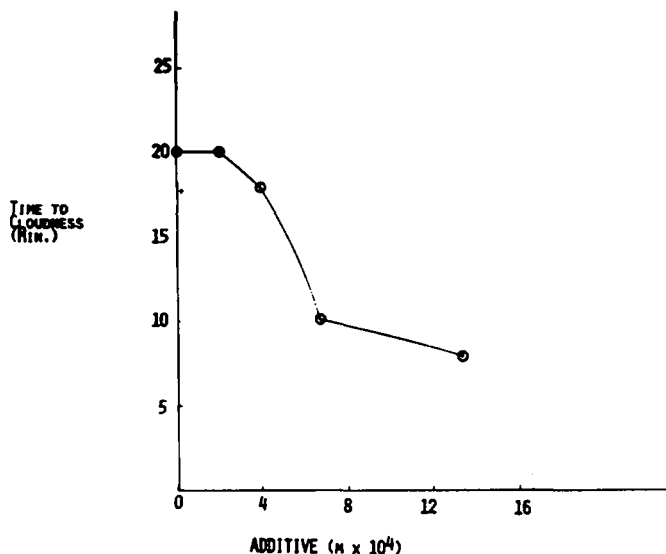
Fig. 5. Salt of 1-pentanesulfonic acid and triethylamine; M = mole ($\times 10^4$) additive per 0.006 mole Hylene MP and 0.006 mole Epon 812.

polyurethane formation is the Epon 812 epoxy resin. The number of free hydroxyl and carboxylic acid (approximately one COOH per 3 moles of polyester) terminal groups on the polyester backbone is extremely small. The probability of a major role of the polyester terminal groups in reactions with dip chemicals during cure is quite low.

The polyurethane adhesive–polyester bond is pictured primarily as a physical interaction rather than of a chemical nature. Iyengar[20] reported that the polyurethane from methylenebisphenylene diisocyanate and Epon 812 has a cohesive energy density of 10.5. Poly(ethylene terephthalate) has a cohesive energy density of 10.3. Thus, compatibility between these two networks would be quite high. Therefore, the probability for adhesion by the diffusion theory of Voyutskii[21,22] exists in the absence of any yarn finish and when nonsulfated finishes are employed.

Besides thermodynamic compatibility between the polyester and polyurethane, a limited but real potential for hydrogen bonding between the N—H groups of the polyurethane and the ester groups of the polyester is possible.

The sulfated finish and compounds containing carboxylic acid groups and sulfonic acid groups acted as inhibitors for the unblocking of Hylene MP and altered the chemistry of the cure reaction. Furthermore, the modified reaction product, possibly because of low molecular weight and/or reduced crosslinking, may act as a weak boundary layer for adhesion. Therefore, in the presence of the sulfated finishes the weak boundary layer theory of adhesion as proposed by Schonhorn[23] and Sharpe[24] appears most applicable.

References

1. T. J. Meyrick and J. T. Watts, *Proc. Instr. Rubber Ind.*, **13**, 52 (1966).
2. O. Bayer, *Angew. Chem.*, **A59** (9), 257 (1949).
3. C. J. Shoaf (to du Pont), U.S. Pat. 3,307,966, (Mar. 7, 1967).
4. Inventor Unknown (to ICI), Belgium Pat. 674,528 (1966).

5. J. Mather, *Brit. Polym. J.*, **3**, 58 (1971).

6. T. J. Redston, W. F. Bernholz, and C. Schlatter, *Text. Res. J.*, **43**, 325 (1973).

7. J. H. Saunders and K. C. Frisch, *Polyurethanes—Chemistry and Technology*, Part 1, Wiley, New York, 1962.

8. J. E. Herweh and W. J. Kauffman, *Tetrahedron Lett.*, 809, 1971.

9. C. H. Schramm (to J. T. Baker Chemical Co.), U.S. Pat. 3,334,110, (Aug. 1, 1967).

10. G. P. Speranza and W. J. Peppel, *J. Org. Chem.*, **23**, 1922 (1958).

11. R. R. Hampton, *Rubber Chem. Technol.*, **45**, 546 (1972).

12. L. J. Bellamy, *Infra-Red Spectra of Complex Molecules*, 2nd ed., Methuen & Co., London, 1957, p. 222.

13. A. E. Nesterov et al., *Vysokomol. Soedin., Ser. A.*, **9**(12), 2630 (1967); *Chem. Abstr.*, **68**, 50164f (1968).

14. H. Sato, *Bull. Chem. Soc. Japan*, **39**(11), 2335 (1966); *Chem. Abstr.*, **66**, 18941e (1967).

15. J. N. Bronsted, M. Kilpatrick, and M. Kirkpatrick, *J. Amer. Chem. Soc.*, **51**, 428 (1929).

16. P. V. Zimakov, *Zhir. Fiz. Khim.*, **30**, 1904 (1956); *Chem. Abstr.*, **51**, 7811 (1957).

17. R. E. Parker and N. S. Issacs, *Chem. Rev.*, **59**, 733 (1959).

18. H. Wasserman and J. Aubrey, *J. Amer. Chem. Soc.*, **78**, 1726 (1956).

19. J. H. Brewster, *J. Amer. Chem. Soc.*, **78**, 1726 (1956).

20. Y. Iyengar and D. E. Erickson, *J. Appl. Polym. Sci.*, **11**, 2311 (1967).

21. S. S. Voyutskii, *Adhesives Age*, **5**, 30 (1962).

22. S. S. Voyutskii, S. M. Yagnyatinskaya, L. Ya Kaplunova, and N. L. Garetovskaya, *Rubber Age*, **105** (2), 37 (1937).

23. The Ministry of Technology, *Adhesion Fundamentals and Practice*, Gordon and Breach, New York, 1969, p. 12.

24. L. H. Sharpe, *J. Adhesion*, **4**, 51 (1972).