Physical Characterization of Incompatible Blends of Polymethylmethacrylate and Polycaprolactone

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Synopsis

Blends of polymethylmethacrylate (PMMA) and poly-ε-caprolactone (PCL) were prepared and characterized. The analysis of the glass transition temperature indicates no compatibility of the two polymers, which segregated into two distinct phases. The fracture strength of the blends can be explained on the basis of a constitutive model of spheres of PCL embedded in a PMMA matrix. The trend of water sorption confirms the hypothesis of phase segregation of PCL in the glassy matrix of PMMA.

INTRODUCTION

In recent years, increasing attention to ecological problems has given rise to a growing interest in biodegradable polymers. Earlier studies on the degradation of synthetic polymers were initiated by the desire to avoid degradation, thereby obtaining long-life materials. Several papers have been devoted to analyzing the environmental factors effecting the performance of polymers. Degradation caused by humidity and thermal spiking,[1-3] photooxidation, and microbial attack,[4] have been extensively studied in order to prevent the failure in service of polymeric materials. Since the early seventies, these studies have constituted a useful basis for analyzing the mechanism of degradation of plastics in order to solve the ecological problems caused by their improper disposal.

Plastics, which essentially consist of an organic backbone, can be more or less easily destroyed depending on the nature of the links bonding the monomers in the main chain. As an example, a polyester can be more easily hydrolyzed than a polymethylenic chain, due to the presence in the backbone of ester links, which are noticeably sensitive to acids and bases. Moreover, not only the chemical constitution of a macromolecule is crucial for degradation; its degree of order in the solid state also plays an important role in determining the rate of depolymerization.

It is well known that the rate of diffusion of gases and liquids is higher in an amorphous polymer than in a crystalline one.[5] Therefore, it is expected that of two polymers having the same chemical constitution, the amorphous one shows higher attack by environmental agents (i.e., oxygen and water) than the crystalline material.

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At the moment the most challenging problem in the degradation of polymers is to match the time scale of the process of bio- (or photo-) degradation with the cost and the required performances of the materials. For example, poly-ε-caprolactone (PCL) is a widely used biodegradable polymer, but its relatively high cost reduces its potential applications.[6–9]

Beside the problems related to the life of plastic articles created for short-term use, there is a relatively new field of application of biodegradable polymers. It relates to the use of plastics as biomaterials. The increasing use of biodegradable polymers in medicine, as sutures, surgical implants, and components for controlled release formulation of drugs, requires knowledge concerning the biodegradability of these synthetic polymers. Also in this field the degradation of the article, in the desired time scale, must take into account the cost of the raw materials and the manufacturing process.

One possible way to overcome these strategical and market problems is to blend two roughly incompatible polymers having two different rates of degradation. The morphology of the resulting blend will be therefore characterized by the presence of a matrix (essentially the less degradable polymer) containing a second phase of the more degradable component. Once the latter has left the blend, a number of voids, whose dimensions depend on the form and the extent of the second phase, will be present in the continuous phase, therefore increasing its degradation rate. The proper balancing of the two polymers in the blend will take into account the cost of the raw materials and govern the extent of degradation of the system.

The purpose of this work is to verify this hypothesis for blends prepared from polymethylmethacrylate (PMMA) which is almost not degradable, with poly-ε-caprolactone (PCL), which is biodegradable. The two parent polymers were chosen on the basis of their tremendous differences in the rate of degradation coupled with a strong difference in market cost. PCL is a semicrystalline polymer, relatively expensive, easily degradable. PMMA is a low-cost amorphous material, with such a low rate of degradation that it can be almost considered nondegradable. This paper deals with the preparation, morphological, and mechanical characterization of blends of PMMA and PCL; work is in progress on the study of degradation of the blends.

EXPERIMENTAL

One of the most critical problems in the preparation of a multicomponent system is the optimum mixing of the different phases. In our case, mechanical blending of PCL and PMMA was not satisfactory, due to the different sizes of the particles of the two polymers. Therefore, in order to achieve a uniform dispersion, the raw materials were previously dissolved in a mutual solvent, and the resulting homogeneous solution was used to obtain blends by casting on a glass plate. For this purpose PMMA (high molecular weight polymethylmethacrylate by BDH) and PCL (poly-ε-caprolactone by Aldrich) were dissolved in boiling diethylendioxide (chemical grade dioxane by Rudi Pont).

Thin films of the blends were obtained by means of the phase inversion technique, by dipping in distilled water glass plates previously coated with the solution of PMMA/PCL (90/10; 80/20; 70/30; 60/40 wt %). The films ob-

tained in this way were dried at 40°C for 24 h under vacuum to remove the residual solvent and were then compression molded into 2 mm-thick sheets at 130°C. Samples of pure PMMA and pure PCL were directly prepared by compression molding.

In order to verify the effect of the extent of mixing of the parent polymers on the mechanical properties of the blends, some samples were prepared by dissolving PCL in methylmethacrylate followed by polymerization of the monomer using azoisobisbutyronitrile (AIBN 0.1% b.w.) as initiator. The polymerization was carried out at 60°C for 5 h and then at 90°C for 2 h. On these samples, mechanical and dynamic-mechanical tests were performed.

To evaluate the behavior of the blends during the degradation of PCL, the samples were dipped in 5% KOH ethanol solution to quickly hydrolyze the PCL in the matrix of PMMA. The samples were first dried and weighed, then were placed in the solution of KOH and recovered at different times. After drying, the samples were weighed to evaluate the loss of PCL.

The glass transition temperatures and the melting temperatures of the specimens were measured by means of a Mettler DSC (differential scanning calorimeter) Model TA300 at a heating rate of 10°C/min in a nitrogen atmosphere. Micrographs were performed using a Hitachi scanning electron microscope (SEM) Model S-2300. Gold-coated samples were prepared in an Emscope model SC 500 Sputter.

Dynamic-mechanical spectra were scanned using a dynamic-mechanical spectrometer (Dynastat (Imass)) instrument at a frequency of 10 Hz and a heating rate of 10°C/min. The mechanical properties of the samples were studied by an Instron universal testing machine Model 1112. The samples were cut in a dumbell shape according to ASTM D638-86 Type. An extension rate of 5 mm/min was used.

The water absorption experiments were performed by placing the samples in a bath at 25°C, and the water gain was determined by weighing the specimens at given time intervals, until an asymptotic value of water uptake was reached.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves for the prepared blends and the parent polymers. The large endotherm at 60°C is due to the melting of crystalline PCL. The area of this peak increases with the increasing amount of the PCL in the blend. Besides the melting peak, the glass transition temperature of the amorphous PMMA is also easily detectable at 120°C. The glass transition temperature of the amorphous fraction of PCL is observable only for the pure polymer at −60°C.

One of the most powerful criteria to check the compatibility of two polymers in a blend is the analysis of the glass transition temperature. Several theories[10,11] have been developed in order to relate the variation of the T_g for the parent polymers with their compatibility in the alloy.

Table I reports the T_g of PMMA for the blends having different compositions (the T_g of the amorphous fraction of PCL has not been reported due to its poor resolution). The small T_g depression of the PMMA phase in the blend of the order of only 5% with the higher content of PCL is indicative of very small compatibility with PCL.

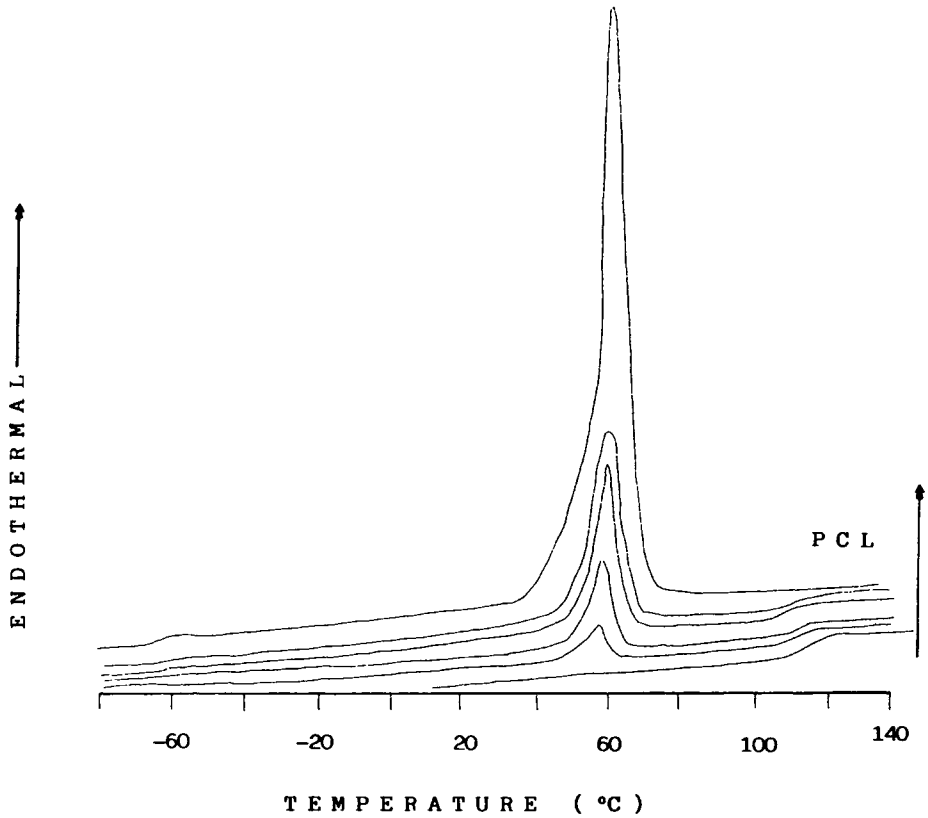

Fig. 1. DSC thermograms of blends and components. Heating rate was 10°C/min (nitrogen atmosphere).

A low compatibility between PCL and PMMA is also confirmed for the samples prepared by polymerization of PMMA directly in the blend. In fact, Figures 2(a)-(e) show the dynamic-mechanical spectra of PMMA, PCL, and the relative blends. The large peak of the loss factor present at 140°C, can be ascribed to the glass transition temperature of PMMA, and its position does not change with the composition of the blend.

The higher values of T_g, as revealed by dynamic-mechanical tests with respect to the calorimetric analysis, are due to the different techniques of measurement and not to the different methods followed for the preparation of the blends. In fact, the DSC analysis performed on these blends indicated a T_g for PMMA

TABLE I
Glass Transition Temperature (T_g) and Crystallinity [X_c, see Eq. (1)] for the Blends; % PCL is the Weight Percentage of PCL in the Blends

% PCL	0	10	20	30	40	100
T_g (°C)	108	106	104	103	102	
X_c	—	0.31	0.40	0.42	0.43	0.49

very close to that obtained on the other set of samples, prepared by direct mixing of the two polymers (Table II).

The effect of PCL in the blend is reflected in the increasing lowering of storage modulus (M') for the blend at the melting temperature of PCL. The decreasing of the modulus indicates a plasticizing effect of the molten PCL on the glassy matrix of PMMA.

Table I also shows the amount of crystalline phase X_c of PCL in the blends. The values of X_c were evaluated on the basis of the following equation:

$$X_c = Q_f/32.4W_{\mathrm{PCL}} \tag{1}$$

where Q_f is the heat of melting the blend as obtained by DSC measurements; 32.4 (cal/g)[12] is the enthalpy of melting of the pure sample of PCL fully crystallized and W_{PCL} is the content of PCL in weight percent in the blend.

The value of X_c slightly increases with the amount of PCL in the blend. This trend is consistent with that previously found for T_g, and confirms a very small compatibility for the two polymers. In other words, PCL and PMMA segregate in two distinct marginally interacting, phases. The results from the mechanical characterization confirm this hypothesis. Figure 3 shows the Young's modulus (E) as a function of the volumetric fraction of PCL in the blend. E is slighthy decreasing with the increasing amount of PCL.

A "self-consistent" approximation can be used in order to explain this trend. According to this model, the composite structure of the blend consists of spherical dispersed phase particles embedded in a continuous body having the elastic properties of the composite. In Kerner's well known derivation,[13] the average mechanical properties in the model structure (subjected to tensile deformation) are equated to those in the corresponding homogeneous body. An analysis, relative to the bulk modulus K yields

$$\frac{K_c}{K_1} = \frac{\Phi_1 K_1 + (\beta_1 + \Phi_2)K_1}{(1 + \beta_1\Phi_2)K_1 + \beta_1\Phi_1 K_2} \tag{2}$$

where K_c is bulk modulus of the composite, K_1 is bulk modulus of the matrix, Φ_1 is volumetric fraction of the matrix, Φ_2 is volumetric fraction of the filler (PCL), β_1 is $(1 - \nu_1)/2(1 - 2\nu_1)$, and where ν_1 is the Poisson ratio of the matrix. In our case $\nu_1 = 0.4$.[14] K_1 and K_2 can be evaluated on the basis of the Young's modulus of PMMA and PCL, and on the Poisson ratios of pure PMMA and PCL. A value of 0, 46 was considered for the Poisson ratio (ν) of PCL.

If the hypothesis is held that the Poisson ratio of the blend dose not substantially change with the composition, eq. (2) relates the Young's modulus of the blend with the volumetric fraction of PCL. The curve of the above equation fits the experimental data of Figure 3 very well. This indicates that the dispersed-sphere morphology approximation is correct.

The fracture stress of the blends decreases with the increasing content of PCL (Fig. 4). This general trend agrees with the analysis presented by Nicolais and Narkis[15] relative to the strength of particulate composites. They have shown that the mechanical stress to failure decrease with increasing filler content in rigid matrix particulate composites. In the case of poor adhesion between filler

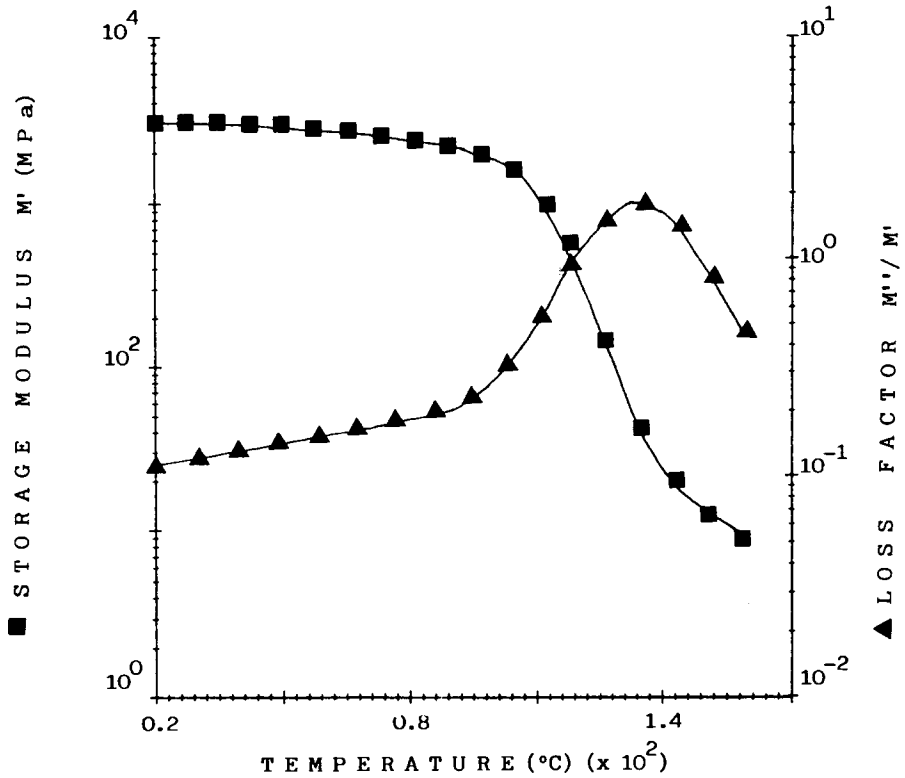

Fig. 2(a). Storage modulus and loss factor of PMMA.

and polymer, the particles cannot carry the load. The load is carried only by the continuous phase. The authors suggest, on geometrical consideration, the following equation for the case of nonadhesion

$$\sigma_{\text{rel}} = 1 - 1.21\Phi^{2/3} \tag{3}$$

where Φ is the volumetric fraction of filler. If σ_m is the strength of the matrix material and σ_c the strength of the "composite," σ_{rel} can be expressed as

$$\sigma_{\text{rel}} = \sigma_c/\sigma_m \tag{4}$$

As shown in Figure 4 the experimental data can be well correlated by the theoretical curve.

Water sorption data expressed as percent of water gain of the weight of the dry polymer *vs.* $t^{1/2}/l$, where l is the thickness, are shown in Figure 5. The trend of water uptake is Fickian, with an initial linear increase followed by an asymptotic value. From the slope of the initial part the diffusion coefficient of water into the blend can be evaluated.

Figure 6 shows the asymptotic water content for each sample. The presence of the maximum at 30% of PCL is probably connected to the interface interactions between the two phases. In fact the blends can contain microcracks

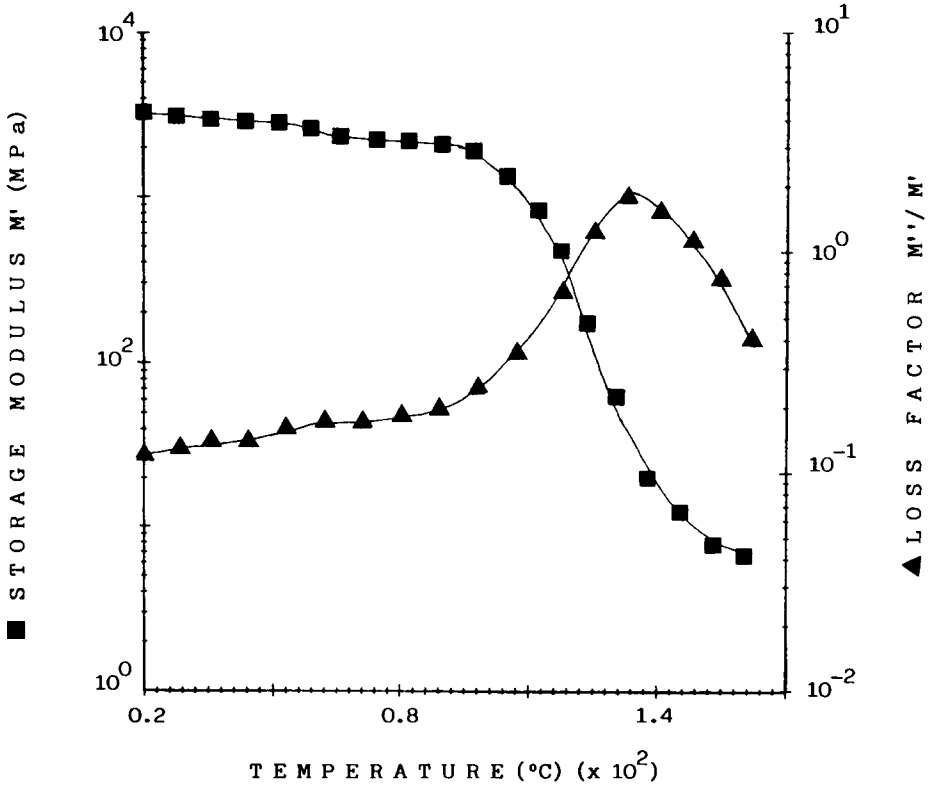

Fig. 2(b). Storage modulus and loss factor of 90/10 PMMA/PCL.

several microns thick near the interface separation area. This might be due to the complex phenomenon of solidification of the samples after the compression molding processing. In fact, during the cooling from 130°C, PCl crystallizes at about 60°C in a glassy matrix of PMMA, and this can cause internal stresses, probably responsible for microcrack formation. These microcracks can hold clusters of water molecules, thus increasing the equilibrium value of water uptake. The surface interface region has a maximum value for a certain content of PCL, and this explains the maximum in the asymptotic water content. The reduction of water sorption after 30% wt % of PCL is due to a lower water content absorbed by the crystalline PCL.

In other words, the hypothesis for the water sorption phenomenon in these blends is based on the assumption of the double mechanism of water diffusion in glassy polymer. It is well known[1,16] that, in glassy polymers, water can be dissolved as clusters in the frozen-in holes of the glassy matrix. While the ordinary Henry law controls the dissolution of water molecules, the content of clusters in the extra free volume need several parameters (pressure, T_g, hole content, temperature) in order to be explained. According to this dual mode mechanism, it can be assumed that in the microcracks, water can be allocated as a cluster, while it is present as ordinary dissolved water in the rubbery fraction of PCL.

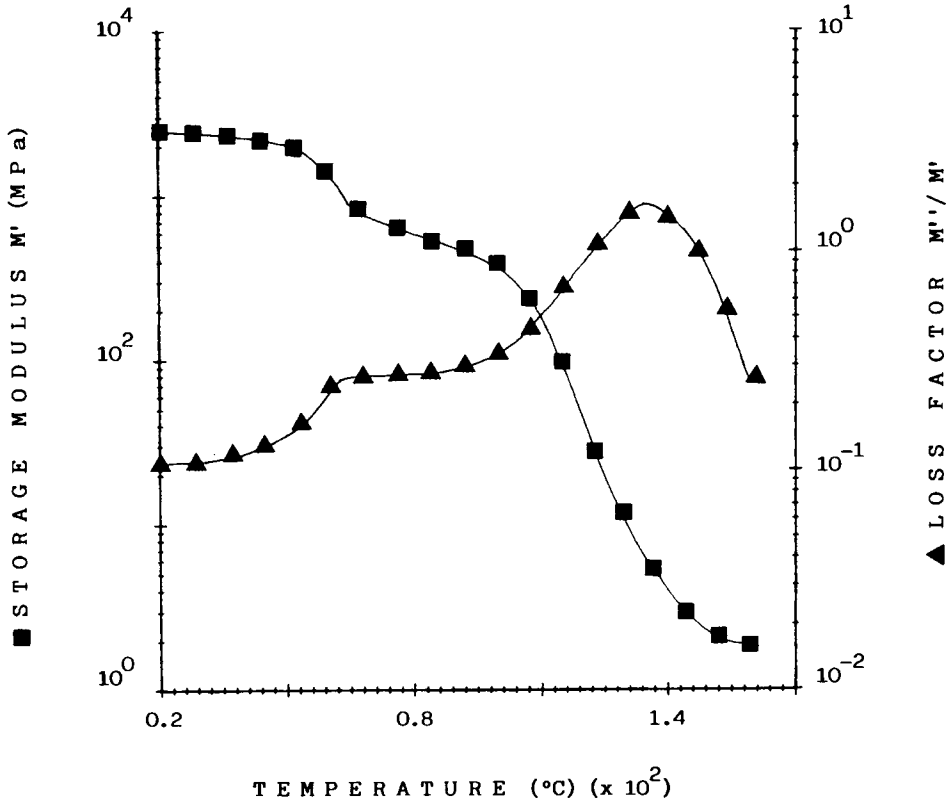

Fig. 2(c). Storage modulus and loss factor of 80/20 PMMA/PCL.

The initially linear relationship in Figure 5 indicates that the sorption phenomenon is diffusion-controlled. According to Crank,[17] the solution of the differential equation for sorption by diffusion in the initial stage allows values of the diffusion coefficient D_s to be obtained by

$$D_s = \pi/16(t^{1/2}/l)^2 \tag{5}$$

where $(t^{1/2}/l)$ is the value that corresponds to the intersecting point of the initial linear interpolation curve with the horizontal asymptote when $t \rightarrow \infty$. The diffusion coefficients are reported in Table III.

The results indicate that the presence of PCL reduces, by about 30%, the diffusion coefficient of PMMA. This is a further indication that PCL can introduce microcracks in the blend. In fact the process of diffusion becomes slower if microvoids, where water can aggregate, are present. However, the data are too scattered to evaluate variations of the diffusion coefficient with the different PCL content.

Table IV shows the loss of PCL, the glass transition temperature, and the Young's modulus E of the hydrolyzed samples. When the PCL content in the blend decreases, the T_g of the samples and the T_g of pure PMMA became very close. But, while the T_g of the blends increases continuously with the loss of PCL, E is almost the same while 75% of PCL is still into the sample.

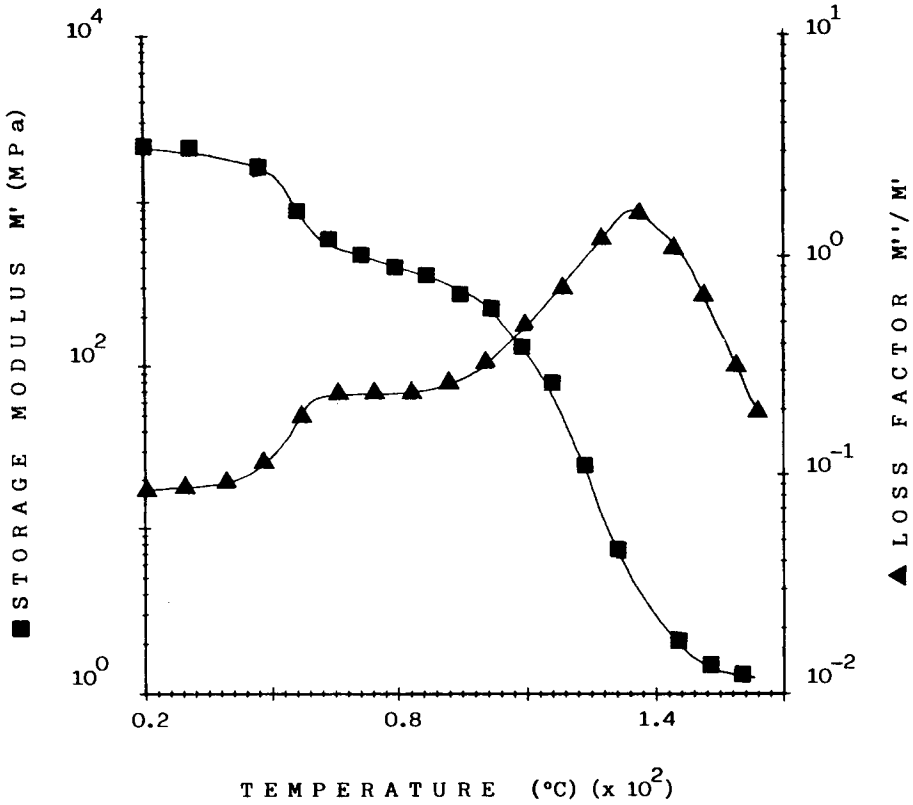

Fig. 2(d). Storage modulus and loss factor of 70/30 PMMA/PCL.

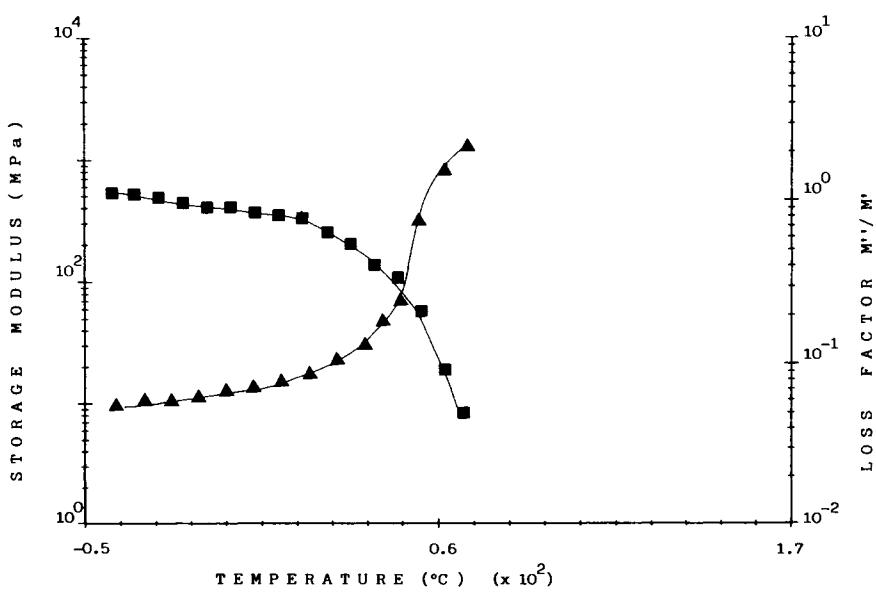

Fig. 2(e). Storage modulus and loss factor of PCL.

TABLE II
Glass Transition Temperature (T_g) and Crystallinity [X_c, see Eq. (1)] for the Blends Prepared by Polymerization of PMMA Directly in the Blend. % PCL is the Weight Percentage of PCL in the Blends

% PCL	0	10	20	30	100
T_g (°C)	102	100	101	99	
X_c	0	0.29	0.41	0.50	0.50

Micrographs of the specimens during the hydrolysis experiments are reported in Figure 7 for three different times of aging. They show a sharp boundary between the hydrolyzed and unhydrolyzed region: On the left the material shows changes in morphology due to the damage of the structure. Hydrolysis of PCL probably produces lower molecular weight substances which counterdiffuse, leaving the structure and producing more microvoids inside. As expected, with increasing hydrolysis time, the thickness of the hydrolyzed region increases, therefore raising the number of voids inside PMMA.

CONCLUSIONS

Blends of PMMA and PCL were prepared and characterized. The presence of PCL does not substantially affect the glass transition of PMMA. This in-

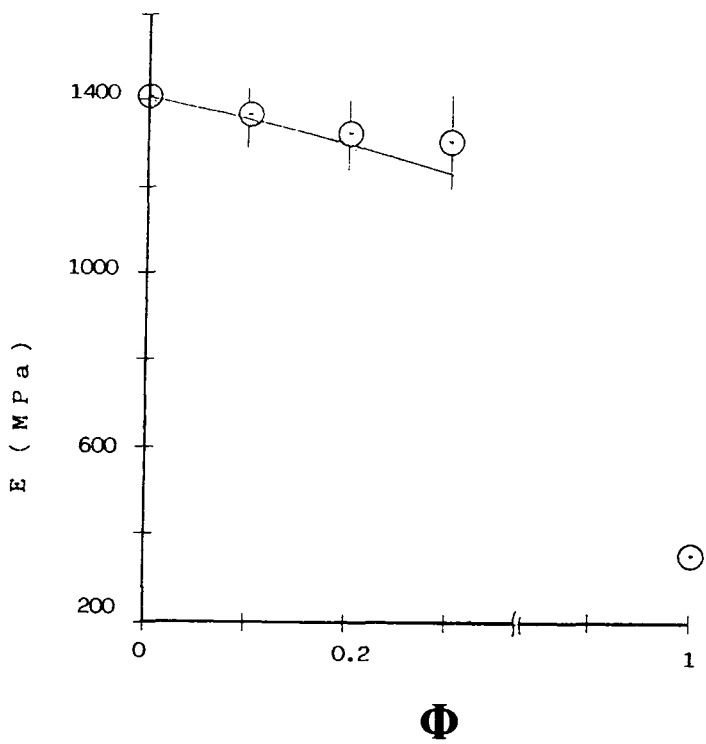

Fig. 3. Young's modulus (E) of the blends. The curve is calculated by equation (2).

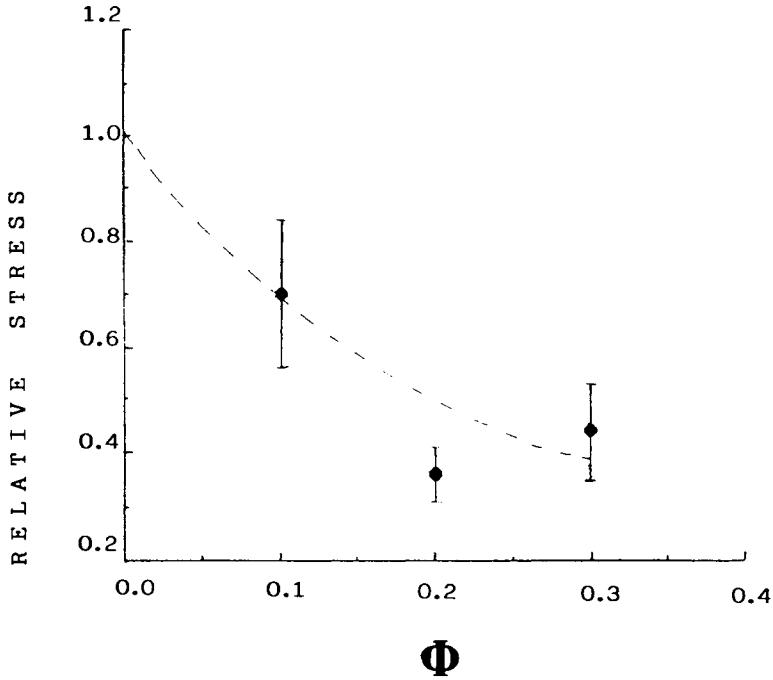

Fig. 4. Relative strength of the blends. The dashed line represent a plot of the Nicolais-Narkin equation, which predicts the strength of particular reinforced composites with brittle matrix.

dicates that the two polymers are incompatible in the blend. The Young's modulus of the blends decreases with the increasing PCL content. The trend is well represented if a spherical morphology of PCL, poorly interacting with PMMA,

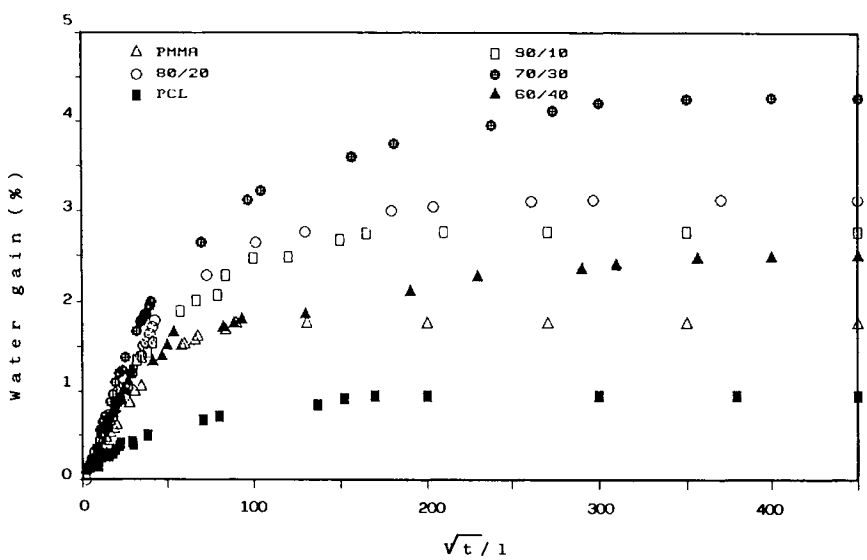

Fig. 5. Water sorption data for blends and components.

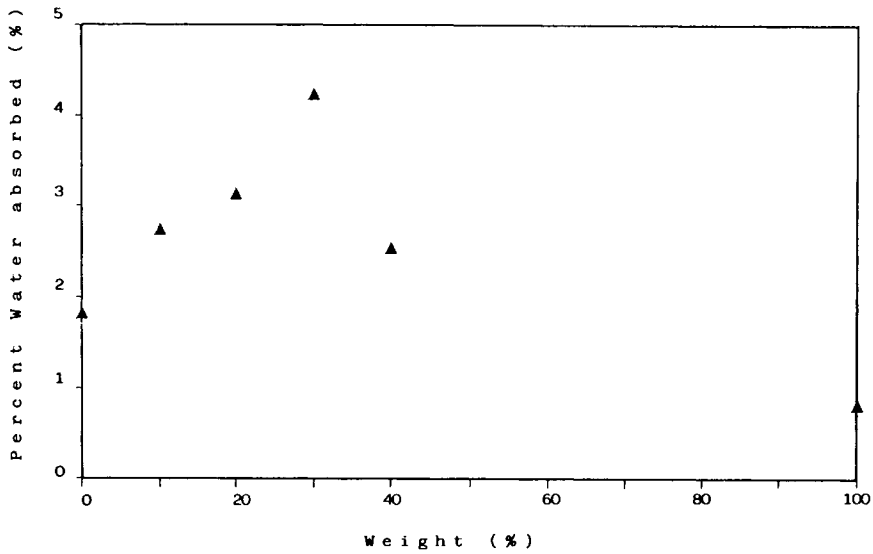

Fig. 6. Equilibrium percent water absorbed by the blends and the components.

is assumed. The transport properties of the blends are strongly affected by their biphasic nature. However, if the content of PCL is maintained lower than 20%, the water transport behavior of the blend is close to that of pure PMMA.

All these considerations lead to the conclusion that if the relative amount of PCL in the blend is low (of the order of 20–30%), the physical and long term properties of the blend are practically the same as pure PMMA. This means that, at least for this model system, the properties of the blends are those of the less degradable and cheaper component. This is very important, because it means that these blends can be potentially utilized for all those applications expected for the less degradable phase. In this way, the goal of getting a biodegradable material at a relatively low cost can be easily reached.

TABLE III
Diffusion Coefficient (D_s) Calculated by Equation (5) for Different Weight Percentage of PMMA (% PMMA)

% PMMA	100	90	80	70	60
D_s (cm^2/s) 10^8	2.2	1.5	1.5	1.5	1.5

TABLE IV
Glass Transition Temperature (T_g), Percentage Loss of PCL and Young's Modulus (E) of the Hydrolyzed Sample (80/20 PMMA/PCL) vs. the Hydrolysis Time

Time (h)	0	1	2	3	9	24
T_g (°C)	104	—	—	106	—	107
Loss (%)	0	8	15	23	40	85
E (GPa)	1.40	1.38	1.37	1.4	1.17	1.06

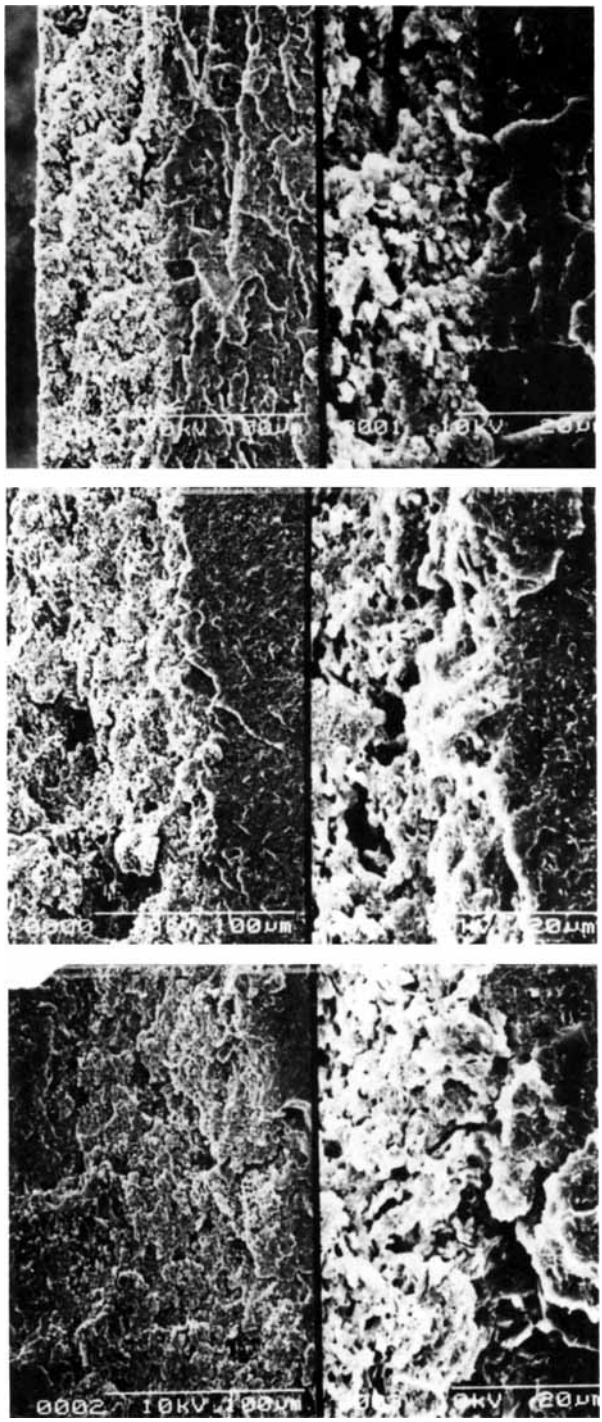

Fig. 7. SEM photomicrographs of the blend 80/20 PMMA/PCL. From the top: 3 h, 9 h, and 24 h in KOH. For each micrograph 400 and 1500 magnifications.

Work is in progress to carry out enzymatic and microbial degradation of these blends and to study their properties.

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