Preparation of Block Copolyetheramides and their Properties as Hot Melt Adhesives

ANDREW TEH HU, RUEY-SHI TSAI, and YU-DER LEE,*

*National Tsing Hua University, Department of Chemical
Engineering, Hsinchu, Taiwan, Republic of China 30043*

Synopsis

  Block copolyetheramides were prepared by incorporating polyether into polyamide through melt polycondensation of polyetherdiamine, piperazine, dimer acid, and ε-caprolactam. Bulk properties of block copolyetheramide, such as tensile strength, tensile modulus, elongation at break, hardness, and impact strength, were evaluated with respect to composition. Investigation on the lap shear strength and T-peel strength of block copolyetheramide hot melt adhesive showed that the lap shear strength was more composition-dependent. Moisture and elevating test temperature also reduced the lap shear strength significantly.

INTRODUCTION

   According to their solidification process, polymer adhesives can be grouped into three categories: chemical reaction type, solvent type, and hot melt type. The hot melt adhesive has become very popular in the last decade because it is convenient and fulfills the environmental requirements.[1-4] Although EVA copolymer is the most frequently used hot melt adhesive, polyesters and polyamides have increased their shares in the market since the former is unsuitable in a high temperature surrounding.[5-9]

   The use of polyamides as hot melt adhesive was found as early as 1959.[10,11] Since then many reports, especially patents, have appeared in the literature. Polyamides hot melt adhesive can be classed into four kinds in accordance with their compositions:

   (1) Polycaprolactam modified with dimer acid, aliphatic or aromatic diacid and diamine,[12-20] carboxy-terminated polybutadiene,[21] polyether diamine,[22] and poly(tetramethylene glycol).[23]

   (2) Polyamides synthesized directly from diacid and diamine.[24-28]

   (3) Polyoxypropylene diamine series.[29-32]

   (4) Polyamide blends.[33-36]

   In this study block copolyetheramide is prepared by incorporating polyether into polyamide through melt polycondensation of polyetherdiamine, piperazine, dimer acid, and ε-caprolactam. The effect of compositions on impact strength and adhesion strength was investigated. The bulk properties were also determined in relation to the adhesion strength.

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*To whom all correspondence should be addressed.

EXPERIMENTAL

Reactants

Polyoxypropylene diamine (Jeffamine D-2000; denoted as J-2000) with molecular weight of 2000 was supplied by the Texaco Chemical Co. Piperazine was Merck reagent grade and ϵ-caprolactam was obtained from China Petrochemical Development Corp. Dimer acid (Pripol 1010) with acid value of 191-197 meq/g was supplied by Unichema Chemie.

Synthesis of Block Copolyetheramides

The following is a typical synthesis reaction. To a four-necked 1000-mL flask equipped with stirring system, condenser, thermocouple, nitrogen gas inlet, and heating mantle, 200 g of ϵ-caprolactam (1.77 mol), 207.7 g of J-2000 (0.1 mol), 17.9 g of piperazine (0.21 mol), and 175.1 g of dimer acid (0.31 mol) were added. The reactants were heated to 232°C at a stirring speed of 200 rpm under nitrogen. After 30 h of reaction, the system was put under vacuum for 2 h. The product was extracted with water by Soxhlet extractor till constant weight. The yields were about 93–95%. The obtained product was dried at 100°C *in vacuo*.

Two series of block copolyetheramides were synthesized. The mole ratio of diamine (J-2000 and piperazine) to diacid (dimer acid) was always kept at 1 in order to obtain high molecular weight. In the first series (J-series), the mol% of ϵ-caprolactam and diacid were held constant, but the amounts of J-2000 and piperazine varied. Table I lists the compositions for the J-series based on phr (parts per hundred parts of ϵ-caprolactam). In the second series (C-series) the amount of ϵ-caprolactam varied. The compositions for the C-series based on phr (parts per hundred parts of J-2000) are listed in Table II.

End Group Analysis and Inherent Viscosity

The inherent viscosity at 30°C in *m*-cresol at a concentration of 0.5 g/dL was determined by Ubbelohde viscometer. The amine number (meq KOH/g) for each sample was determined by titrating its phenol/methanol (weight ratio = 70:30) solution with aqueous HCl standard solution, and the acid

TABLE I
Charged Monomer Composition of J-Series

	J(0)	J(1)	J(2)	J(3)	J(4)
			phr[a] (mole fraction)		
ϵ-Caprolactam	100.0	100.0	100.0	100.0	100.0
	(74%)	(74%)	(74%)	(74%)	(74%)
Dimer acid	88.0	88.0	88.0	88.0	88.0
	(13%)	(13%)	(13%)	(13%)	(13%)
J-2000	0.0	30.1	60.2	103.9	150.9
	(0%)	(1.3%)	(2.5%)	(4.3%)	(6.3%)
Piperazine	13.6	12.0	10.8	9.0	6.9
	(13.0%)	(11.7%)	(10.5%)	(8.7%)	(6.7%)

[a] Based on 100 parts of ϵ-caprolactam.

TABLE II
Charged Monomer Composition of C-Series

	C(1)	C(2)	C(3)
		[phr^a (mole fraction)]	
J-2000	100.0	100.0	100.0
	(6.8%)	(4.3%)	(2.5%)
ε-Caprolactam	49.2	96.2	192.3
	(59.2%)	(74.0%)	(85.0%)
Dimer acid	84.4	84.4	84.4
	(20.4%)	(13.0%)	(7.5%)
Piperazine	8.6	8.6	8.6
	(13.6%)	(8.7%)	(5.0%)

^{a} Based on 100 parts of J-2000.

number for each sample was obtained by dissolving the sample in benzyl alcohol and then titrating it with KOH benzyl alcohol standard solution.

Thermal Properties

The thermal properties of block copolyetheramides were determined by Perkin-Elmer DSC-2 and the heat of fusion of the sample was obtained by comparing it with the heat of fusion of Indium taken as 6.8 cal/g.

Tensile Properties and Hardness

The tensile properties of compression molded sheet were measured in accordance with ASTM D-638 with crosshead speed of 5 mm/min. The hardness (Shore D) was determined via durometer from Testing Machine Inc.

Impact Strength

A RIT-8000 Impact Tester from Rheometrics Inc. with clamp diameter of 1 in. and impact speed of 2000 in./min was used to measure the impact strength of the 3.0-mm-thick compression-molded sheets of block copolyetheramides. The impact force which the samples could resist was monitored as the probe of diameter 1.57 cm impacted the sample. The integrating value of impact force vs. penetrated distance curve gave total impact energy that the sample could absorb, and the impact strength was obtained by dividing this value with the thickness of the sample.

Adhesion Strength of the Block Copolyetheramides Used As Hot Melt Adhesive

Aluminum was chosen as the adherend and its surface was treated as follows. Aluminum was dipped in trichloroethylene for 24 h, followed by rinsing with water. The cleaned aluminum was then dipped in a $Na_2Cr_2O_7/H_2SO_4$ solution ($Na_2Cr_2O_7 : H_2SO_4 : H_2O = 1 : 10 : 30$ by weight) at 60°C for 2 h. Finally it was washed with water and dried.

The block copolyetheramide adhesive films were obtained by compression molding. The adhesion joint was then obtained by pressing the film between
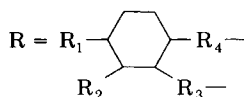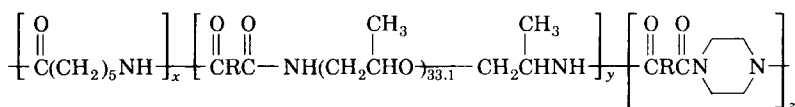
two pieces of treated aluminum adherend at preselected temperature and pressure (see Tables IX and X). Lap shear strength was determined according to ASTM D1002-72 with crosshead speed of 2 mm/min. T-peel strength was measured in accordance with ASTM D1876-71 with crosshead speed of 200 mm/min.

The effect of moisture absorption on lap shear strength was determined according to ASTM D-570 on samples aged in humidity chamber at 60°C, 95% relative humidity.

RESULTS AND DISCUSSION

Characterization of the Polymerization

The melt polycondensations of ϵ-caprolactam, dimer acid (Pripol 1010), piperazine, and polyetherdiamine (J-2000) gave block copolyetheramides with chemical structure shown below:

$$\left[\begin{array}{c} O \\ \| \\ \overline{C(CH_2)_5 NH} \end{array}\right]_x \left[\begin{array}{c} O \quad O \quad\quad\quad CH_3 \quad\quad\quad\quad CH_3 \\ \| \quad \| \quad\quad\quad | \quad\quad\quad\quad | \\ CRC\!-\!NH(CH_2CHO)_{33.1}\!-\!CH_2CHNH \end{array}\right]_y \left[\begin{array}{c} O \quad O \\ \| \quad \| \\ CRCN\!\!\bigcirc\!\!N \end{array}\right]_z$$

$$R = R_1 \!\!\bigcirc\!\! R_4\!- $$
$$R_2 \quad R_3\!-$$

$$R_1 + R_2 + R_3 + R_4 = 28 \text{ carbons}$$

The measured acid number, amine number, and inherent viscosities for the J-series and C-series are listed in Tables III and IV, respectively. Since the acid plus amine number (corresponding to end group content) and the inher-

TABLE III
Acid Number, Amine Number, and Inherent Viscosity of J-Series

	J(0)	J(1)	J(2)	J(3)	J(4)
Acid number (eq/g)	2.5	3.2	2.9	2.3	2.7
Amine number (eq/g)	1.4	1.5	1.0	0.9	0.7
Acid number + amine number (eq/g)	3.9	4.7	3.9	3.2	3.4
η_{inh} (dL/g)	0.65	0.50	0.57	0.58	0.59

TABLE IV
Acid Number, Amine Number, and Inherent Viscosity of C-Series

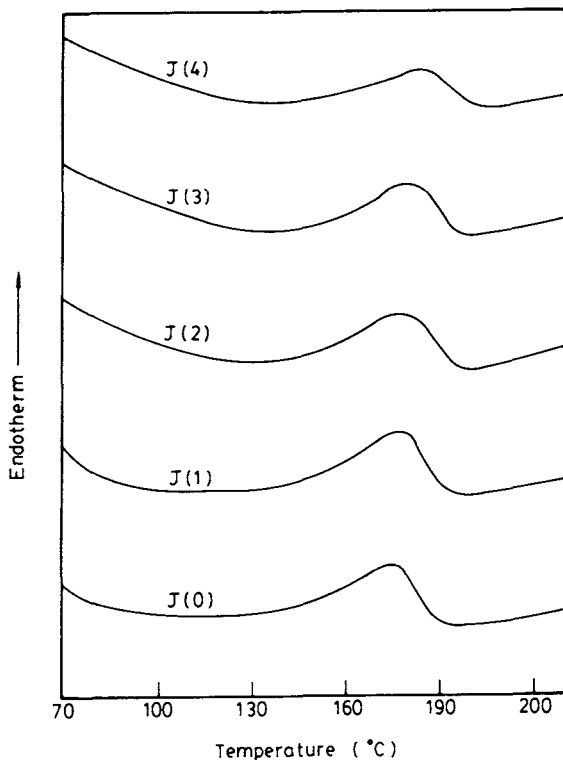|	C(1)	C(2)	C(3)
Acid number (eq/g)	1.7	2.4	2.8
Amine number (eq/g)	1.1	0.9	1.6
Acid number + amine number (eq/g)	2.8	3.2	4.4
η_{inh} (dL/g)	0.56	0.58	0.56

Fig. 1.   DSC thermograms of J-series.

ent viscosity of all samples do not vary significantly, it is concluded that molecular weight differences do not cause any variation in properties.

Thermal Properties

The DSC thermograms of the J-series are shown in Figure 1. T_m of each polyethramides of the J-series was about 180°C as shown in Table V. The heat of fusion and relative crystallinity of the J-series are also listed in Table V. Since the mole ratio of ε-caprolactam to diacid (or diamines) of the J-series was the same and equal to 5.7 : 1, the copolymerization effect of diacid and diamines on the T_m of polycaprolactam segment was the same, even though

TABLE V
T_m, Heat of Fusion, and Relative Crystallinity of J-Series

	J(0)	J(1)	J(2)	J(3)	J(4)
T_m (°C)	175	175	177	180	183
Heat of fusion (cal/g)	16.9	15.0	13.7	9.6	5.9
Relative crystallinity[a] (%)	33.8	29.9	27.3	19.2	11.8

[a] Relative crystallinity was obtained by dividing the heat of fusion with the heat of fusion of fully crystallized nylon 6 (50 cal/g[37]).
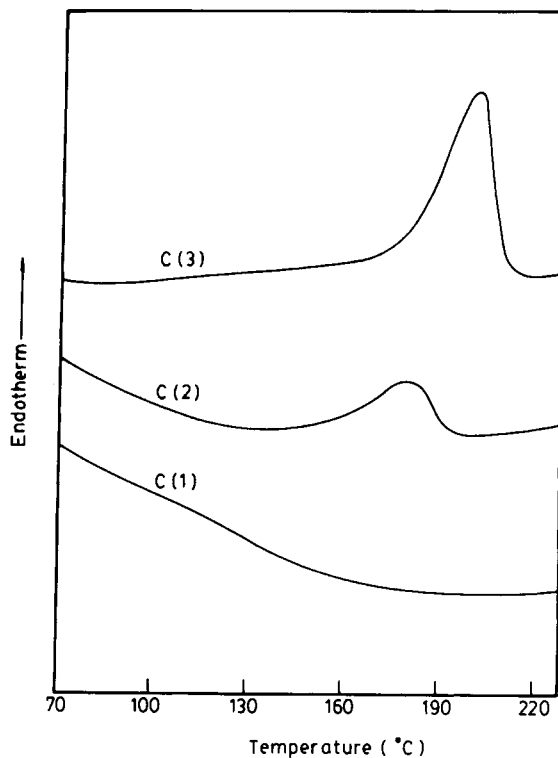
Fig. 2.   DSC thermograms of C-series.

the J-2000 content was different; therefore, similar T_m was found in the J-series. However, the relative crystallinity decreased as the content of J-2000 increased as shown in Table V. Since only the polycaprolactam segment could crystallize in these block copolyetheramides, any increase in the content of J-2000 would decrease the weight fraction of ϵ-caprolactam and therefore the relative crystallinity.

The DSC thermograms of the C-series are shown in Figure 2. T_m, heat of fusion, and the relative crystallinity of the C-series are listed in Table VI. The mole ratio of ϵ-caprolactam to diacid of C(1) was equal to 2.9 : 1, and, since the polycaprolactam block length was too short to crystallize, no melting peak

TABLE VI
T_m, Heat of Fusion, and Relative Crystallinity of C-Series

	C(1)	C(2)	C(3)
T_m (°C)	—	180	200
Heat of fusion (cal/g)	0	9.6	25.1
Relative crystallinity[a] (%)	0	19.2	50.2

[a] Relative crystallinity was obtained by dividing the heat of fusion with the heat of fusion of fully crystallized nylon 6 (50 cal/g[37]).

TABLE VII
Tensile Properties and Hardness of J-Series

	J(0)	J(1)	J(2)	J(3)	J(4)
Tensile strength at break (psi)	2270 ± 110	1700 ± 90	1310 ± 80	870 ± 70	570 ± 45
Tensile yield strength (psi)	1500 ± 70	1100 ± 60	800 ± 135	650 ± 30	320 ± 15
Tensile modulus (psi)	18,500 ± 600	16,200 ± 500	8400 ± 250	6500 ± 200	4900 ± 130
Elongation at break (%)	130 ± 60	210 ± 75	250 ± 70	250 ± 65	150 ± 50
Shore D hardness	63	56	48	37	35

was observed as shown in Figure 2. On the other hand, the mole ratio of ϵ-caprolactam to diacid of C(3) was equal to 11.4 : 1, and a T_m of 200°C was observed due to longer block length of polycaprolactam. The relative crystallinity increased as the content of ϵ-caprolactam increased in the C-series.

Tensile Properties and Hardness

The tensile strength at break, tensile yield strength, tensile modulus, elongation at break, and Shore D hardness of the J-series and C-series are listed in Tables VII and VIII, respectively. For the J-series, as the content of J-2000 increased, the crystallinity decreased and the strength, modulus, and hardness decreased as well. In the case of the C-series, the strength, modulus, and hardness increased as the content of ϵ-caprolactam increased.

Impact Strength

The polyetheramide samples could not be broken by a pendulum type impact tester (Izod impact tester). Therefore, their impact strength was determined by a fast speed probe-type impact tester, RIT-8000. The sample was impacted with a probe at a speed of 2000 in./min. The impact forces that the sample could resist vs. the distances which the probe penetrated through it were monitored. The impact strength was obtained by integrating the force vs. distance curve as the total impact energy that the sample could absorb.

TABLE VIII
Tensile Properties and Hardness of C-Series

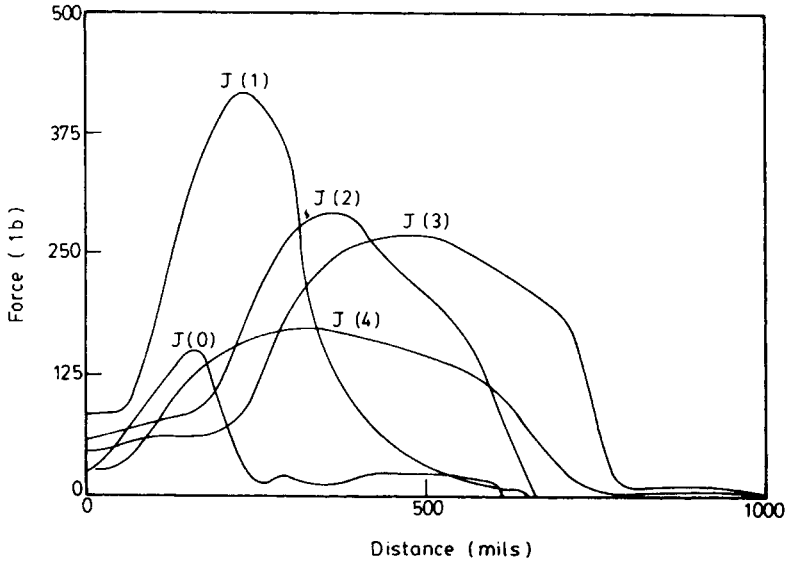|	C(1)	C(2)	C(3)
Tensile strength at break (psi)	150 ± 20	870 ± 70	1800 ± 90
Tensile yield strength (psi)	95 ± 10	650 ± 30	—
Tensile modulus (psi)	4700 ± 150	6500 ± 200	28400 ± 900
Elongation at break (%)	40 ± 15	250 ± 100	270 ± 80
Shore D hardness	18	37	54

Fig. 3.   The impact force vs. distance relationship for J-series.
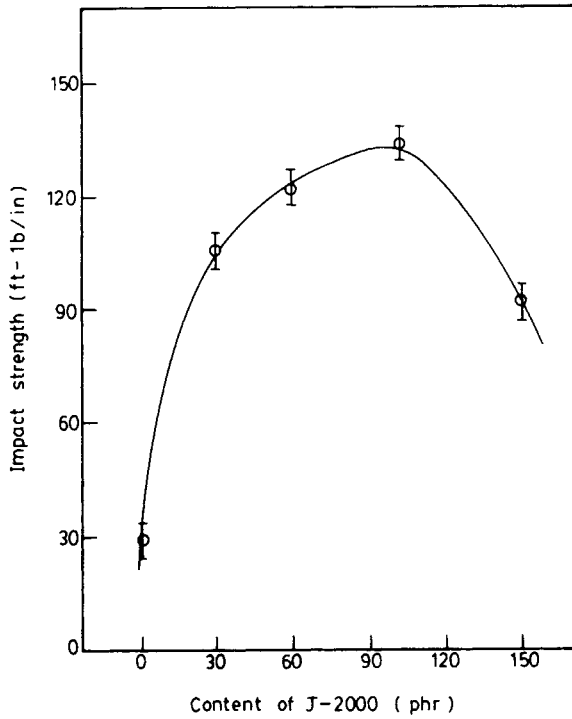

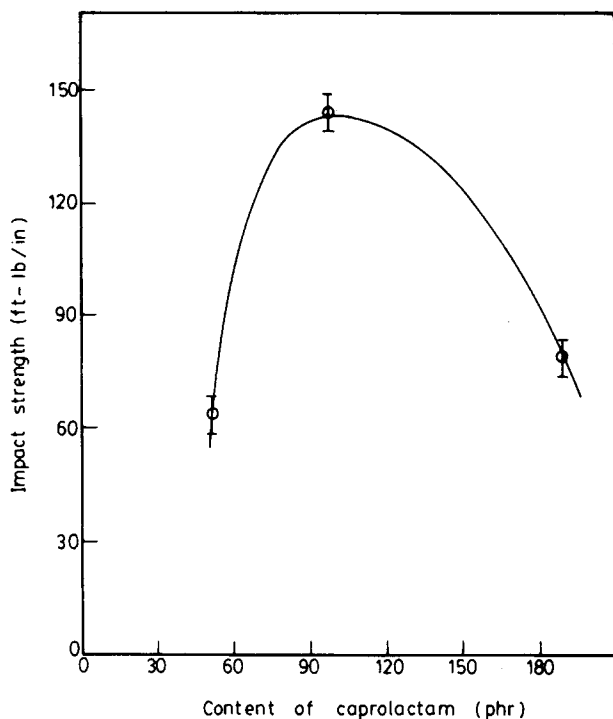Fig. 4.   Impact strength of J-series.

Fig. 5.   Impact strength of C-series.

The force versus distance relationship for J-series is shown in Figure 3, and the effect of composition on the impact strength for J-series is shown in Figure 4.

When J-2000 was not present, as at J(0), the impact strength was low as shown in Figure 4. But with the presence of J-2000, the impact strength increased considerably and reached a maximum when its content was around 104 phr. This phenomenon could be explained as follows: As the content of J-2000 increased, the hardness and modulus decreased; thus the impact force which the samples could resist also decreased, as shown in Figure 3. On the other hand, the distance that the sample could resist impact force increased as the content of J-2000 increased, also as shown in Figure 3. Therefore, a maximum impact strength which was related to the total absorbed impact energy would exist at a certain J-2000 content, and that was about 104 phr. Although the hardness or modulus of J(0) was very high, before it could resist high impact force, it was broken and its impact strength was low. Obviously, the introduction of flexible polyether part (J-2000) would increase the impact strength.

Figure 5 shows the effect of composition on the impact strength of the C-series. For the same reason, the impact strength reached a maximum when the content of ε-caprolactam was about 96 phr. Although C(3) and J(0) had about same content of ε-caprolactam (50% by weight), the impact strength of C(3) was higher than that of J(0). It was further evidence that introducing polyether into the main chain did increase the impact strength.

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TABLE IX
Effects of Aging at 60°C, 95% Relative Humidity on the Lap Shear Strength (psi) of J-Series[a]

	J(0)	J(1)	J(2)	J(3)	J(4)
No aging	1990 ± 300	1600 ± 240	1260 ± 200	1120 ± 150	800 ± 120
3 days	1510 ± 230	1180 ± 180	640 ± 110	530 ± 100	330 ± 90
7 days	1230 ± 210	960 ± 150	600 ± 110	450 ± 100	270 ± 50

[a]Adhesion temperature and pressure for hot melt adhesive were 190°C and 80 psi respectively.

TABLE X
Effects of Aging at 60°C, 95% Relative Humidity on the Lap Shear Strength (psi) of C-Series[a]

	C(1)	C(2)	C(3)
No aging	200 ± 50	1120 ± 150	1600 ± 240
3 days	130 ± 30	530 ± 100	880 ± 120
7 days	110 ± 30	450 ± 100	480 ± 110
Adhesion temperature[b] (°C)	135.0	190.0	210.0

[a]Adhesion pressure for hot melt adhesive was 80 psi.
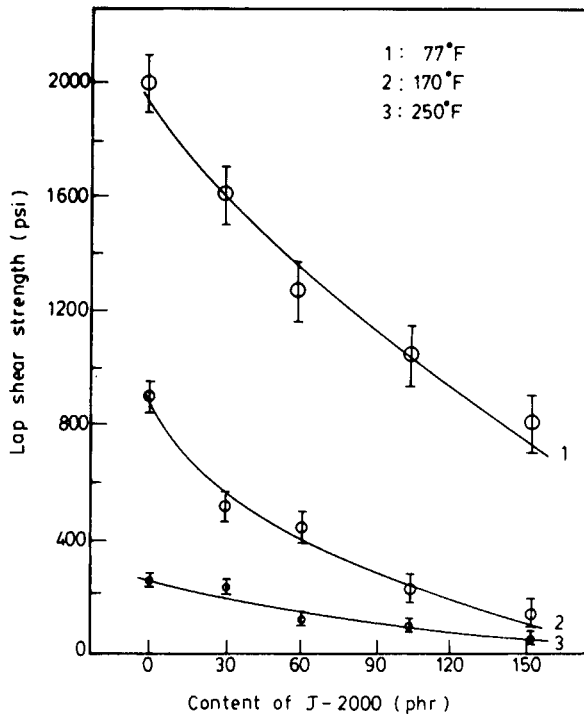[b]For hot melt adhesive.

Fig. 6. Lap shear strength of J-series at different testing temperatures (°F): (1) 77; (2) 170; (3) 250.
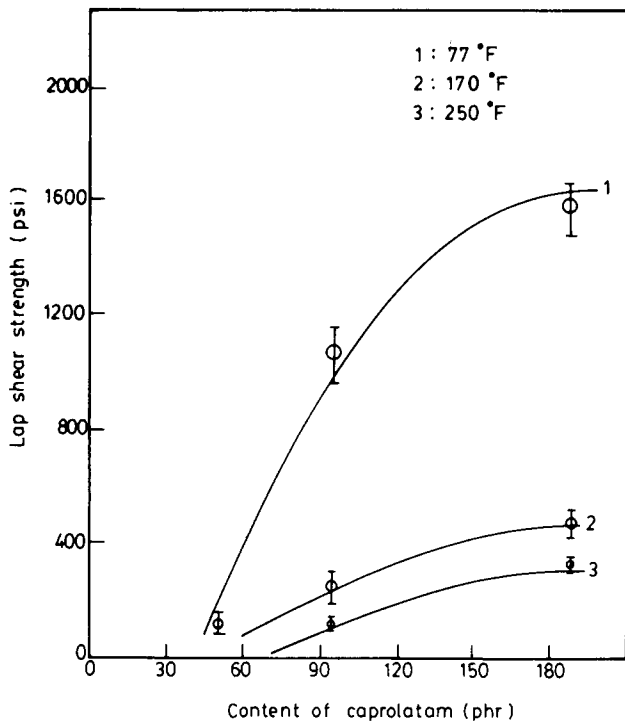
Fig. 7.   Lap shear strength of C-series at different testing temperatures (°F): (1) 77; (2) 170; (3) 250.
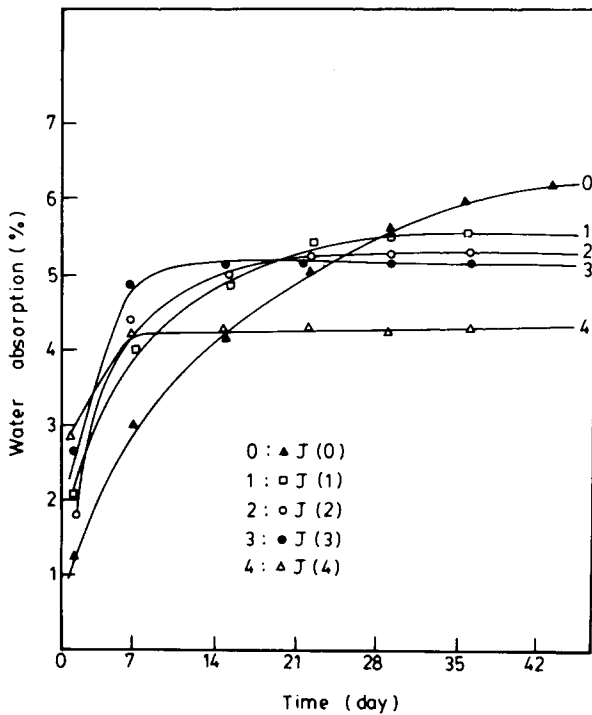

Fig. 8.   Moisture absorption of J-series: (0, ▲) J(0); (1, □) J(1); (2, ○) J(2); (3, ●) J(3); (4, △) J(4).
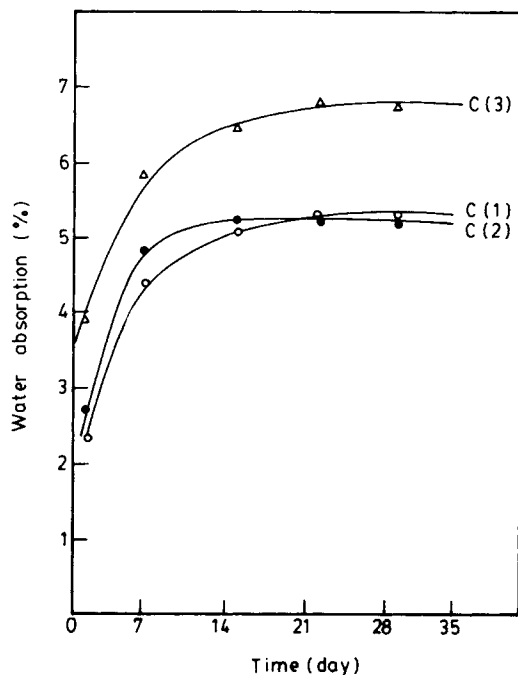
Fig. 9.   Moisture absorption of C-series.

Lap Shear Strength

The adhesion strength of this hot melt adhesive depended more or less on the adhesion conditions. In this paper, the adhesion conditions are listed in Tables IX and X, respectively. The effect of composition and test temperature on the lap shear strength of the J-series is shown in Figure 6. As the content of J-2000 increased, the hardness and strength decreased (the cohesion force also decreased) and so did the lap shear strength. As was expected, elevating the test temperature decreased the lap shear strength too.

The lap shear strength of the C-series is shown in Figure 7. Increasing the content of ϵ-caprolactam increased the lap shear strength. Also, higher test temperature resulted in lower lap shear strength value.

Polyetheramides absorb moisture easily due to their strong hydrogen bonding. The water absorption characteristics for the J-series and C-series are shown in Figures 8 and 9, respectively. The wt% of absorbed water increased rapidly in 1 week and then approached a saturated value. The absorption of moisture would plasticize polyetheramides and weaken the bonding joint as shown in Tables IX and X for samples aged for 3–7 days at 60°C, 95% relative humidity and cause the lap shear strength to fall significantly.

TABLE XI
T-Peel Strength of J-Series

	J(0)	J(1)	J(2)	J(3)	J(4)
T-peel strength (pli)	9.9 ± 3.8	9.5 ± 3.6	9.9 ± 3.3	11.0 ± 3.8	9.9 ± 4.2

TABLE XII
T-Peel Strength of C-Series

	C(1)	C(2)	C(3)
T-peel strength (pli)	10.6 ± 3.5	11.0 ± 3.8	10.4 ± 4.5

T-Peel Strength

The T-peel strengths of the J-series and C-series are listed in Tables XI and XII, respectively. No significant difference in T-peel strength was observed with the change in polyetheramide composition.

CONCLUSION

Polycaprolactam is unsuitable as hot melt adhesive because of its high T_m. Thus dimer acid and diamine were added to lower the T_m and J-2000 was incorporated to increase flexibility. The end product of such polymerization is a block copolyetheramide. The bulk properties of the block copolyetheramide depend on the composition and affect the adhesion strength, especially the lap shear strength, very much. If the composition is properly controlled, a block copolyetheramide hot melt adhesive with high impact strength and good adhesion strength could be obtained.

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