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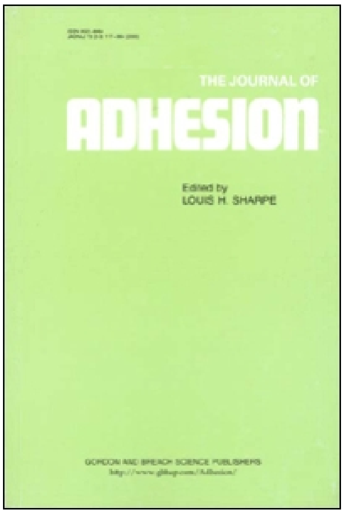

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Effect of Predrying Time on the Strength of Solvent-Welded Polyamide-11 Joints

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The failure in tension of polyamide-11 solvent-welded joints has been studied, with a special emphasis on the effect of predrying the adhesive at 40°C before mating. During the initial 30 minutes of predrying the fracture strength increased to a maximum value. Thereafter, the fracture stress decreased toward an equilibrium value. This general behavior occurred with notched and unnotched tensile specimens. The initial increase in strength is associated with the increase in concentration of polymer at the mating interface. The subsequent decrease in strength is associated with a decrease in the mobility of the polymer molecules at the mating interface as the concentration of solvent at the mating interface decreases by evaporation. It was found that the small amount of polymer that is initially dissolved in the adhesive has no effect on the fracture stress or its relationship to predrying time. It is concluded that polymer is dissolved in the adhesive in order to adjust its viscosity so that it can be conveniently applied to the surface.

KEY WORDS solvent welding; polyamide-11; nylon; adhesive joint strength; predrying; fracture mechanics; morphology.

INTRODUCTION

Solvent welding is a useful joining technique for thermoplastic polymers, including PVC, ABS, polycarbonate and polyamide. An important application for polyamide-11 is its use in gas piping sytems.[1] Only a few studies on solvent welding have been published. Most of them deal with either PVC[2,3,4,5] or polycarbonate.[6,7,8,9]

The adhesion in solvent-welded joints originates in interdiffusion of polymer chains between superficial layers of the adherends which have been softened by the solvent. Dissolved polymer may be added to the adhesive, as in the present case, in order to facilitate the gap filling between mismatching surfaces and to control the viscosity of the adhesive.

The solvent diffuses from the applied adhesive into the bulk polymer, generating a plasticized region in which the chain mobility is enhanced.[2,6] Concurrently, polymer from the bulk diffuses into the adhesive. Yue[4] showed on PVC that the greater the degree of plasticization, as generated by very good solvents, the more

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*Corresponding author.

significant the improvement of adhesion. Thus, strong solvent welds are produced with solvents having the greatest ability to dissolve the polymer and not with solvents which could diffuse most rapidly into the adherends.

In order to evaluate the adhesive strength, a notched tensile test was used although most adhesives are investigated with lap shear tests. A well-defined notch was used in order to reduce the scatter in the fracture stress and also to obtain a value for K_{IC}, the critical stress intensity factor. In order to obtain reproducible values of the fracture strength it was necessary to control the smoothness of the surface, clamping pressure, thermal history of the resin and the predrying time. The variables that were investigated were smoothness of the surface, pressure during drying, thermal history of the resin and predrying. The influence of the time of predrying on the fracture strength and its relationship with morphology are the focus of this article. Predrying refers to the time between the application of the adhesive on the surface of the adherends and their mating. Licata and Haag[8] found a continuous decrease in the strength of solvent-welded polycarbonate with increasing predrying time but, for the polyamide-11, an initial increase in the strength was followed by a decrease.

EXPERIMENTAL

Materials

Commercial polyamide-11 was provided by Atochem North America under the name of Rilsan BESNO TL. 5 mm thick plaques were compression molded at 210°C and quenched at a rate of about 40°C/min, then cut and milled into 5 × 25 × 30 mm specimens. One of the 5 × 25 mm faces (the useful surface) was polished metallographically with 600 grit paper.

The adhesive, consisting of a mixture of cresol-like solvents and less than 10% of dissolved polyamide-11, is produced under the brand name of Nylink-1 by Industrial Pipe Systems (Australia).

Preparation of the Specimens

A stress concentration was introduced in the adhesive joint in the form of a 3 mm deep notch as shown in Figure 1. The notch was made by covering part of the bonding surface with a 45 μm thick piece of Scotch® tape. The piece of tape was stuck onto one of the surfaces before the adhesive was applied, thus forming a barrier between the surfaces to be mated. Once the adhesive had been brushed on both surfaces, the final mating was completed in a minimum time of 20–30 sec. The predrying time, the time prior to mating, ranged from 5 min. to 4 hours, during which the two half specimens were stored at 40°C. The final specimen was lightly clamped and dried at 40°C for 7 days, thus allowing the bond to reach full strength as shown in Figure 2.

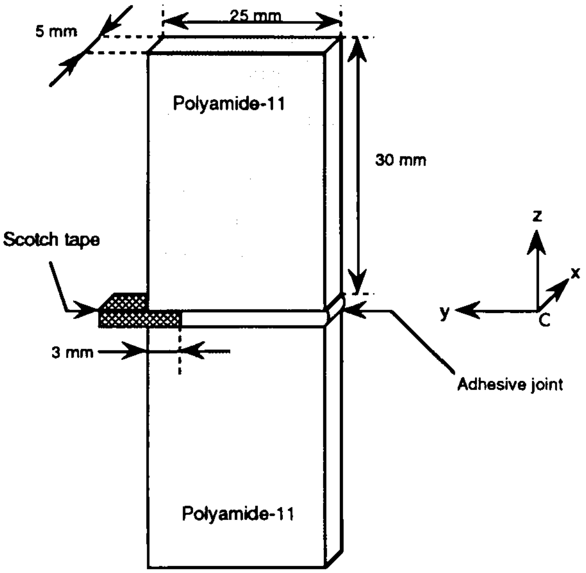

FIGURE 1 Specimen geometry.

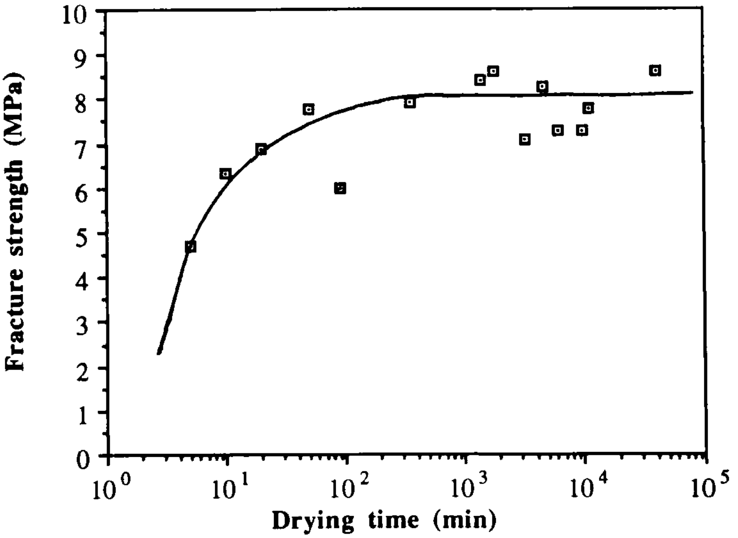

FIGURE 2 Fracture strength *versus* drying time at 40°C. (7 days = 10^4 min).

Tensile Tests

Tensile tests were performed on an Instron machine at a constant crosshead speed of 0.02 inch/min and at room temperature. All the specimens exhibited curves characteristic of brittle-type failures. For each condition of predrying, a set of 7 specimens was tested. Sometimes more than one set of 7 specimens was tested for a given condition of predrying. The standard deviation within the set was usually less than 15%, for notched specimens, but only sets exhibiting a standard deviation below 10% have been taken into account. Tensile tests were also done with un-notched specimens whose standard deviation in fracture stress was about 20%, with sets of only 4 specimens. The reported fracture strength is the load divided by the un-notched cross section area.

Measurement of the Adhesive Joint Thickness

For each condition of predrying, the thickness of the final adhesive layer, Δ, was measured at 3 different spots using optical microscopy. The average value was used. In order to measure Δ, the final adhesive layer was clearly exposed by polishing the (y-z) surface (Fig. 1) and etching with concentrated hydrochloric acid. In a few cases, the specimen was notched with a razor blade and then rapidly fractured at low temperature along the (x-z) plane. The fracture surface was then examined in the SEM in order to measure Δ.

RESULTS

A. Drying process The process after mating is called drying or curing. The effect of drying time at 40°C on the strength of unpredried specimens is shown in Figure 2. Half of full strength is reached in 5 minutes and full strength is achieved in a few hours. In the regular experiments, the drying time was 7 days (10^4 min) at 40°C for each condition of pre-drying. It is assumed that the equilibrium strength was achieved after 7 days for all conditions of pre-drying even though Titow *et al.*[6] showed that some solvent always remains in the final adhesive layer despite the length of the drying time or the application of specially-designed heat treatments.

B. Pre-drying time Figure 3 shows the effect of predrying time on the fracture strength. For the minimum predrying time of about 20 seconds the strength is 7.7 MPa. After 5 minutes the strength is 13 MPa and then it reaches the maximum of 14.6 MPa in 30 minutes. Thereafter, the strength decays to a value of 9 MPa after about 240 minutes of predrying.

The question arises as to how the notch itself influences the way that the predrying time affects the strength. Figure 4 shows the results without a notch. The same general behavior is observed in that a maximum still occurs in the range 0–60 minutes of predrying, whereas with the 3 mm deep notch the strength at zero time and at the maximum are 7.7 and 14.6 MPa, respectively. The corresponding

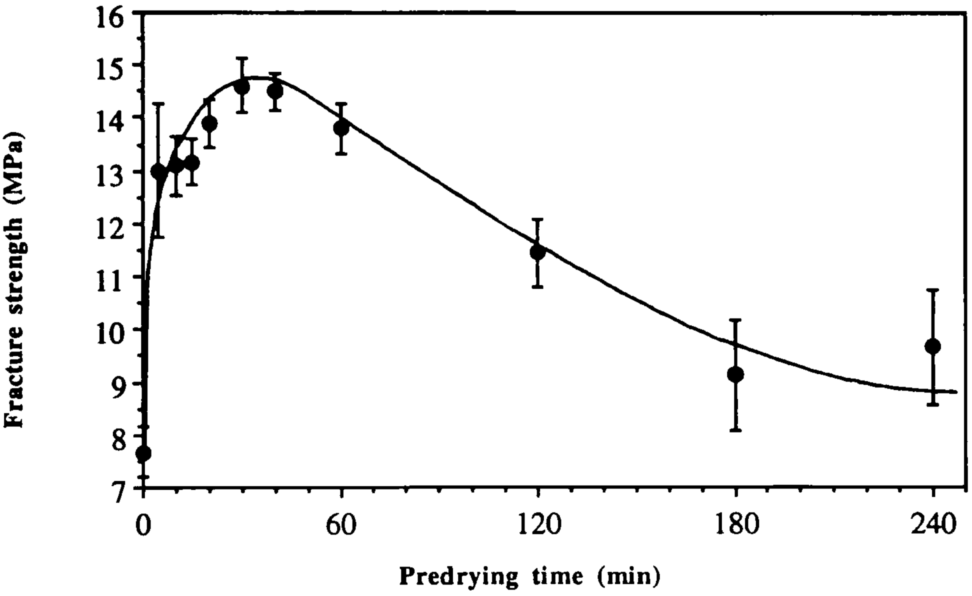

FIGURE 3 Fracture strength *versus* predrying time at 40°C for notched specimen.

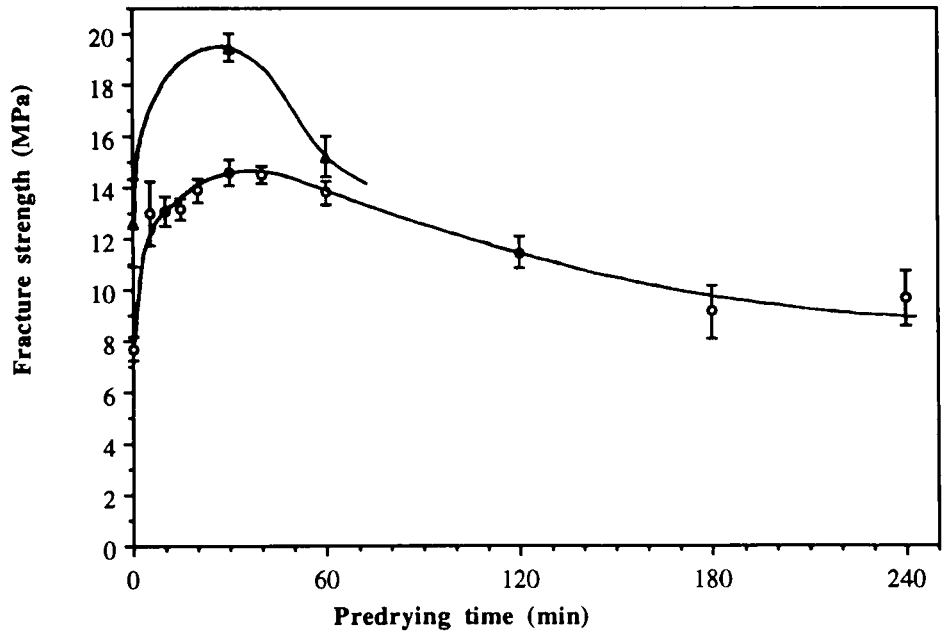

FIGURE 4 Fracture strength *versus* predrying time at 40°C for Δ-unnotched specimen and O-notched specimen.

strengths without a notch are 12.6 and 19.5 MPa. Probably, a critical stress intensity, K_{IC}, determines fracture where

$$K_{IC} = Y \sigma_f a^{1/2} \tag{1}$$

where Y is the usual geometric factor, σ_f is the fracture stress and a is the notch depth. Therefore, the unnotched joint behaves as if it had a natural or effective notch whose depth, a, is between

$$a = \frac{3}{(12.6/7.7)^2} = 1.1\ \text{mm} \quad \text{and} \quad a = \frac{3}{(19.5/14.6)^2} = 1.7\ \text{mm}$$

The scatter in fracture stress is about 20% without the notch compared with, usually, less than 10% with a notch.

C. Effect of dissolved polyamide in the adhesive The Nylink-1 adhesive has about 5% polyamide dissolved in it. Table I compares the effect on strength for adhesives with and without dissolved polyamide. These results show that the dissolved polyamide has no effect on the strength for the 20-second predried and 30-minute predried specimens. From this experiment, it is concluded that the solvent-plasticized polyamide in the bulk is responsible for the strength of the bond and that polyamide is dissolved in the adhesive in order to obtain a convenient viscosity while applying it.

TABLE I
The effect of dissolved polyamide on fracture stress

	Strength (MPa)	
Specimen	**20 sec. Predrying**	**30 min. Predrying**
With dissolved Polyamide	7.7 ± 0.5	14.6 ± 0.5
Without dissolved Polyamide	8.2 ± 0.7	13.3 ± 1.1

D. Morphology of the bond Figures 5a, b, and c show the bond for predrying times of 0, 40 and 120 minutes. For predrying times up to 40 minutes the microstructure of the bond appears to be homogeneous for a microscopic resolution of about 0.3 μm. For 120 minutes of predrying voids are visible. However, the voids are not easily observed in Figure 5 because they are lenticular and are best seen when exposed on the x-y plane. Presumably these voids originate early in the predrying stage and then increase in size with increasing predrying time. Possibly these voids contribute to the decline in strength beyond the maximum value at 30 minutes of predrying time.

Figure 6 shows that the bond thickness, Δ, shown in Figure 5, increases with predrying time. It is observed that the adhesive layer becomes more tacky and viscous as the predrying time increases as a result of evaporation of the solvents and diffusion of bulk polymer into the adhesive. Also, when the two halves of the specimen are clamped together some of the adhesive layer is extruded; the amount extruded decreases with increasing predrying time. Presumably the increase in

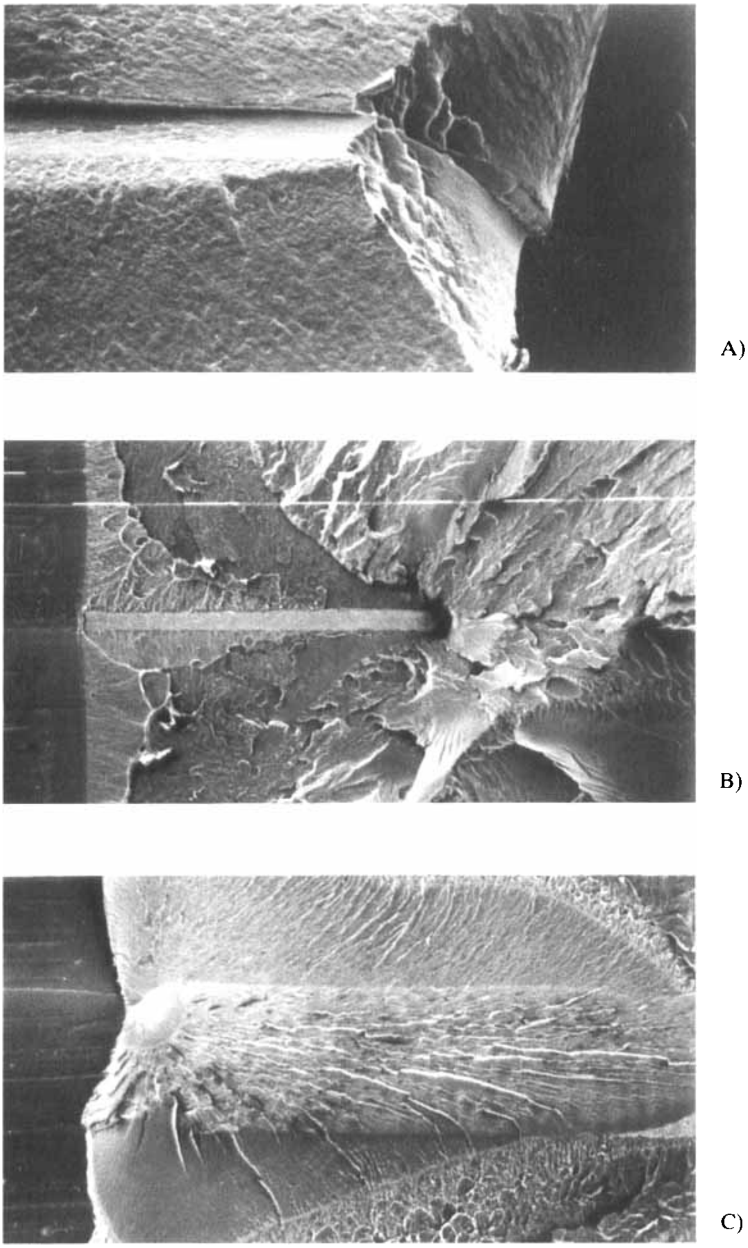

FIGURE 5 Micrographs of the adhesive joint showing variation in thickness of the adhesive layer for various predrying times. The parallel lines are the boundaries of the adhesive layer: A) The adhesive layer is 10 μm thick after 20 sec. of predrying and the boundaries of the adhesive layer as viewed on the left side of the micrgraph run in the y direction; B) The thickness is 34 μm after 40 min. of predrying. C) The thickness is 272 μm after 120 min. of predrying.

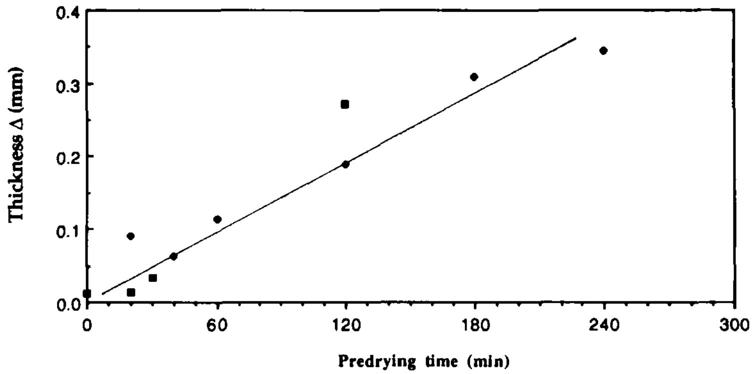

FIGURE 6 Thickness of the adhesive joint *versus* predrying time, ■ by SEM ♦ optical.

viscosity with predrying time causes the amount of extruded material to decrease and, as a result, the amount of the final adhesive layer is greater.

DISCUSSION

The critical stress intensity factor, K_{IC}, is obtained from equation (1) where, from Reference 10, the value of $Y = 2.15$ for our specimen geometry. K_{IC} *versus* predrying time is shown in Table II.

The effect of predrying time on the fracture stress as exhibited by Figure 4 is related to the amount of entanglement that occurs at the mating interface. The amount of entanglement at the mating interface depends on the concentration of polymer and on its mobility. Thus, the results in Figure 4 can be explained in terms of the effect of predrying time on the concentration and mobility of polymer at the mating interface. Prior to mating the adherends, polymer diffuses into the adhesive so that there is a concentration gradient between the bulk polymer and the free surface. The concentration of polymer in the adhesive layer increases with predrying time as reflected by the increase in viscosity. When the two surfaces are joined, part of the adhesive layer is squeezed out. Thus, the mating interface at which entanglement occurs between the two halves of the specimens is somewhere between the free surface and the original surface of the bulk polymer. The degree

TABLE II
K_{IC} *versus* predrying time

Predrying time (min)	0	5	10	15	20	30	40	60	120	180	240
K_{IC} (MPa·m$^{1/2}$)	0.84	1.56	1.62	1.58	1.71	1.76	1.73	1.63	1.37	1.09	1.17

of entanglement that occurs at this mating interface during drying depends on the concentration of polymer and its mobility at the mating interface.

Now, Figure 4 can be explained. The strength increases initially because the concentration of polymer increases with predrying time and while the concentration of solvent is sufficient to give the molecules adequate mobility to entangle. For much longer predrying times the concentration of polymer at the mating interface continues to increase, but there is also a greater loss of solvent which reduces the mobility. Also, at the free surface, the loss of solvent becomes so high that a thin skin of nearly solid polymer may form. The skin may not be completely squeezed out or fragmented during mating and will be a barrier to the entanglement of molecules from each half of the joint. In simple terms, Figure 4 may be explained as follows. The degree of entanglement is given by:

$$E = f_c(t) \cdot f_M(t) \tag{2}$$

where $f_c(t)$ is a function of the concentration of polymer molecules, which increases with predrying time. $f_M(t)$ is a function of the mobility of polymer molecules, which decreases with predrying time. Thus, equation (2) has a general form which produces a maximum value in strength at an intermediate predrying time as shown in Figure 4. There are several factors which can affect $f_c(t)$ and $f_M(t)$. $f_c(t)$ will depend on the molecular weight of the polymer and its crystallinity. $f_M(t)$ will depend on the compatibility of the solvent with the polymer, the amount of swelling in the polymer and the volatility of the solvent. The predrying temperature should have an important effect on the diffusivity of the polymer into the adhesive.

The notch is most effective for drying times less than about 30 minutes. Thereafter, the difference in fracture stress between the notched and unnotched specimen decreases. Two factors probably contribute to the decrease. At the longer predrying times, a thin skin of solid polyamide forms at the surface because the solvent rapidly evaporates and, when the surfaces are mated, the skin forms a barrier against the entanglement of molecules from the two halves. This barrier is probably fragmented during clamping. As a result, the interface contains unbonded regions. Secondly, the strength of the adhesive layer decreases with longer predrying time because the voids which form increase with time.

With respect to strength of the polyamide bond, it is interesting to note that the maximum tensile strength of the adhesive bond (19.5 MPa without a notch) is about one-half the tensile yield point of the polyamide.

Yue and Chui[5] suggested that the polymer which is dissolved in the adhesive may provide a "gap filling" capability so that micro-roughness within the joint can be smoothed out, thereby reducing stress concentrations. In our case, 5% of dissolved polymer had no effect on the strength. Yue and Chui[5] found that the strength of bonded PVC continuously decreased as the amount of dissolved polymer in the THF solvent increased from 0 to 20%. On the other hand, in the PVC/methyl ethyl ketone system, 2% dissolved PVC increased the strength but 5 to 20% dissolved PVC continuously decreased the strength. These results, and the results of the present investigation, suggest that the amount of dissolved polymer in the adhesive should be dictated by the amount required to produce a viscosity which facilitates the application of the adhesive onto the surface of the polymer adherends.

CONCLUSIONS

1. The fracture strength of solvent welded polyamide-11 increases with predrying time up to a maximum value after 30 minutes at 40°C.
2. The strength decreases slowly after the maximum and tends toward an equilibrium value.
3. The relationship between fracture strength and predrying time can be explained in terms of the change with time of the concentration and mobility of the polymer at the mating interface.
4. The composition of the adhesive includes about 5% polymer, but the fracture strength does not change if the polymer is absent. Probably the polymer is added to the adhesive to achieve a convenient viscosity during its application.
5. A specimen that is precisely notched at the weld interface exhibits less scatter in its fracture strength than an unnotched specimen.

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