Flow-Induced Mixing of Blends of Poly(ethylene–vinyl acetate) and Solution Chlorinated Polyethylene

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ABSTRACT: A rheooptical device was constructed to monitor phase changes in polymer blends undergoing constant stress, simple shear flow. Light scattering experiments during shear flow of blends of poly(ethylene-*co*-vinyl acetate) (EVA) and solution chlorinated polyethylene (SCPE) indicated that stress improves the miscibility of the two polymers. This is interpreted in terms of a stress-dependent phase diagram in which the phase boundary of a polymer mixture that exhibits a lower critical solution temperature is shifted upward in temperature due to the application of stress. The phenomenon required a critical stress, but in the case of the EVA/SCPE, this was relatively low and improvements in miscibility were observed at temperatures of nearly 30 °C above the cloud point.

Introduction

The literature is rich with reports of polymer blends and their mechanical properties, and numerous attempts have been made to relate the ultimate properties to the blend microstructure. Recent research has focused on theoretical predictions and experimental studies of polymer–polymer miscibility under equilibrium conditions[1] and the kinetics of phase separation in partially miscible blends[2-5].

Surprisingly few studies have considered the phase behavior of a polymer blend removed from static equilibrium. This is likely to be important during processing where transient stress fields and temperature gradients are encountered. Because of the relatively high viscosities of polymers, the times required for equilibration of the chain conformations or, in the case of blends, the morphology following a change in the temperature, pressure, or stress may be long. When vitrification or crystallization occurs before an equilibrium phase structure is achieved, as may happen when a blend is quenched following melt extrusion or injection molding, the final blend morphology may be more representative of the melt than that expected from thermodynamic arguments. As a consequence, the miscibility behavior and morphology of a polymer blend in a stress field (i.e., under processing conditions) and the kinetics of how the phase behavior changes during a transient in the stress field are expected to influence the ultimate structure and properties of the blend.

Over the past 30 years there have been numerous studies of deformation-induced changes in the solubility of polymer solutions in low molar mass liquids. This subject has been reviewed by Rangel-Nafaile et al.[6] The majority of this literature reports phase demixing when polymer solutions were deformed, though there have also been reports of phase mixing. Kramer and Wolf[7] observed both shear-induced mixing and shear-induced demixing for a single polymer/solvent system depending on the polymer molar mass and concentration.

Relatively few authors have considered the effect of deformation on liquid–liquid phase behavior in polymer blends, and the majority of the reports[8-14] have been within the past several years. The primary observation has been flow-induced miscibility, though Katsaros et al.[14] also reported flow-induced demixing.

The first report of the phenomenon of flow-induced miscibility of a polymer blend was made by Mazich and Carr[8] who studied the system of polystyrene (PS) and poly(vinyl methyl ether) (PVME)[15] with a cone and plate rheometer. Relying on the observation of a discontinuity in the viscosity versus temperature curve at constant shear stress, they concluded that in simple shear flow (SSF), phase separation occurred from 2 to 7 °C above the quiescent cloud point. They explained their results in terms of the application of strain energy, and the effect was more pronounced when the magnitude of the applied strain energy was comparable to the energy decrease that would result if the system were allowed to equilibrate under quiescent conditions.

Katsaros et al.[9] used a planar extensional flow to study flow-induced miscibility of PS/PVME blends. They developed a lubricated stagnation flow by the impingement of two rectangular jets in a specially built die with hyperbolic walls. The cloud point was detected by a change in turbidity of the blend, and their paper discussed changes in clarity at a constant temperature above the cloud point of the quiescent blend after the onset of the flow. In general, these authors found that flow-induced miscibility occurred in times of the order of seconds or minutes. They observed miscibility not only in the stagnation region, which was in planar extension, but also near the die walls where the material underwent shear flow. Miscibility occurred first in the regions of highest extension. They found that the time required to induce miscibility decreased with increasing flow rate, though quantitative conclusions were not possible owing to the fact that the strain and residence time in the die were not homogeneous.

Lyngaee-Jorgensen and Sondergaard[10] developed a semitheoretical model for the transition from two phases to one for a polymer blend undergoing SSF. Their model predicted the critical shear stress required for the transition, and the authors proposed using shear to prepare miscible blends at temperatures at which the quiescent melt would be within the spinodal region of the phase diagram for a system exhibiting a lower critical solution temperature (LCST). If the shear were then stopped, spinodal decomposition should occur. They suggested

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Table I
Material Parameters

polymer	% VA	wt % Cl	T_g, °C	$10^{-4}\bar{M}_n$	$10^{-5}\bar{M}_w$	refractive index
SCPE		54.8	33	2.9	1.27	1.51
EVA	45		−25	4.75	1.14	1.42

that this "shear-jump" scheme would produce interconnected morphologies comparable to those observed by temperature jumps into the spinodal region.

Using a cone and plate viscometer equipped with glass fixtures so that light scattering could be measured during SSF, Lyngaee-Jorgensen and Sondergaard[11] studied the shear-induced miscibility of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN). Their reported light scattering results, however, were measurements of melt turbidity. They observed a rheological "transition" at a higher stress, but in qualitative agreement with the loss of turbidity as the shear stress was increased isothermally. The rheological transition was taken as the stress at which viscosity–shear rate data of the PMMA/SAN blends deviated from a master curve of reduced variables constructed with data for the pure components. Calculations of the critical shear stress using the model developed in the earlier paper[10] were in reasonable agreement with the experimental values.

Pistoor and Binder[12] generalized the phenomenological mean-field theory describing concentration fluctuations and spinodal decomposition of binary polymer liquids to include SSF. They predicted the collective scattering function for temperature jumps into the spinodal region for blends undergoing shear. For low shear rates the initial structure factor was nearly isotropic and growth of the scattering pattern during spinodal decomposition was also isotropic. Only at long times did the scattering function become anisotropic. For high shear rates, however, the scattering function in the one-phase region was anisotropic (i.e., the coils were no longer spherical) and scattering during spinodal decomposition was highly anisotropic. No experimental data were presented.

In this paper, we describe the development of a rheooptical apparatus for studying light scattering during SSF of polymer blends and some initial results of the effect of shear on the phase behavior of a 50/50 blend of poly(ethylene-*co*-vinyl acetate) (EVA) and solution chlorinated polyethylene (SCPE).

Experimental Section

Materials. Poly(ethylene-*co*-vinyl acetate) (EVA) was obtained from ICI (Evatone 45) and was fractionated with benzene and 2-propanol. 2-Propanol was added to a 2 wt % solution of EVA in benzene until the solution became turbid. The solution was heated to 50 °C in order to redissolve the precipitated polymer and then slowly cooled to room temperature. The supernatant liquid was removed and the precipitated polymer fraction was redissolved in chlorobenzene and precipitated in methanol. This precipitate was dried in air at room temperature for 1 day and finally under vacuum at 50 °C for a week.

Solution chlorinated polyethylene (SCPE) was prepared by photochlorination of a commercial linear polyethylene obtained from BDH. Polyethylene was dissolved in chlorobenzene at 135 °C, and chlorine was bubbled through a vigorously stirred solution under a nitrogen atmosphere. The reaction was initiated with a 60-W tungsten lamp, and the chlorine content was controlled by adjusting the reaction time. The resulting polymer was fractionated by using the same procedure described above for EVA.

The characteristics of the fractions used in this study are given in Table I. The molar mass averages were obtained by gel permeation chromatography.

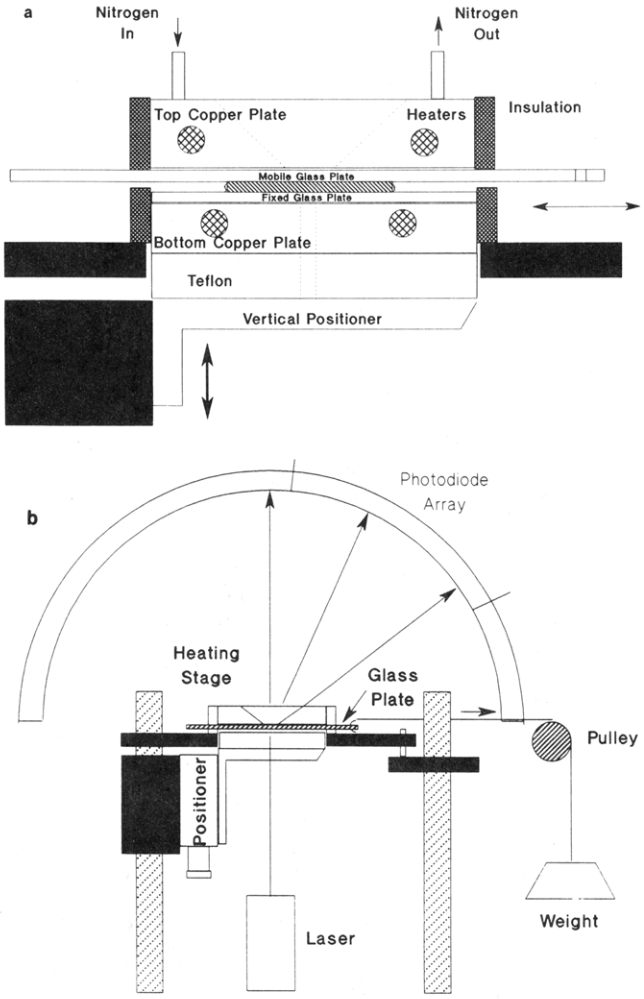

Figure 1. Schematic of rheooptical shear apparatus: (a) shear fixture; (b) light scattering setup.

Clear films of 50/50 blends were cast from tetrahydrofuran onto a glass microscope slide that was used as the bottom plate of the shear fixture. The thickness was controlled by the concentration of the casting solution and ranged from 60 to 70 μm. The raised area at the edge of the cast film was removed prior to the shear experiment.

Shear Apparatus. A schematic of the custom built rheooptical apparatus is shown in Figure 1. Constant stress, uniaxial shear was applied to the thin polymer film sandwiched between parallel glass plates by means of a weight and pulley attached to the upper plate. The fixed bottom plate was a standard 76 × 25 mm microscope slide, and the mobile top plate was 140 × 25 mm. The usable travel of the top plate was limited to about 5 mm, which limited the total allowable strains to less than about 100%. Heat was supplied by five 25-W soldering iron heaters mounted in two copper blocks above and below the glass plates. Thermal conductivity between the blocks and glass plates was enhanced by aluminum foils, and the gap between the heating blocks was purged with nitrogen to maintain an inert atmosphere and to reduce temperature gradients in the system. Temperature was controlled with a FGH Controls Ltd 900 Series PID controller with a temperature stability of 0.2 °C between 30 and 250 °C. The temperature could also be cycled or ramped with an effective heating rate of 1 °C/min. For axial shear flow between parallel plates the shear stress is constant across the thickness of the sample[16] and can be calculated from the following equation

$$\sigma = Mg/A$$

where M is the mass (grams) of the weight attached to the pulley, g is the gravitational acceleration, and A is the contact area of the film (m^2). The mass load was corrected by subtracting

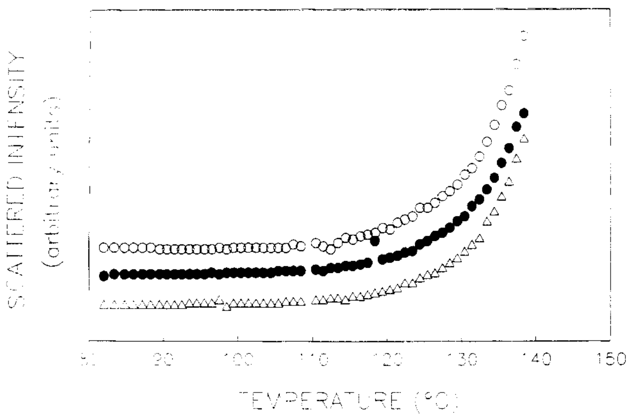

Figure 2. Light scattering intensity as a function of temperature at three scattering angles, (○) 24°, (●) 32°, and (△) 36°, for an unsheared 50/50 SCPE/EVA blend. The heating rate was 1 °C/min.

out the mass needed to overcome the friction in the system. Experimental stress values ranged from 0.8 to 23 kPa.

The shear apparatus was mounted on an anodized aluminum platform and positioning stage attached to a stainless steel support frame. The platform was painted matte black to minimize light reflections. An Aerotech, Inc., ATS 300m micrometer positionable stage was used to control the gap between the shear plates.

Light Scattering Apparatus. The light source was an Aerotech Model 1105P He/Ne laser (λ = 633 nm) mounted normal to the shear assembly. The scattered light was detected by a custom-built photodiode array mounted on a semicircular frame at a radius of 16 cm from the sample. The array consisted of two movable banks of 16 diodes each, which provided a total angular range of 62°. The diode detectors were connected to a multiplexer and a 12-bit A/D converter interfaced to a BBC Model B computer. The entire apparatus, except for the computer and interface, was contained inside a light-proof box.

The experimentally measured light intensities were corrected for parasitic scattering by subtracting the scattered intensities obtained from the glass plates in the absence of a sample. The photodiodes were normalized by measuring the scattering from milk, which scatters light uniformly at all angles. The refractive indices of the blends and the glass were similar, and correction was made for refraction of the light through the fixture.

Thermal Analysis. Glass transition temperatures of the blends and the starting polymers were measured with a Perkin-Elmer differential scanning calorimeter, DSC-2. The samples were encapsulated in aluminum pans, and the measurements were made under a nitrogen atmosphere at a rate of 20 °C/min.

Results and Discussion

The cloud point of a 50/50 blend was determined from turbidity measurements using the same apparatus described above, but without applying shear. Films of the blends were heated at a rate of 1 °C/min, and the cloud point was defined as the temperature corresponding to the change in slope of the scattered light intensity. Typical experimental data are shown in Figure 2. EVA/SCPE exhibited LCST behavior and the cloud point of the 50/50 mixture was 117 °C. The experimental value was independent of the angle of the detector between 3 and 45°. The glass transition temperature (T_g) of the miscible blend was -5 °C, and the T_g's of the individual component polymers are given in Table I. All T_g's were sufficiently below the cloud point such that the possible formation of a rigid included phase during the phase demixing part of the experiment was not a problem.

Figure 3 shows the time-dependent light scattering intensity during shear deformation at various temperatures, measured at a constant scattering angle of 10° and a constant shear stress of 23 kPa. At 90 °C (curve A) the blend was in the one-phase region, and as expected no change in scattering intensity occurred when the blend was sheared. At 120 °C (curve B) the blend was about 3 °C above the cloud point. The gradual increase in the scattered light intensity with time before the onset of shear was due to phase demixing. During that time the sample appearance changed from optically clear to opaque, which was an indication of phase separation. Upon shearing, the scattering intensity decreased, though it never reached the initial value for the one-phase melt in the time frame of the experiment. Curve C is for a shear experiment run at 140 °C, 23 °C above the cloud point. Again, the scattered light intensity increased as the blend phase separated before the start of the shearing experiment. Shear was applied for 10 s, during which time the scattered light intensity decreased indicating some phase mixing. When the shearing was stopped, the scattering intensity increased again as a result of phase demixing, thus demonstrating the reversibility of the flow-induced mixing. At 145 °C, 28 °C above the quiescent cloud point, the scattering intensity increased monotonically with time, even during the application of shear. Thus, no phase mixing occurred during shear at 145 °C, which indicates that the blend was in the two-phase region of the deformation-dependent phase diagram at that temperature. That is, for a shear stress of 23 kPa, the phase boundary for the 50/50 blend was between 140 and 145 °C.

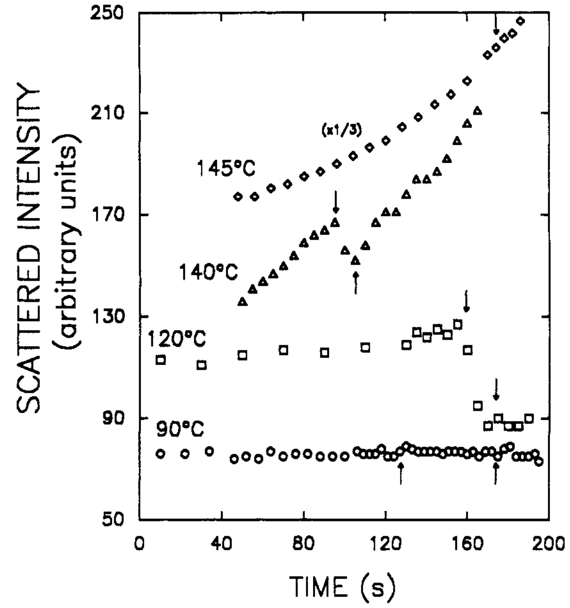

Figure 3. Scattered light intensity during shear flow for a 50/50 SCPE/EVA blend at four different temperatures measured at a constant scattering angle of 10° and a constant shear stress of 23 kPa. Shear began at the time indicated by the first arrow on each curve. A second arrow on the same curve indicates cessation of shear.

Scattering intensity data as a function of time for the 50/50 blend at 130 °C and a shear stress of 17 kPa are shown in Figure 4 for several scattering angles. The qualitative behavior of the time- (strain-) dependent scattering was the same over the entire scattering curve. The scattered light intensity decreased with increasing shearing time, i.e., increasing strain (strain = shear rate × time). The magnitude of the decrease in scattering intensity, however, decreased with increasing angle. This is what one would expect if the result of shearing was to first break up the larger domains that scatter at lower angles.

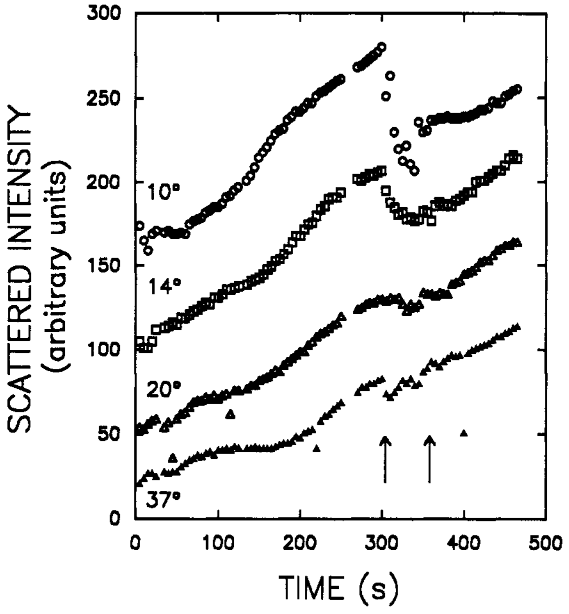

Figure 4. Scattered light intensity as a function of time measured at four scattering angles. The arrows have the same meaning as in Figure 3.

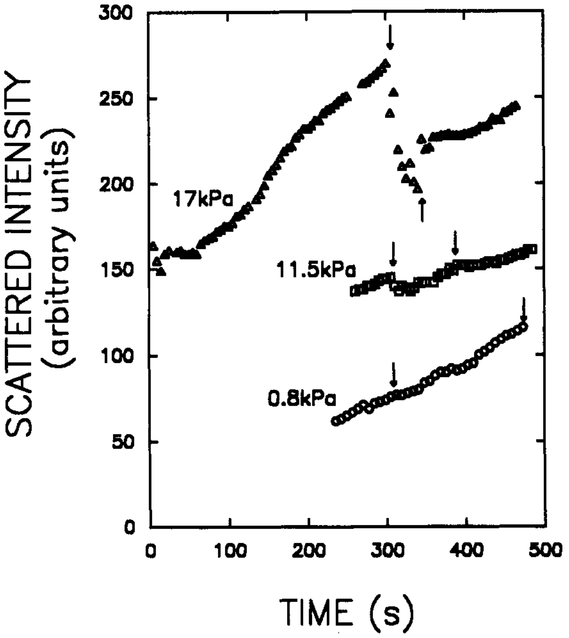

Figure 5. Scattered light intensity versus time as a function of applied shear stress for a 50/50 SCPE/EVA blend at 130 °C. The arrows have the same meaning as in Figure 3.

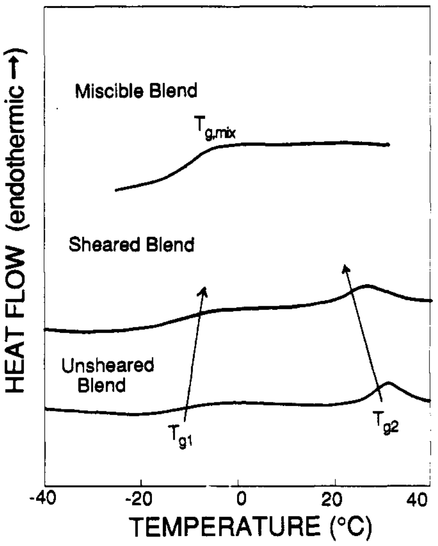

Figure 6. DSC thermograms for 50/50 SCPE/EVA blends as a function of thermal and shear history; (a) unheated, unsheared blend; (b) heated, sheared blend; (c) heated, unsheared blend. The thermal and stress histories are described in the text.

The effect of shear stress on flow-induced mixing at 130 °C is shown in Figure 5. The curves correspond to applied shear stress of 0.8, 11.5, and 17 kPa, respectively. At the lowest shear stress no phase mixing was observed, while at the highest shear stress, phase mixing occurred as is evident from the sharp drop in the scattered light intensity. The effect of a stress of 11.5 kPa was less clear. It appeared that some phase mixing occurred upon the application of shear, but the initial drop in scattering intensity was followed by a slow increase during the shear experiment. Thus, there appeared to be a competition between mixing and demixing processes, and one might conclude that this stress is close to the "critical stress" required for flow-induced phase mixing. The magnitude of this critical stress was consistent with the order of magnitude of the predicted and experimental values of the critical stress reported for PS/PVME blends by Lyngaae-Jorgensen and Sondergaard.[10,11]

An important question that arises from these observations and those of other researchers is whether the changes in light scattering intensity represent molecular mixing of the polymers or simply a reduction in the phase-separated domain size. Recent fluorescence experiments by Larbi et al.[13] showed that for PS/PVME blends near the cloud point, mixing on a molecular scale occurred when the blend was subjected to shear flow. For the EVA/SCPE blend described in the present communication, a cast film was heated on a hot stage at 130 °C and allowed to phase separate for a short time. The film became visibly cloudy. Shear flow was then applied manually to one half of the film by moving a coverslip over it, and then both sides of the film were quenched with liquid nitrogen. Figure 6 shows the subsequent DSC analyses of the sheared and unsheared parts of the film as well as a separate miscible blend sample that did not experience the 130 °C temperature. The unheated film had only a single T_g at about −5 °C, which was consistent with a one-phase morphology. Both heated blends exhibited two-phase morphologies as evidenced by two T_g's in the DSC scan. In the case of the sheared blend, however, the T_g's were shifted to higher and lower temperatures for the EVA and SCPE transition, respectively. This was due to increased miscibility of the two polymers in this blend as a result of the deformation, though complete miscibility was not attained at the strain employed in this experiment.

Conclusions

Light scattering experiments during shear flow of EVA/SCPE blends indicated that stress improved the miscibility of the two polymers. This is interpreted in terms of a stress-dependent phase diagram in which the phase boundary of a polymer mixture that exhibits lower critical solution temperature is shifted upward in temperature due to the application of stress. The phenomenon required a critical stress, but in the case of the EVA/SCPE, this was relatively low and improvements in miscibility were observed at temperatures of nearly 30 °C above the quiescent cloud point. Although DSC results of a separate experiment indicated that complete miscibility may not have been achieved in the experiments reported here, this is thought to be a limitation of the maximum strains allowed by the equipment used rather than refutation of the flow-induced mixing argument. Future experiments will employ a rotary shear device in order to overcome the strain limitations of our present equipment.

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Notes

Characterization of Polymer Surfaces after KrF Laser Ablation by Infrared Spectroscopy

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Introduction

Pulsed ultraviolet laser radiation can lead to clean and precise material removal at the irradiated site of polymer surfaces. This phenomenon was discovered in the early 1980s using an excimer laser[1,2] and was termed ablative photodecomposition.[2] It has been reported that the absorption of laser light in polymers is governed by Beer's law and that the etch depth exhibits a logarithmic dependence on the incident laser fluence above a threshold value.[3-6] The penetration depth of ultraviolet laser light is usually greater than the etch depth, so that the surface left behind after ablation has been exposed to laser light. So far, the properties of only a few polymer surfaces after ablation have been studied by means of X-ray photoelectron spectroscopy (XPS) and wet chemical techniques.[7-9] In the case of two polymers, poly(ethylene terephthalate) (PET) and polyimide (PI), the oxygen-to-carbon atomic ratio at the surfaces after 193-nm laser ablation was found to decrease significantly.[7] A further study on PET suggested that the fresh surface created after ablation consisted of some oligomer.[8] In this note we report the results of attenuated total reflection infrared (ATR-IR) spectroscopy studies on modified PET and PI surfaces remaining after 248-nm laser ablation. The characterization of modified surfaces is performed with the spectral subtraction method.

Experimental Section

PET films (Toray Industries Inc., Lumirror, 70 μm thick) and PI films (Ube Industries Ltd., Upilex-S, 20 μm thick) were used as received. Laser pulses (248 nm, 20-ns fwhm) were produced from Lambda-Physik EMG 160 excimer laser at 1 Hz. The energy of the pulses was measured with a Gentec ED-200 joulemeter. On the basis of the threshold fluence for the ablation at 248 nm of PET (130 mJ/cm^2)[4] and of PI (27 mJ/cm^2 or 80 mJ/cm^2),[4,5] both polymer films were irradiated at a fluence of 145 mJ/cm^2 to obtain the fresh surfaces after ablation, using a quartz lens and a metal mask of 1.0-cm^2 area. Laser irradiation was carried out with a single laser pulse in air.

The IR spectra were recorded on a Digilab FTS-40 Fourier transform infrared spectrometer by an ATR attachment using a KRS-5 internal reflection element (IRE) at a nominal 45° angle of incidence. A total of 64 spectral scans were averaged at a resolution of 4 cm^{-1}.

Results and Discussion

The IR spectrum of an original PET film is shown in Figure 1a. The main absorption bands[10,11] associated with C=O (502 and 1716 cm^{-1}), C–O (1099 and 1245 cm^{-1}), and the aromatic ring (725, 872, and 1331 cm^{-1}) appear in the spectrum. The IR spectrum of a laser-irradiated PET film is shown in Figure 1b. The same absorption bands are observed in this spectrum; however, the relative intensity of an absorption band at 725 cm^{-1} is greater than that for the original PET film.

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