Adhesion and morphology of PVDF/PMMA and compatibilized PVDF/PS interfaces

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The morphology of the interface between miscible and immiscible polymer pairs was investigated. For the PVDF/PMMA system, which has a highly exothermic enthalpy of mixing, complex structures suggest the occurrence of bulk convective motion at the contact area between the two polymer melts. The immiscible pair PVDF/PS, displays a smooth interface under similar conditions. A simple method for testing compatibilizers is described. Using this method, styrene–methylmethacrylate random copolymers and PMMA were investigated as compatibilizers for the PVDF/PS blend. PVDF/PMMA/PS (1:1:1) ternary blends show some heterogeneity with small domains but their maximum tensile strength is of the same magnitude as that of PVDF/PMMA blends.

(Keywords: immiscible polymer pairs; PVDF; PMMA; PS; compatibilizers)

INTRODUCTION

More than 50 miscible polymer blends are currently commercially available. Their properties and applications are well reviewed in the literature[1–5]. Miscibility of high molecular weight polymers is a consequence of specific intermolecular interactions such as hydrogen bonding, ionic interactions and n–π complex formation[6,7]. Mixing occurs during processing of polymer blends with intensive transfer of polymer chains at the polymer–polymer interfaces until an homogeneous material is obtained. Results of theoretical and experimental work have been reported in the literature, concerning the interdiffusion of polymer pairs[8–21], assuming a continuous concentration gradient at the interface.

Miscibility is not an essential requirement for a useful commercial polymer blend. A large number of immiscible blends are known today as very important commodity and engineering materials. Good examples are the impact-modified polymers. However, suitable mechanical properties are only achieved with good adhesion between the polymer phases[22,23]. Adhesion can be improved through the use of compatibilizers. In this work a simple test for evaluation of compatibilizers is described, as well as the morphology of bonded polymer interfaces. Compatibilizer performance in improving mechanical properties of immiscible polymer blends can be determined by their contribution to increasing adhesion of macroscopic polymer interfaces. Among the most effective compatibilizers are block and graft copolymers[24,25]. However, random copolymers are receiving greater attention as compatibilizers[22,26–32] due to their particular thermodynamic behaviour. Even when intermolecular interactions in homopolymer–random copolymer systems are not strong enough to contribute to exothermic heats of mixing, repulsive intramolecular interactions due to immiscible segments in the copolymer may be responsible for a favourable mixing.

The use of a homopolymer as a compatibilizer and the behaviour of ternary blends have not received much attention in the literature, although some examples have been reported[22,33–37]. In this work, the performance of styrene–methylmethacrylate random copolymers and poly(methylmethacrylate) in the compatibilization of blends of polystyrene and poly(vinylidene fluoride) is also investigated.

EXPERIMENTAL

Poly(vinylidene fluoride) (PVDF) Kynar 461 ($T_g = -35$°C. $T_m = 155$–160°C, $M_w = 4.4 \times 10^5$ and $M_n = 7.6 \times 10^4$ g mol^{-1}) was kindly supplied by Pennwalt SA, São Paulo. Poly(methylmethacrylate) (PMMA) Oroglas ($T_g = 105$°C) was purchased from Rohm and Haas Co. This was characterized by gel permeation chromatography ($\bar{M}_w = 7.04 \times 10^5$, $\bar{M}_n = 4.09 \times 10^5$, $\bar{M}_z = 9.99 \times 10^5$ g mol^{-1}) with a u.v. detector. Polystyrene (PS) ($T_g = 100$°C) was kindly supplied by Proquigel, São Paulo. Gel permeation chromatography (g.p.c.) gave $\bar{M}_w = 3.02 \times 10^5$, $\bar{M}_n = 1.56 \times 10^5$, $\bar{M}_z = 5.36 \times 10^5$ g mol^{-1}. Random styrene–methylmethacrylate (SMMA) copolymers of different styrene content were prepared according to the method of Thomson[38]. The monomers were distilled, mixed in a glass tube and heated for 48 h at 50°C, followed by 24 h at 90°C. Initiator was 2,2′-azobisisobutyronitrile.

Preparation of polymer–polymer adhesive joints

Polymer cylinders of 1 cm diameter and 3 cm length were obtained using the system described in *Figure 1*. The mould was made of steel, with a steel jacket fitted with electric heaters. The system was adapted to a laboratory (Schwing Siwa) press, maximum pressure equal to 4.8 MPa.

The cylinder surfaces were carefully polished with 600 mesh sand paper, washed and dried. Pairs of different polymers were pressed together in the same mould described in *Figure 1*. The samples were previously

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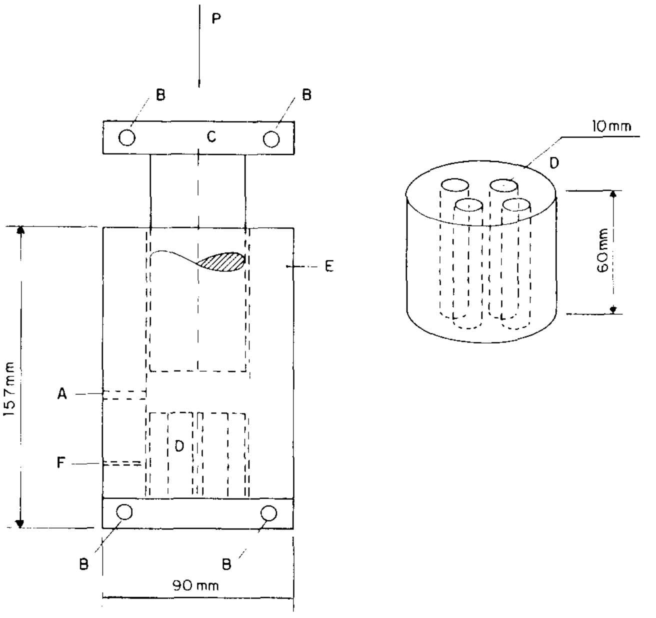

Figure 1 Steel mould for the preparation of polymer joints: (A) vacuum connection, (B) cooling fluid in/outlet, (C) pressing head, (D) mould, (E) mould jacket and (E) thermocouple well

evacuated during 30 min and heated under 300 atm. PVDF/PMMA and PVDF/PS joints were heated at 185 or 145°C. PMMA/PS joints were heated to 135°C. The temperature was controlled within ±5°C with a chromel–alumel thermocouple in the steel mould.

PVDF/PS joints for compatibilization tests were obtained in the following way. A copolymer solution was dropped on the PVDF surface and the solvent ($CHCl_3$) was evaporated in order to obtain a thin copolymer film ($5\,mg\,cm^{-2}$). The cylinder was pressed against PS at 185°C and 300 atm for 1 h. Some tests were also performed in a similar way except that the copolymer film was changed to a PS/PMMA blend with 9.4% of PS.

Adhesion tests

The polymer joints were evaluated measuring their maximum strength at breaking in an EMIC–MEM 500 tensile machine with a crosshead rate of $0.5\,mm\,min^{-1}$. Results are shown in *Tables 1* and *2*.

Scanning electron microscopy (SEM)

One of the components of the polymer joint was dissolved in a selective solvent. Chloroform is a good solvent for PMMA and PS and does not swell or cause any change on PVDF surfaces as observed by microscopy. PVDF/PMMA and PVDF/PS joints with and without the compatibilizer film were immersed in chloroform for 6 h. The solvent was renewed 10 times during this period. Solvent was finally eliminated through freeze drying. Freeze drying was chosen instead of evaporation at room temperature in order to minimize any effect of the leaving solvent on the remaining structure at a temperature at which PVDF has higher mobility. The remaining polymer surfaces were covered with a thin layer (350 Å) of gold through sputtering or gold evaporation and observed in a Jeol T-300 scanning electron microscope.

In order to verify the solvent effect on a polymer blend of the same components of the joints, films of PVDF/PMMA of different compositions were obtained by casting from dimethylformamide solutions. The films were carefully dried and immersed in chloroform in the same way as for the polymer joints. The remaining films were freeze-dried, gold-coated and observed in the scanning microscope.

Transmission electron microscopy (TEM)

A thin cut of the PMMA/PVDF joint was obtained in an ultramicrotome in the perpendicular direction to the interface. The sample was observed in a Zeiss EM-902 transmission electron microscope. This microscope is fitted with a magnetic filter which allows the selection of monochromatic inelastic electrons[39] and gives an image with high contrast even without conventional staining. For the PVDF/PMMA interface, electrons with energy loss of 61 eV were chosen to increase contrast. PMMA appears darker than PVDF, in contrast to conventional elastic imaging.

Polymer blends

PVDF/PMMA, PMMA/PS and PVDF/PS polymer blends with and without compatibilizer were obtained in a Brabender Plasticorder PLE 331/DC 36-200 mixer at 190°C and $40\,rev\,min^{-1}$. The mixing time was 10 min. Sheets (1 mm thick) were obtained pressing the previously mixed polymer blends. Tensile strength measurements were performed in samples of 85 × 6 × 1 mm in the EMIC tensile machine. Results are shown in *Table 3*. Parts of the polymer sheets were fractured in liquid nitrogen, covered with gold and observed in the SEM.

Table 1 Adhesion tests: maximum tensile strength of polymer–polymer joints pressed at 300 atm

Polymer pair	Pressing time (min)	T (°C)	Maximum tensile strength (MPa)
PVDF/PMMA	60	185	21.5 ± 4.8
		145	2.2
	150	185	20.4 ± 2.6
		145	10.3
	360	185	20.5 ± 5.6
PVDF/PS	60	185	0
		145	0
	150	185	0
		145	0
	360	185	0
PMMA/PS	60	135	18.3 ± 3.3
	150	135	19.9 ± 1.0
	360	135	19.6 ± 1.3

Table 2 Influence of compatibilizer on the adhesion of PVDF/PS joint pressed for 1 h at 185°C and 300 atm

Compatibilizer	Maximum tensile strength (MPa)
PMMA	23.2 ± 2.7
SMMA with 4.8% S	20.8 ± 2.8
SMMA with 9.6% S	19.4 ± 2.2
SMMA with 20% S	14.4 ± 2.5
SMMA with 30% S	12.8 ± 2.1
SMMA with 40% S	9.4 ± 0.4
SMMA with 50% S	0
PMMA/PS blend with 9.4% PS	13.6 ± 3.3

Table 3 Maximum tensile strength of (1:1) polymer blends obtained in the Brabender mixer

Polymer blend	Maximum tensile strength (MPa)
PVDF/PS	24.4 ± 2.5
PVDF/PMMA[a]	43.2
PMMA/PS	30.4 ± 9.0
PVDF/PS with 2% PMMA	21.5 ± 1.9
PVDF/PS with 5% PMMA	23.5 ± 2.4
PVDF/PS with 10% PMMA	35.1 ± 0.4
PVDF/PS with 20% PMMA	33.6 ± 2.8
PVDF/PS with 33% PMMA	46.5 ± 2.5

[a]Ductile fracture (strength at break = 29.0 MPa)

RESULTS AND DISCUSSION

Mechanical tests

Polymer–polymer and polymer–compatibilizer–polymer joint strengths. The joint strength of thermoplastic polymers due only to physical attraction is low and is of the order of magnitude of the surface energy. In order to achieve useful practical values for the joint strength, there must be a mass transport across the interface which is believed, as discussed in the literature[13], to be a consequence of a pure chain diffusion process. Wu[13] proposed that in order to achieve a strong adhesive bond, polymer chains must diffuse to form an interfacial thickness of at least one entanglement mesh size and thus to favour a cohesive fracture, instead of an interfacial fracture. In the case of smaller interfacial thickness, interfacial fracture takes place[40]. In cohesive joints, failure does not occur at the interface but at some small distance from it. Typical examples are joints between identical or compatible polymers when the interactions between their entangled chains are so strong that their separation gives rise to large scale local deformation. Adhesion between identical polymer samples has a fundamental importance in crack healing and technical welding and has been extensively studied[40–43].

Considering the interdiffusion in joints of different polymers, characteristic interfacial thickness is predicted to be inversely proportional to the Flory–Huggins interaction parameter[44,45]. This agrees with the prediction of de Gennes according to which the rate of polymer molecules moving across the interface between miscible pairs is proportional to the interaction parameter and to the chain mobility[19,20]. Interdiffusion in pairs of different polymers has been studied using different methods[8–18]. Its low magnitude should be the limiting factor to the formation of a strong joint, whenever mixing is to be expected on thermodynamic grounds. However, as discussed below, for miscible pairs the movement of polymer molecules through the interface is enthalpically very favourable and there is a possibility that it occurs with convection. Convection in this case contributes even more by increasing the interface thickness and the joint strength, because it can generate rough, mechanically bonded interfaces. Thicknesses and joint strengths in this case should be above those predicted by theories which take into account only pure interdiffusion. *Table 1* shows the maximum tensile strength values obtained in adhesion tests of different polymer–polymer joints pressed at 300 atm. Higher values of maximum tensile strength were obtained for PVDF/PMMA joints than for PVDF/PS and PMMA/PS joints in the same conditions. Differences in the joint strength for different pressing contact times could only be observed in joints obtained at temperatures well below the melting temperature of PVDF. At 185°C even after only 1 h the PVDF/PMMA joint strength has already a very high value, indistinguishable from those obtained after longer pressing times. At 145°C, which is below PVDF melting temperature, chain mobility is already high enough to favour adhesion.

Table 2 shows how the PVDF/PS joint strength changes using a thin film of compatibilizer between the pure polymer cylinders. PMMA seems to be the best compatibilizer. The joint strength decreases as the styrene content is increased in the SMMA copolymer. This result is to be expected, following the arguments given.

Block and graft copolymers are frequently used as compatibilizers for immiscible polymer blends[24,25]. In these cases each block is at least partially miscible with one of the blend components and the copolymer is located at the interfaces between the immiscible phases, increasing the adhesion between them. Some examples of random copolymers as compatibilizers have also been reported in the literature[7,22,24–32]. Miscibility in polymer blends has always been related to specific intermolecular interactions. The miscibility between random copolymers and homopolymers can be even higher than expected when only intermolecular interactions are considered. Intramolecular repulsions occur when the different segments in the copolymer are mutually immiscible, making an important contribution to the enthalpy of mixing which turns out to be more exothermic. In random copolymers of SMMA the intramolecular repulsion is not high since the Flory–Huggins parameter for PMMA and PS has a small positive value.

Joint strength and interaction energy. The results obtained for PVDF/PS joint strength with random SMMA copolymers of different styrene content as compatibilizers can be correlated with values for the interaction energy, *B*, for mixing segments. *B* for the PVDF/SMMA and PMMA/SMMA pairs can be obtained from the literature data of the Flory–Huggins interaction parameter, χ, for PVDF/PMMA[13], PMMA/PS[16] and the solubility parameters, δ, for PVDF and PS[46], using the following equations[22]:

$$B_{ij}/RT = \chi_{ij}/V_{ij} \qquad (1)$$

where V_{ij} is the segmental molar volume for a pair of polymers i and j

$$B_{ij} = (\delta_i - \delta_j)^2 \qquad (2)$$

The value of δ for PVDF was taken as 11 cal$^{1/2}$ cm$^{-3/2}$, estimated from data for the best solvents of PVDF, dimethylacetamide ($\delta = 10.2$ cal$^{1/2}$ cm$^{-3/2}$) and dimethylformamide ($\delta = 12.1$ cal$^{1/2}$ cm$^{-3/2}$) (ref. 47). Substituting data from the literature, $\chi_{PMMA/PVDF} = -0.7$, $\chi_{PMMA/PS} = 0.01$, $\delta_{PS} = 8.9$ cal$^{1/2}$ cm$^{-3/2}$, the following *B* values were obtained:

$$B_{PMMA/PVDF} = -17.3 \times 10^6 \text{ J m}^{-3}$$

$$B_{PMMA/PS} = 0.2 \times 10^6 \text{ J m}^{-3}$$

$$B_{PVDF/PS} = 18.4 \times 10^6 \text{ J m}^{-3}$$

B values can be obtained for the interaction between the SMMA copolymers and each homopolymer of the joint,

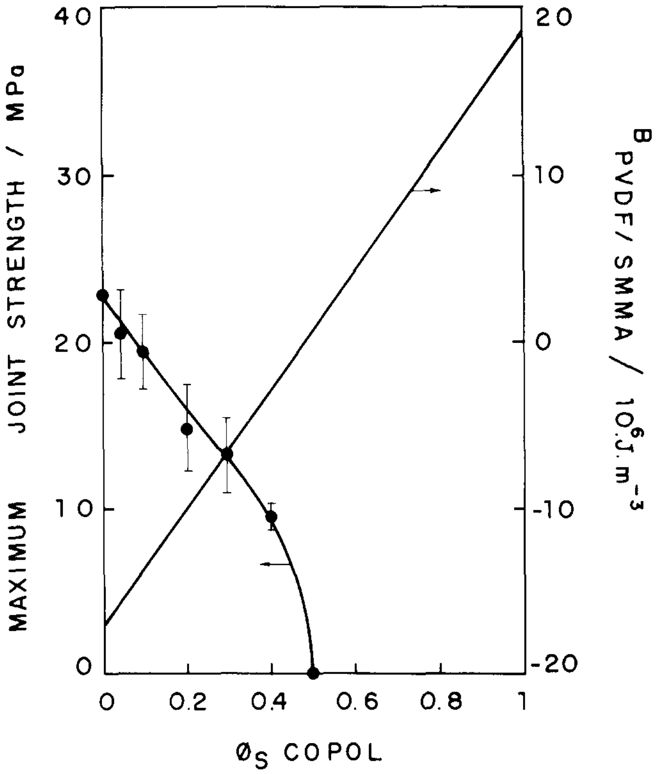

Figure 2 Interaction energy for segment mixing, *B*, and maximum joint strength as a function of styrene content in the SMMA random copolymer

PVDF and PS:

$$B_{\mathrm{PVDF/SMMA}} = B_{\mathrm{PS/PVDF}}\phi_{\mathrm{S}}^{\mathrm{COPOL}} + B_{\mathrm{PMMA/PVDF}}\phi_{\mathrm{MMA}}^{\mathrm{COPOL}} - B_{\mathrm{PS/PMMA}}\phi_{\mathrm{S}}^{\mathrm{COPOL}}\phi_{\mathrm{MMA}}^{\mathrm{COPOL}} \quad (3)$$

and

$$B_{\mathrm{PS/SMMA}} = B_{\mathrm{PS/PMMA}}\phi_{\mathrm{MMA}}^{\mathrm{COPOL}} - B_{\mathrm{PS/PMMA}}\phi_{\mathrm{S}}^{\mathrm{COPOL}}\phi_{\mathrm{MMA}}^{\mathrm{COPOL}} \quad (4)$$

where $\phi_{\mathrm{S}}^{\mathrm{COPOL}}$ and $\phi_{\mathrm{MMA}}^{\mathrm{COPOL}}$ are volume fractions of styrene and methylmethacrylate in the SMMA copolymer.

Values for $B_{\mathrm{PS/SMMA}}$ vary between 0 and 0.2 J m^{-3} for the whole range of styrene content. For $B_{\mathrm{PVDF/SMMA}}$ the variation is high and can be observed in *Figure 2*. For styrene contents higher than 0.5, $B_{\mathrm{PVDF/SMMA}}$ values are positive corresponding to an unfavourable interaction which is confirmed by the very small values of maximum tensile strength for PVDF/compatibilizer/PS joints.

Tensile strength of polymer blends. Blends of the same polymers and compatibilizers used in the polymer joints were obtained in the Brabender mixer and their maximum tensile strengths were measured as shown in *Table 3*. Polymer pairs which give the higher joint strength values are also the components of blends with higher maximum tensile strength. PVDF/PS blends with 10% PMMA have maximum tensile strength 40% higher than those without compatibilizer.

Homopolymers are seldom used as compatibilizers. Not many ternary polymer blends are reported in the literature[22]. The interaction energy for mixing polymer segments, *B*, can be obtained for a PVDF/PMMA/PS ternary blend using values of $B_{\mathrm{PMMA/PVDF}}$, $B_{\mathrm{PVDF/PS}}$ and $B_{\mathrm{PMMA/PS}}$. This can be calculated using the following equations[22]:

$$B = B_{\mathrm{PMMA/PVDF}}(\phi_{\mathrm{PMMA}})^2/1 - \phi_{\mathrm{PVDF}} + B_{\mathrm{PVDF/PS}}(\phi_{\mathrm{PS}})^2/1 - \phi_{\mathrm{PVDF}} + \Delta B[\phi_{\mathrm{PMMA}}\phi_{\mathrm{PS}}/(1 - \phi_{\mathrm{PVDF}})^2] \quad (5)$$

where ϕ_i is the volume fraction of component i and

$$\Delta B = B_{\mathrm{PMMA/PVDF}} + B_{\mathrm{PVDF/PS}} - B_{\mathrm{PMMA/PS}} \quad (6)$$

B values for the PVDF/PMMA/PS ternary blend were obtained as a function of composition, as shown in *Figure 3*.

For $\phi_{\mathrm{PMMA}}/(1 - \phi_{\mathrm{PVDF}})$ values above 0.55, *B* is negative. This explains the very high value of maximum tensile strength in *Table 3* for a blend of PVDF/PMMA/PS (1:1:1) ($\phi_{\mathrm{PMMA}}/(1 - \phi_{\mathrm{PVDF}}) = 0.5$) which is comparable to the value for the PVDF/PMMA miscible blend.

MORPHOLOGY

Blends obtained by casting

PVDF/PMMA blends obtained by film casting show globular structures when treated with $CHCl_3$ (*Figure 5*). PMMA is extracted from the PVDF/PMMA blend film and a porous layer of PVDF is left behind. Because $CHCl_3$ is a nonsolvent for PVDF, the porous surface layer shrinks, decreasing the PVDF–$CHCl_3$ contact area. The order, size and number of the globular structures vary with the initial PMMA content: 1:2 PVDF/PMMA blends (*Figure 5*) show a larger number of globular structures per unit area than 1:4 blends, but the former have a smaller diameter. This is expected because a denser layer results after PMMA extraction. Similar structures

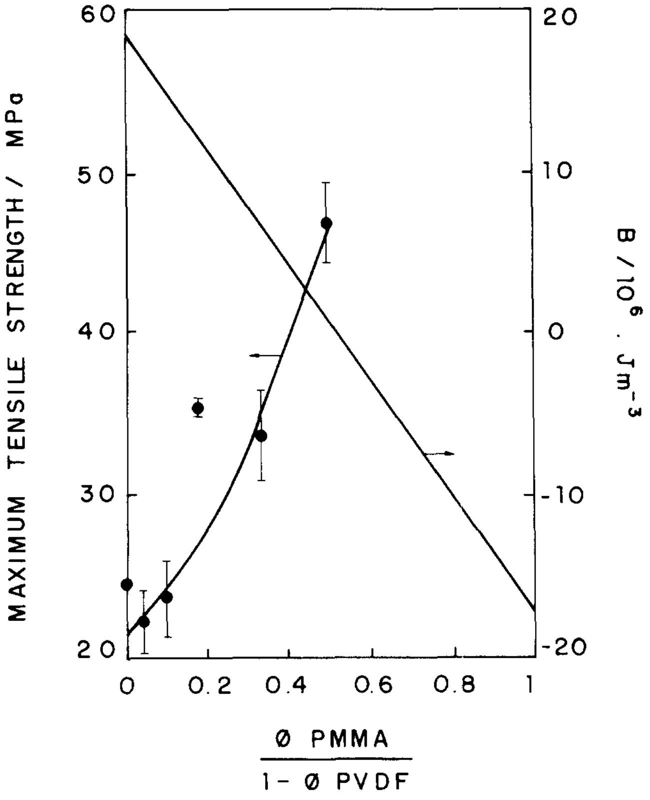

Figure 3 Interaction energy for segment mixing, *B*, and maximum tensile strength as a function of composition of the PVDF/PMMA/PS ternary blend

were always observed for blends of different compositions immersed in $CHCl_3$. Blends with PMMA content higher than 97% dissolved in $CHCl_3$.

Morphology of polymer–polymer interfaces

PVDF surfaces were pressed against PMMA at 300 atm and 185°C. After cooling, they were immersed in $CHCl_3$ in order to dissolve PMMA and examined by SEM (*Figure 4a*). These surfaces show complex structures in contrast to those which were pressed against PS (*Figure 4b*). A smooth surface can be observed also in PMMA/PS joints, after PS extraction with cyclohexane (*Figure 4c*). It is well known that PVDF and PMMA form miscible blends in contrast to the other pairs. This suggests that strong miscibility is related to the development of surface roughness in these experiments.

As compared to cast films, PMMA extraction from the interface of PVDF/PMMA joints develops a completely different morphology. Crazing-like structures are observed. These kinds of structures were observed also for the same polymer joints pressed at lower pressures (0.1 atm, *Figure 6*).

If the joint interfaces were homogeneous, as expected for those obtained by pure interdiffusion, the morphology would be similar to that observed also by SEM for the blend films. Thin cuts of the interface observed in the TEM (*Figure 7*) confirm its inhomogeneity, which can also be observed in micrographs presented in the

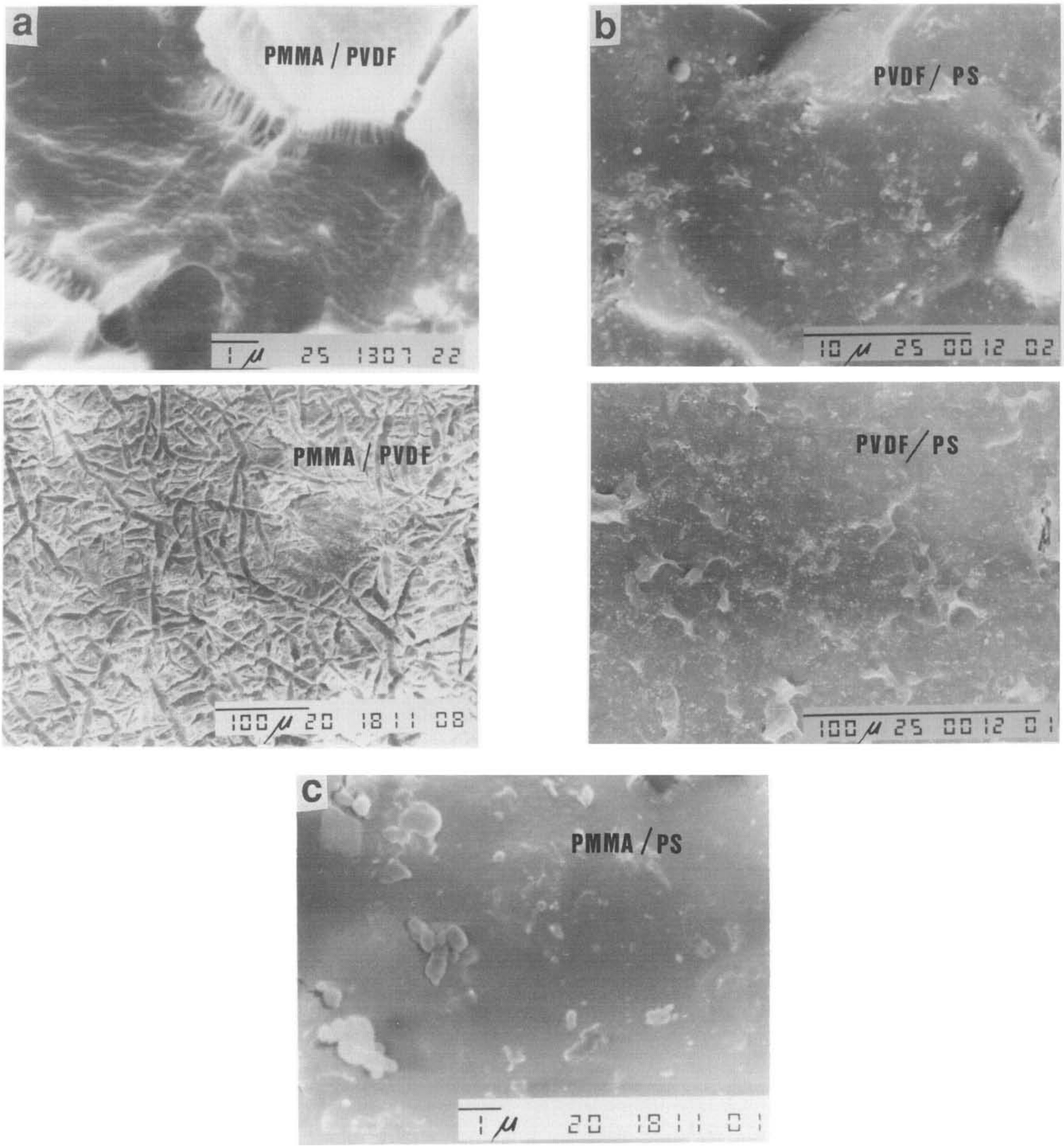

Figure 4 SEM of PVDF surfaces pressed against (a) PMMA and (b) PS at 300 atm and 185°C, after extraction with chloroform. (c) SEM of PMMA surfaces pressed against PS at 300 atm and 135°C, after extraction with cyclohexane

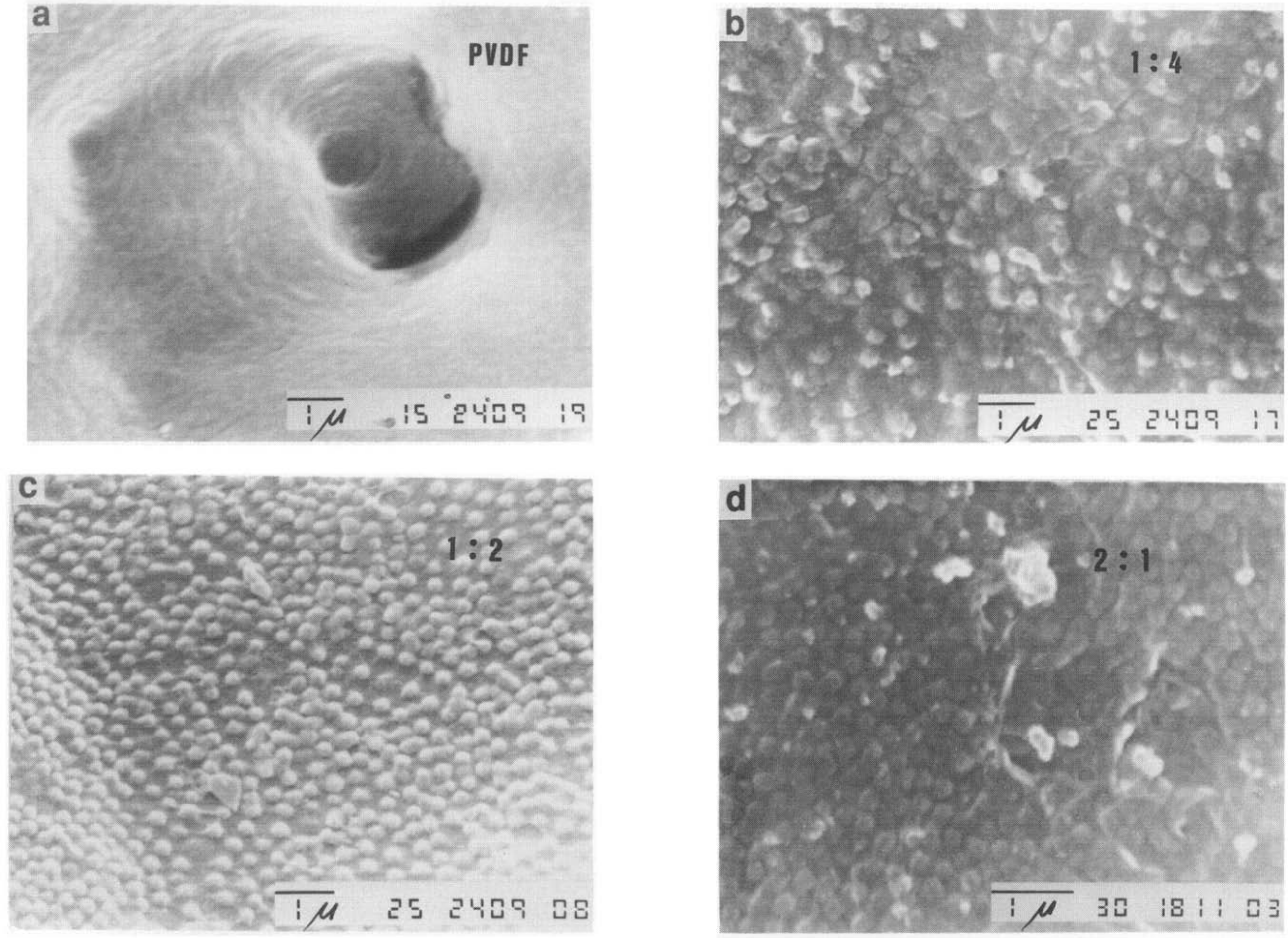

Figure 5 SEM of (a) PVDF and (b)–(d) PVDF/PMMA blends obtained through casting in dimethylformamide, dried and immersed in chloroform. Composition: PVDF/PMMA (b) 1:4, (c) 1:2 and (d) 2:1

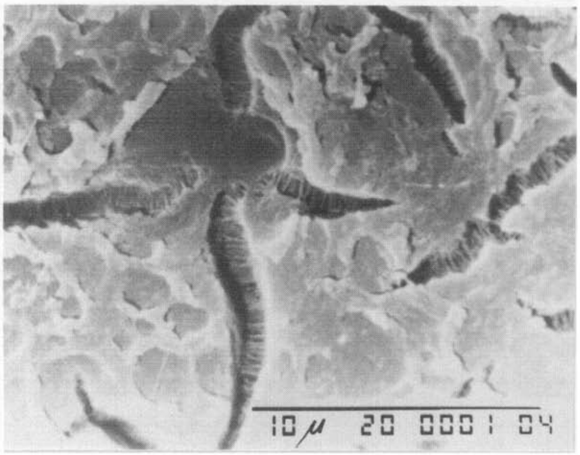

Figure 6 SEM of PVDF surfaces pressed against PMMA at 185°C and 0.1 atm after extraction with chloroform

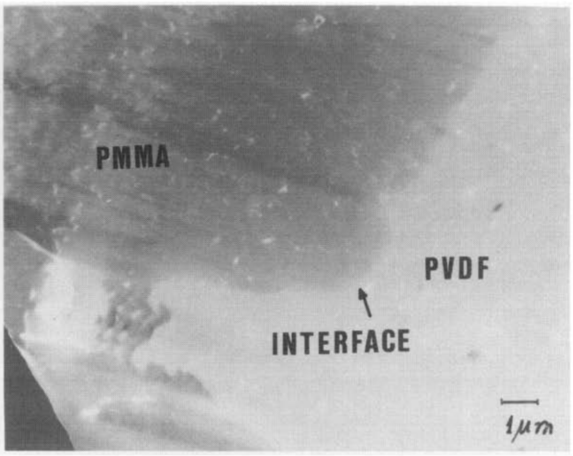

Figure 7 Transmission electron micrograph of the PVDF/PMMA interface with inelastic monochromatic electrons ($\Delta E = 61$ eV)

literature[48]. One way to explain the observed morphologies is to consider that convection occurs at these interfaces, instead of pure interdiffusion which is normally assumed in the literature[13]. The enthalpy of mixing in the PVDF/PMMA system is very favourable to mixing, due to hydrogen bonding interactions[49]. Fluctuations of the polymer–polymer interfacial tension may favour convective movements at the interface in order to minimize the interfacial energy. Free-energy decreases with geometrical expansion of the interface, wherever the interfacial tension is lower and consequent contraction of the interface takes place wherever the interfacial tension is higher. This is the well known Marangoni effect[50].

Composto, Kramer and White[15] also consider that the segment flux across a polymer–polymer interface is not wholly diffusive. Because the diffusion fluxes of polymers A and B across the interface may differ (and this is probably the case for PVDF/PMMA), a bulk (or convective) flow occurs to compensate for volume excesses. This bulk flow may also be understood as a response to the pressure gradient created at the interface as assumed by Brochard, Jouffroy and Levinson[51]. Some experimental work supports the theory which predicts that diffusion is controlled by the slower moving component[11,51,52]. Sillescu[53] claims that diffusion is controlled by the faster component which agrees with results of Green *et al.*[54]. Brochard and de Gennes[55] proposed a hybrid fast–slow theory, considering that the slower moving component is swollen like a gel by the faster one and the interface moves backwards. In this theory, for shorter diffusion distances a pressure gradient develops and the results follow the slow theory.

Another way to describe the formation of polymer interfaces which could also explain the observed inhomogeneity is to consider the fractal nature of the diffusion front[56].

Morphology of compatibilized interfaces

When SMMA copolymers (*Figure 8*) were used as compatibilizers, the same crazing-like structures were observed but with a smaller frequency for the same area. The morphology changes with the styrene content. For copolymers with styrene content greater than 40% the morphology is similar to that observed for PVDF/PS joints. When a PMMA/PS blend (10% PS) was used as compatibilizer, the same macroscopic morphology was observed, but the internal fibrillar structure which occurs with copolymers with the same styrene content was changed into small spherical cavities. This morphology may occur due to segregation of PS domains by the PVDF and PMMA.

Morphology of polymer blends obtained by melt-mixing

Blends of the same polymers used in the polymer joints were obtained from the melt in a Brabender mixer and their morphology was observed by SEM after fracturing them in liquid nitrogen. All the blends were obtained in the same conditions. PVDF/PS blends have a very rough morphology showing rather large phase domains (*Figure 9b*), while PVDF/PMMA blends are well dispersed after the same mixing time (*Figure 9a*). Polymer pairs which give joints with higher adhesion also form better dispersed blends in the Brabender mixer. Blends with smaller domain sizes also showed better mechanical properties (*Table 3*) and lower values of interaction energy as discussed above. When a fractured sample of a ternary PVDF/PMMA/PS (1:1:1) is observed by SEM (*Figure 9e*), a well but not completely dispersed structure is seen. The morphology is similar to that of binary PMMA/PS blends which have a rather low value of Flory–Huggins interaction parameter ($\chi = 0.01$) (ref. 16). *Figure 10* shows how the phase domains of a PVDF/PMMA/PS blend decrease with increasing PMMA content. The domain size is not zero for PVDF/PMMA blends because the mixing time was not enough for complete dissolution.

Adhesion between two different polymers is directly related to the interfacial tension which governs the mutual miscibility and the size of phase domains obtained by mixing the polymer pair. For immiscible polymers such as PVDF/PS, the interfacial tension, σ, is high. A typical order of magnitude for σ is 10^{-2} ($\mathrm{N\,m^{-1}}$). If phase domains have radii R in the order of 10^{-6} m, $\sigma/R = 10^{4}\ \mathrm{N\,m^{-2}}$ (ref. 57). During the mixing process, shear stresses for polymer melts can be well below this value and an effective mixture is not attained. PMMA and PS have a lower interfacial tension, the adhesion between them is higher and smaller domains may be obtained with low shear stresses. Poor physical properties of incompatible blends such as maximum tensile strength may be assigned to low adhesion at the polymer–polymer interfaces.

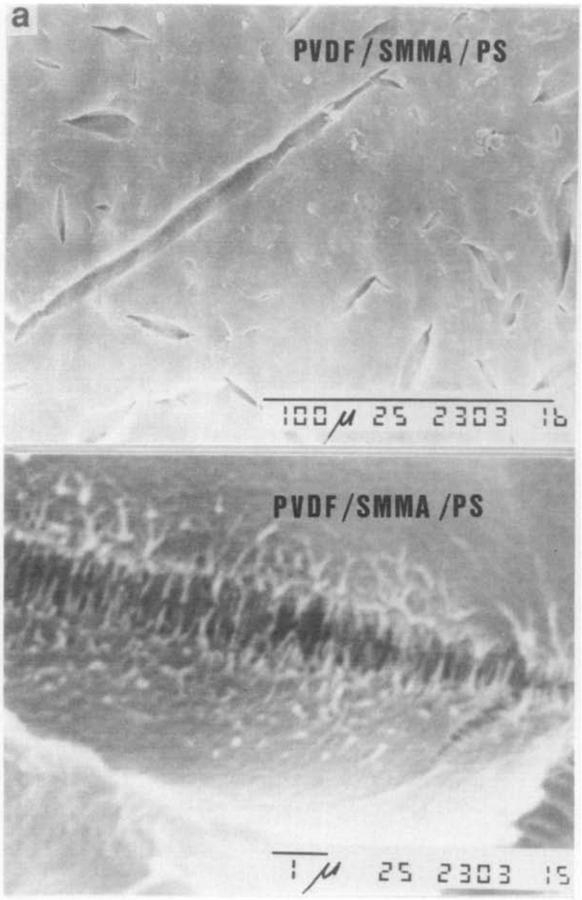

Figure 8 SEM of PVDF surfaces pressed against (a) SMMA copolymer with 5% styrene and (b) PMMA/PS blend with 10% PS at 185°C and 300 atm

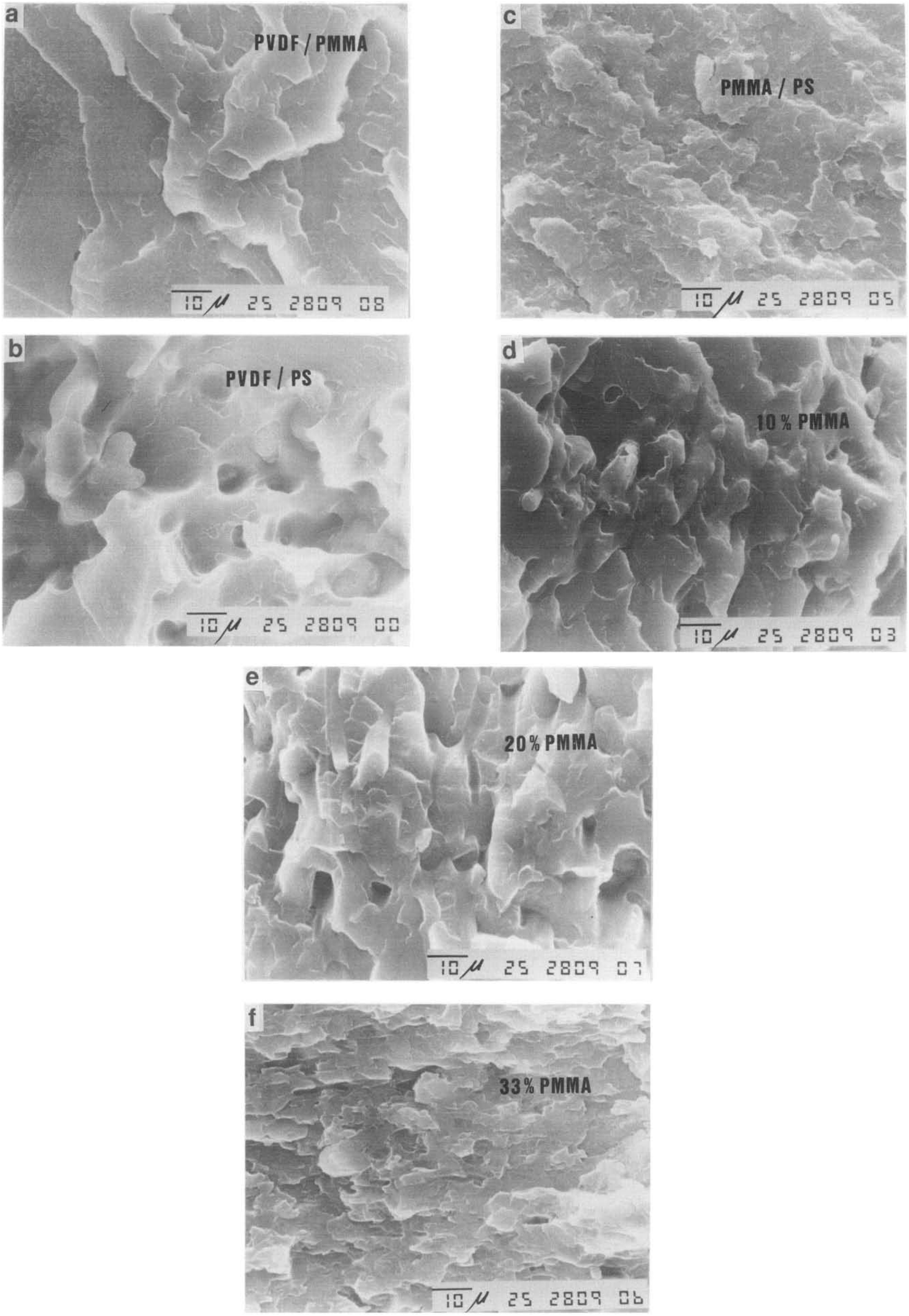

Figure 9 SEM of fracture surfaces of (a) PVDF/PMMA, (b) PVDF/PS, (c) PMMA/PS and PVDF/PS with (d) 10, (e) 20 and (f) 33% of PMMA, obtained in the Brabender mixer at 190°C

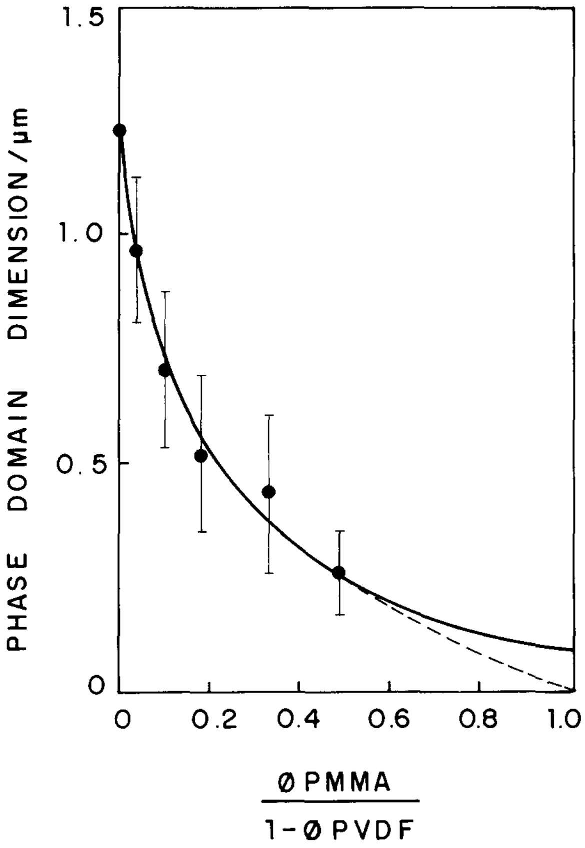

Figure 10 Size of phase domains in a PVDF/PMMA/PS ternary blend obtained in a Brabender mixer at 190°C, as a function of PMMA content

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