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Temperature dependent optical properties of a synthesis blend of poly(methyl methacrylate) and vinyl rubber

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The temperature dependent optical properties of a poly(methyl methacrylate) (PMMA) ethylene-co-vinylacetate (EVA) blend (PMMA–EVA) were investigated in order to study its thermo-optical behaviour in the temperature range 30–70 °C. The thermal coefficients of the refractive index d*n*/d*t* of PMMA–EVA, PMMA and EVA were measured as a function of the temperature. The observed trend of the thermal coefficients is related to a first-order phase transition of the EVA component. A comparison with the results of calorimetric investigations by differential scanning calorimetry (DSC) is also reported. The possible use of this material in optics is described.

1. Introduction

In recent years glassy polymers have been reported as showing large optical non-linearities, which is a key feature for their use in electro-optical technologies [1, 2]. In this respect, poly(methyl methacrylate) (PMMA) has been proposed as an interesting material, either for its intrinsic birefringency [3] or for its capability to be a host polymer accommodating non-linear guest molecule [4].

Some optical properties were investigated of PMMA ethylene-co-vinylacetate (EVA) (PMMA–EVA), a synthetic blend prepared by a special technique in which the acrylic matrix is polymerized by a radical process in the presence of the EVA copolymer [5].

The blend of PMMA and EVA exhibits a very peculiar and interesting optical behaviour. In fact, it is almost totally transparent at room temperature (that is, its transparency is close to that of pure PMMA), whereas at higher temperatures it becomes opaque. It has been shown that this temperature-dependent opacification can be ascribed to the onset of a light-scattering phenomenon; taking into account the microstructure of the blend, the description of this kind of scattering can be carried out in the Rayleigh–Gans approximation [8]. The optical transparency at room temperature is due to the effect of the equalization of the refractive indices of the two components of the blend, at this temperature.

The propagation of a light beam in a two-component, heterogeneous medium like PMMA–EVA, with static optical inhomogeneities, may give rise to a non-linear scattering due to a non-linearity of the refractive indices n_P and n_E of the two components. Relevant non-linear optical phenomena occur [9] when the light-induced part, Δn_{NL}, of the refractive-index difference, $\Delta n = n_P - n_E$, has a sign opposite to, and a value comparable with, the difference, Δn_L, between the linear parts of the refractive index of each component; some important applications of this phenomenon in laser physics has been reported in *liquid* suspensions [10]. In the case of PMMA–EVA, a non-linear optical behaviour of thermal origin may occur: the light-induced changes of the refractive index result from thermal heating following irradiation with a power light beam and are proportional to the temperature coefficient d*n*/d*t* of the refractive index.

This paper reports on the measurements of the thermal coefficient of the refractive index d*n*/d*t* of PMMA–EVA, PMMA and EVA, as a function of the temperature, in the range between room temperature and 70 °C. The observed trend of the thermal coefficients is related to a first-order phase transition of the EVA component. This interpretation is confirmed by

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comparison with the results of calorimetric investigations by differential scanning calorimetry (DSC). The possible use of this material in optics is described.

2. Materials and methods

The EVA copolymer, kindly supplied by Dupont, has a vinylacetate content of 20% by weight and an inherent viscosity ($c = 0.25$ g per 100 ml toluene) of 1.04 dl g^{-1}. PMMA ($M_W = 150\,000$) was purchased from BDH, MMA monomer was used as-received from Fluka. The PMMA–EVA blend was prepared starting from the dissolution of the EVA elastomer in the MMA monomer in a ratio of 7/93 by weight. At this point 0.5 wt % of benzoyl peroxide was added with stirring, and the temperature was raised to 80 °C. When the viscosity increased to a critical level (normally after about 100 min), the solution was poured into a mould consisting of two polished glass plates separated by teflon spacers sealed by adhesive tape at the four corners and held together by springs. The mould was kept for 12 h in an oven at 70 °C, followed by a finishing cycle of an additional 3 h at 100 °C.

At the completion of the polymerization process, precipitation of rubber occurs and a complex morphology is obtained, in which the minor phase is constituted by EVA droplets entrapping some PMMA particles. Such a microstructure is represented schematically in Fig. 1 and can be described as a multicore-shell structure (the so-called salami structure). A concentration of 7% w/w EVA is sufficient to strongly improve the mechanical properties of PMMA [5, 6, 7].

A Mettler System TA-3000, equipped with a control and programming unit (microprocessor TC 10 A), was used for thermal analysis. The system was provided with a calorimetric cell DSC-30, which allowed temperature scans from − 170 to 600 °C. Measurements of the thermal coefficient of the refractive index of PMMA and PMMA–EVA at $\lambda = 633$ nm were carried out using a very sensitive interferometric technique; the thermal range explored was 20–70 °C. In the case of EVA, measurements of the refractive index at $\lambda = 589$ nm were performed on a thin slab using an Abbe refractometer; data were taken every 10 min with 2 °C increments, in the range 20–70 °C. The temperature coefficient dn/dt of this refractive index was determined numerically.

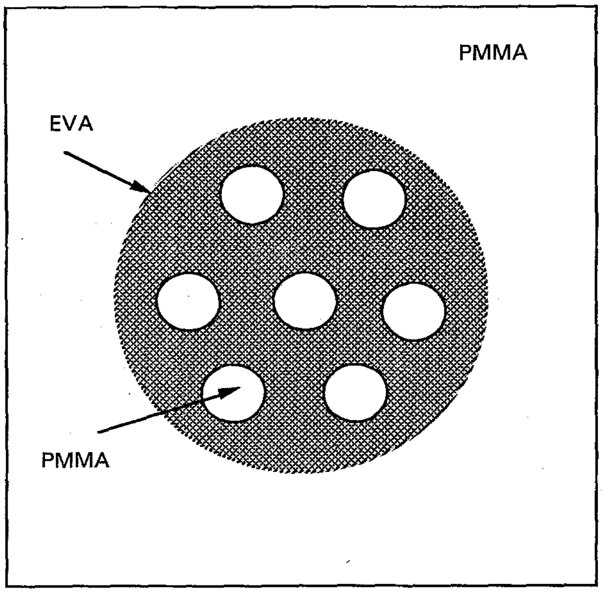

Figure 1 A schematic representation of rubber-toughened PMMA obtained by reactive blending with EVA.

3. Results

The thermal properties of EVA rubber and the PMMA–EVA blend have been analysed in the DSC experiments reported in Figs 2 and 3, respectively. Fig. 2a shows the DSC melting trace for EVA and Fig. 2b shows the crystallization trace. The EVA rubber has two clear melting peaks (at about 50 °C and 90 °C) and two clear crystallization peaks (at about 65 °C and 40 °C). Figs 3a and 3b show DSC traces for the melting and crystallization, respectively; of PMMA–EVA. The PMMA–EVA blend shows weaker melting and crystallization peaks between 50 °C and 90 °C and between 70 °C and 25 °C. Fig. 3a also shows a transition of PMMA–EVA at about 110 °C; this corresponds to the glass transition of PMMA.

Figs 4 and 5 show the trend of dn/dt (at constant pressure) against temperature, t, for PMMA–EVA and for EVA, respectively, in the range 20–70 °C. The

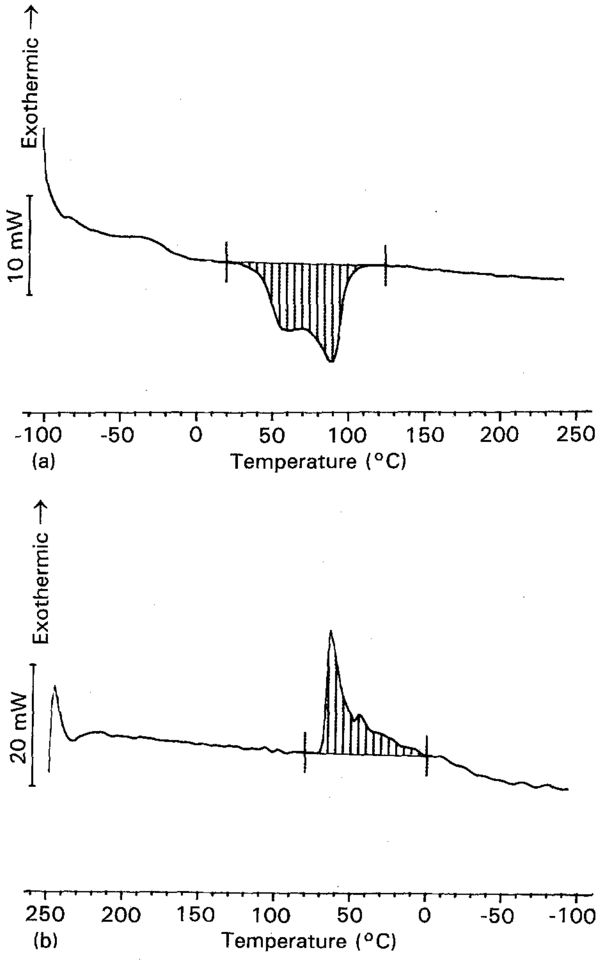

Figure 2 DSC traces of EVA: (a) melting, and (b) crystallizing.

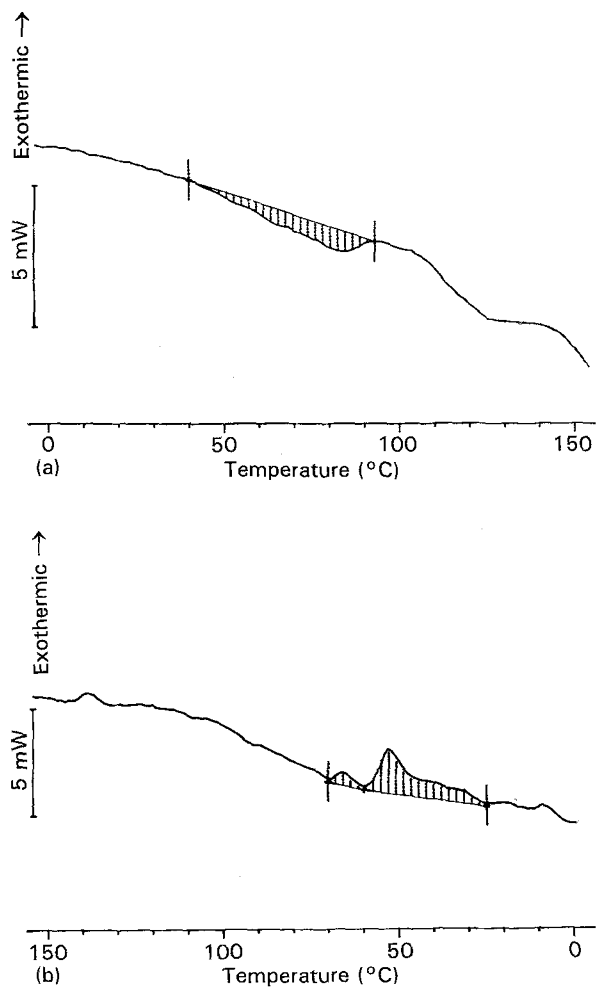

Figure 3 DSC traces of the PMMA–EVA blend during: (a) melting and (b) crystallization.

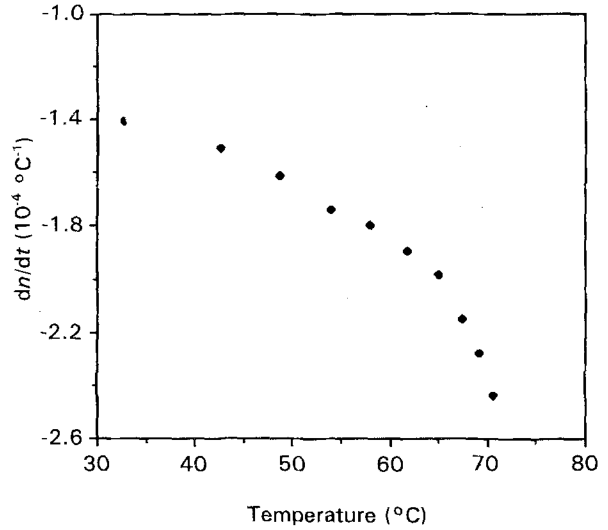

Figure 4 A plot of d*n*/d*t* against temperature for PMMA–EVA ($\lambda = 633$ nm).

measured value of d*n*/d*t* for PMMA is d*n*/d*t* = -1.2×10^{-4} °C^{-1} at any temperature in the same range. In EVA rubber, d*n*/d*t* is a decreasing function of temperature and shows discontinuity at about 65 °C (Fig. 5); d*n*/d*t* for the PMMA–EVA blend shows an analogous trend (Fig. 4).

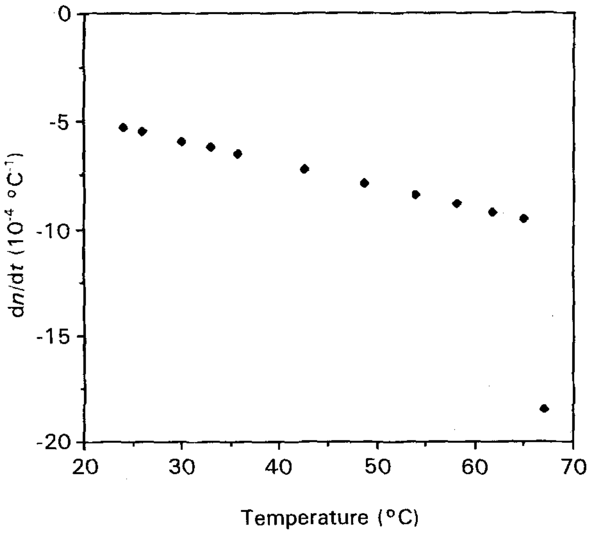

Figure 5 A plot of d*n*/d*t* against temperature for the EVA copolymer ($\lambda = 589$ nm).

4. Discussion

The good mechanical properties and the peculiar transmittance characteristics of the blend demonstrated in previous works [5, 8] are due to the particular (multicore) structure that we have realized. In fact, a blend prepared by melt-mixing 7 p.h.r. (parts per hundred resin) or EVA with PMMA in a Brabender-like apparatus is completely opaque at any temperature. The usual, multistage industrial process for the production of special, tough PMMA is to add rubber particles in large amounts (20–30 wt%). The rubber particles are produced industrially by a suspension process in which an outer shell of a cross-linked, rubbery, butylacrylate-styrene copolymer is polymerized around a PMMA core. The morphology of the microstructure of this tough-PMMA fabrication process is shown in Fig. 6. Our PMMA–EVA fabrication process is very simple when compared to the industrial

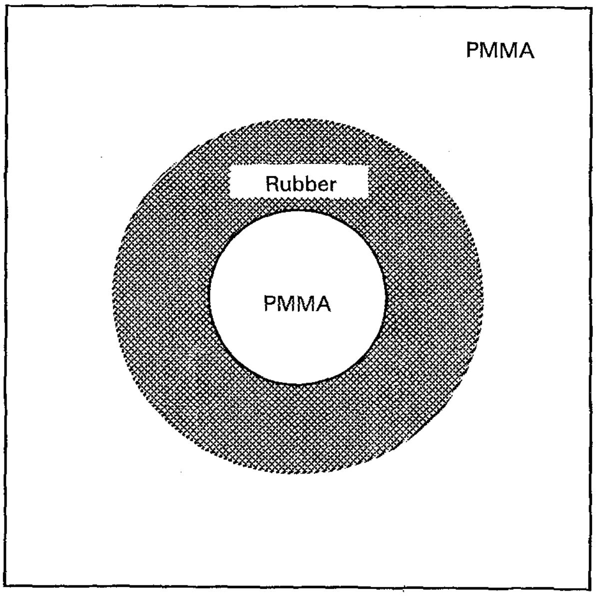

Figure 6 A schematic representation of an industrially produced, rubber-toughened PMMA.

process described. Moreover, a low rubber concentration suffices to improve the impact properties of the PMMA.

The first-order phase transitions of the blend and its EVA component (Figs 2 and 3) are attributed to the fusion of EVA, which has some residual crystallinity because of the presence of polyethylene sequences along the polymeric chains. The multiple melting and crystallization temperatures observed in the DSC traces of the copolymer result from the randomness of the length of crystallizable polyethylene sequences; the difference between the transition temperatures in the melting and the crystallization processes is due to an "undercooling" effect.

The peculiar thermo-optical behaviour of the PMMA–EVA blend can be ascribed to its EVA component. The optical behaviour of EVA, at temperatures lower than the transition temperature, T_0, is related to its temperature-decreasing high values of dn/dt. Note that the low average temperature rate used in the measurements, and the occurrence of a discontinuity in the dn/dt versus temperature curve just at the location of the transition temperature, exclude the possibility of non-equilibrium thermodynamical conditions. In the same temperature range, PMMA has a constant dn/dt value; thus, the trend of the dn/dt curve for PMMA–EVA (Fig. 4) is dominated by the behaviour of EVA. At room temperature (25 °C, $\lambda = 589$ nm) the refractive indices and the thermal coefficients, dn/dt, of PMMA and EVA are, respectively, $n_p = 1.4916$ and $dn_p/dt = -1.2 \times 10^{-4}\,°C^{-1}$, and $n_E = 1.4938$ and $dn_E/dt = -5.4 \times 10^{-4}\,°C^{-1}$. As a consequence of the "highly interconnected structure" obtained in the synthesis blend, the light scattering is proportional to the square of the difference in the refractive indices [8]. At room temperature, the light scattering is very small and is approximately zero at about 30 °C. When the temperature increases, the refractive index of the copolymer changes more steeply than the acrylic matrix; hence, the difference between the indices increases gradually with temperature. In turn, this produces an increasing of the scattering up to the transition temperature, where the sample becomes completely opaque. We also verified that this phenomenon is reversible [9]. Finally, notice that at room temperature both the difference Δn_L and the difference between the temperature coefficients of the refractive indices (proportional to Δn_{NL}) are typical of those heterogeneous media which exhibit non-linear scattering [10, 11]. We believe that some effects usually associated with non-linear light scattering (for example, self-transparency and optical bistability) could also occur in PMMA–EVA. This would suggest the use of this blend in laser physics.

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