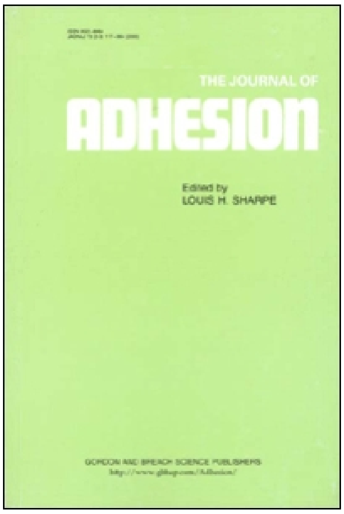

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Strength and Microstructure of Solvent Welded Joints of Polycarbonate

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The relationship of joint strength of solvent welded joints of polycarbonate to their microstructure is investigated. We used three solvents – butanone, acetone, and cyclohexanone – to test the effect of solubility parameters, and a mixture of cyclohexanone with ethanol to test the effect of a cosolvent; the effect of variation of welding temperature on both the joint strength and the microstructure is also investigated. Three fracture modes in shear, tensile and tear tests are analyzed. Polycarbonate treated with butanone has maximum joint strength. Cyclohexanone at 78 vol% in ethanol produces the maximum joint strength of polycarbonate. The joint strength of polycarbonate joints welded with cyclohexanone increases with the temperature at which the weld is made. Comparing microstructure with joint strength, tongues, equiaxed dimples and elongated dimples are responsible for the maximum shear, tensile and tear strength, respectively.

KEY WORDS: Solvent welding; polycarbonate; solubility parameter; microstructure; joint strength; cosolvent.

1. INTRODUCTION

The phenomenon of solvent welding of polymeric materials is well-known but poorly understood. Polymeric materials treated with solvent welding are confined to thermoplastic polymers, for example polystyrene, polycarbonate, poly(methyl methacrylate), poly(vinyl chloride), etc.[1] Titow[1] observed that residual solvent concentrated in the bonding zone (solvent-affected zone) of polycarbonate or polysulphones. In addition to a solvent-affected zone, Menges *et al.*[2] and Yue and Cherry[3] found a soft residual final joint layer sandwiched between two solvent-affected zones. The extent of solvent welding relies on the ability of solvent to dissolve the polymer but is not related to the size of the solvent-affected zone in the polymer.[4] According to the model of critical principal strain,[5] Yue and Chui[6] found that a large critical principal strain corresponds

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* Corresponding author.

to a large intrinsic weld strength. These investigators never addressed the relationship of welding strength to fractography.

Fractography relates the topography of the fracture surface to the causes or basic mechanisms of fracture.[7] The basic mechanisms of fracture in metals and the response of metals to various environments were collected in the Metals Handbook.[8] The effect of rate of loading and molecular weight on fracture morphology of poly(methyl methacrylate) was summarized by Wolock *et al.*[9] The fractography of solvent welding of poly(methyl methacrylate) was investigated by Lin *et al.*[10]

Crack healing is known for various materials.[11–14] The morphology of polycarbonate treated with acetone[15] differs from that of poly(methyl methacrylate) treated with methanol[11] or with ethanol.[12] To promote adhesion, the solvent is required to plasticize the surface of the polymer. Cyclohexanone is a good solvent for poly(vinyl chloride), producing excellent adhesion, but butanone is a poor one producing a poor weld strength.[14] Therefore, we investigated the strength and microstructure of solvent welded joints of polycarbonate. Three solvents, acetone, cyclohexanone, and butanone were used to compare the joint strength. The effects of welding temperature and concentration of solvent on joint strength were also tested.

2. EXPERIMENTAL

Polycarbonate (General Electric Company, USA) had the form of 5.5 mm or 2.2 mm thick Lexan® 9034 sheet. Pieces of dimensions 35 mm × 7 mm × 5.5 mm for tensile tests, 70 mm × 7 mm × 5.5 mm for shear tests, and 20 mm × 7 mm × 5.5 mm for tear tests were cut from the sheet. Samples were annealed in vacuum at 120°C for 24 h and cooled in the oven to approximately 25°C. The purpose of the polycarbonate samples being annealed in vacuum is to reduce moisture content and to relieve residual stresses.

Acetone, butanone and cyclohexanone of analytical grade were used for solvent welding. The specifications of these solvents are tabulated in Table I. The solvent was applied to the surface of polycarbonate at 25°C. The two welding surfaces were then brought together and the specimen was mounted under a compressive stress of 0.022 MPa for 5 min. Then the specimen was removed and aged in vacuum at 25°C for four weeks. The specimen geometries for shear, tensile and tear tests are shown in Figure 1(a)–(c), respectively.

TABLE I
Properties of the three solvents used for welding

Solvent	butanone	acetone	cyclohexanone
Molecular weight (g/mole)	72.11	58.08	98.14
Solubility parameter[26] $(cal/cm^3)^{1/2}$	9.27	9.77	9.88
Hydrogen bonding parameter[26] $(cal/cm^3)^{1/2}$	2.5	2.0	3.4
Boiling point (°C)	80	57	156
Density (g/cc) at 20°C	0.80	0.79	0.95

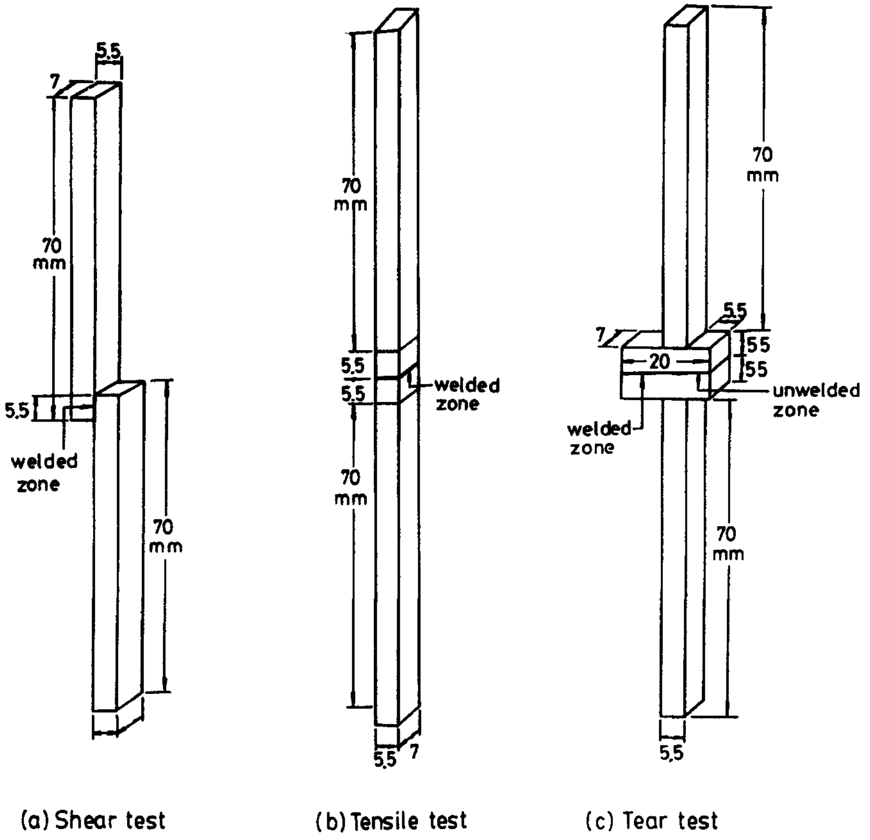


FIGURE 1 Schematic diagrams of various joints to test solvent welding: (a) shear test; (b) tensile test; and (c) tear test.

The effect of cosolvent on joint strength was tested. As ethanol penetrates polycarbonate poorly, it cannot be used for the solvent welding of polycarbonate. Ethanol served to dilute cyclohexanone to assess the effect of concentration of cyclohexanone on solvent welding. The volume fraction of cyclohexanone in the cosolvent was in the range 65%–100% by volume. The mechanical strength was tested at 25°C. The effect of welding temperature on adhesion was tested in the range 25°C–65°C. Before welding, all components of the test specimen, and cyclohexanone were all heated to the welding temperature. Then the process was the same as that of cosolvent treatment. After welding, the specimen was cooled in an oven to 25°C and aged in vacuum at 25°C for four weeks.

Specimens for tear (notch tensile test), tensile and shear tests were mounted on a universal tensile machine with a crosshead speed 0.1 mm/s; tests were made at 25°C. Each data point was the average of three specimens. The morphologies of the fracture surfaces of specimens tested in the various modes were observed with an Olympus BH-2 optical microscope.

3. RESULTS AND DISCUSSION

According to tests of solvent welding of plastics by Titow and coworkers,[16–18] the smaller the concentration of solvent after desorption, the smaller is the diffusivity. Hence, residual solvent remains after welding, but decreases with increasing duration of desorption in vacuum. The joint strength increases with the duration of desorption until it reaches a plateau. Figure 2 shows typical data for shear strength *versus* duration of desorption after acetone welding. The maximum strength of polycarbonate occurs after desorption for more than three weeks. Shear and tensile strengths are defined as failure loads divided by welded area; tear strength implies the maximum load (not failure load) divided by welded area.

3.1 Solubility Parameter Effect

The solubility parameters of solvents are listed in Table I; the solubility parameter of polycarbonate is 9.5. The effect of solubility parameter on shear strength, τ, tensile strength, σ_{tn}, and tear strength, σ_{tr}, of the various joints is illustrated in Table II. The shear strength and tear strength decrease in the order: butanone, acetone and cyclohexanone. The tensile strengths of joints of polycarbonate solvent-welded with these three solvents are approximately the same within experimental error and they appear to be insensitive to solubility parameter. However, the strengths of these joints are only about one-third to one-fourth that of the bulk tensile strength of virgin polycarbonate (i.e., bulk polycarbonate not previously exposed to solvents). According to Tables I and

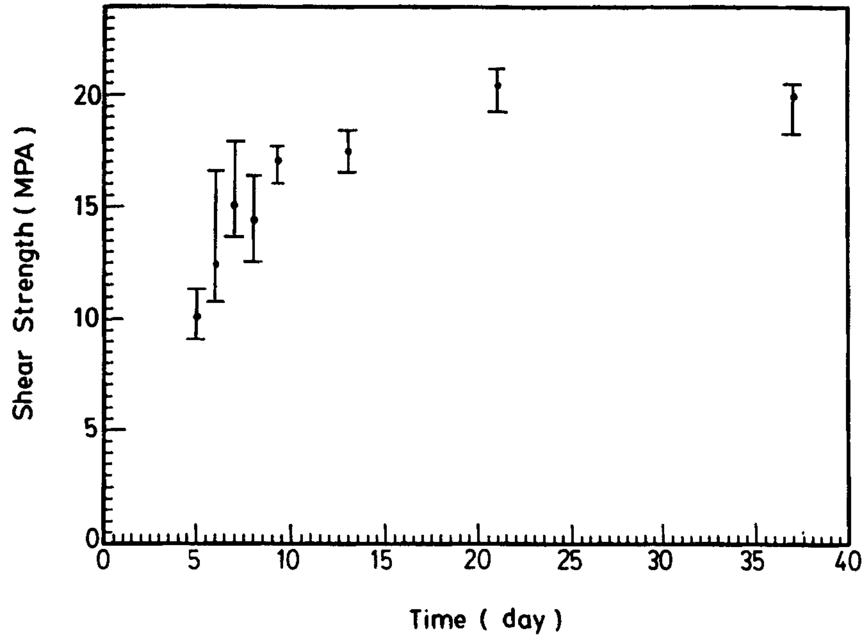


FIGURE 2 Shear strength of polycarbonate joints after acetone welding *versus* period of desorption.

TABLE II
Solubility parameter and joint strengths

Solvent	butanone	acetone	cyclohexanone	Virgin*
Shear strength, τ (MPa)	25.7 ± 1.9	21.3 ± 1.1	10.2 ± 1.3	-
Tensile strength, σ_{tn} (MPa)	25.3 ± 1.4	20.9 ± 1.2	22.8 ± 1.9	89.9
Tear strength, σ_{tr} (MPa)	9.5 ± 0.8	7.8 ± 0.4	5.0 ± 0.4	–

* Virgin implies a bulk polycarbonate without solvent treatment

II, the closer the solubility parameters (not the hydrogen bonding parameter) between solvent and polycarbonate, the greater is the joint strength.

In addition to residual solvent, solvent-induced spherulites cause decreased strength of polycarbonate. The solvent-induced spherulites are randomly distributed. Crystallized polycarbonate is harder than amorphous polycarbonate.[19] The strength of crystallized polycarbonate is expected to increase because of the reinforced structure of the concrete type in the combination of crystalline and amorphous regions, but this idea is likely incorrect. Miller *et al.*[20] postulated that creation of an interface at areas of order-disorder caused both a large shear force at this boundary and voids within the bulk of the polymer. These boundary flaws and voids then propagate as crazes or cracks at stresses less than the strength of the polymer. The morphology of shear fracture surfaces of joints of polycarbonate treated with butanone, acetone and cyclohexanone is shown in Figures 3(a)–(c), respectively. The morphologies of shear fracture surfaces arising from these three solvents resemble fuzzy tongues, distinct tongues, and clouds, respectively. According to visual observations, shear fracture surfaces arising from butanone appear milky white, whereas those arising from acetone appear slightly opaque. The fracture surfaces are different because the shear deformation produces a different microdeformation process.

The morphologies of tensile fracture surfaces of joints of polycarbonate treated with various solvents are shown in Figures 4(a)–(e). The morphology of tensile fracture surface arising from butanone consists of equiaxed dimples and hackles as shown in Figure 4(a) and (b), respectively. These dimples and hackles are not intermixed, but separate from each other. Of the two features of tensile fracture surfaces after acetone welding, one is composed of many small equiaxed dimples as shown in Figure 4(c) and the other consists of small patches as shown in Figure 4(d). These dimples and patches are not intermixed, but separate from each other. Tensile fracture surfaces arising from cyclohexanone appears filled with fine spherulites as shown in Figure 4(e).

The appearances of a tear fracture surface of polycarbonate after welding with butanone, acetone and cyclohexanone are shown in Figure 5(a)–(d), respectively. The morphologies of tear fracture surfaces after welding with butanone and cyclohexanone consist of large elongated dimples (Fig. 5(a)) and small spherulites (Fig. 5(d)), respectively. Of the two features of tear fracture surfaces after acetone welding, one is composed of many small equiaxed dimples (Fig. 5(b)) near the unwelded zone, and the other consists of patches containing many striations (Fig. 5(c)) far from the unwelded zone.

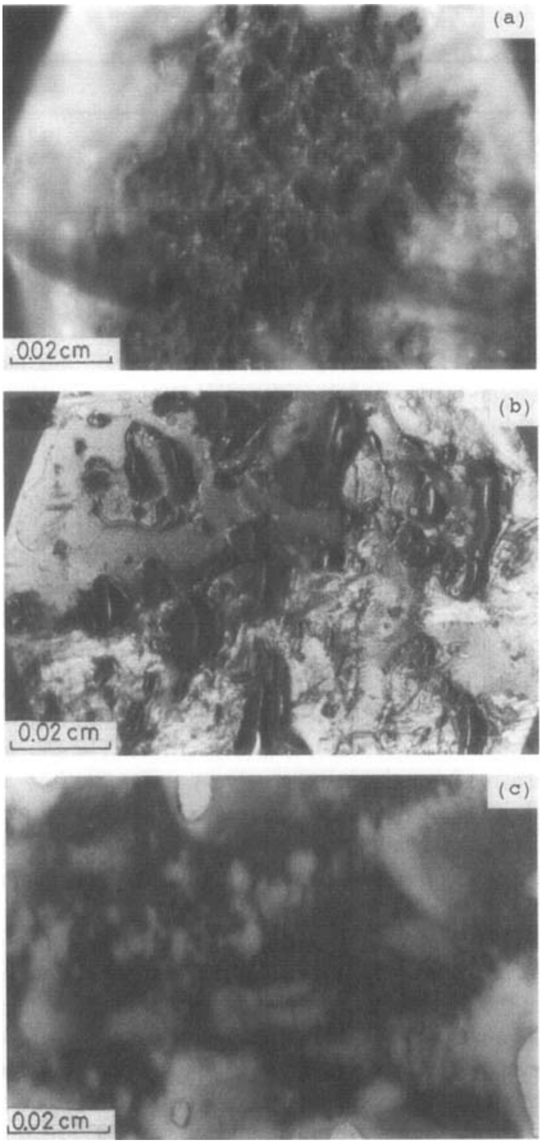


FIGURE 3 Morphologies of shear fracture surfaces for various solvent welds: (a) butanone, (b) acetone, and (c) cyclohexanone.

3.2 Effect of Cosolvent

Cosolvent or synergism effects in a ternary system (solvent 1, solvent 2 and polymer) are well established.[21,22] In certain systems, such as the so-called classic cosolvent systems,[23,24] synergism occurs when two poor solvents (essentially non-solvents) give a mixture capable of dissolving high molecular weight polymer over a wide range of temperature. Ethanol cannot transport into polycarbonate, but cyclohexanone and ethanol are completely miscible near 25°C, and the efficiency of dissolving polycarbonate varies with the volume ratio of their mixtures. Hence, the capability of solvent welding depends on the concentration of cyclohexanone. Concentrations of cyclohexanone in the range 65–100% by volume were tested. The effect of concentration of cyclohexanone on the joint strength is presented in Table III. Cyclohexanone at 78 vol% in ethanol yields the maximum joint strength. When the concentration of cyclohexanone was less than 60 vol%, no adhesion of polycarbonate was observed.

In order to understand the mechanism of the effect of cosolvent on joint strength, we investigated the fractographies of the surfaces resulting from various fracture modes. The morphologies of shear fracture surfaces for varied concentrations of cyclohexanone in ethanol are shown in Figures 6(a)–(f). The features of the shear fracture surface for pure cyclohexanone are shown in Figure 3(c). When the concentration is in the range 65–78 vol%, the shear fracture surface consists of many tongues, and the size of tongue increases with the concentration of cyclohexanone. Beyond 78 vol% cyclohexanone, the shear fracture surface resembles clouds; the size of the cloud increases with the concentration of cyclohexanone. Comparing the microstructure with the shear

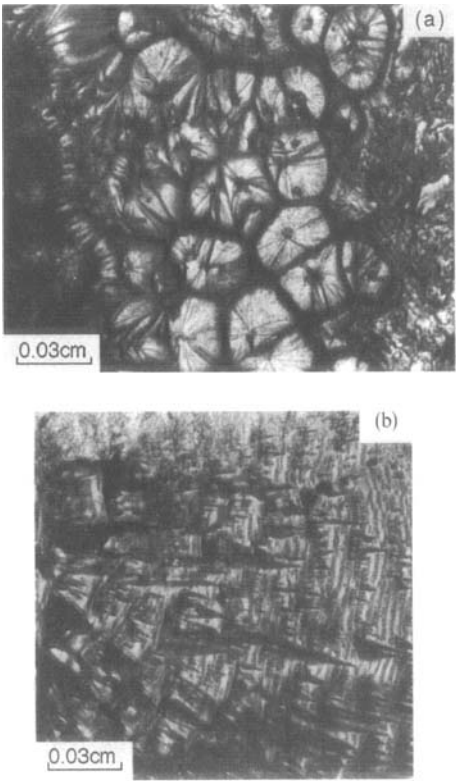


FIGURE 4 Morphologies of tensile fracture surfaces for various solvent welds: (a) and (b) butanone, (c) and (d) acetone, and (e) cyclohexanone.

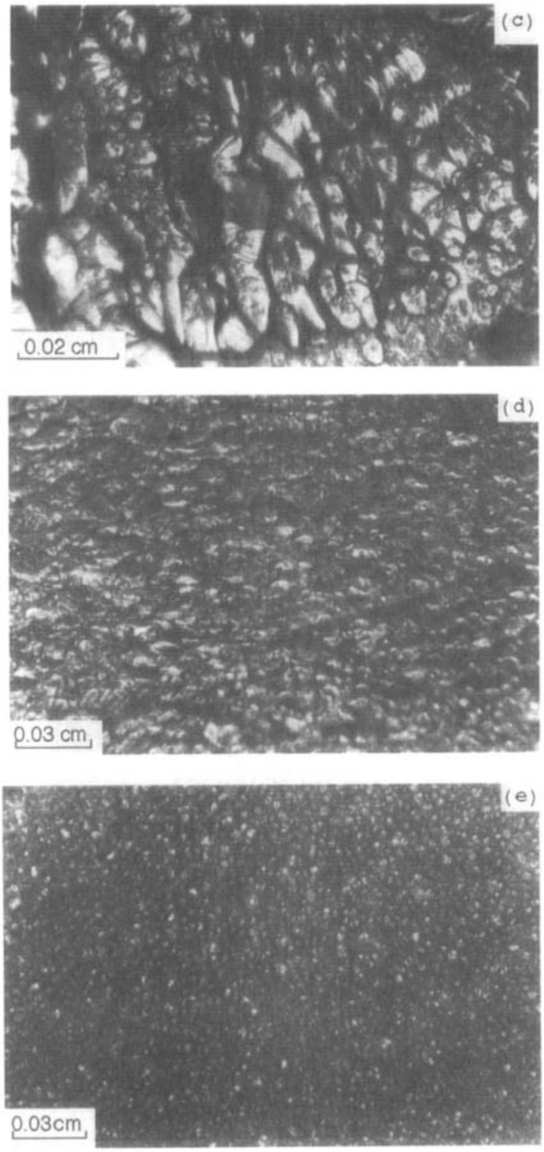


FIGURE 4 (*Continued*).

strength, we find that the morphology has a larger shear strength for a tongue than for a cloud. As the shear fracture surface of polycarbonate treated with 78 vol% cyclohexanone corresponds to the greatest extent of tongues, it has the largest shear strength.

Figures 7(a)–(f) show the features of tensile fracture surfaces of polycarbonate treated with cyclohexanone at various concentrations in ethanol. The features of the tensile fracture surface for joints made with pure cyclohexanone appears in Figure 4(d). The tensile fracture surface at 65 vol% and 70 vol % consists of many hackles. The morphologies of the tensile fracture surface for 74 vol% and 78 vol% resemble equiaxed dimples and elongated dimples, respectively. Features of the tensile fracture surfaces for cyclohexanone concentrations greater than 84 vol% resembles spherulites. Comparing the microstructure with tensile strength of joints, we found that the morphology of the tensile fracture surface of polycarbonate treated with cyclohexanone at 78 vol% corresponding to the maximum tensile strength exhibits dimples.

Figures 8(a)–(f) show the morphologies of tear fracture surfaces for cyclohexanone at various concentrations in ethanol. The morphology of the tear fracture surface for pure cyclohexanone appears in Figure 5(d). The tear fracture surfaces at concentrations less than 74 vol% resemble hackles; the tear fracture surface at 78 vol% resembles elongated dimples, and tear fracture surfaces for concentrations greater than 84 vol% resemble spherulites. In relation to the surface features and tear strength, the dimples correspond to the largest tear strength.

3.3 Effect of Temperature

The interaction of solvent and polymer increases with temperature. The uptake of solvent in polycarbonate decreases with increasing temperature but that in poly(methyl methacrylate) has the opposite trend. Ethanol is not an effective solvent for poly(methyl methacrylate) at 25°C but a good solvent at 87°C[25] and CCl_4 induces crack healing of polycarbonate above 40°C.[13] The effect of temperature on welding of polycarbonate with cyclohexanone is shown in Table IV. The joint strength increases with increasing welding temperature. The effect of welding temperature is more pronounced in the shear test than in the tensile and tear tests. The features of shear fracture surfaces of polycarbonate treated with cyclohexanone are shown in Figure 9(a)–(d) for temperatures 25, 45, 55, and 65°C, respectively. The shear fracture

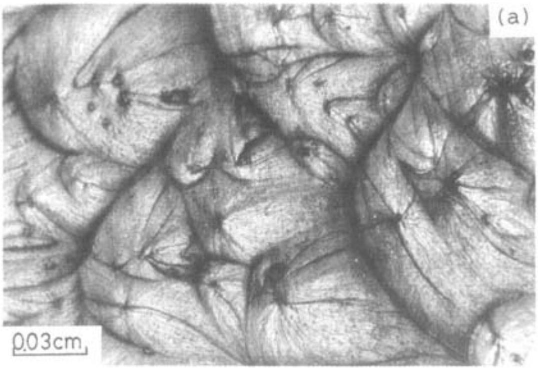


FIGURE 5 Morphologies of tear fracture surfaces for various solvent welds: (a) butanone, acetone, (b) near welded zone, (c) far from welded zone, and (d) cyclohexanone.

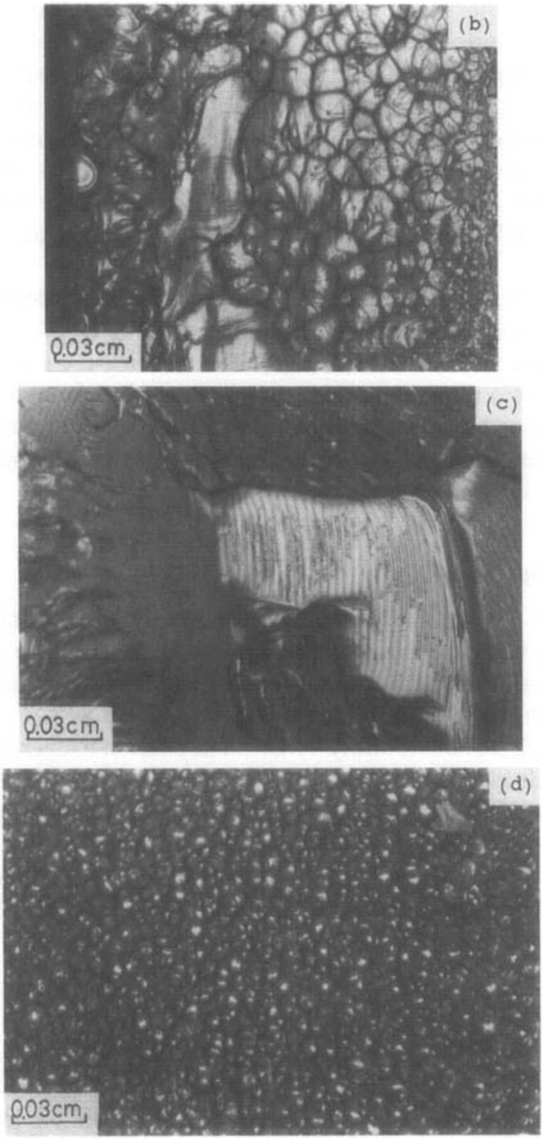


FIGURE 5 (*Continued*).

surface of polycarbonate resembles clouds when solvent-welded at a temperature less than 55°C and tongues at 65°C. The morphologies of tensile fracture surfaces are shown in Figures 10(a)–(d) corresponding to welding temperatures of 25, 45, 55, and 65°C, respectively. Tensile fracture surfaces exhibit fine spherulites at 25°C and equiaxed dimples for temperatures above 45°C. The size of the dimples increases with temperature. The tensile fracture surface of polycarbonate having the largest dimples corresponds to the greatest tensile strength. The morphologies of tear fracture surfaces are shown in Figures 11(a)–(d) for welding temperatures of 25, 45, 55, and 65°C, respectively. With the exception of spherulites at 25°C, the morphologies for temperature above 45°C exhibit elongated dimples, the size of which increases with temperature. The largest elongated dimple corresponds to the maximum tear strength.

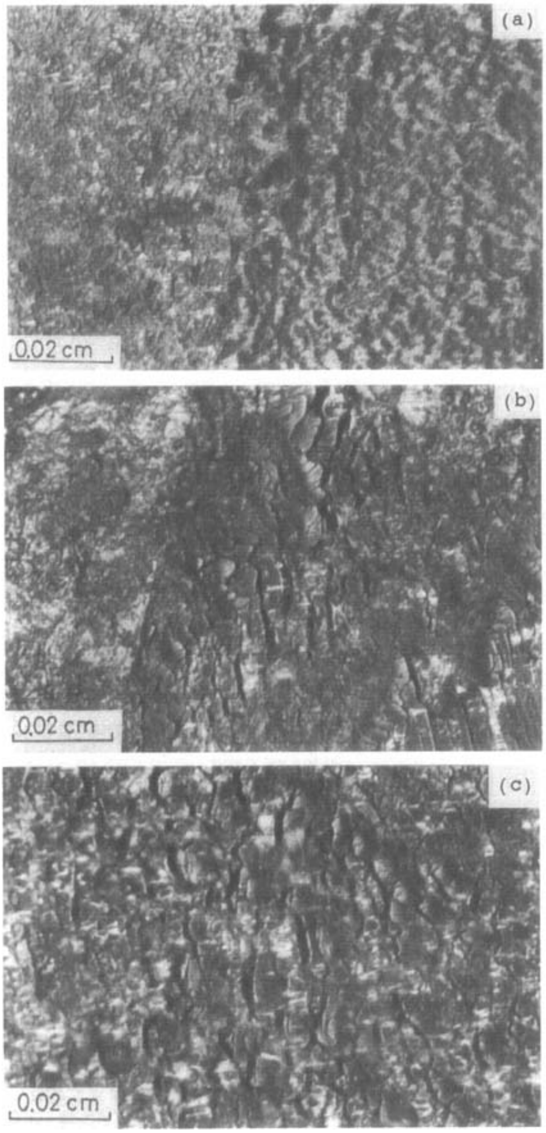


FIGURE 6 Morphologies of shear fracture surfaces of welds made with cyclohexanone at various concentrations (vol%) in ethanol: (a) 65, (b) 70, (c) 74, (d) 78, (e) 84, and (f) 92.

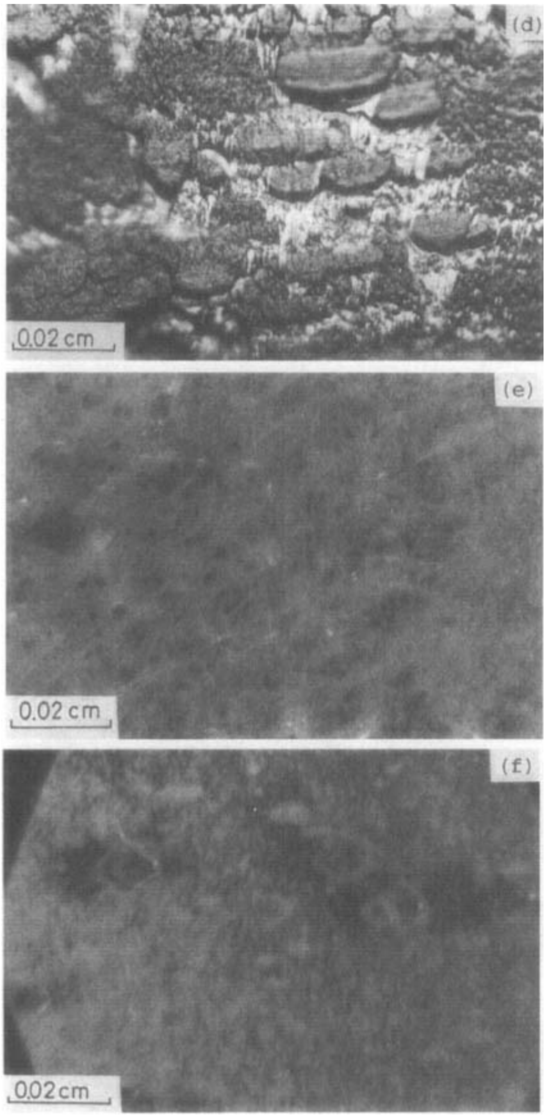


FIGURE 6 (*Continued*).

3. DISCUSSION

The feature of tongues corresponds to the maximum shear strength of polycarbonate. Tongues were also observed on shear fracture surfaces of poly(methyl methacrylate).[10] Shear fracture surfaces of metals feature oval dimples, not tongues.[8] Tongues, however, are occasionally observed on cleavage fracture in metals. They are formed, when a

TABLE III
Effect of cyclohexanone concentration in ethanol on shear strength, τ, tensile strength, σ_{tn}, and tear strength, σ_{tr}, of solvent-welded polycarbonate joints

Concentration (vol%)	τ (MPa)	σ_{tn} (MPa)	σ_{tr} (MPa)
65	14.6 ± 2.5	22.1 ± 1.6	5.4 ± 0.7
70	14.9 ± 2.6	23.9 ± 5.2	5.7 ± 0.9
74	17.2 ± 2.7	24.3 ± 1.1	5.5 ± 1.1
78	18.7 ± 1.9	27.8 ± 3.0	7.2 ± 0.9
84	13.5 ± 0.7	22.0 ± 1.6	4.7 ± 0.1
92	11.3 ± 0.4	23.9 ± 1.6	5.0 ± 0.1
100	10.2 ± 1.3	22.8 ± 1.9	5.0 ± 0.4

cleavage surface differs slightly from the cleavage plane and moves a short distance along a twin direction.[8] However, polymeric materials have no twin structure. It is found that the shear strength increases with the size of tongue. A tongue is nucleated at a place of weak bonding for shear loading. As a result, if the tongues are of larger size,

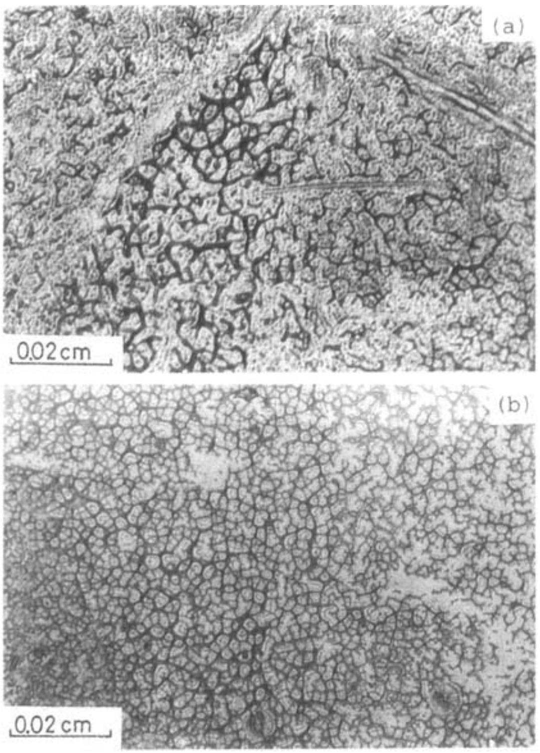


FIGURE 7 Morphologies of tensile fracture surfaces of welds made with cyclohexanone at various concentrations (vol%) in ethanol: (a) 65, (b) 70, (c) 74, (d) 78, (e) 84, and (f) 92.

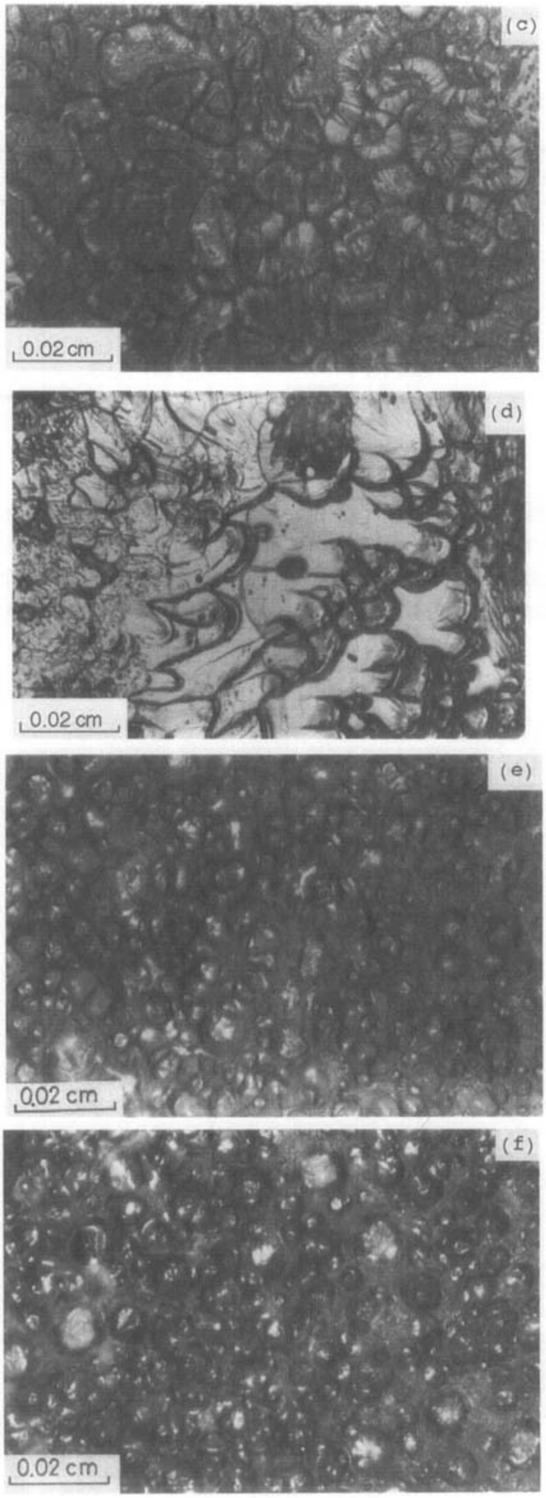


FIGURE 7 *(Continued).*

and fewer in number per unit area, then the area of weak bonding will be smaller and the shear strength will be higher. A detailed analysis of tongue formation on the joint surface of polymer will be undertaken. Both polymers and metals have equiaxed dimples and elongated dimples for tensile and tear fracture tests, respectively. The dimples of polymers are larger than those of metals. In general, the joint strength

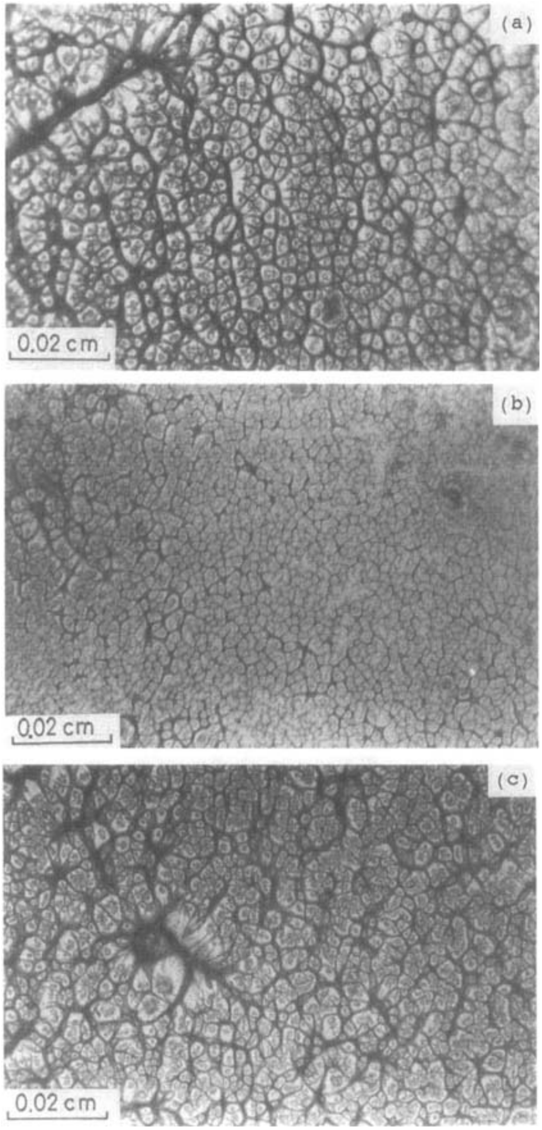


FIGURE 8 Morphologies of tear fracture surfaces of welds made with cyclohexanone at various concentrations (vol%) in ethanol: (a) 65, (b) 70, (c) 74, (d) 78, (e) 84, and (f) 92.

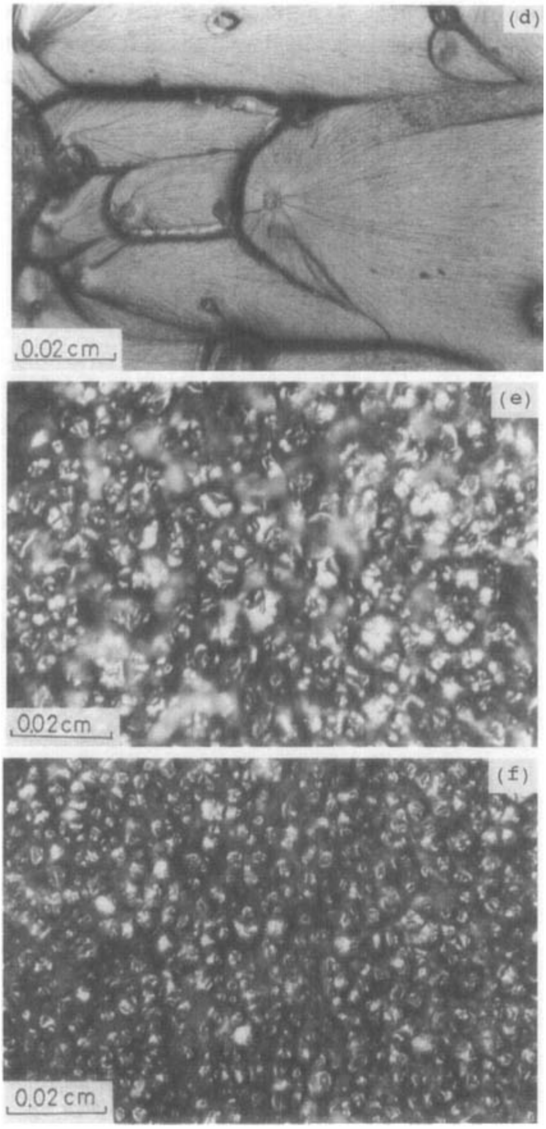


FIGURE 8 (*Continued*).

TABLE IV
Effect of welding temperature on shear strength, τ, tensile strength, σ_{tn}, and tear strength, σ_{tr}, of joints of polycarbonate solvent-welded with cyclohexanone

T(°C)	25	45	55	65
τ(MPa)	10.2 ± 1.3	14.6 ± 0.6	19.1 ± 0.2	25.6 ± 0.9
σ_{tn}(MPa)	22.8 ± 1.9	31.0 ± 1.4	32.1 ± 2.0	37.2 ± 1.5
σ_{tr}(MPa)	5.0 ± 0.4	7.7 ± 0.4	8.3 ± 0.2	9.3 ± 0.2

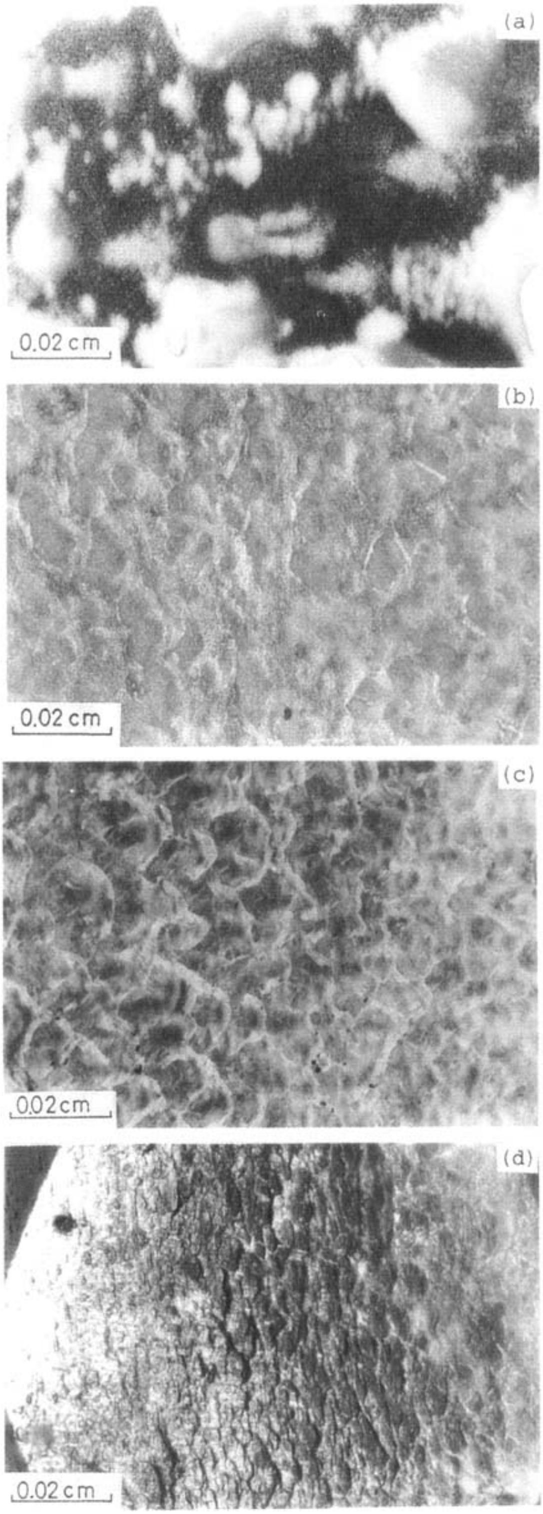
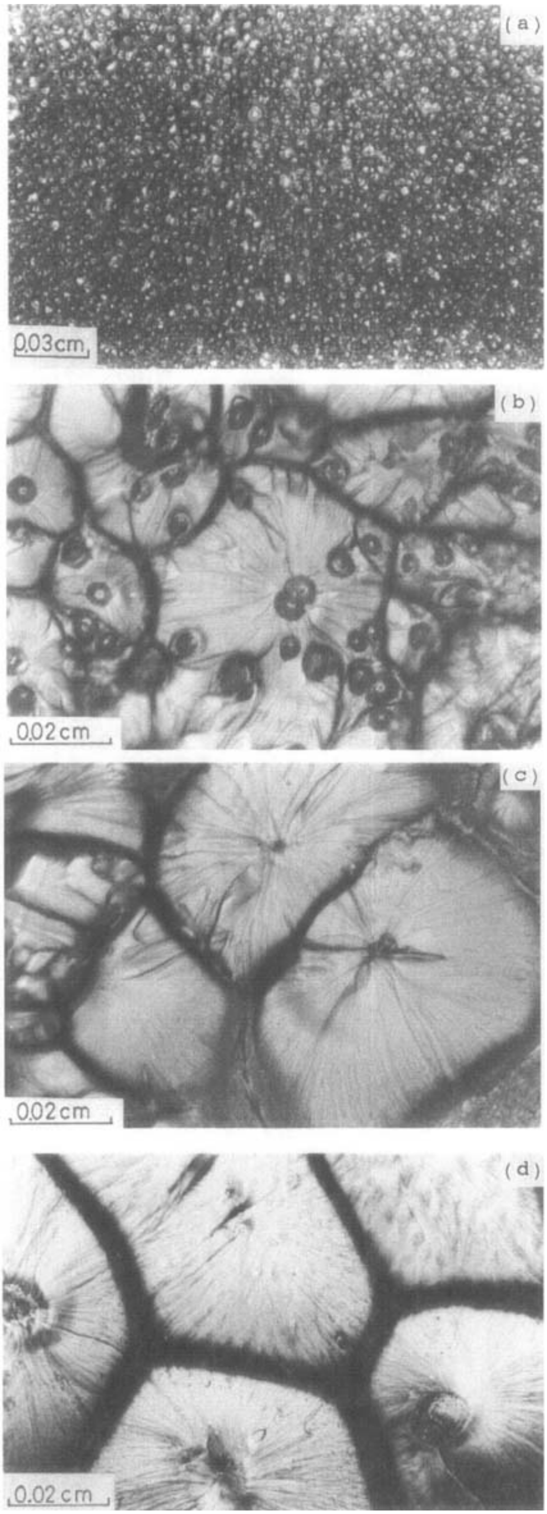


FIGURE 9 Morphology of shear fracture surfaces of welds made with cyclohexanone at temperatures (a) 25°C for $\tau = 11.5$ MPa, (b) 45°C for $\tau = 15.2$ MPa, (c) 55°C for $\tau = 20.3$ MPa, and (d) 65°C for $\tau = 26.5$ MPa.


(a)
0.03cm
(b)
0.02cm
(c)
0.02cm
(d)
0.02 cm

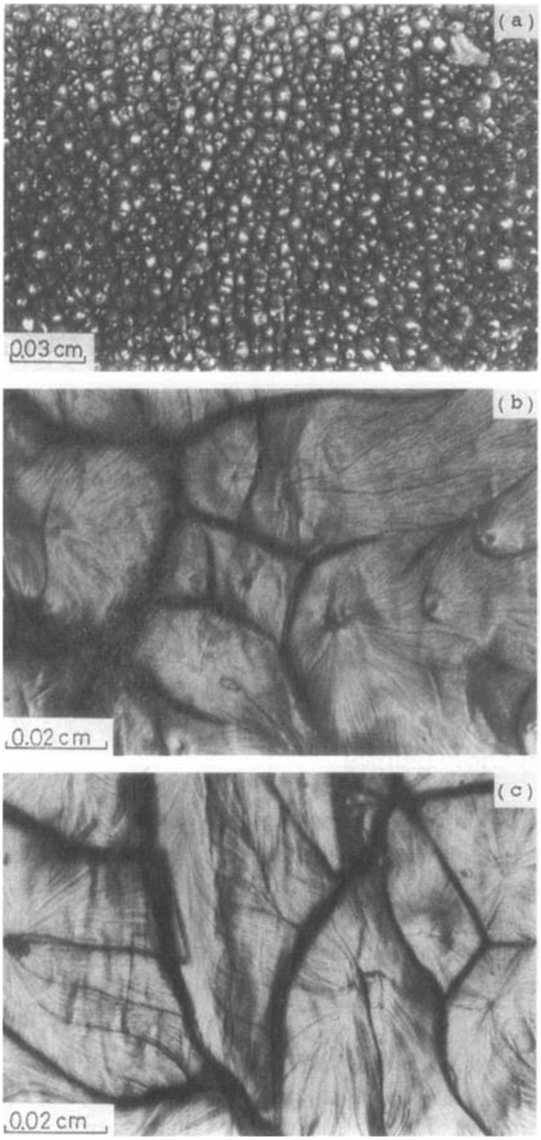


FIGURE 11 Morphology of tear fracture surfaces of welds made with cyclohexanone at temperatures (a) 25°C for $\sigma_{tr} = 5.4$ MPa, (b) 45°C for $\sigma_{tr} = 8.1$ MPa, (c) 55°C for $\sigma_{tr} = 8.5$ MPa, and (d) 65°C for $\sigma_{tr} = 9.5$ MPa.

FIGURE 10 Morphology of tensile fracture surfaces of welds made with cyclohexanone at temperatures (a) 25°C for $\sigma_{tn} = 23.7$ MPa, (b) 45°C for $\sigma_{tn} = 32.4$ MPa, (c) 55°C for $\sigma_{tn} = 34.1$ MPa, and (d) 65°C for $\sigma_{tn} = 38.7$ MPa.

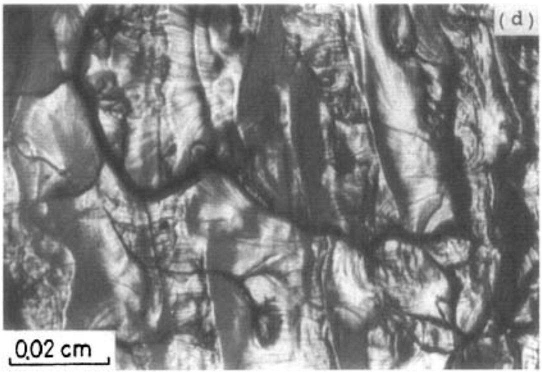


FIGURE 11 (*Continued*).

(tensile and tear) increases with the size of the dimples. A dimple is nucleated at a place of weak bonding for tensile and tear loadings. Thus, the more dimples per unit area, the greater the area of weak bonding and the lower the joint strength. The feature of the virgin polycarbonate is the same as the feature within the dimples. The virgin polycarbonate is stronger because it does not contain the areas of weak bonding from which the dimple nucleates.

4. SUMMARY AND CONCLUSIONS

Strength and microstructure of solvent welded joints of polycarbonate were investigated. The failure strengths in shear, tensile, and tear modes were measured and related morphologies were examined. Three solvents, butanone, acetone, and cyclohexanone were employed. Mixtures of cyclohexanone with ethanol were used to access the effect of a cosolvent. The effect of welding temperature on the joint strength and microstructure was also investigated. Some important results are summarized as follows.

1. Features of tongues, equiaxed dimples, and elongated dimples are responsible for maximum shear, tensile and tear strengths, respectively.
2. Butanone as the welding solvent gives the highest joint strengths, followed by acetone and cyclohexanone.
3. When the concentration of cyclohexanone in ethanol is less than 60 vol%, no welding is observed. Polycarbonate treated with cyclohexanone at 78 vol% has the maximum joint strength.
4. Joint strength of polycarbonate treated with cyclohexanone increases with the welding temperature.

Acknowledgement

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