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Changes of polymer morphology caused by u.v. irradiation: 2. Surface destruction of polymer blends

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The morphology of poly(methyl methacrylate)/polystyrene and poly(vinyl acetate)/polystyrene blends with different compositions was investigated by scanning electron microscopy. The multiphase structure and surface damage of blends caused by highly energetic, polychromatic u.v. irradiation is presented. It was found that photodegradation of polymer blends was initiated at the phase boundary or in the phase of the less stable polymer. The changes which occur in interfacial interactions, probably caused by the formation of polar groups during photo-oxidation, are discussed.

(Keywords: polymer blends; u.v. irradiation; morphology)

INTRODUCTION

The morphology of polymer blends has a great influence on their behaviour. In the case of homogeneous, miscible blends, when the Gibbs free energy ΔG_m is less than zero (i.e. negative), physical and mechanical properties are usually additive but sometimes synergism or antagonism of properties occurs. In thermodynamically immiscible blends (when $\Delta G_m \geq 0$), phase separation takes place and domains of one polymer are more or less regularly distributed in the continuous phase of the second polymer, called the matrix[1–5]. The prediction of properties of fully or partially immiscible blends is much more complicated, mainly because the mixtures may exhibit many different morphologies.

The morphology of immiscible blends depends on the nature of the polymers as well as on the ratio of components. Generally, the lower the amount of one component, the smaller and better distributed its phase. Conversely, sometimes the lower volume fraction component can be also promoted to provide the continuous phase[6]. Besides the kind and ratio of ingredients, other factors influencing the morphology of polymer blends include: hydrophilicity of the polymers, the adhesion and interfacial tension between them, mobility of macrochains, molecular weight and its distribution, temperature and the procedure of blend preparation, (i.e. the kind of casting solvent, the presence or absence of elongation fields, and the ratio of the relative viscosities of the dispersed and continuous phases)[1,5,7–10].

Polymer surface analysis may be performed by various methods, for instance attenuated total reflectance (ATR) spectroscopy, electron spectroscopy for chemical analysis (ESCA) photoacoustic spectroscopy (PAS) and contact angle measurements[11,12]. Recently, inverse gas chromatography was used to examine the surfaces of solid polymers and their dispersive properties[13,14]. One of the most popular methods widely applied for the study of polymer blends is scanning electron microscopy (SEM)[15–20]. The main advantage of SEM is its high resolving power and very high magnification.

The aim of this work was to study the morphology changes caused by u.v. irradiation in two immiscible blends, poly(methyl methacrylate)/polystyrene and poly(vinyl acetate)/polystyrene, with different compositions.

EXPERIMENTAL

Table 1 lists the commercial polymers chosen for morphology studies of polymer blends. Polymers were purified by precipitation from benzene solutions by non-solvents. Blends of PMMA/PS and PVAc/PS with different ratios of components were prepared by the mixing of 2% polymer solutions. Thin polymer films ($\sim 20\,\mu$m) were obtained by casting of polymer solutions.

Polymers were photodegraded in air atmosphere at room temperature using a high pressure mercury lamp (HPK 125 W; Philips, Holland). Intensity of the incident light was $32\,\mathrm{mW\,cm^{-2}}$.

Surfaces of the polymer blends were examined using a Novascan 30 scanning electron microscope at an acceleration voltage of 15 kV. Samples were coated with gold prior to examination.

Differential scanning calorimetry (d.s.c.) analysis of the samples was performed on a Polymer Laboratories PL DSC at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$. Indium was used as a calibration standard. The glass transition temperature of the polymer samples was taken by applying the mid-point method.

RESULTS AND DISCUSSION

Investigated blends of PMMA/PS and PVAc/PS are immiscible, the first indication of immiscibility being the

Table 1 Polymers used for morphology studies

Abbreviation	Common name	IUPAC name
PMMA	Poly(methyl methacrylate)	Poly[1-(methoxycarbonyl)-1-methylethylene)]
PVAc	Poly(vinyl acetate)	Poly(1-acetoxyethylene)
PS	Polystyrene	Poly(1-phenylethylene)

Table 2 Physical parameters characterizing PS, PMMA and PVAc

Polymer	Refractive index[a] n_d^{20}	Glass transition temperature (°C)	Solubility parameter at 25°C[a] $\delta\ 10^{-3}\ (\mathrm{J\ m^{-3}})^{1/2}$	Surface tension at 20°C[b] γ (mN m^{-1})	Polarity[b] x^p (mN m^{-1})
PS	1.592	104	17.4–21.1	40.7	0.17
PMMA	1.466	103	18.4–19.5	41.1	0.28
PVAc	1.490	44	18.0–22.6	36.5	0.33

[a] From ref. 21. [b] From ref. 1

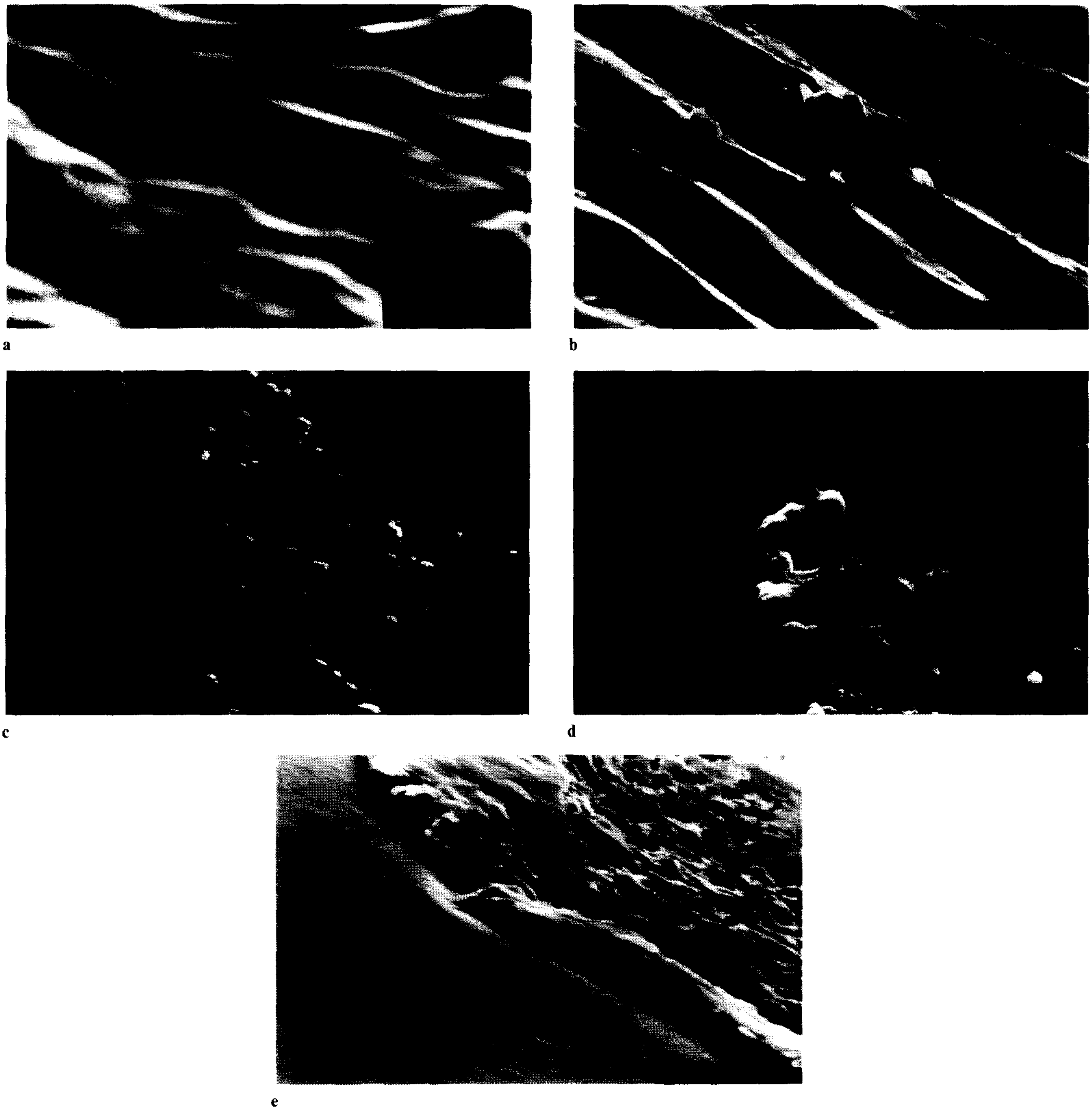


Figure 1 SEM microphotographs of (a) undegraded PMMA and PMMA/PS blends with different ratios of components: (b) 99/1, (c) 95/5, (d) 90/10 and (e) 80/20

turbidity of the films prepared. Although the differences between the refractive indices of PMMA and PS as well as of PVAc and PS are significant (*Table 2*), in the case of a very low amount of one polymer (1–2 wt%) in the matrix of the second component, samples were clear and transparent, indicating the presence of well dispersed small particles. Samples containing >3 wt% of the second (included) polymer were always opaque.

Immiscibility of PVAc and PS was confirmed by d.s.c. measurements. The blends of PVAc/PS showed two glass transition temperatures, differing by as much as 60°C (*Table 2*). Only in the blend containing a very small amount of one component (e.g. 1 wt%) was the sensitivity of d.s.c. too low for its detection. In the case of PMMA/PS blends, the glass transition temperatures of both components are almost the same and it was impossible to conclude their separation by this method.

It is necessary to note, that theoretical predictions of miscibility on the basis of polymer solubility parameters do not always give the correct result. Experimental or theoretically calculated values of the solubility parameter for the same polymer vary widely, depending on the method used (*Table 2*). Furthermore, all contributions to the solubility parameter—polar, non-polar and hydrogen-bonding—must be taken into account.

However, even if phase separation is not observed visually and is not revealed by d.s.c., it can be observed by SEM. The microstructures of PMMA and PMMA/PS blends of different composition are shown in *Figures 1a–e*. Pure PMMA exhibits a somewhat wrinkled surface (*Figure 1a*). Addition of 1 wt% PS to the PMMA matrix results in inhomogeneity of the samples (*Figure 1b*). PS particles, generally smaller than 0.5 μm, are distributed irregularly but larger particles (~ 1–2 μm) also occur randomly. The 95/5 blend of PMMA and PS shows a more dense distribution of PS particles but their size is similar to those found in 99/1 PMMA/PS blend (*Figure 1c*). These small PS inclusions have a tendency to exist close to other similar particles and, consequently, coalescence is observed. When the amount of PS exceeds 10 wt%, separated larger domains with irregular shapes are formed (*Figure 1d*). In addition to these domains, small dispersed PS grains are still present in the PMMA matrix. The boundary between the PMMA and PS phases is demonstrated in *Figure 1e*. It is clearly seen that the degree of roughness of both homopolymers is different. PMMA is more smooth compared with the rough, corrugated surface of PS.

The microphotographs in *Figure 2* show the surface damage of the same samples caused by u.v. irradiation. Cracks occur in pure PMMA after a relatively long time of photodegradation. There are no changes in the PMMA surface for the first 6 h of irradiation and then a network of cracks develops quickly. It seems probable that surface defects or small impurities can be initiation points of film breakage (*Figure 2a*). In PMMA/PS blends with increasing amounts of PS, the cracks are formed earlier than in pure PMMA (e.g. after 4 h of u.v. irradiation). *Figures 2b–d* demonstrate that destruction of the blends can start in places of high inhomogeneity of the sample. It is probable that not only chain scission

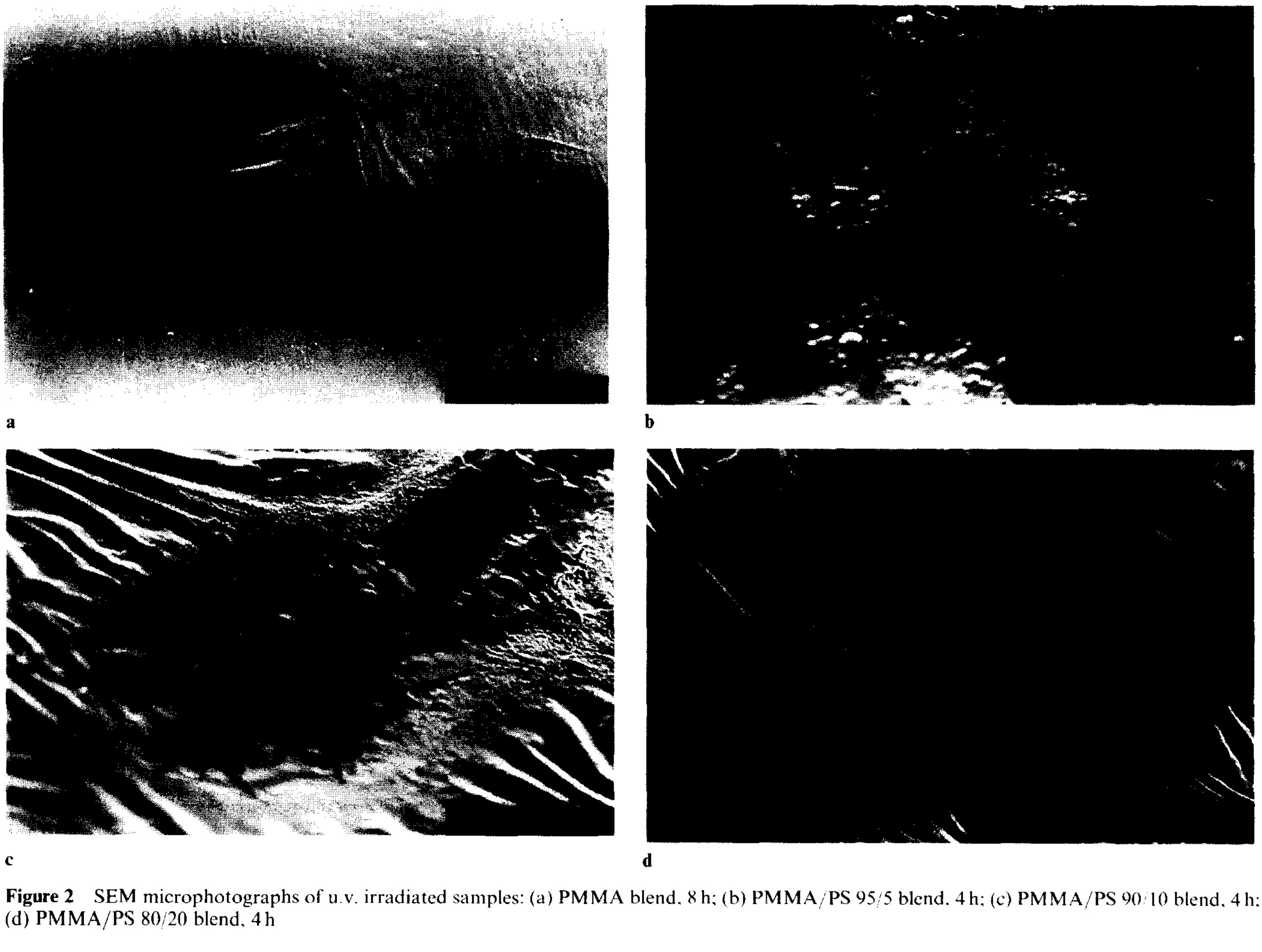


Figure 2 SEM microphotographs of u.v. irradiated samples: (a) PMMA blend, 8 h; (b) PMMA/PS 95/5 blend, 4 h; (c) PMMA/PS 90/10 blend, 4 h; (d) PMMA/PS 80/20 blend, 4 h

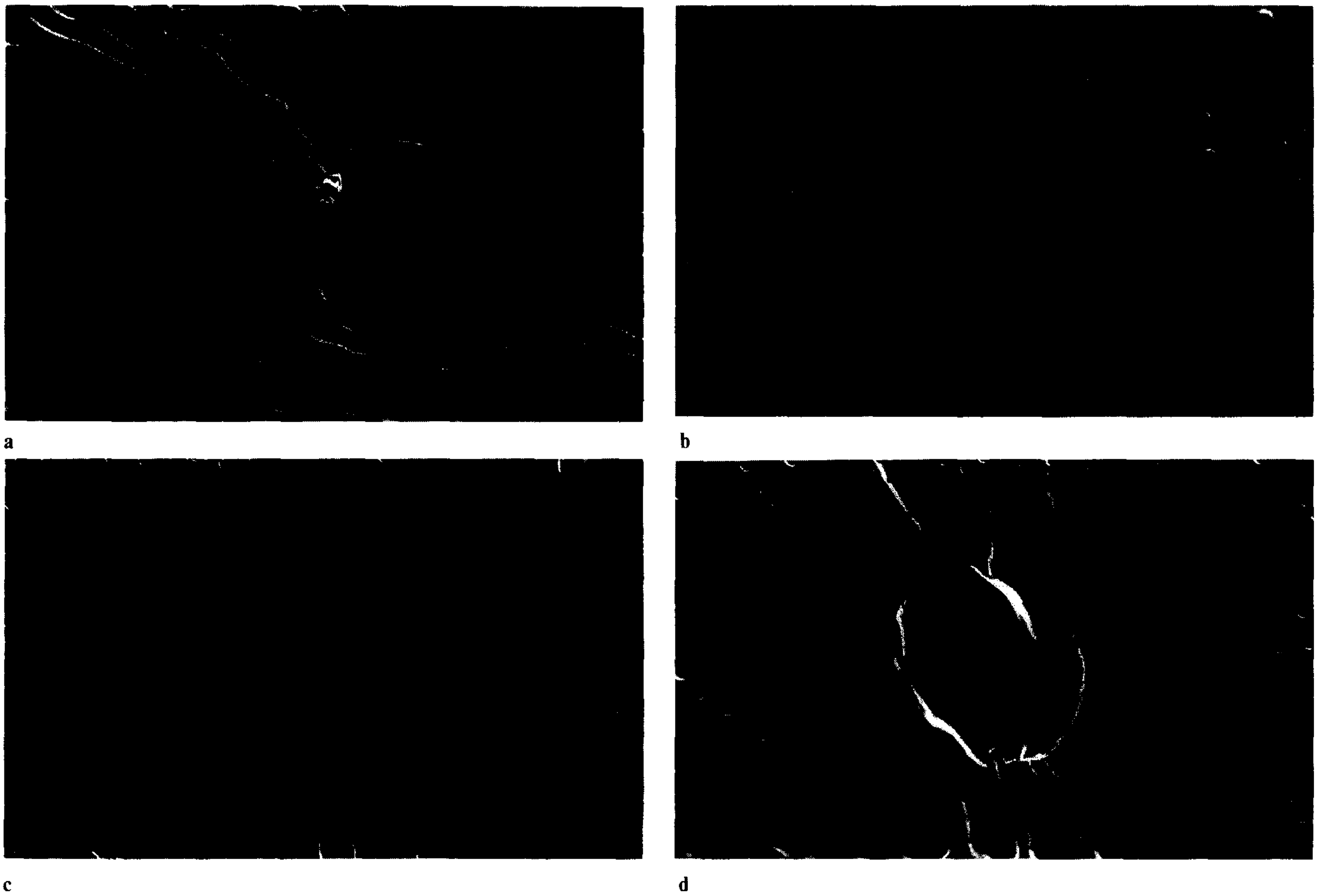


Figure 3 SEM microphotographs of: (a) undegraded PMMA/PS 5/95 blend, (b)–(d) PMMA/PS 10/90 blend, irradiated for 5 h

reactions are responsible for the breaks—the two different phases can undergo shrinkage to different extents and this could be what causes the internal strains and stresses, leading to efficient crack formation.

In the blends with a prevalent amount of PS a different surface morphology was observed (*Figure 3*). A low amount of PMMA (1–5 wt%) in PS is observed as irregular inclusions from 2 to 10 μm in size (*Figure 3a*), but higher amounts of PMMA (10–20 wt%) result in more regular spherical or ellipsoidal domains randomly distributed in the PS phase (*Figure 3b*). It is interesting to note that these domains are covered by a continuous PS phase. Such covering of PMMA particles by a thin layer of PS could suggest that PMMA is protected against u.v. irradiation. However, it was reported[22] that PS/PMMA blends were always more sensitive to photodegradation than the pure polymers. The production of carbonyl and hydroperoxide groups was greatly accelerated by the presence of even a small amount of PS or PMMA, which act as sensitizers. It seems more probable that processes of energy transfer between both polymers in the blend take place during their accelerating degradation. The mutual acceleration effect can also be explained by the formation of small active radicals created upon u.v. irradiation in one of the polymers, which can migrate and initiate the photodegradation and photo-oxidation of second, more resistant polymer. In addition, the turbidity of sample, due to the heterogeneous structure of the blend, can result in the increase of the optical path and thus the amount of light absorbed by the sample[22]. SEM observations indicate that degradation proceeds from the surface to the polymer bulk.

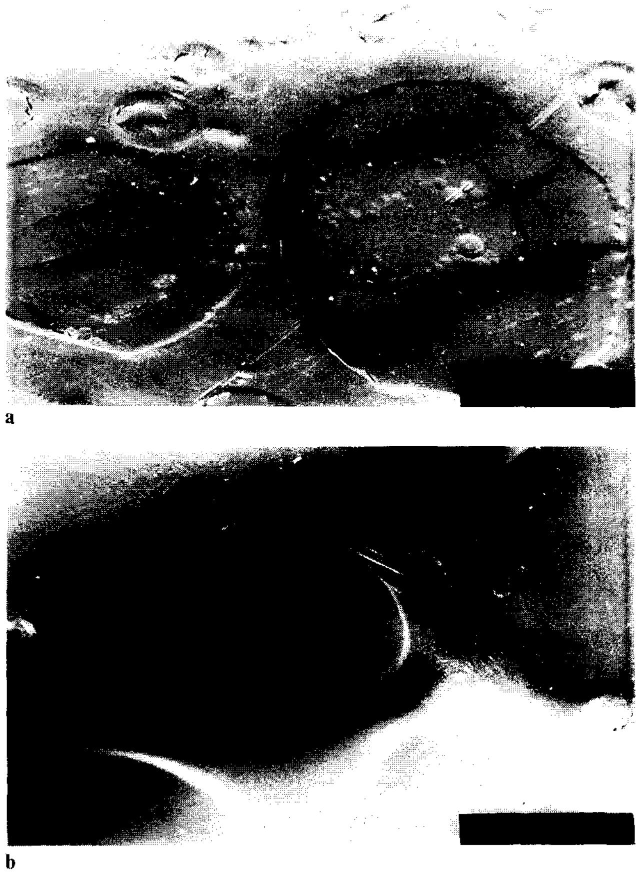


Figure 4 SEM microphotographs of PMMA/PS blends irradiated for 4 h: (a) 40/60 blend and (b) 60/40 blend

Cracks were not observed in PS/PMMA blends with a prevalent amount of PS until after 8 h u.v. irradiation but the formation of blisters and holes took place earlier, mainly in the PS phase. Voids resulting from the evolution of gaseous products were occasionally formed in the PMMA phase (*Figure 3b*). The average size of the holes observed varied from 1 to 20 μm. *Figure 3c* shows these holes at higher magnification. On the basis of *Figure 3d*, one can imagine that the present blister is full of volatile degradation products and it will break in the next stage of photodestruction. Smaller craters are formed earlier and they are uniformly distributed on the film surface.

Figures 4a and *b* demonstrate the morphologies of photodegraded PMMA/PS blends with two different intermediate compositions: 40/60 and 60/40, respectively. Phase inversion is observed. Differences between both samples occur in the size of the oval domains, which are larger in the 40/60 PMMA/PS blend (200–2000 μm) in contrast to the smaller domains in the 60/40 PMMA/PS blend (20–100 μm). It is seen distinctly that surface breaking occurs in the PMMA phase: in the matrix in the case of blend 60/40 PMMA/PS, but in the large dispersed islands blend in 40/60 PMMA/PS. This confirms previous findings that PMMA is less stable for photodegradation processes than PS, detected by viscosimetric measurements. These results are in good agreement with data of the quantum yield of chain scission (for $\lambda = 253.7$ nm used)[23], i.e. $1.7\text{–}3 \times 10^{-2}$ in PMMA and significantly lower in PS film $\sim 5.5 \times 10^{-4}$.

Most of the films exhibit a highly wrinkled surface morphology which is probably caused by weak van der Waals' attraction forces between polymer chains. It is interesting to mention that this planar arrangement of the surface depends on the side of the samples considered. Our blends were obtained by the mixing of two polymer solutions and pouring on to glass plates, and it appears that the sides of the samples obtained by this method are not identical. Characteristic oriented wrinkles, mentioned above, were observed on the air-side of samples; the reverse side (glass side) was smoother with numerous small surface defects. In fact, the image of the latter side is similar to the structure of glass obtained by a polymer replica. It was suggested that the wrinkled surface texture tends to vanish after extended storing time, which indicates that relaxation processes take place[24]. Differences between the two sides of polymer films obtained by casting were also described by Muellerleile *et al.*[25]. On the basis of contact angle measurements of PMMA, Briggs *et al.*[26] have concluded that the migration of low-molecular-weight impurities from the bulk of the film to the film–air interface is responsible for different properties of both polymer sides.

The next set of microphotographs (*Figures 5a–d*) shows the morphology of the second blend investigated: PVAc with PS. The nature of domains in this blend is different. In 40/60 PVAc/PS blend, the average size of PVAc domains in the PS matrix is $\sim 10\text{–}100$ μm. Simultaneously, smaller internal particles, with diameters of $\sim 1\text{–}8$ μm were observed to be incorporated into these relatively large islands. This clearly indicates that PVAc/PS possesses a multiphase structure. The domains formed in 60/40 PVAc/PS blend are larger within 50 to 300 μm. Domains are not smooth, their folded surfaces indicating

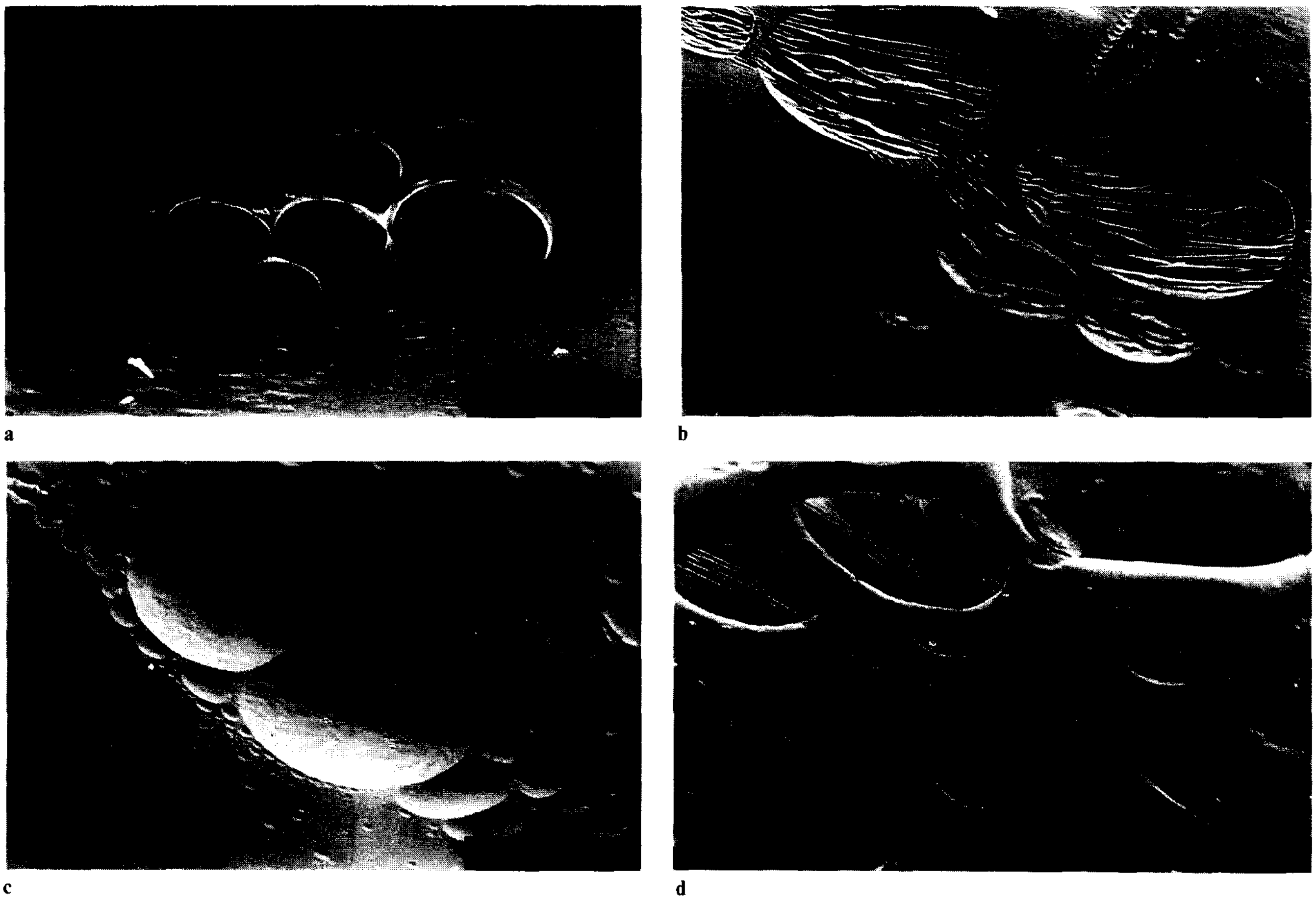


Figure 5 Morphology of PVAc/PS blends: (a) 40/60 undegraded; (b) 60/40 undegraded; (c) 40/60, irradiated for 4 h; (d) 60/40, irradiated for 4 h

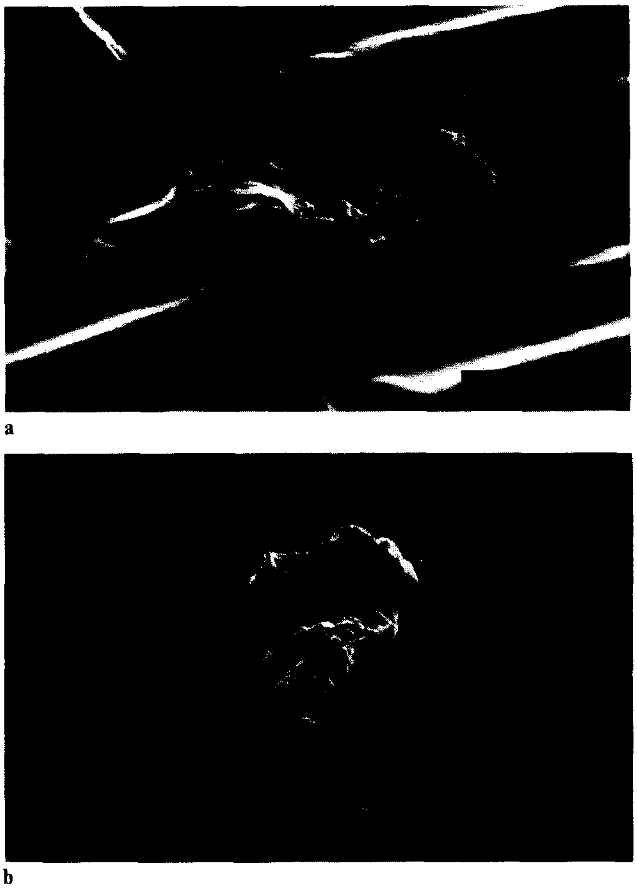


Figure 6 Different types of inclusions in the polymer matrix: (a) PVAc/PS 10/90 blend and (b) PVAc/PS 90/10 blend

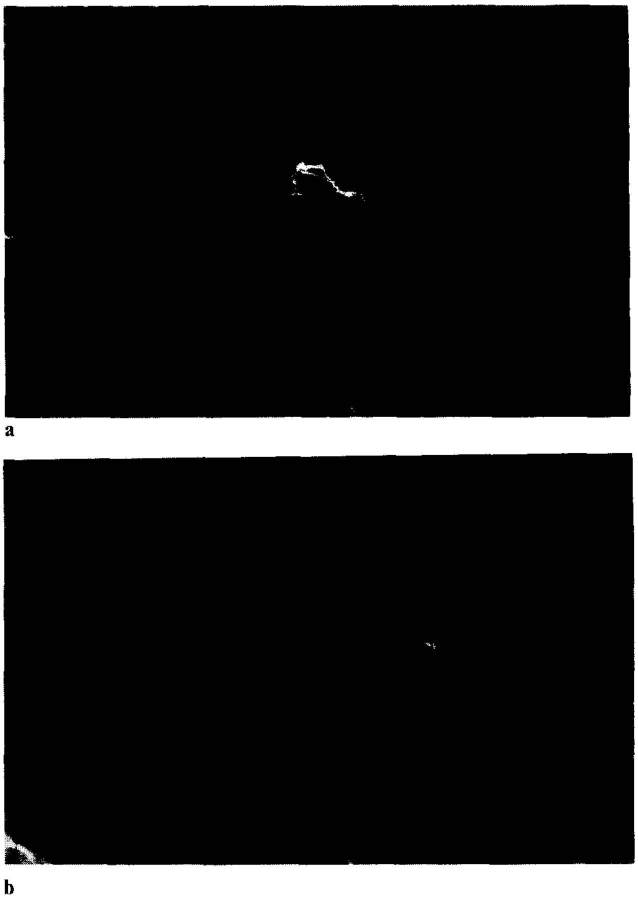


Figure 7 Morphology of PVAc/PS 5/95 blend irradiated for (a) 2 h and (b) 4 h

that internal stresses resulting in shrinkage may occur to different extents in both phases. Strain due to shrinkage develops particularly at the phase boundary. *Figures 5c* and *d* show the microcracks formed in PVAc/PS blends upon u.v. irradiation. It is seen that PVAc is less stable and degradation starts in this phase (*Figure 5c*). In the second case (*Figure 5d*) crack formation is observed mainly on the phase boundary.

Similar results have recently been reported by Getlichermann and co-workers for polyethylene (PE)/PIP blends[27,28]. It was demonstrated that photo-oxidation of the matrix of immiscible blends can be easily and homogeneously initiated by the dispersed, less stable phase, even when it is present in low amounts. Non-homogeneous degradation of PE/PIP blend takes place mainly at or near the polymer interface. It was pointed out that small PIP fragments may migrate into the PE phase and act as a photoinitiator. The mechanism of degradation of each component of the blend is strongly modified by interaction with the other component.

Such regular, oval domains as in *Figure 5* are not always observed in PVAc/PS blends. In the case of PVAc/PS with a low amount of one component (1–10 wt%), irregular inclusions with different size and shape exist. An example of such an irregularity is presented in *Figure 6*. Small, distributed particles of one polymer cause disturbances in the folded surface of the matrix, as is shown in *Figures 7a* and *b*. Moreover, in the photodegraded PVAc sample containing 1–10 wt% of PVAc, distinct, circular regions around small PVAc inclusions are formed after u.v. irradiation. This is probably caused by chemical interactions between both components of the mixture on the phase boundary. Oxidized products formed during u.v. irradiation (mainly carbonyl and hydroxyl groups) change the macromolecular polarity and some interaction between functional groups, including hydrogen bonding, can take place near the border of both polymers. Even very weak interaction forces may lead to a small amount of clustering or other non-random arrangement of polymer segments. Such behaviour of photodegraded immiscible blends has recently been suggested[29]. It should be pointed out that such circles were not observed in non-degraded films.

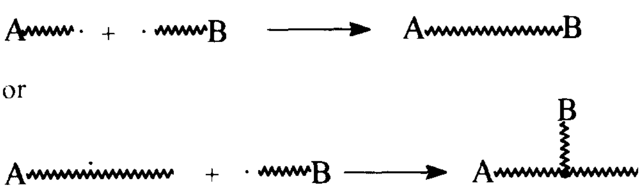
The improvement of blend compatibility resulting from the photo-oxidation of normally immiscible types of PE has also been reported by Trojan *et al.*[30]. The reduction of polymer molecular weight due to chain scission leads to higher mobility of macrochains. Thus, interactions between different groups as well as inter-diffusion of macromolecular segments are easier and more probable.

According to Dee and Sauer[31], a specific interaction occurs between the phenyl ring of PS and the ether side chain of poly(methyl vinyl ether) in PS/PVME blends. Analogous interactions can take place in both blends investigated here.

Another explanation for the increase of polymer miscibility during u.v. irradiation is the possibility of formation of a small amount of copolymer. Because the mechanism of polymer photodegradation is free radical in nature, it is reasonable to assume that accidental recombination of macroradicals coming from both polymers takes place giving a low amount of copolymer:

Table 3 Parameters characterizing interfacial region in PMMA/PS and PVAc/PS blends (ref. 1)

Polymer blend	Interfacial tension at 140°C (mN m^{-1})	Interfacial thickness (Å)	Work of adhesion at 140°C (mJ m^{-2})
PMMA/PS	1.7	160	62.4
PVAc/PS	3.7	31	57



Such copolymers may then act as typical compatibilizers, enhancing the miscibility of both components.

Moreover, the increase of the polymer polarity during irradiation causes changes of their surface tension and of the interfacial tension in the blend. Literature values of the surface tension of PS, PMMA and PVAc (at 20°C, in N m^{-1} are given in *Table 2*. This parameter has a similar value—about 41 mN m^{-1}—for PS and PMMA but it is lower in the case of PVAc—36.5 mN m^{-1} (*Table 2*). Low-molecular-weight additives with low surface tension are known to modify the surface of polymers. Such products are created during photo-oxidative degradation of polymers and their blends[23] and can reduce the surface tension. This may enhance the surface activity.

The interfacial tension value of PMMA/PS is about half that in PVAc/PS (*Table 3*). This in turn influences the interfacial thickness (degree of interdiffusion of polymer segments), which is significantly larger in PMMA/PS than in PVAc/PS blend. The thickness of the diffuse interface increases as the compatibility increases. In addition, interfacial tension decreases with decreasing difference between the polarities of two phases. Thus, the many different functional groups existing in the oxidized polymers and even the small amount of accidentally formed copolymer lead to bridging of the interface and reduction of the interfacial tension between the polymer components. The result of this is that adhesion between the blend components is promoted. It seems very probable that the circular regions observed in the photo-oxidated sample of PS/PVAc in *Figures 7a* and *b* are the result of changes in polarity, adhesion and interfacial tension caused by u.v. irradiation.

CONCLUSIONS

Peculiarities of the morphology of immiscible components in polymer blends—phase distribution, size and shapes of domains—are clearly seen using SEM, even if other methods (for example d.s.c.) do not give successful results. SEM studies of u.v. irradiated blends reveal the mutual interactions between blend components and allow us to detect parts of the polymers with less resistance to u.v. irradiation. Weak points, where degradation starts, are usually in the places of the greatest inhomogeneity or in the interface area. It was shown that the polymer morphology near the phase boundary changes after u.v. irradiation probably because of the increase of interaction forces between the separated phases due to the polarity of oxidized polymers.

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