

## Interaction of Nylon Polymers with Epoxy Resins in Adhesive Blends

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### Synopsis

Blends of nylon-epoxy resins are used as adhesives. It is found by swelling tests that the epoxy resin crosslinks the nylon. By the failure of poly-*N,N'*-diisobutyl-hexamethyleneadipamide to cure and by the failure of pre-reactions of the nylon with phenyl glycidyl ether, it is shown that the epoxy resin reacts with the nylon through the amide hydrogen. The effect of the epoxy cure on increasing the brittle strength and on decreasing the yield strength of the nylon is discussed in terms of stresses in the adhesive joint.

### I. INTRODUCTION

It has generally become known that adhesives with high peel strength can be prepared from blends of nylon polymers with epoxy resin.<sup>1</sup> Because of this interest, the nature of the interaction between a bisphenol A-based epoxy resin and a nylon-type polymer was investigated.

It had been reported earlier that the epoxide ring does not react with the amide hydrogen.<sup>2,3</sup> On the other hand, it is known that ethylene oxide can be grafted onto polyhexamethylene adipamide.<sup>4a,5</sup> The latter report<sup>5</sup> suggested that at the high temperatures used in forming the adhesive bond the diepoxide could cure such polymers by addition of the amide hydrogen to the epoxide ring.

Swelling data presented here show that such crosslinking does occur. In addition, it is shown that the resulting cured blend has an increased brittle strength as well as a decreased yield strength. This is believed to be one reason for the improved joint strength of the nylon-epoxy blend over the nylon alone.

### II. EXPERIMENTAL

The polymer used was an alcohol-soluble nylon commercially available as Zytel 61. (Du Pont trademark). The number-average molecular weight of the polymer was 25,000.

The polymer was dissolved in hot ethanol to give a 14% (w/w) solution. Epon 828 (Shell trademark) was added to the solution while the latter was still warm. If dicyandiamide was used as an additional curing agent, it was stirred in the mixture after it had cooled down to near room tempera-

ture. The dicyandiamide was added in the ratio of one part per ten parts of Epon 828.

As soon as a seemingly homogeneous mixture was produced, the mixture was cast into a  $6\frac{1}{2} \times 10$  in. Pyrex dish and allowed to air-dry in the hood until the end of the day. The dish with its semitacky film was then dried overnight in a vacuum oven at  $50^{\circ}\text{C}$ . and 28 in. Hg. The film usually pulled loose from the dish during drying and was easily removed. The product was a semiopaque flexible sheet with small patches of varying clarity. The clarity and flexibility of the sheet increased with the Epon 828 content.

Adhesive joints were prepared by using 7075-T6 Alclad aluminum strips measuring  $1 \times 3 \times 0.063$  in. The strips were vapor degreased with Triclene (Du Pont trademark for solvent grade trichloroethylene) and then etched for  $\frac{1}{2}$  hr. at  $70^{\circ}\text{C}$ . in a cleaning bath containing three liters of water 100 g. of sodium dichromate, and 550 ml. of concentrated sulfuric acid. The strips were washed with cool tap water and distilled water and then dried in a circulating air oven at  $50^{\circ}\text{C}$ .

Simple lap joints were made with 0.5 in. overlap by pressing an uncured film of the adhesive between strips at  $177^{\circ}\text{C}$ . for 1 hr. under light pressure (about 100 lb. on the pressure gage). The final thickness of the adhesive was about 0.001 in. or less. The joints were pulled apart under tension (tensile-shear test) at a 4 in. jaw separation and a rate of approximately 0.2 in./min. Six joints were used in each test.

The swelling tests were run on cured sheets of adhesive measuring about 0.03 in. thick. The solvent used was 2,2,3,3-tetrafluoropropanol obtained by distilling C-3 Fluoroalcohol (Du Pont trademark for a mixture of fluoroalcohols) and taking a cut at  $106\text{--}109^{\circ}\text{C}/760$  mm. to give a material with  $n_D^{25}$  1.3203. Sufficient sodium trifluoroacetate which had been recrystallized from dioxane and ethanol was added to the tetrafluoropropanol to give a 0.1*N* solution. Before the swelling tests were run, the adhesive was cured at  $177^{\circ}\text{C}$ . for 3 hr., then extracted with boiling ethanol and with tetrafluoropropanol to remove the nongel fraction. The dried samples were then swollen at room temperature in tetrafluoropropanol until equilibrium was reached. The excess solvent was removed by blotting the surface of the samples with paper towels.

The yield strengths of the bulk polymer were determined on an Instron tensile tester at a pull rate of 20 in./min. and an initial jaw separation of 4 in. The samples of polymer were rectangular strips measuring  $5 \times 0.5$  in. and varied in thickness from 0.01 to 0.02 in. The samples were pulled at room temperature.

The brittle strengths were determined by an impact test on an unnotched sample using the same standard equipment as for a Charpy test (ASTM-D-256-56).<sup>6</sup> The samples measured  $4 \times 1 \times 0.03$  in. and were placed across the two knife edges having a  $2\frac{1}{4}$  in. separation so that the broader surface of the sample was struck. The samples were first cooled in liquid nitrogen ( $-196^{\circ}\text{C}$ .) and then tested immediately.

The *N,N'*-dialkylated polyhexamethylene adipamide was prepared by the melt polymerization of *N,N'*-diisobutylhexamethylenediamine and adipic acid.<sup>4b</sup> The number-average molecular weight was about 3800.

X-ray examination of films of the polymers was made on a G. E. Model XRD-5 diffractometer using nickel-filtered  $\text{CuK}\alpha$  radiation at a setting of 50 kv. and 15 ma. The slit settings were 3, 0.1, and 3°. The measurements were made with a recording Geiger detector and scaler set for a time constant of 4 sec. and gain of 500 at a scan rate of 2° ( $2\theta$ )/per min. The scan was from  $2\theta = 10$  to 30°. The polymer samples were the same as those used in determining the yield and brittle strength, having been cured at 177°C. for 3 hr. between 1/4 in. aluminum blocks coated with Teflon (Du Pont trademark) in a press and then air cooled to room temperature outside the press (air-quenched).

### III. RESULTS

#### A. Joint Strength

A comparison of the strengths of adhesive joints containing the nylon-epoxy blend with those containing the nylon alone shows that the epoxy doubles the strength (Table I). For both materials, the effect of varying the application conditions was explored, and the best results are given here. In general, the joint strength initially increased sharply as the dwell time (time the joint was held at 177°C.) was increased until a plateau was reached. Beyond 3 hr., the joint strengths tended to decrease slowly. The initial rapid rise is probably a measure of the rate of wetting<sup>7</sup> of the surface; the later drop, a measure of polymer degradation.

TABLE I  
Adhesive Joint Strength of the Nylon Alone and of the Cured Epoxy Blends

| Sample   | Tensile shear joint strength, psi |           |
|--|-----------------------------------|-----------|
|  | Average                           | Range     |
| Nylon polymer alone                                    | 2860                              | 3600-2400 |
| Nylon polymer + 14.8% Epon 828<br>+ 1.4% dicyandiamide | 6780                              | 7100-6500 |

#### B. Swelling Measurements

The solvent 2,2,3,3-tetrafluoropropanol was used since Beachell and Carlson<sup>8</sup> determined the second virial coefficient for Zytel 61 in 2,2,3,3-tetrafluoropropanol by light-scattering measurements. This value,  $35 \times 10^{-4}$ , was converted to the interaction coefficient,  $\chi$ , by means of Flory's equation:

$$A_2 = (\rho_s/M_s\rho^2) (0.5 - \chi)\mathfrak{F}(J\xi^3) \quad (1)$$

where  $M_s$  was the solvent molecular weight,  $\rho_s$  was the density of the solvent, and  $\rho$  was the density of the polymer. It was assumed that  $\mathfrak{F}(J\xi^3)$

was equal to unity. Actually the value of this function was probably a fractional number so that the derived  $\chi$  was high and the values of  $M_c$  calculated on this basis were probably maximum values. However, on this assumption,  $\chi = +0.09$ .

The molecular weight between crosslinks,  $M_c$ , was calculated by the Flory-Rehner equation for high degrees of swelling:

$$q_m^{5/3} = (M_c/\rho V_1)(0.5 - \chi)/(1 - 2M_c/M) \quad (2)$$

where  $V_1$  is the molar volume of the solvent,  $\rho$  is the density of the polymer,  $M$  is the molecular weight of the polymer before crosslinking, and  $q_m$  is the equilibrium volume swelling ratio. Although the equation was derived for amorphous networks, Valentine<sup>9</sup> found that it can be applied to polymers (nylon 66) which are crystalline in the nonswollen state.

When eq. (2) was applied to cured adhesive blends containing 15% Epon 828, the average  $M_c$  was found to be 8950 (Table II). This figure might indicate that the epoxy resin had crosslinked the polyamide through points along the chain. However, if it was assumed that the polyamide reacted only through the carboxyl and amino endgroups of the polymer, an alternate equation would have to be used in which the term for dangling ends was removed. This turned out to be:

$$q_m^{5/3} = (M/\rho V_1)(0.5 - \chi) \quad (3)$$

TABLE II

Equilibrium Volume Swelling Ratio and Molecular Weight between Crosslinks for Cured Nylon-Epoxy Blends

| Blend composition,<br>% Epon 828 <sup>a</sup> | $q_m$   |                    | $M_c$ (calculated) |
|---|---------|--------------------|--------------------|
|   | Average | Standard deviation |                    |
| 15  | 18.8    | $\pm 0.5$          | 8950               |
| 30  | 10.2    | $\pm 0.5$          | 6000               |

<sup>a</sup> Blend of nylon, Epon 828, and dicyandiamide (10 phr based on Epon) cured at 177°C. for 3 hr. After extraction, swollen at room temperature in 2,2,3,3-tetrafluoropropanol.

Equation (3) assumed that all of the ends of the polyamide chain have become incorporated in multifunctional crosslinks. The molecular weight between crosslinks is now 25,000, and the question is whether or not  $q_m$  for such a system is the same as that determined. It was found that, indeed,  $q_m$  was 18.8 which checked well with value found (Table II).

It was thus apparent that the swelling data alone on this lightly crosslinked adhesive blend could not distinguish between chains crosslinked through the endgroups and those crosslinked through the side. For this reason, a second blend was tried in which a higher concentration (30%) of Epon was used. This figure (Table II) indicated that the epoxy resin did crosslink the polyamide at points along the length of the chain.

### C. Effect of Curing Agent on Cure

A comparison was made of the effect of leaving out the dicyandiamide on the crosslinking of the polymer. The amount of crosslinking was measured by determining the per cent of polymer left after extraction of the cured sample with boiling ethanol. When the dicyandiamide was left out, it was quite apparent that the crosslinking efficiency of the Epon 828 was reduced (Table III).

TABLE III  
Effect of Curing Agent on Crosslinking

| Epon 828, %                               | Gel, % | Remarks                           |
|---|--------|-----------------------------------|
| A. Without dicyandiamide; 3½ hr. cure     |        |                                   |
| 3   | 0      | Completely soluble in hot ethanol |
| 5   | 0      | Slight gel, too little to collect |
| 7   | 26     | Gelatinous                        |
| 14  | 66     | Coherent sheet                    |
| B. With 10 phr dicyandiamide; 3½ hr. cure |        |                                   |
| 5   | 30     | Coherent sheet                    |
| 7   | 70     | Coherent sheet                    |
| 14  | 82     | Coherent sheet                    |

### D. Preparing with Phenyl Glycidyl Ether

Attempts were made to block the endgroups on the supposition that they might be taking part in the curing reaction with the Epon 828. For this purpose, phenyl glycidyl ether was used in the place of Epon 828, and the blend was prepared as described above, 1.8 g. of phenyl glycidyl ether, 10 g. of polymer, and 0.2 g. of dicyandiamide being used. The film was formed as before and cured at 177°C. for 3 hr. The resulting sheet (which was still soluble in hot ethanol) was next extracted with acetone to remove the unreacted phenyl glycidyl ether. This film was then redissolved in ethanol, 1.8 g. of Epon 828 together with 0.2 g. of dicyandiamide was added, and a film formed as before. After being cured at 177°C. for 3 hr., the film was insoluble in both hot ethanol and 2,2,3,3-tetrafluoropropanol. The equilibrium volume swelling ratio of the cured film was 17.4, indicating that the phenyl glycidyl ether treatment had a negligible effect on the subsequent Epon 828 cure.

### E. Interaction of Poly-*N,N'*-Diisobutylhexamethyleneadipamide and Epon 828

To test further the conclusion that the Epon 828 was crosslinking the polyamide by reacting with the amide hydrogen, a nylon 66 was prepared in which all of the amide hydrogen had been replaced with isobutyl groups. The balsamlike isobutylated nylon was subsequently formed into an Epon 828-containing film in the same manner as described above for the nylon.

Long cure times were tried in attempts to cure the film; however, even heating cycles of 177°C. for 50 hr. produced no cures. All of the blends, ranging from 10 to 29% Epon 828, were still soluble in hot ethanol after the curing cycle. No gel fraction was present.

### F. Yield Strength and Brittle Strength

A comparison of the yield strength and brittle strength of the polyamide and of the cured blend (Table IV) shows that the yield strength of the cured blend is lower than that of the polymer alone, while the brittle strength is higher.

TABLE IV  
Yield Strength and Brittle Strength of the Nylon and Epoxy Blends

| Sample   | Yield strength,<br>psi |              | Yield strain, % |              | Brittle strength,<br>ft.-lb. |              |
|--|------------------------|--------------|-----------------|--------------|------------------------------|--------------|
|  | Ave.                   | Std.<br>Dev. | Ave.            | Std.<br>Dev. | Ave.                         | Std.<br>Dev. |
| Nylon polyamide alone                          | 2100                   | ±110         | 6.0             | +0.6         | 0.28                         | ±0.03        |
| Nylon + Epon 828 (15%)<br>+ dicyandiamide (1%) | 1420                   | ±100         | 5.4             | ±0.4         | 0.40                         | ±0.04        |

The brittle strengths were measured by a low temperature impact test; attempts were also made to measure the brittle strength by means of a low temperature flexure test; however, both samples yielded rather than fractured under this condition. The ultimate strength of the samples was much higher.

### G. Crystallinity

The epoxy cure does not appear to change the crystallinity of the nylon (Fig. 1). The x-ray diffraction peak at  $2\theta = 21^\circ$  was not significantly altered either in height or width, indicating that both the per cent crystallinity and the crystallite size were of the same order both for the nylon and the epoxy-cured nylon. The greater opaqueness shown by the epoxy-cured

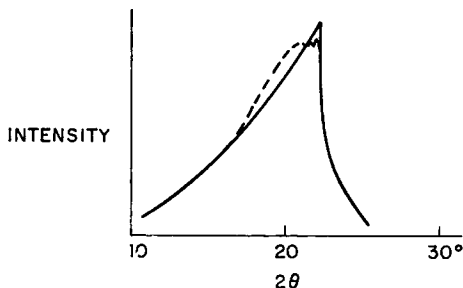


Fig. 1. X-ray diffraction peak for the nylon and epoxy-cured nylon.

samples is ascribed to the presence of some homopolymerized epoxy resin which gives rise to some microheterogeneity.

#### IV. DISCUSSION

The improved strength of adhesive joints containing the cured nylon-epoxy blend undoubtedly involves many factors. The improvement of specific adhesion is probably one of these, but at present there is no agreement on a test which measures specific adhesion.<sup>10</sup> On the other hand, the strength properties of the polymer are also involved and measurable.

Failure of a polymer is either brittle or tough. The transition from one type of failure to the other is generally governed by the temperature, the rate of loading, and the complexity of the stresses. Vincent<sup>11</sup> has con-

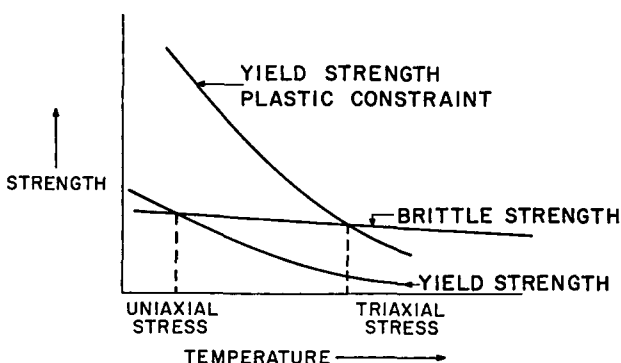


Fig. 2. Schematic diagram of effect of temperature and plastic constraint on brittle-to-tough transition.

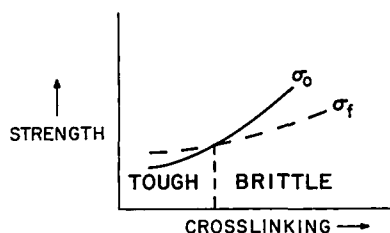


Fig. 3. Schematic diagram of the effect of crosslinking on brittle and yield strength.

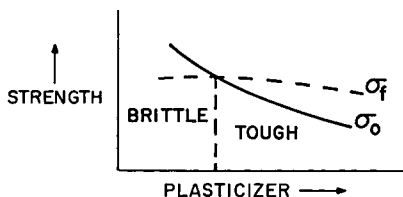


Fig. 4. Schematic diagram of the effect of plasticizer on brittle and yield strength.

sidered at greater length some of the factors affecting this transition. By this treatment, the problem is resolved into the relative magnitude of the yield strength,  $\sigma_0$ , and the brittle strength,  $\sigma_f$ , of the polymer. By this view, the yield strength is the peak load in tough failure, while the stress at break in brittle failure is the brittle strength. When the yield strength is lower than the brittle strength ( $\sigma_0 < \sigma_f$ ), failure is tough. When the yield strength is greater than the brittle strength ( $\sigma_0 > \sigma_f$ ), failure is brittle.

The polymer layer in an adhesive joint is subjected to triaxial stresses owing both to the geometry of the joint and the constraint at the interface.<sup>12</sup> The introduction of triaxial stresses acts to increase the yield strength of the polymer since it is under plastic constraint and cannot flow (Fig. 2).<sup>13</sup>

Two factors which affect the balance of the yield strength and brittle strength and which are applicable to the cured nylon-epoxy blends are crosslinking and plasticization. The effect of crosslinking (Fig. 3)<sup>11</sup> is to increase both the brittle strength and yield strength; however, the yield strength increases more rapidly than the brittle strength, and at high levels of crosslinking the polymer becomes brittle. The effect of plasticizing (Fig. 4)<sup>11</sup> nylons with small amounts of water is to decrease the yield strength; there is no detectable change in the brittle strength. At high loadings of plasticizer, at least with polyvinyl chloride, the brittle strength decreases.

The experimental data on the nylon-epoxy system has shown that the brittle strength is increased while the yield strength is reduced. This change can be interpreted as resulting from a combination of crosslinking and plasticizing of the nylon by the epoxy resin. The crosslinking alone would raise the brittle strength of the nylon as was found; however, the plasticizer would tend to reverse the more rapid rise of the yield strength induced by crosslinking while having little effect on the brittle strength. The net effect of the crosslinking and plasticizing together then would be to raise the brittle strength and either hold constant or reduce the yield strength so that tough failure is favored even under the triaxial stresses in the adhesive joint.

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### Résumé

On utilise des mélanges de nylon et de résines époxy comme adhésifs. On a trouvé par des essais de gonflement que la résine époxy formait des pontages avec le nylon. Par le défaut du poly(*N,N'*-diisobutylhexaméthylèneadipamide) à subir un post-traitement et suite à l'absence de préreactions de la part du nylon avec l'éther phényl-glycidique on montre que la résine époxy réagit avec le nylon par l'intermédiaire de l'hydrogène de l'amide. L'effet du traitement par la résine époxy sur l'augmentation de la force de rupture et sur la diminution de la force de rendement est discuté en termes de tensions dans le joint adhésif.

### Zusammenfassung

Gemische von Nylon mit Epoxyharzen werden als Klebstoffe verwendet. Wie aus Quellungsversuchen hervorgeht, wird das Nylon durch das Epoxyharz vernetzt. Da sich Poly(*N,N'*-Diisobutylhexamethylenadipamid) nicht härten lässt und da eine Vorbehandlung von Nylon mit Phenylglycidyläther unwirksam ist, muss man annehmen, dass das Epoxyharz mit dem Amidwasserstoff des Nylons reagiert. Die in einer Erhöhung der Sprödreissfestigkeit und einer Erniedrigung der Reissfestigkeit des Nylons bestehende Wirkung der Epoxyhärtung wird auf Grundlage der in der Verklebungsstelle wirksamen Spannungen diskutiert.

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