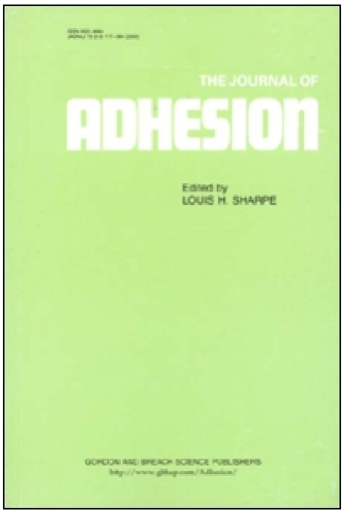

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Effect of Smoothness, Temperature, and Thermal History on the Strength of Solvent Welded Polyamide-11

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Effect of Smoothness, Temperature, and Thermal History on the Strength of Solvent Welded Polyamide-11

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The fracture strength of solvent welded polyamide-11 joints was measured as a function of the time of predrying. The effect of the smoothness of the surface of the adherend, the thermal history of the adherend, and the temperature during the predrying and curing of the bond were investigated. When the adherend surface is polished, the bond is stronger than for a milled surface. For a given predrying time, a higher temperature of predrying gives greater strength as does a higher temperature during curing. The quenched adherend has greater strength than a slow cooled adherend. Under all conditions the fracture strength exhibits a maximum value at an intermediate predrying time. These results are simply explained in terms of the concentration of molecules at the mating surface and the mobility of the molecules during curing.

KEY WORDS Solvent welding; polyamide-11; fracture; surface smoothness; thermal history

INTRODUCTION

Several thermoplastic polymers including PVC, polycarbonate, PMMA and polyamide are commonly joined by solvent-welding. The adhesion in solvent welded joints originates from the interdiffusion of polymer chains between superficial layers of the adherends which have been softened by the solvent. Solvent welding of polyamide-11 is important because it is the method used to join polyamide-11 systems for the distribution of natural gas.[1]

In a first paper by Beaume and Brown[2] about solvent welded polyamide-11, the strength of the bond was found to be highly dependent upon the predrying time, which is the time between the application of the solvent on the surface and the mating of both sides. The fracture strength exhibited a maximum value after about 30 min. of predrying. This dependency was analyzed in terms of concentration of polymer molecules at the mating interface and their mobility during drying (curing).

The influence of other parameters on the strength of the bond is presented now. These parameters are the smoothness of the adherend surface, the thermal history of the adherend and the temperature for predrying and drying. The fracture strength of the solvent welded polyamide-11 specimens was measured with a notched tensile test described in detail in Reference 2.

EXPERIMENTAL

Preparation of the Specimen

Commercial polyamide-11 was provided by Atochem North America under the name of Rilsan BESNO TL and was compression molded and then quenched at a rate of about 40 °C/min or cooled very slowly. The adhesive, consisting of a mixture of cresol-like solvents and less than 10% of dissolved polyamide-11, is produced under the brand of Nylink-1 by Industrial Pipe Systems (Australia).

The specimens shown in Figure 1 consist of two halves which were butt-glued together across their 5 × 25 mm surface. The smooth surfaces were polished metallographically with 600 Grit paper, and the milled surfaces were machined with a standard milling tool. A 3 mm deep notch was introduced in the adhesive joint in the form of a piece of Scotch® tape which prevents any adhesion over the aera of the Scotch® tape. The solvent was applied at 25 °C and then exposed to a given predrying temperature. It took about 20 seconds to apply the solvent. After a given predrying time, the specimens were usually dried for 7 days. Notched specimens were used instead of unnotched specimens because they gave less scatter and also permitted the calculation of a value of K_{IC}. A more detailed description of the specimen is available in Reference 2.

FIGURE 1 Geometry of specimen.

Tensile Test

Tensile tests were performed on an Instron machine at a constant cross head speed of 0.02 inch/min. and at room temperature. All the specimens exhibited a brittle behavior. For each condition a set of 7 specimens was tested. Sometimes more than one set of 7 specimens was tested for a given condition. The standard deviation within the set was usually less than 15%, but only sets exhibiting a standard deviation below 10% have been taken into account except for the milled specimens which exhibited a significantly higher scatter.

RESULTS

Effect of Roughness

Instead of being metallographically polished some surfaces were milled. As shown in Figures 2a and 3a, the surface state is quite different in both cases. Polishing leaves fine scratches while milling produces large grooves with partially torn material which remains on the surface. The fracture strengths of smooth and milled specimens are compared in Figure 4 after various predrying times at 40 °C and curing at 40 °C. Compared with the polished specimens, the scatter is generally larger for the sets of milled specimens. Also, with a few exceptions, their strength is lower than the fracture strength of polished specimens. It is to be noted that, in both cases, predrying for 5 min. generates a large increase in fracture strength compared with the minimum predrying time of about 20 seconds.

The fractured surfaces were examined with the SEM. Figures 2b and 3b show that for predrying times less than 20 seconds, fracture occurs at the interface between the adhesive and the adherend. For longer predrying times fracture occurs within the adhesive for both the smooth and milled specimens (Figures 2c and 3c). A cell structure is observed on the fractured surface in which the cells increase in size as the predrying time increases as shown in Figure 6.

Effect of Thermal History

Two thermal histories were investigated. After compression molding at 210 °C, the polyamide was either quenched at a rate of about 40 °C/min. or slow-cooled overnight. DSC experiments gave a crystallinity of 28.6% for the quenched material and 31.7% for the slow-cooled (SC) material.

The fracture strength *versus* predrying time at 40 °C is shown in Figure 5 for the quenched and SC states. The general variation of the strength with the predrying time is the same for the quenched as for the SC material. A maximum of strength is reached for the same predrying time of 30 min. However, the fracture strength of the slow-cooled specimens is lower than the strength of the quenched specimens for all predrying times except for the minimum predrying time of 20 seconds where the strengths are about the same. Unlike the quenched specimens, the slow-cooled specimens undergo a very fast decay in strength beyond the maximum, so that the final strength is reached after a rather short predrying time of 60 min.

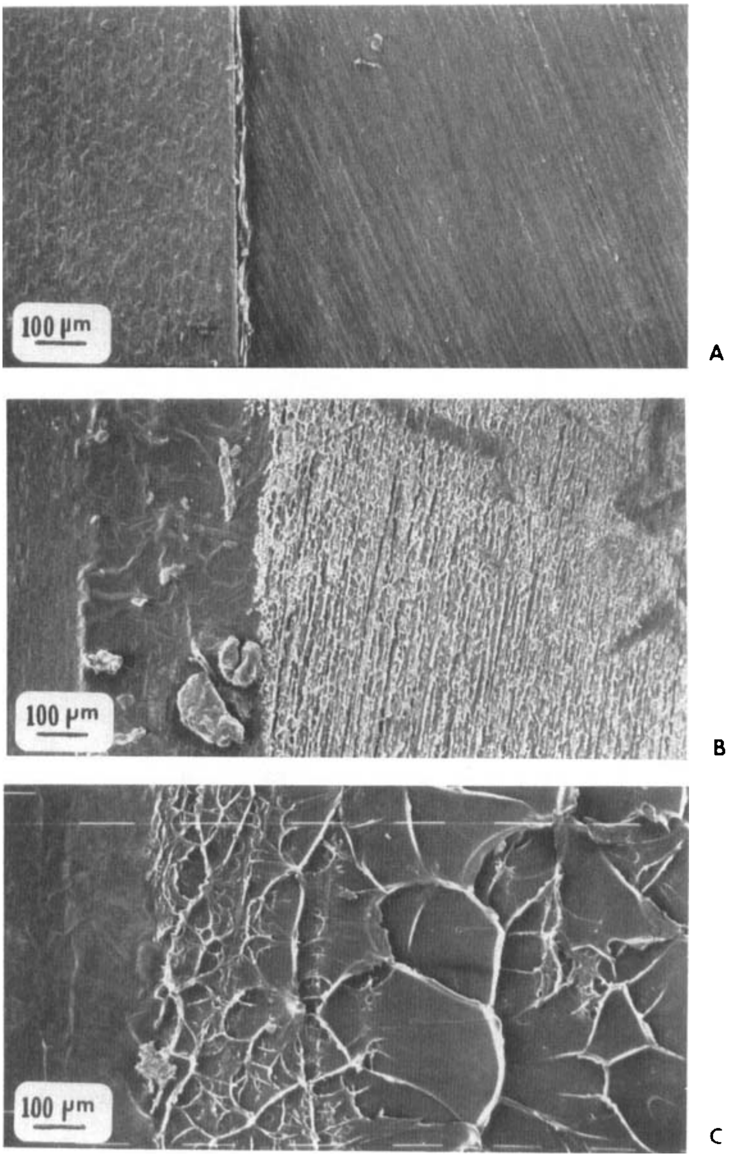

FIGURE 2 Specimens with smooth surface: a) original surface; b) fractured surface after 20 sec of predrying; c) after 10 minutes of predrying.

Micrographs of the fractured surfaces of the quenched and slow cooled states can be compared by viewing Figures 6 and 7. The fractured surface of the quenched state occurs completely within the adhesive after 5 minutes of predrying whereas for the slow cooled state fracture occurs partly at the adhesive bulk interface and partly within the adhesive as shown in Figures 7a and b. For both the quenched and slow cooled states the cell size increases uniformly with predrying time except that for a

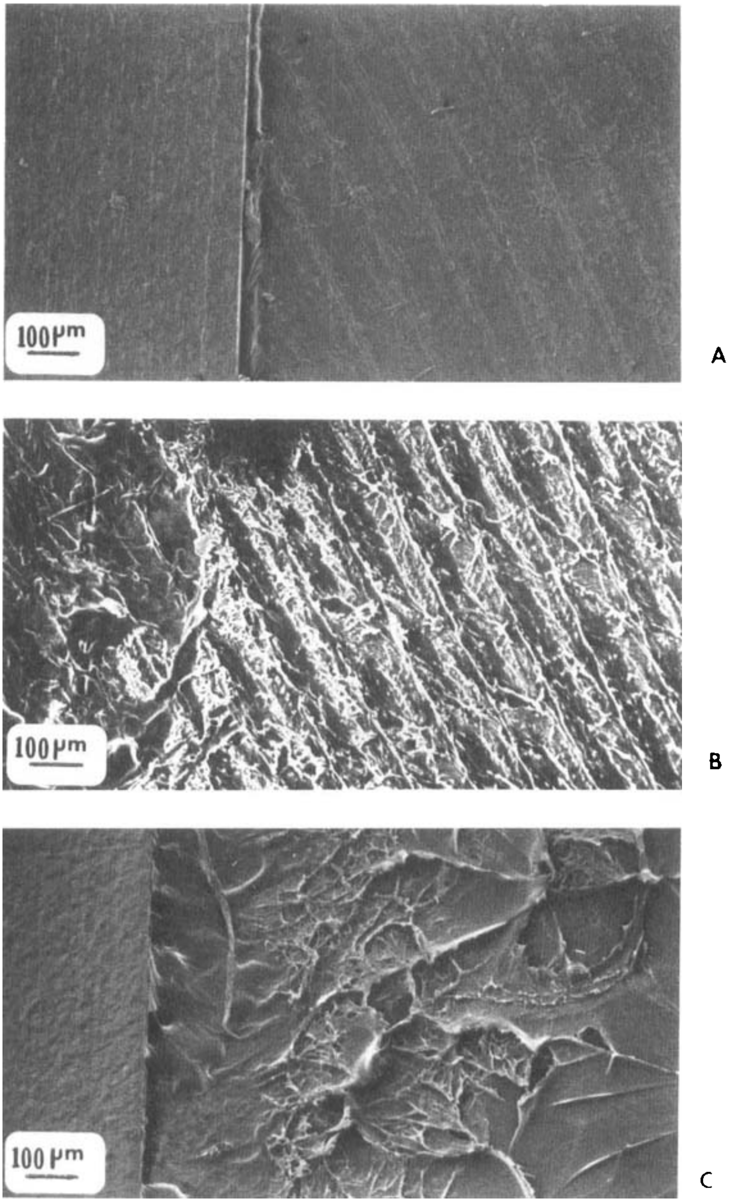

FIGURE 3 Specimens with milled surface: a) original surface; b) fractured surface after 20 sec of predrying; c) after 10 minutes of predrying.

given amount of predrying the cell size is smaller in the slow cooled state. For the slow cooled state, a round particle occurs within the cell. This round particle increases in size with predrying time as does the cell. The partial fracture at the weak adhesive-bulk interface (Fig. 7a) in the slow cooled material accounts for the fact that its strength is less than the quenched state for short predrying times. Probably the round particles

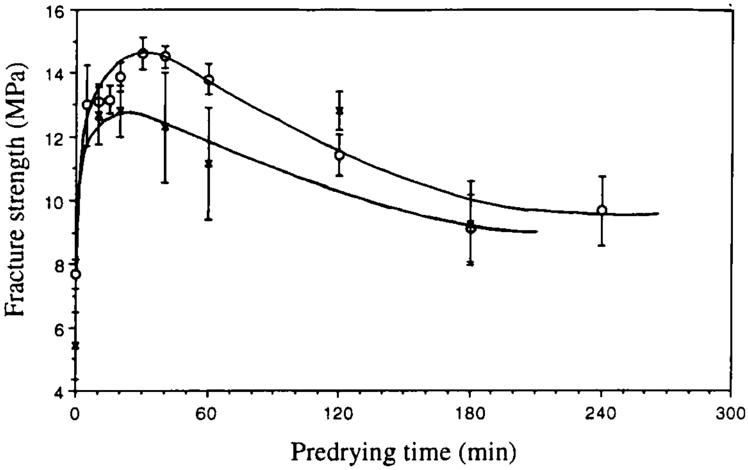

FIGURE 4 Fracture strength *versus* predrying times, predrying and drying temperatures = 40 °C; O—smooth surface; X—milled surface.

within the cells cause the slow cooled state to be weaker than the quenched state and also cause the rapid decrease in strength beyond the maximum value at 30 minutes. Higher magnification pictures of the round particle in the cells of the slow cooled material are shown in Figure 8. At the present time nothing is directly known about the structure or origin of the round particle except that it has only been observed in the slow cooled state.

Effect of Temperature

Four predrying temperatures, 25 °C, 33 °C, 40 °C, and 58 °C, were investigated. The glass transition temperature of polyamide-11 is about 52 °C. The drying temperature

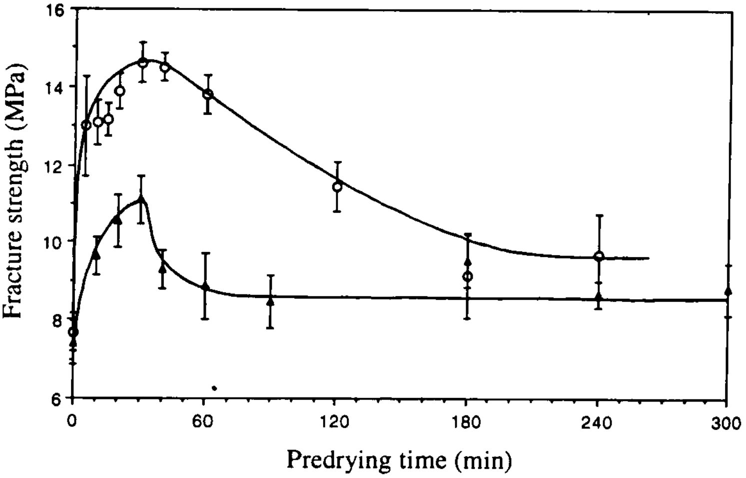

FIGURE 5 Fracture strength *versus* predrying time for predrying and drying temperatures of 40 °C. O—quenched state; Δ—slow cooled state.

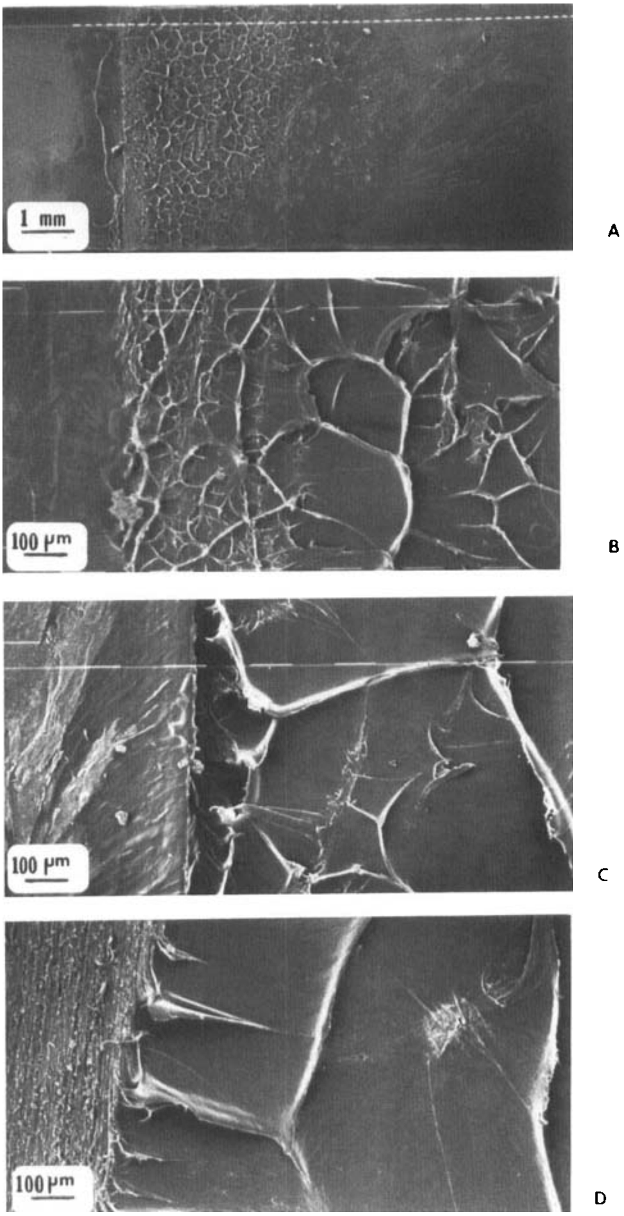

FIGURE 6 Fractured surface of quenched state for various predrying times. A—10 min; B—10 min; C—30 min; D—180 min predrying and drying temperatures = 40 °C.

was the same as the predrying temperature and the drying time was 7 days at 33 °C and 40 °C, 5 days at 58 °C and 3 weeks at 25 °C. Figure 9 shows the effect of predrying time for each predrying temperature. The fracture strength at the minimum predrying time of 20 sec. was the same for all predrying temperatures. All data indicate a maximum in the fracture stress. The maximum value increased as the predrying temperature was

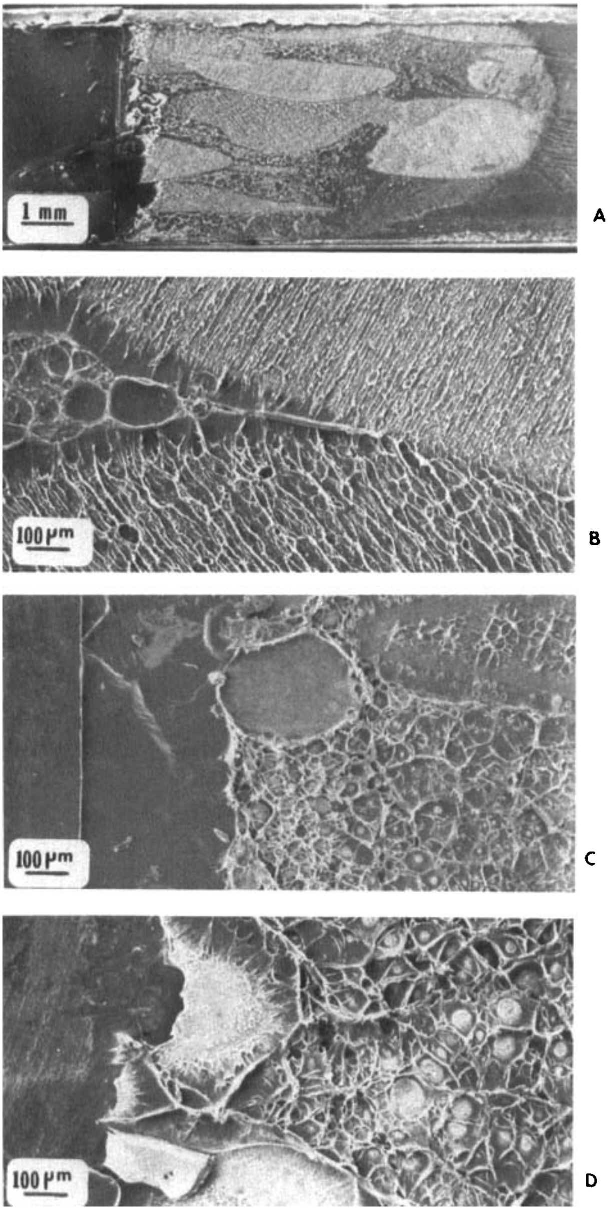

FIGURE 7 Same as Figure 6 except for slow cooled state.

increased. Also, the time to reach the maximum value decreased as the temperature increased. These observations are consistent with the faster kinetics of molecular motions at the higher temperature.

The effect of drying temperature was investigated by first predrying at 25 °C and then drying some specimens at 25 °C for 3 weeks and some at 40 °C for 7 days. The results are

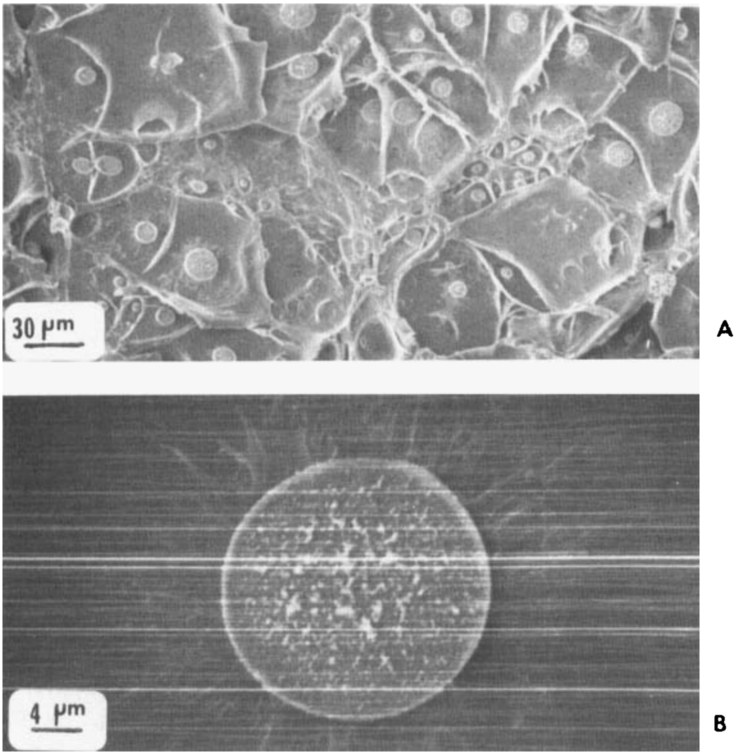

FIGURE 8 Fractured surfaces of slow cooled state after 30 minutes of predrying: a) low magnification; b) high magnification of round particle.

shown in Table I. Except for the minimum predrying time of 20 seconds, the higher drying temperature produces a significant increase in strength. When one compares the effect of changing the predrying temperature for a fixed drying temperature, as shown in Table II, against the effect of changing the drying temperature for a fixed predrying temperature as shown in Table I, it is seen that changing the predrying temperature has a relatively smaller effect.

DISCUSSION

The Model

Practically all the results can be explained in terms of the model shown in Figure 10a and with equation (1) which was used by Beaume and Brown in Reference 2.

The strength after predrying time, t, depends on the degree of entanglement, $E(t)$, that occurs during drying. $E(t)$ is given by:

$$E(t) = C(t) \cdot M(t) \tag{1}$$

TABLE I
The Effect of Drying Temperature after Predrying at 25 °C

Predrying Time(min) at 25 °C	Fracture Strength (MPa) Curing at 25 °C for 3 Weeks	Fracture Strength (MPa) Curing at 40 °C for 7 Days
1/3	8.6 ± 0.7	7.7 ± 0.5
30	8.8 ± 0.8	12.9 ± 1.0
90	8.7 ± 0.6	13.2 ± 0.2

TABLE II
The Effect of Predrying Temperature before Drying at 40 °C for 7 Days

Predrying Time (min)	Fracture Strength (MPa) Predrying at 25 °C	Fracture Strength (MPa) Predrying at 40 °C
1/3	7.7 ± 0.5	7.7 ± 0.5
30	12.9 ± 1.0	14.6 ± 0.5
90	13.2. ± 0.2	12.8

C(*t*) is a function of the concentration of the polymer that diffuses into the adhesive after predrying time, *t*. As shown in Figure 10, *C*(*t*) decreases with the distance from the original bulk-solvent interface AB to the free surface of the solvent. In general, *C*(*t*) at any point in the adhesive layer increases with predrying time and temperature. *M*(*t*) is related to the mobility of the polymer molecules in the adhesive layer during drying,

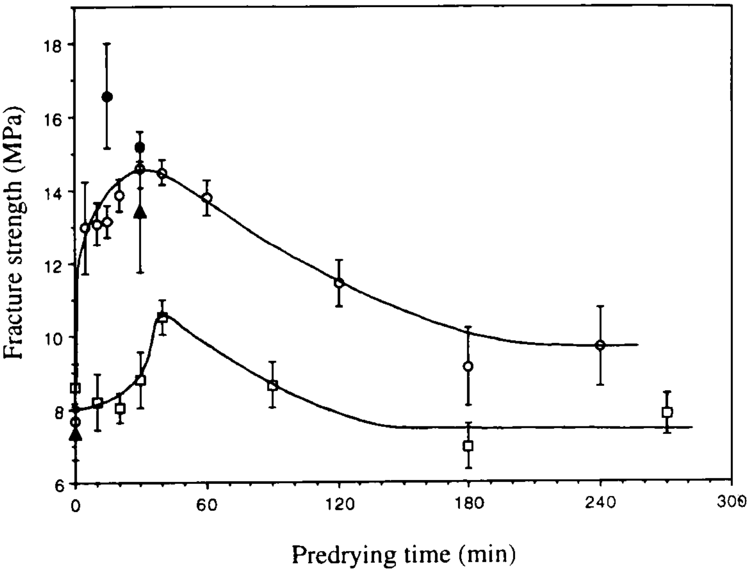

FIGURE 9 Fracture strength *versus* predrying time at various predrying temperatures. □—25 °C; ▲—33 °C; ○—40 °C; ● — 58 °C. Drying temperature same as predrying temperature.

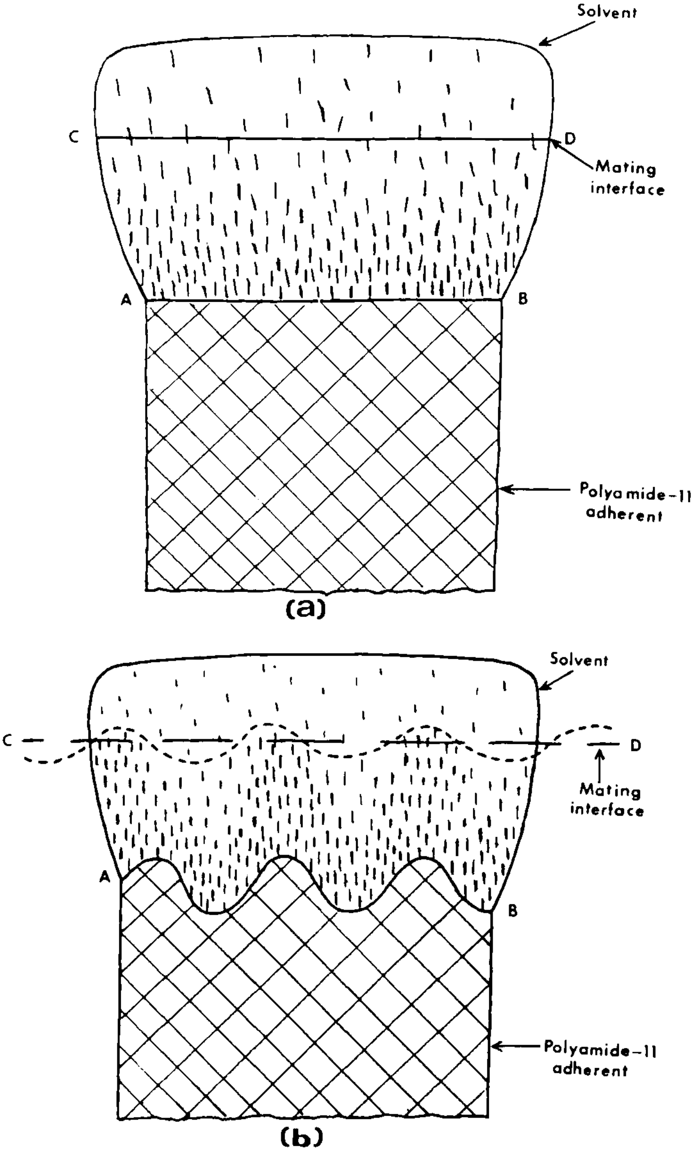

FIGURE 10 Model of the adhesive layer during predrying. Position of mating interface is determined by how much of the adhesive layer is squeezed out during mating. Density of dash lines is related to the polymer concentration: a) for smooth surface; b) for milled surface.

$M(t)$ decreases with predrying time because the solvent concentration in the adhesive layer decreases by evaporation and diffusion.

Since the degree of entanglement is a product of $C(t)$ and $M(t)$, it passes through a maximum value with respect to predrying time as was observed in all the experiments. The entanglement between the two halves of the specimen occurs at the mating interface CD which is the middle of the final adhesive layer. As shown in Reference 2, the thickness of the final adhesive layer increases with predrying time. The reason is as follows: when the two halves of the specimen are clamped together, adhesive is squeezed out and the amount of adhesive that is squeezed out depends on its viscosity. The viscosity of the adhesive layer increases with predrying time because the concentration of polyamide in the solvent increases with time while the amount of solvent decreases by evaporation and diffusion into the bulk polymer.

During drying, entanglement takes place between molecules from each half of the specimen. The degree of entanglement and thus the fracture stress depends on the concentration of the molecules at the mating surface and their mobility which depends on the solvent concentration in the vicinity of the mating surface. Now the effect of surface roughness, thermal history, and the temperature will be explained in terms of the above model.

Surface Roughness

Figure 10b is useful for explaining the effect of surface roughness. Since the original interface AB between the adhesive and the bulk polymer is rough, then it is expected that the concentration of polymer that diffuses into the adhesive will reflect this roughness. If the concentration of polymer varies along the mating plane, then the degree of subsequent entanglement after mating will not be uniform. Possibly this effect may account for the lower fracture stress and for the fact that the scatter in fracture stress from the rough specimen is much greater than that from the smooth specimen.

Thermal History

Slow cooling produced a greater crystallinity than quenching. Therefore, it is expected that the rate of solution of the bulk polymer into the solvent will be less for the slow cooled state than for the quenched state. Consequently, the concentration at the mating interface will also be less. Since usually the diffusion rate and rate of evaporation should not vary greatly with concentration of polymer, the change in fracture stress with predrying time is expected to have the same general form for the slow cooled and quenched state, as shown in Figure 5. For both states the shape of the curve up to the maximum is the same except that the value of the fracture stress is less for the slow cooled state. The maximum value of the fracture stress occurs at 30 minutes for both states. A big difference between the slow cooled and quenched states is the rate of decrease of the fracture stress beyond the maximum. The slow cooled state decreases in strength much more rapidly. Possibly this behavior is caused by the occurrence of the round particles (Figs. 7 and 8) which may produce an embrittlement effect.

The source of the round particles in the slow cooled state is not known. Possibly, slow cooling produces some very perfect regions of crystallinity which are very difficult to dissolve. During drying some of the polymer molecules may precipitate on these residual crystals and form the round particle. If this is true, it would mean that less molecules would be available for forming entanglements with molecules in the other half of the specimen. Then, the fracture stress would be less than if all molecules participated in the entanglement process.

Temperature Effect

When the temperature of predrying is decreased, the diffusion of the molecules into the adhesive is slower. Thus, for a given predrying time the concentration of molecules at the mating interface will be less, as will be the fracture stress, in agreement with Figure 9. Also, the change in fracture stress with respect to predrying time should exhibit a change in kinetics when the temperature is changed. Figure 9 shows that the shape of the functional relationship between fracture stress and predrying time before the maximum is convex upward at 40 °C and concave upward at 25 °C. This indicates that the diffusion rate is less at 25 °C. Also, the time to reach the maximum strength is 40 minutes at 25 °C, 30 minutes at 40 °C, and 15 minutes at 58 °C. The maximum strength increased from about 11 MPa to about 17 MPa as the predrying temperature went from 25 °C to 58 °C.

In the above experiments, the temperatures of predrying and drying were the same. The question arises as to how much of the increase in strength with temperature depends on the predrying and how much on the drying. A comparsion of Tables I and II suggests that increasing the drying temperature has a greater influence on the maximum strength than an equal increase in the predrying temperature. Whereas the strength has a maximum value at some intermediate value of the predrying time, it increases monotonically to an equilibrium value during drying.[1]

The contribution of predrying and drying to the final strength can be simply described. During predrying, polymer dissolves into the solvent to form the adhesive layer where the amount dissolved increases with temperature and time. Also, solvent evaporates and diffuses into the polymer so that the viscosity of the adhesive layer increases with time and temperature. The degree of entanglement during drying depends on the concentration of polymer in the adhesive layer and the mobility of the molecules. The concentration of polymer is partly determined by the concentration of polymer that exists at the mating interface after predrying and partly from the additional diffusion of polymer from the bulk during drying. The initial mobility of the molecules is determined primarily by the concentration of solvent that remains in the adhesive layer after mating. The mobility of the molecules during drying gradually diminishes as the amount of solvent in the adhesive layer diminishes, so that the fracture strength approaches an equilibrium as the drying time increases. An increase in temperature not only accelerates the approach toward equilibrium, but it also increases the equilibrium value of the fracture stress.

The maximum value of 17 MPa for the fracture stress that was obtained in these experiments was for a notched quenched specimen with a polished surface that predried at 58 °C for 15 minutes and dried at 58 °C. Probably this value could have been produced after about 1 hr. of drying time instead of 5 days. In the previous paper it was found that without a notch, the fracture strength was 13% greater than with the 3 mm deep notch. Thus, for the experimental conditions used in this investigation, the greatest fracture strength would have been 23 MPa without a notch. It is important to know that this value is about 50% less than the tensile yield point of quenched bulk polyamide-11.

CONCLUSIONS

1. For all conditions, the fracture strength goes through a maximum value as a function of the predrying time.
2. The maximum in the fracture strength is greater for the adherend with a smooth surface than for a rough surface.
3. The maximum in strength is greater for quenched material than slow cooled material.
4. The maximum in strength increases with predrying temperature and with the drying temperature.
5. For a given change in temperature the effect of drying on the maximum fracture stress is greater than the effect of predrying.

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