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Effect of solvent and cosolvent on friction welding properties between part of PMMA with PVC

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The effect of distilled water, methanol, ethanol, acetone and cosolvent (comprising ethanol and distilled water, the volume fraction of ethanol in the cosolvent was $10V_f\%$ and $20V_f\%$) on the friction welding properties between parts of PMMA with PVC is investigated. Treatment with those solvents, $20V_f\%$ cosolvent and $10V_f\%$ cosolvent promote about 360%, 280% and 110% more bonding strength than without any solvent treatment. The tensile fracture morphology of welded PMMA with PVC has three zones: the non-plasticized central zone (Fud), the plasticized peripheral zone (Fpl), and the partly plasticized zone between Fud and Fpl (Fpd). Comparing tensile fracture morphology and residual solvent with bonding strength, it has larger Fpd regions, no Fud in the central part and less residual solvent is responsible for better bonding strength. *© 2003 Kluwer Academic Publishers*

1. Introduction

General methods for joining thermoplastics involve adhesive bonding and welding [1–2]. Welding here includes solvent welding [3]; spin friction welding [4]; vibration welding [5]; hot press welding [6, 7]; hot-gas welding [8]; infrared heating welding [9]; resistance welding [10]; linear friction welding [11] and ultrasonic welding [12]. Solvent welding is a process in which thermoplastics are plasticized with a good solvent and then pressed together to form a bond [13]. Spin friction welding, in which one substrate is fixed while the other is given a controlled angular velocity and brought into contact with the former to cause friction heat and molecular motion to form a bond. Advantage of spin friction welding is high welding quality, simplicity, high speed, and reproducibility. Major parameters of friction welding include friction pressure, forge pressure, spinning time and burn off length.

Wool and O'Connor [14] proposed five steps for welding thermoplastics: rearrangement of molecular chains; approach of two welding surfaces; wetting; interdiffusion and the randomization of molecular chains. According to Kim and Wool [15] the interdiffusion and the randomization of molecular chains could be designated by the reptation model [16] proposed by de Gennes [17] and Doi [18]. Voyoutskii [19] showed that polymeric bonding is based on mutual interdiffusion molecular chains to achieve an effective diffusion distance (ΔX); this comes from Einsteinian formula: $\langle \Delta X^2 \rangle = 2D\Delta t$; where D is the diffusion coefficient, and Δt is the diffusion time. According to Wool *et al.* [20] while we are using welding for thermoplastic, the operating temperature should be higher than the glass transition temperature (T_g), because with the help of thermal activity, the entangled molecular chains untie for mobility and interdiffusion. According to Kausch and Jud [21], bonding strength is based on the degree of chain entanglement.

Traditionally, for welding incompatible PMMA with PVC by spin friction welding is difficult to attain better bonding strength. This research proposes a method by treating with solvent or cosolvent on the welding surface and then spins friction welding between parts of PMMA with PVC. In this way, on the welding zone can be eliminated residual stress and the bonding strength is increased while consuming less material.

2. Experimental procedure

2.1. Materials preparation

PMMA rods (weight-average molecular weight $\sim 2 \times 10^5$) and PVC rods (weight-average molecular weight $\sim 4.7 \times 10^4$) are cut for welding specimens whose standard is shown in Fig. 1. Carbimet paper of 1200 grit is used for polishing the welding surface, and finally polished with 0.3 μm Al_2O_3 slurries followed. The purpose of polishing is given during friction pressure for two specimens to have close contact. Then, the specimens are kept at 50°C for 24 h for annealing and then the annealed specimens are cooled to room temperature to eliminate residual stress on the welding surfaces.

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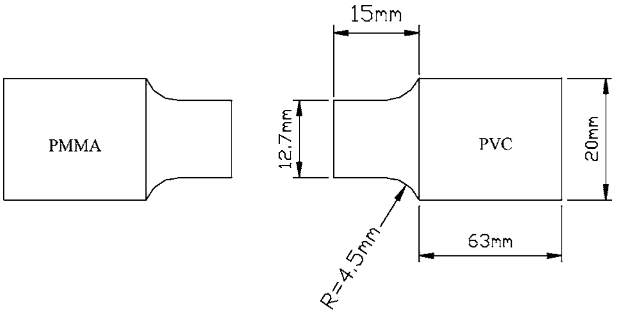

Figure 1 Schematic of specimens.

2.2. Spin friction welding

An apparatus for PMMA with PVC spin friction welding is shown in Fig. 2. The welding surface of the work pieces was degreased prior to welding. During spin friction welding, the PMMA specimen is rotated while the PVC remains stationary, and to make ensure good contact, 0.65 MPa friction pressure is exerted for PMMA with PVC welding with AC motor of 460 rpm for 5 s of spinning time. Then, 5 s forge pressure, the same as the spin friction pressure, is applied immediately to complete. The effects of solvent and cosolvent on friction welding properties were tested. The welding surfaces of the two specimens were contacted closely and then treated with 1×10^{-6} m^3 distilled water, methanol, ethanol, acetone and cosolvent by capillarity before spinning friction. Then friction welding is completed immediately to avoid volatilization of solvents or cosolvents. Thus, the solvent should remain at the interface in the presence of gravity prior to welding or in the presence of centrifugal forced during welding. The specifications of these solvents are tabulated in Table I. The cosolvents were comprised ethanol and distilled water. The volume fraction of ethanol in the cosolvent was 10V$_f$% and 20V$_f$%. After friction welding, the specimen was aged in vacuum at 25°C for 3 weeks for desorption treatments until weight has no change. It is noteworthy to mention that both welding surfaces were treated with solvent or cosolvent at room temperature using the same friction welding conditions, the welded work pieces have no bonding strength.

TABLE I The properties of solvent

	Solvent			
Properties	Distilled water	Methanol	Ethanol	Acetone
Molecular weight (g/mol)	18	32	16	58.08
Solubility parameter (J/m^3)$^{1/2}$	46800	28600	25800	19540
Boiling point (°C)	100	64.7	78.2	57
20°C density (kg/m^3)	1000	801	797	790

2.3. Microstructure observation

Metallographic specimen sections were prepared from each weld using standard practice through 1200 grit carbimet paper polishing. Final polishing was performed using a 0.05 μm Al_2O_3 particulate suspension. After polishing, various heat affected zone across the welds were examined using OPTIPHOT-100 Nikon optical microscopy were etched using acetone.

2.4. Tensile test and fractography

The fringes from the welded PMMA with PVC were machined before tensile testing. Tensile test was performed at room temperature on a universal tensile machine with a crosshead speed of 1 mm/min. The bonding strengths were calculated from the load at failure, divided by the original cross section area. Three measurements were taken for each of the bonding strengths to calculate their average data. After 4 min of gilding of the tensile fracture surface, the tensile fracture morphology was observed with a JEOL-JSM 840A scanning electron microscope.

3. Results and discussion

3.1. Wetting zone

The wetting zone of welded PMMA with PVC without solvent treatment is shown in Fig. 3a. The wetting zone is limited and only appeared in the central zone. This is because PMMA has lower wear resistance than PVC and the degree of wear will increase in radius

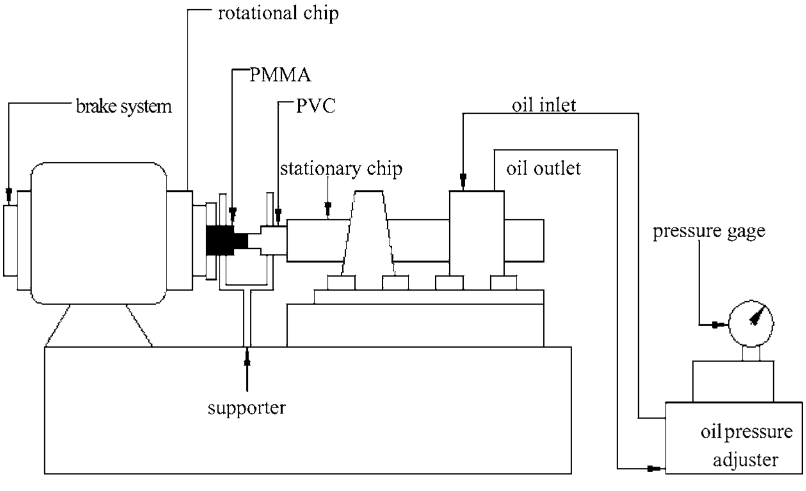

Figure 2 Schematic of friction welding system.

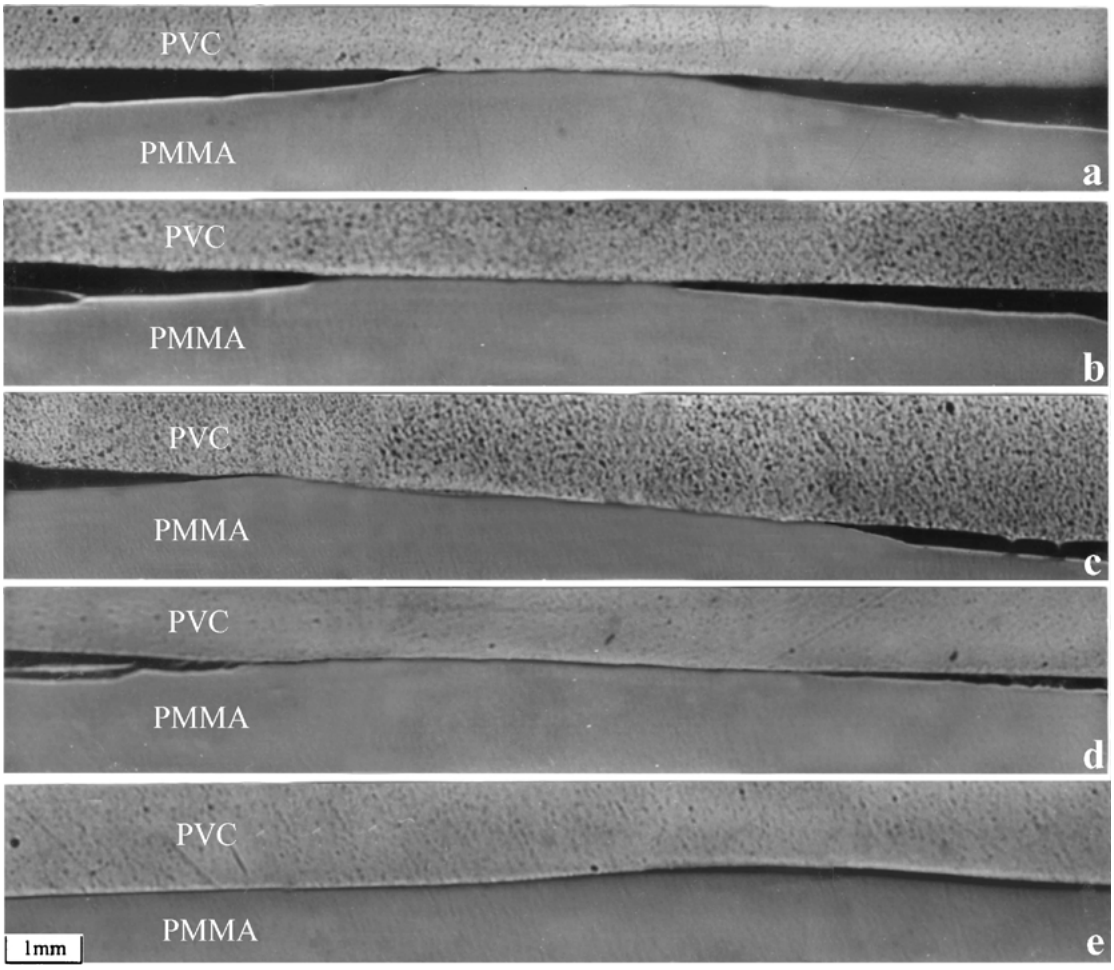

Figure 3 Light optical microscope (OM) morphologies for welding zone: (a) without solvent treatment, and treated with (b) distilled water, (c) methanol, (d) ethanol, and (e) acetone.

during mutual spin-friction. Thus, the peripheral zone of PMMA is more easily spun out of the matrix than PVC, and decreases the opportunities for wetting with PVC and PMMA while forge pressure is being applied. The welded PMMA with PVC treated with distilled water, methanol, ethanol and acetone forms apparent wetting zone is shown in Fig. 3b–e, respectively. The reason is that the friction heat helps solvent transport to welding surfaces, decreases the effective glass transition temperatures ($T_{g,\text{eff}}$) and promotes plasticization of the welding surface, and then increases the wetting zone of each other while forge pressure is being applied. The area of the wetting zone is, in decreasing order of size, as follows: acetone, ethanol, methanol, and distilled water. Because the solubility parameter between acetone and PMMA is very close as shown in Table I, it causes easy flow of the polymer, melting a tacky layer that forms in the welded zone of PMMA, which will be squeezed while forge pressure is being applied and makes the two welded planes to have extensive wetting as shown in Fig. 3e. On treatment with ethanol, methanol and distilled water, no tacky layer forms on the welded interface, which will not be squeezed while forge pressure is being applied. Additionally, the difference of the solubility parameter between ethanol, methanol, distilled water and PMMA, ethanol is smaller and distilled water is larger, so the area of the wetting zones treated with ethanol are larger and those treated with distilled water are smaller as shown in Fig. 3b–d, respectively. The wetting zone of welded PMMA with PVC with cosolvent treatment is shown in Fig. 4, where we can find the area of wetting zone, treated with $20V_f\%$ cosolvent is larger than that treated with $10V_f\%$ cosolvent.

3.2. Tensile fracture morphology

The tensile fracture surface morphologies of welded PMMA with PVC without treating with solvent has three zones is shown in Fig. 5: (1) The central zone (Fud), which has a "worn surface" morphology in the both welding parts; (2) The peripheral zone (Fpl), which has a "rippling" fracture morphology in the PMMA welding part and a "plasticized pile-up" fracture morphology in the PVC welding part. Because the plasticized flow of PMMA is easily spun out of the matrix and decreases the wetting zone in the peripheral region, the fracture morphology of the Fpl zone in both welding parts have no relationship; (3) The middle section (Fpd), which has a partly plasticized "dot" fracture morphology in the both welding parts. The reason for the "dot" fracture morphology that forms in the Fpd zone is that the molecular chains of welded PMMA with PVC will penetrate into the matrix of each other and entangle in the overlap zone. When welding PMMA with PVC under a tensile stress, the straightening of molecular

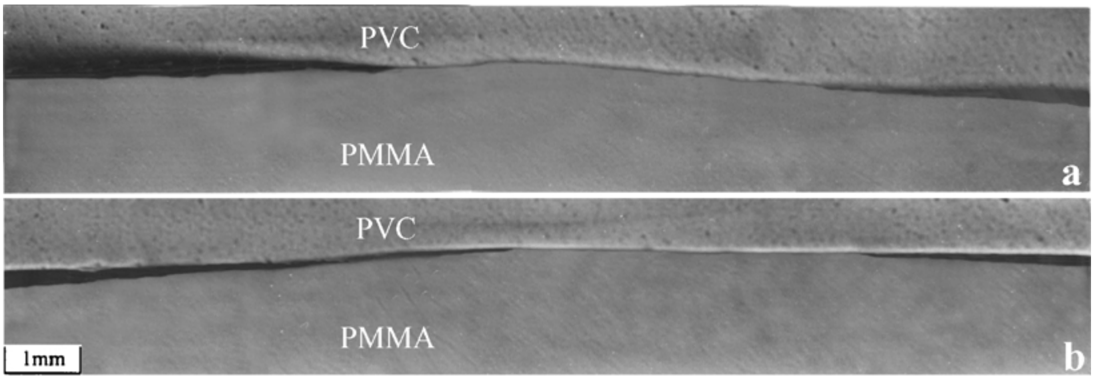

Figure 4 OM morphologies for wetting zone, treated with: (a) $10V_f\%$ cosolvent and (b) $20V_f\%$ cosolvent.

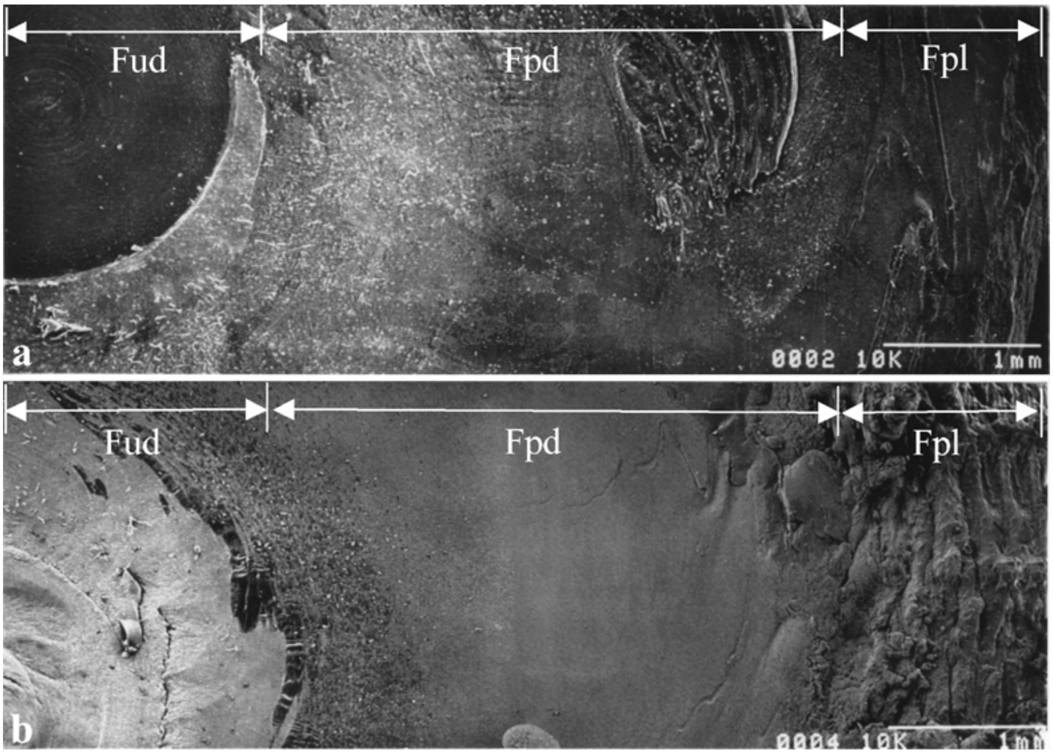

Figure 5 Scanning electron microscope (SEM) morphologies for tensile fractures without solvent treatment: (a) PMMA and (b) PVC.

chains starts in the overlap zone of molecular chains cell. The molecular chains are aligned along the tensile direction, the molecular chains in neighborhood of the overlap zone disentangle, the position of the stress concentration is here; oriented molecular chains will also be at the final breaking "dot" under the action of an tensile load. The fracture morphology after treating with distilled water is shown in Fig. 6. The area of the "dot" fracture morphology is larger than those without solvent treatment. Although distilled water is a poor solvent (essentially non-solvent) for PMMA and PVC, a little distilled water is still transported to both of the welding parts to activate the partial plasticization of the molecular chains by the friction temperature, and increases the wetting zone for interdiffusion of the molecular chains each other. The tensile fracture morphology after treating with the methanol, ethanol and acetone are shown in Figs 7–9, respectively. A larger area of the "dot" fracture morphology appears on the Fud zone, but a part of the PVC has clung to the Fpd zone of PMMA. The area of clung zone is, in decreasing order of size, as follows: acetone, ethanol, and methanol. The reason is that the closer the solubility parameters between solvent and PMMA with PVC, the greater are the plasticized and welded regions in both wet zones. Compared with Figs 6–9, the order of the area of effective welding zones including the "dot" fracture morphology and the part of the PVC clinging to the PMMA, from largest to smallest is acetone, ethanol, methanol and distilled water.

The fracture morphology treated with $10V_f\%$ cosolvent and $20V_f\%$ cosolvent is shown in Figs 10 and 11, respectively, in which the $20V_f\%$ cosolvent effective welding zone is more striking than that of the $10V_f\%$ cosolvent.

3.3. Bonding strength

The bonding strength of welded PMMA with PVC while treated with and without solvent and cosolvent, are shown in Table II. The bonding strength of joints of welded PMMA with PVC with four solvents is

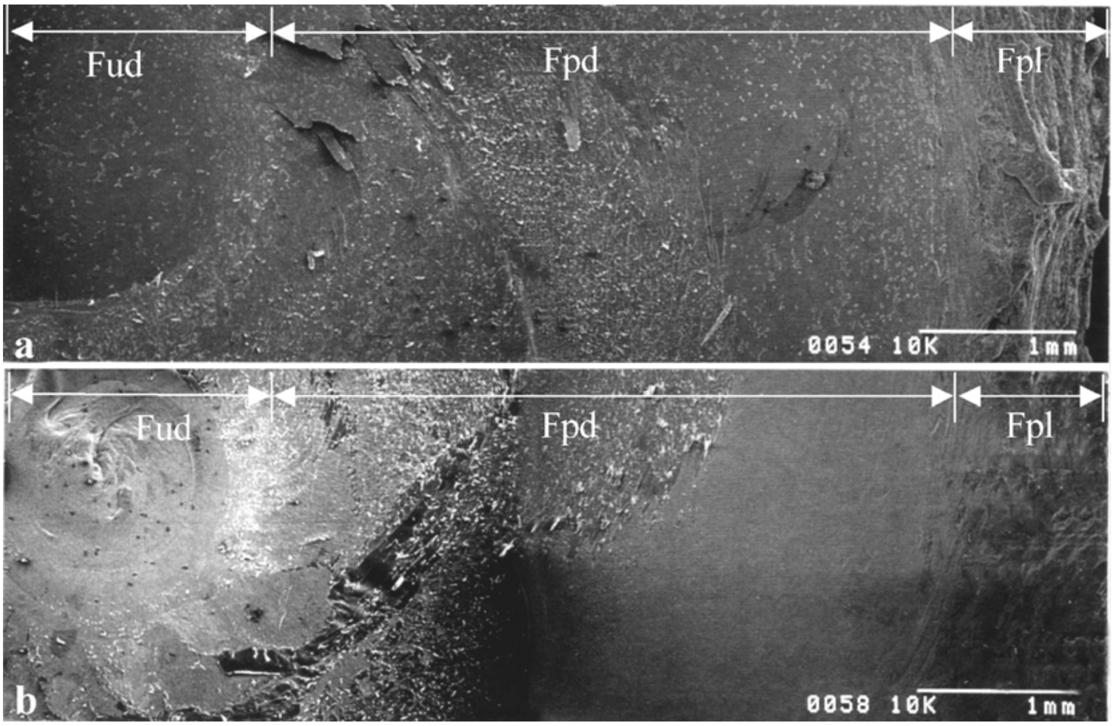

Figure 6 SEM morphologies for tensile fractures, treated with distilled water: (a) PMMA and (b) PVC.

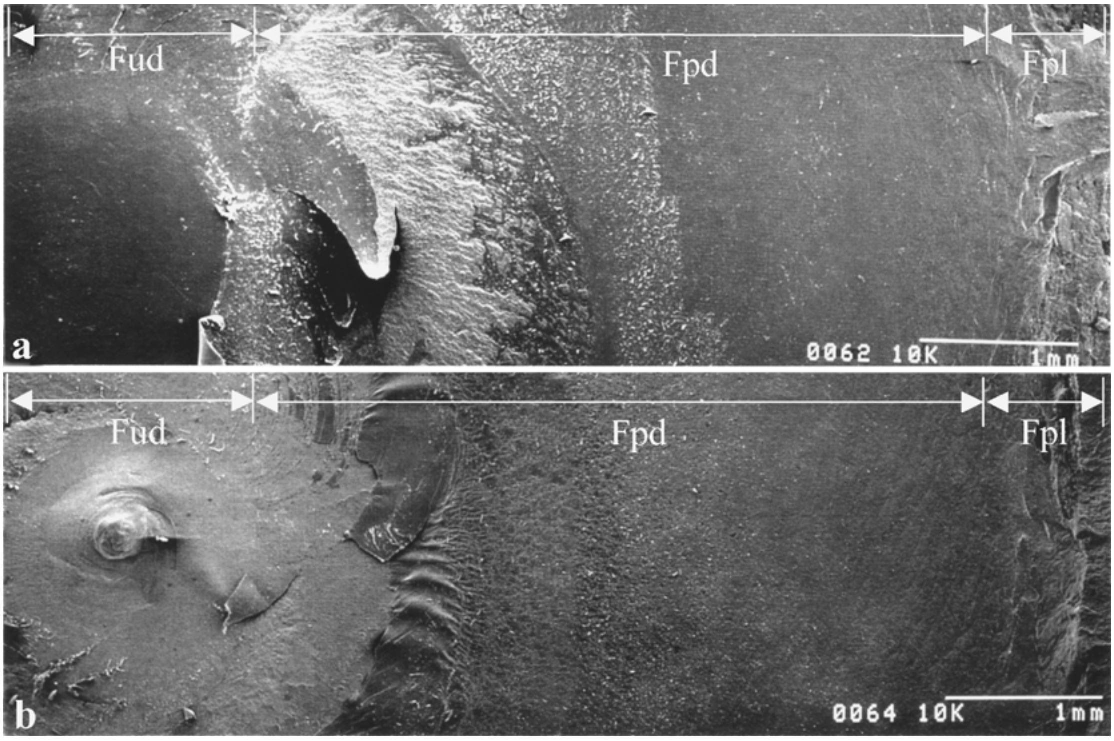

Figure 7 SEM tensile fracture morphologies, treated with methanol: (a) PMMA and (b) PVC.

approximately the same within experimental error and they appear to be insensitive to solubility parameter (not the hydrogen bonding parameter). However, the bonding strength of these joints with solvent treatment are about 360% that of the bonding strength without solvent treatment. Ethanol at $20\text{V}_\text{f}\%$ and $10\text{V}_\text{f}\%$ in distilled water promotes 280% and 110% bonding strength compared with that without solvent treatment. Traditionally, joining incompatible PMMA with PVC by spin friction welding has three disadvantages: (1) the PMMA's glass transition temperature (102°C) is higher than that for PVC (82°C), when friction temperature is over 82°C, the PVC welding part is plasticized but the PMMA has not plasticized yet; for welded PMMA with PVC to achieve better bonding strength they must be simultaneously plasticized and wetted so that interdiffusion of molecular chains occurs. The so-called plasticization comes from the friction temperature being so much higher than the glass transition temperature, so that the chain is apt to activate under these conditions; (2) for

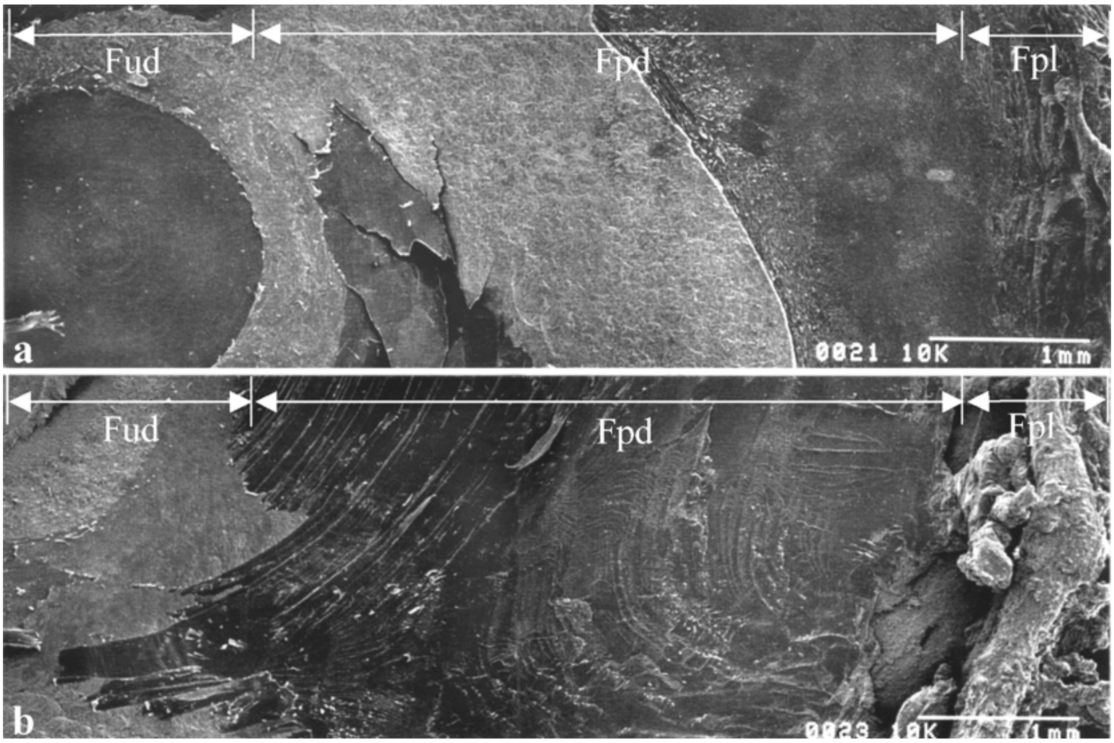

Figure 8 SEM tensile fracture morphologies, treated with ethanol: (a) PMMA and (b) PVC.

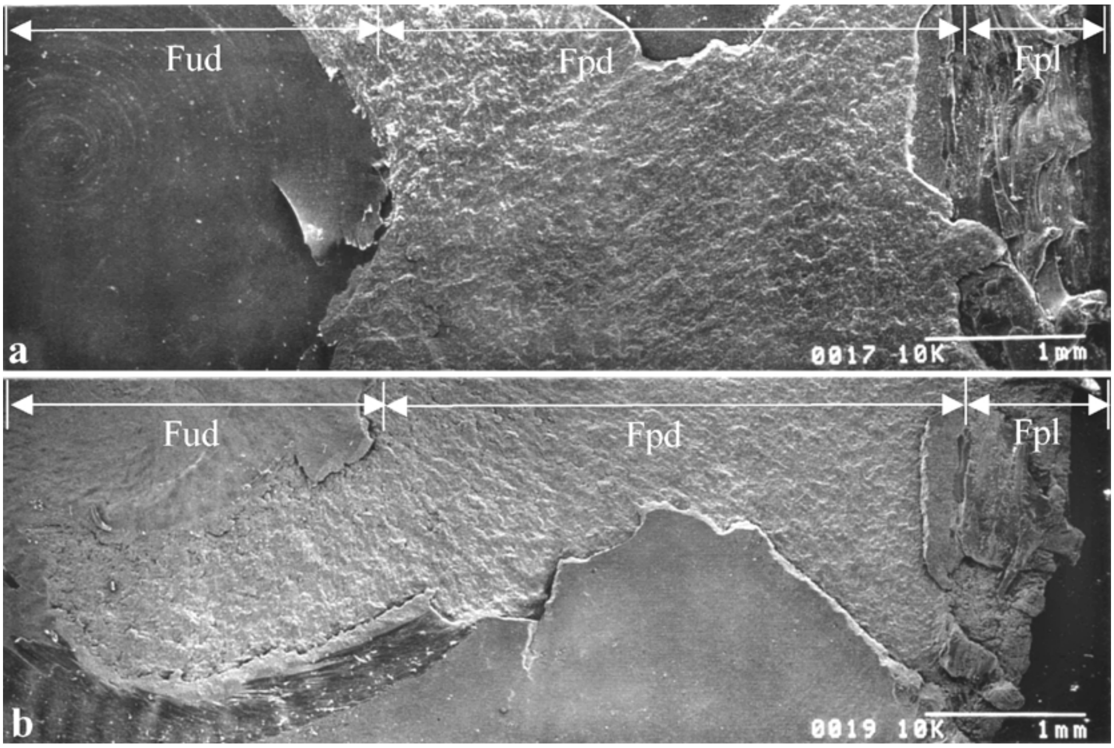

Figure 9 SEM tensile fracture morphologies, treated with acetone: (a) PMMA and (b) PVC.

wear resistance, PMMA is lower than PVC, the periphery zone of the PMMA will be earlier spun out of the matrix than PVC, and decrease the area of effectively welding zone, thus decline the bonding strength; (3) when spinning friction is stopped at the moment of forge pressure, the previous friction heat will be lost immediately [22], and the heat activation will be reduced. The purpose of this research is to resolve these problems, when distilled water, methanol, ethanol and acetone transport into both welding parts at the same time in spin friction, and can reduce the effective glass transition temperature in both the welding parts. Because the amount of solvent transport into PMMA is larger than into PVC, the reduction in the glass transition temperature will be larger in PMMA. This will thus reduce the differences between the effective glass transition temperatures of the PMMA and PVC, namely reduce the incompatible degree between PMMA and

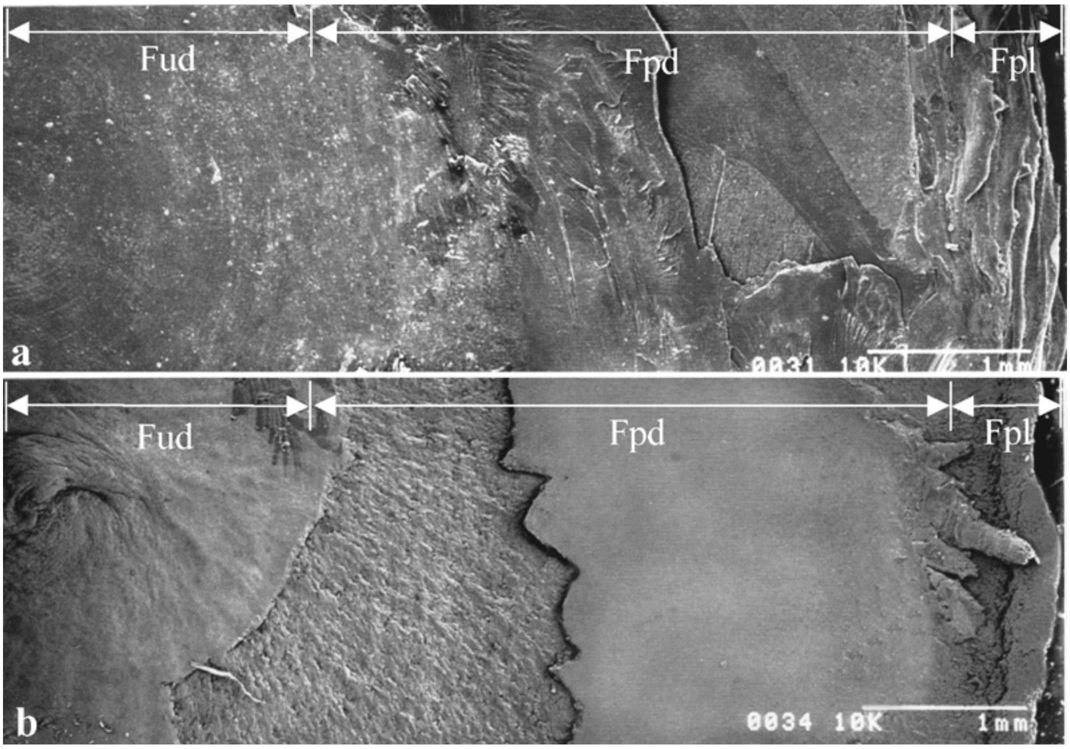

Figure 10 SEM tensile fracture morphologies, treated with $10V_f\%$ cosolvent: (a) PMMA and (b) PVC.

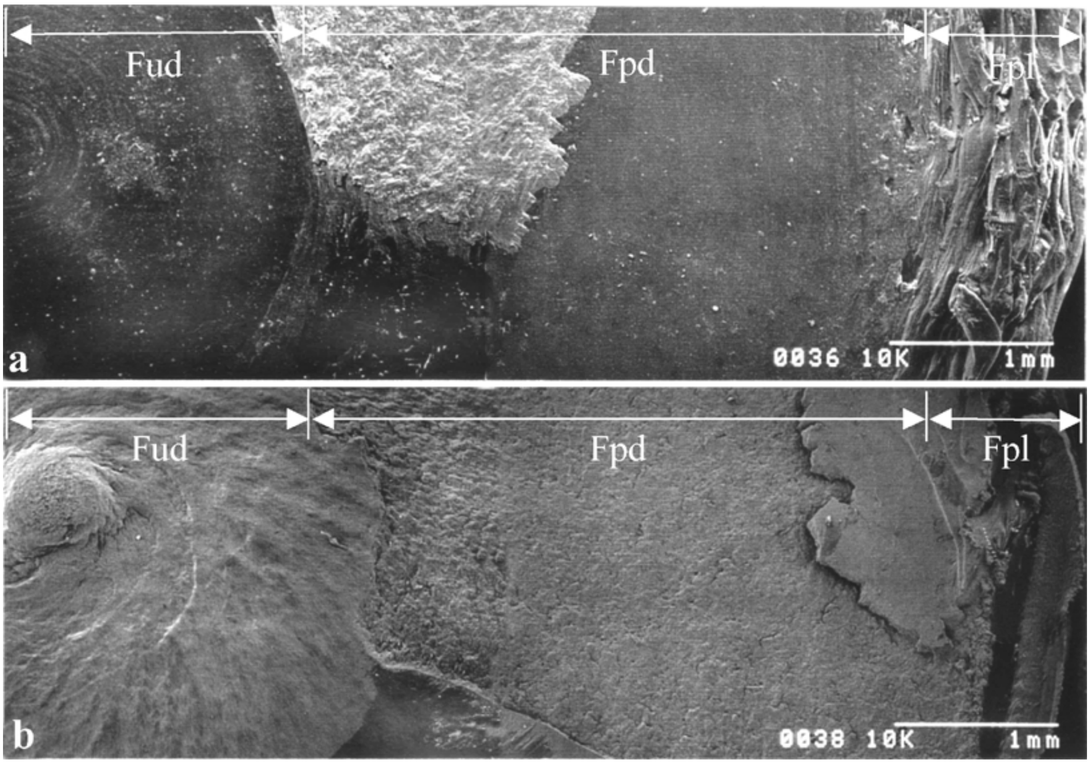

Figure 11 SEM tensile fracture morphologies, treated with $20V_f\%$ cosolvent: (a) PMMA and (b) PVC.

PVC, and the time for the plasticization of both welding parts will be approximately the same rather than spin out the plasticized part, thus the welded PMMA with PVC have an effective interdiffusion. In addition, the residual solvent still remain in both welding parts, it is not easy to speedily raise the effective glass transition temperature, while spinning friction welding ceases and forge pressure is added. Also, these solvents can eliminate the residual stress in the welded zone.

Comparing fracture morphology with bonding strength and residual solvent, the percentage of each solvent left on the welding zone during desorption in vacuum is the following: 0.03% of distilled water, 0.3% of methanol, 2% of ethanol and 6% of acetone. The solvent left on the welded zone will reduce the bonding strength of welded PMMA with PVC. Thus, the positive factor (effective welding zone) and negative factor (residual solvent) will affect the bonding strength

TABLE II Bonding strength of welded PMMA-PVC treated with and without solvent and cosolvent

Solvent	Bonding strength (MPa)
Without treatment	2.9
Distilled water	13.6
Methanol	13.8
Ethanol	13.4
Acetone	13.7
$10V_f\%$ cosolvent	6.2
$20V_f\%$ cosolvent	11.3

simultaneously. This is to say, the welded zone will have a larger area of the "dot" fracture morphology and the PVC clung to the Fpd zone of PMMA, and less residual solvent remaining in the welded zone, and this is responsible for better bonding strength.

4. Conclusions

The effect of solvent and cosolvent on bonding strength and microstructure of spin-friction welded between parts of PMMA with PVC were investigated. The failure strength in tensile loading was measured and related fracture morphologies were examined. Four solvents, distilled water, methanol, ethanol, acetone were employed. Mixtures of ethanol with distilled water were used to access the effect of a cosolvent. Some results are summarized as below:

1. Treatment with solvent and cosolvent can obtain a better wetting zone, the welding zone in decreasing order of size are as follows: acetone, ethanol, methanol, distilled water, $20V_f\%$ cosolvent, and $10V_f\%$ cosolvent;
2. Tensile fracture morphologies includes three zones: (1) the central zone (Fud) as worn surface, (2) the peripheral zones (Fpl), as plasticized "rippling" and plasticized "pile-up" fracture morphology for PMMA and PVC, respectively and (3) the middle zone (Fpd), as the "dot" fracture morphology or the part of the PVC Fpd zone where it tears from matrix to remain clung to the PMMA. In Fpl, there is no approach or wetting between PMMA and PVC.
3. Treatment with distilled water, methanol, ethanol and acetone, promote about 360%, $20V_f\%$ cosolvent and $10V_f\%$ cosolvent promote 280%, and 110% more bonding strength than occurs without solvent treatment, because they have larger plasticized Fpd, which have no Fud in the central part.
4. For welding PMMA with PVC, treatment with distilled water is readily available and nontoxic, and not only raises the bonding strength but is also a potential bonding method.

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