

Acrylate/EVA Reactive Blends and Semi-IPN: Chemical, Chemical–Physical, and Thermo-Optical Characterization

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ABSTRACT: In the present work, blends between poly(methyl methacrylate) (PMMA) or its copolymer with butyl methacrylate P(MMA-co-BMA) and poly(ethylene-co-vinyl acetate) (EVA) rubbers obtained applying the reactive blending principles were deeply investigated to clarify the chemistry of the system. A copolymeric phase, which is created *in situ*, was isolated and its chemical structure was determined through NMR analysis. The blends were also crosslinked with a flexible dimethacrylate to realize semi-

interpenetrated networks. The blends were characterized for their properties of interest (mechanical and optical behaviors). Particularly, an accurate investigation of the optical properties as a function of the temperature was performed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2926–2935, 2006

Key words: blending; graft copolymers; interpenetrated networks; reactive processing; refractive index

INTRODUCTION

Acrylic glasses are a class of material very important, as they match outstanding optical properties and easy of processing with low price. These properties allow poly(methyl methacrylate) (PMMA) to face the competition of bisphenol-A-based polycarbonate, the other very important, transparent, rigid polymer, in commercial and residential glazing.

In the early 70', impact-modified acrylic resin grades were developed for injection molding and extrusion.^{1,2} The soft impact modifier phase was either an acrylic of low T_g (e.g., poly(*n*-butyl acrylate) or styrene-butadiene rubbers. The refractive indices are matched to maintain transparency, but at the high content needed for a detectable improvement of the impact properties (normally 30% of soft phase) a strong decrease (of about 30%) of the flexural modulus is detected, which limits the application of the material.

In previous papers,^{3,4} we have reported that, by means of *in situ* polymerization of MMA in the presence of an ethylene-vinyl acetate copolymer (EVA), it was possible to obtain an impact grade PMMA (up to four times increase in the Izod values) without significantly depressing the modulus. This was possible due to the very low content (7%) of EVA employed, and to the blending process, really a reactive blending⁵ with the formation of a graft copolymer.

In the present article, we extend our studies to the preparation, based on the same principles, of EVA-modified acrylic polymers having as acrylic phase a methyl methacrylate/butyl methacrylate (MMA/BMA) copolymer, which is more commonly used for acrylic glasses than PMMA. Moreover, we aim also to prepare and characterize semi-interpenetrated networks (semi-IPN) with the use of a crosslinker of the acrylic polymer (to study the influence of a crosslinker on the T_g and mechanical properties).⁶ We also intend to investigate on the structure of the graft copolymer, which forms as a consequence of inter-reaction between the EVA rubber and growing PMMA chains. Finally, we aim to study the optical behavior of the blends as a function of temperature.

EXPERIMENTAL

Materials

EVA copolymer, kindly supplied by Dupont, with a vinyl acetate content of 18.6% by weight and a melt flow index of 2.5 dg/min. PMMA (BDH), $M_w = 1.16 \times 10^5$ Da.

Methyl methacrylate (MMA), butyl methacrylate (BMA), and 1,4-butandiol-dimethacrylate (BDDM) were Fluka products and used without any purification. All the solvents were of analytical degree and used as received.

Techniques

The inherent viscosities of neat PMMA and of PMMA extracted from the blends were determined with an

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Ubbelohde viscometer at $T = 25^\circ\text{C}$ and $c = 0.50\text{ g/dL}$ in chloroform solution. The viscosimetric molecular weight, M_{v} , was obtained by applying the Mark-Howink equation.

The infrared spectra were recorded using a Perkin-Elmer System 2000 FTIR spectrophotometer on films obtained by solution casting.

NMR experiments were carried out on a Bruker AM-400 spectrometer operating at 400 MHz. Samples were prepared by dissolving about 35 mg of polymers (PMMA, EVA, EVA-*g*-PMMA) in 0.75 mL of chloroform (CDCl_3 - d_3 , 99% D). All peaks were referenced to CDCl_3 at 7.27 ppm for ^1H spectra. NMR analysis was performed at 298 K. ^1H spectra were acquired using 16 scans with 16 K data points (zero-filled to 32 K before FT). For the characterization of EVA-*g*-PMMA, double quantum filtered correlated spectroscopy (DQF-COSY)⁷ was recorded. The data file consisted of 512 points and 4098 points in the ω_1 and ω_2 dimensions. Free induction decays (FIDS) were multiplied in both dimensions with weighting functions and the data points were zero-filled to 1 K in ω_1 prior to Fourier transformation.

Calorimetric analysis was performed on 10–15 mg of sample, at a heating/cooling rate of $10^\circ\text{C}/\text{min}$, using a Mettler DSC-30 differential scanning calorimeter (DSC). The glass transition temperature, T_g , was taken at the midpoint of the transition step in the second heating run after quenching.

Scanning electron microscopy (SEM, Philips SEM XL20) was performed on smoothed surfaces after exposure to *n*-heptane vapors (20 min) to remove the EVA phase. Samples were coated with a Pd/Au alloy.

Tensile testing was performed using an Instron machine Mod. 4500 on $1.6 \times 4.5 \times 50\text{ mm}^3$ specimens (obtained by compression molding), at $T = 110^\circ\text{C}$ and at a constant crosshead speed of 10 mm/min.

Transmittance measurements, as a function of temperature, have been performed by means of an optical Axioskop microscope manufactured by Zeiss, equipped with a halogen lamp operating in the visible light (λ from 380 to 760 nm), and provided with an automatic exposure meter. The exposure time, needed to impress in the camera a photographic film of a given sensitivity, is recorded as a function of temperature by a suitable digital apparatus. The optical microscope is equipped with a hot stage (Linkam TH 600), internally controlled by a nitrogen atmosphere and connected with a temperature controller. The specimens undergo thermal cycles (from RT up to 100°C and *vice versa*) at two different heating/cooling rates (2 and $0.5^\circ\text{C}/\text{min}$).

Synthesis procedures

PMMA was prepared by a conventional radical process initiated by an organic peroxide (0.2 wt %).

Following an already described procedure³ slightly modified, the PMMA/EVA blends were prepared in a three-necked flask, equipped with a refrigerator and a mechanical stirrer, by dissolving 3.15 g of the elastomer EVA in 30 g (32 mL) of MMA. Dibenzoyl peroxide (DBPO) (0.06 g), corresponding to 0.2 wt %, were added to this solution and the temperature was raised to 70°C . After 1 h, 15 g of MMA containing 0.03 g of DBPO were also added. The final ratio between EVA and MMA was 7/93 by weight. The transparent solution was let to polymerize under vigorous stirring (600 rpm/min) until the viscosity reached a critical level (normally after a total time of about 100 min), and was then poured into a preheated mold, consisting of two glass plates separated by a rubbery gasket and held together by springs. The mold was kept in an oven heated to 70°C for 12 h. Finally, the blend was further postpolymerized at 120°C for 3 h.

An analogous procedure was adopted for the blends containing BMA as comonomer. In this case, 3.15 g of EVA were dissolved in a mixture of 36 g (38 mL) of MMA and 9 g (10 mL) of BMA (ratio MMA/BMA/EVA = 80/20/7 by wt).

To obtain crosslinked blends (semi-IPN), 0.53 or 1.06 g of BDDM, corresponding to 0.5 and 1% by moles, respectively, were also added together with the DBPO. The polymerization was then performed in the same experimental conditions.

RESULTS AND DISCUSSION

Synthesis of blends

The blends were obtained by a simple method already reported in our previous works, which has been slightly modified to better control the chemio-rheology of the system. The EVA copolymer is dissolved in liquid methacrylic monomers (either MMA or a 80/20 mixture of MMA and BMA), and then the temperature is raised to 70°C to allow a first stage of polymerization (prepolymerization). During this stage, the efficiency of stirring is of fundamental importance, as an inversion of phase occurs at a given level of viscosity of the system (usually after about 100 min). For this reason, a gradual addition of MMA is necessary in the case of PMMA/EVA binary blends, as the viscosity of this system during polymerization increases quickly, and the phase inversion is hindered in spite of the mechanical stirring. This is not the case of MMA/BMA copolymer, probably due to the increased elasticity of the growing poly(MMA-*co*-BMA) chains. The subsequent curing step was effected in a mold at 70°C for 12 h. The temperature must be carefully controlled to avoid the monomer to boil, with the consequent formation of microbubbles inside the material, which act as defects. A further postcuring step at higher temperature (120°C) was then performed to complete the polymerization. The EVA employed in the present

work has a high molecular weight and a content of VA units of 18% by weight, as these characteristics were demonstrated to give the best matching properties in the blend.⁴

To investigate on the effect of a crosslinking agent on morphology and optical properties of blends, different amounts of a dimethacrylate, namely BDDM, were added. In this way, only the acrylic phase was crosslinked and a semi-interpenetrated network (semi-IPN) was generated. The degree of crosslinking influences the morphology of the material, as the domains' dimensions of the dispersed phase depends on the length of the segments between two crosslinking points in such systems.

Codes and composition of the prepared blends were reported in Table I.

Chemical characterization of blends

The blends were prepared by "reactive blending," a methodology which consists in the polymerization of a component (in our case, PMMA) in the presence of a second preformed component (EVA), with the aim to create *in situ* a copolymer between the two phases, which acts as a compatibilizing agent. In fact, as the monomer concentration decreases, chain transfer from a growing PMMA chain to EVA becomes favored. The macroradical EVA can initiate the polymerization of a new PMMA chain, with formation of an EVA-g-PMMA grafted copolymer.

To confirm the above hypothesis, extractions with a selective solvent were performed on the M93 blend to isolate the copolymer. The blend was then treated with boiling acetone in a Soxhlet apparatus for prolonged time to extract the PMMA phase.

The soluble fraction was recovered by removing the acetone by roto-vapor. FTIR analysis of this fraction showed that it really consisted of plain PMMA, whose molecular weight, M_v , as obtained by viscosimetry, was 9.15×10^4 Da, which is comparable with that of a PMMA prepared in the same experimental conditions, in absence of EVA (M100 sample, $M_v = 9.47 \times 10^4$ Da). The insoluble residue (corresponding to around 8% b.w.) was recovered by filtration, and dried and characterized

TABLE I
Codes and Composition of the Synthesized Blends

Codes	MMA (wt %)	BMA (wt %)	EVA (wt %)	BDDM (mol %)
M100	100	—	—	—
M93	93	—	7	—
M93/0.5	93	—	7	0.5
M93/1	93	—	7	1
MB80	80	20	7	—
MB80/0.5	80	20	7	0.5
MB80/1	80	20	7	1

TABLE II
¹H NMR Chemical Shifts of EVA-g-PMMA Copolymer

Polymer	Nucleus	δ (ppm)
PMMA	CH ₂	0.81–1.08
	CH ₂	1.58–1.98
	OCH ₃	3.66
EVA-g-PMMA	CH*	2.18
	CH ₂ *	1.48
EVA	CH _{2a,b}	1.25
	CH _{2,c}	1.5–1.6
	CH ₃	2.02
	CH	5.2

through NMR and DSC techniques (see next paragraphs). It turned to be a copolymeric phase consisting of EVA grafted with PMMA chains (EVA-g-PMMA).

It is also important to note that, in the case of M93/0.5 and M93/1 blends, no soluble phase at all was extracted, confirming the full crosslinking of the acrylic phase through BDDM.

NMR analysis of the copolymer

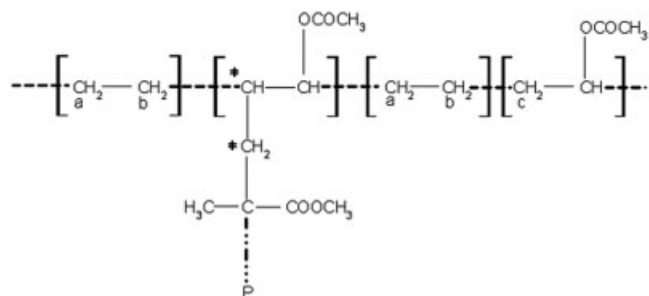
Monodimensional and bidimensional Fourier Transform ¹H NMR analysis was performed on the EVA-g-PMMA copolymer as extracted from the M93 blend. Chemical shifts are reported in Table II. The assignments of the peaks relative to PMMA and EVA chains have been obtained on the basis of the ¹H spectra of plain polymers that were also acquired.

The proton spectrum of the copolymer showed, together with the signals characteristic of PMMA and EVA, two new resonances, at 2.18 and 1.48 ppm, respectively, attributed to the CH of EVA and to the CH₂ of PMMA on which the grafting reaction does occur, as sketched in Scheme 1. Such a structure was unambiguously confirmed also by bidimensional DQF-COSY analysis (Fig. 1), which allowed correlating protons located on adjacent C atoms. In particular, the new signal at 2.18 ppm attributed to the CH of EVA involved in the grafting showed correlations with both the CH_{2b} (1.25 ppm) and CH (5.2 ppm) resonances of EVA as well as with the CH₂ resonance (1.48 ppm) of the grafted PMMA.

Because of peak overlapping, it was impossible, instead, to give an evaluation of the length of the PMMA grafted chains.

The degree of grafting of PMMA onto EVA was estimated from the ratio between the intensities of the signal attributed to the CH_{2c} and that attributed to CH* in the spectrum of EVA-g-PMMA copolymer. The ratio was 2.5, which means that ~ 1 each of 2.5 units (about 40%) of vinylacetate moles along the EVA brings a PMMA chain grafted on it.

It is reasonable that the vinylacetate units of EVA onto which a PMMA chain can graft are those linked



Scheme 1 Chemical structure of the EVA-g-PMMA copolymer.

to an ethylene unit, as steric hindrance effects should make unlikely the grafting of PMMA onto consecutive VA units. This means that an high content of VA units in the EVA copolymer does not necessary imply a high grafting degree of PMMA, as the percentage of isolated VA units decreases increasing the VA content of EVA copolymer. This consideration can probably justify the better mechanical properties of the blends obtained using an EVA with 18 wt % of VA with respect to an EVA at higher content of VA (36%).⁴

Morphological analysis

SEM micrographs were taken on smoothed surfaces after etching with *n*-heptane to extract the EVA phase. The typical morphology of the system is

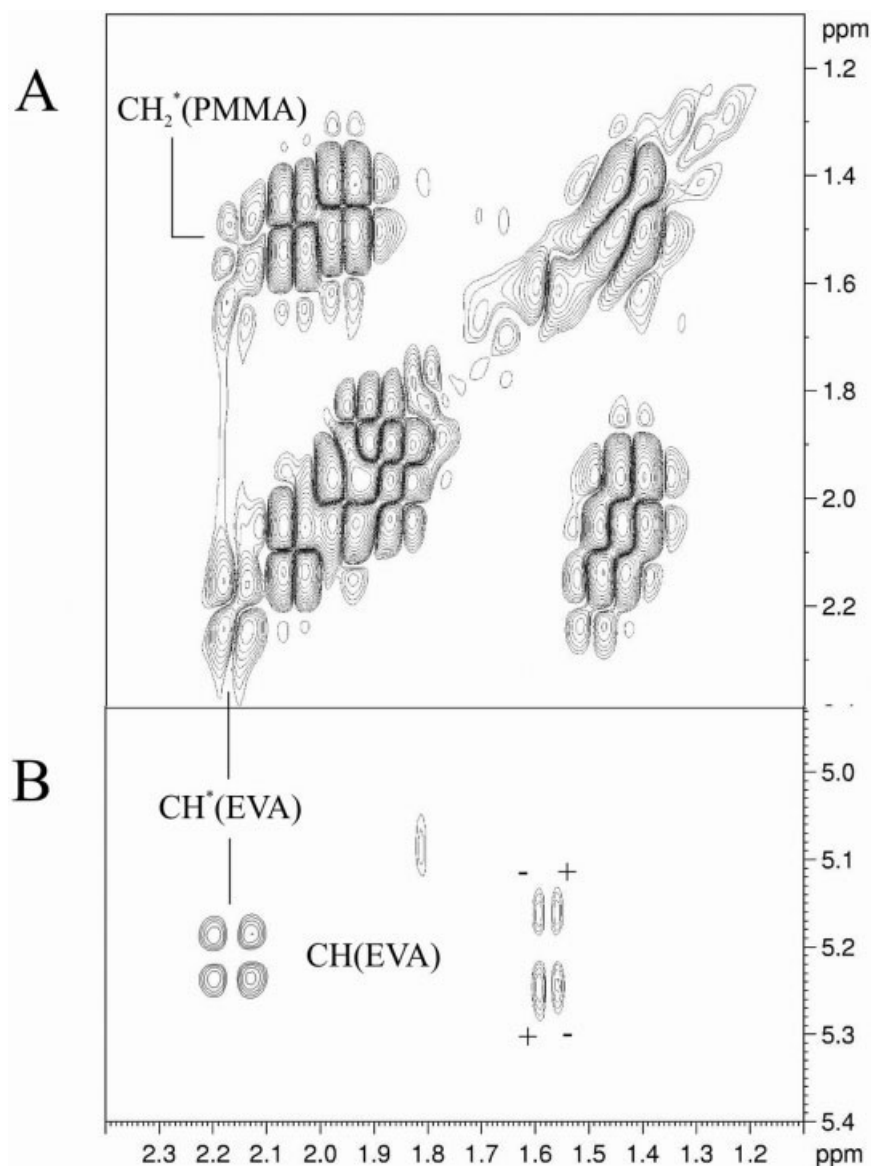
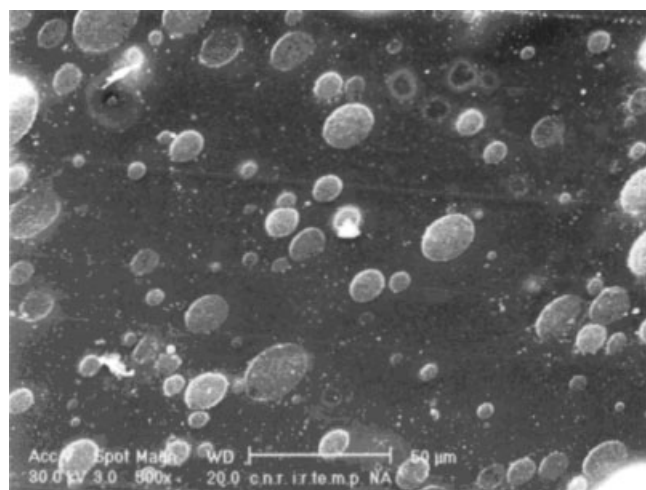
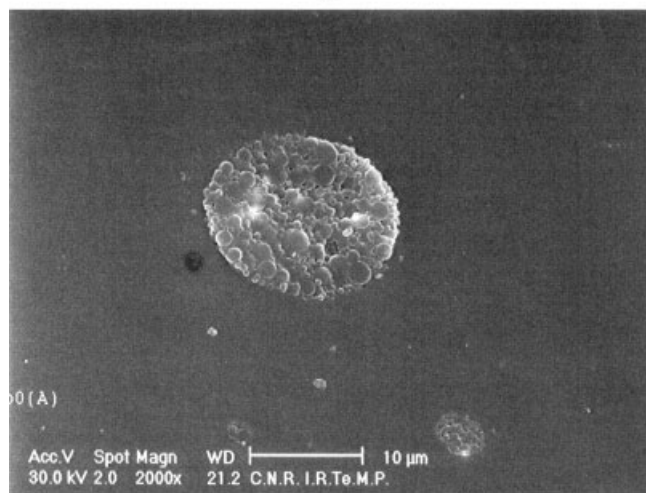


Figure 1 DQF-COSY spectrum of EVA-g-PMMA copolymer at 400 MHz in CDCl_3 , 300 K. Only the peaks discussed in the text are labeled. The sign pattern of peaks (+, -) is also reported.



(a)



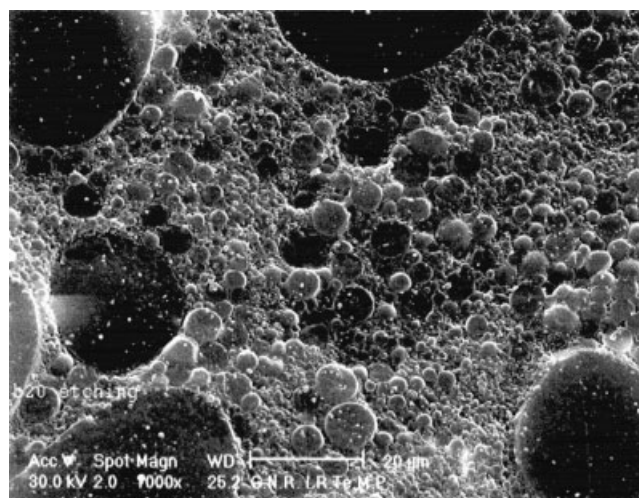
(b)

Figure 2 SEM micrographs at different magnitude of a smoothed surface of M93 blend after etching.

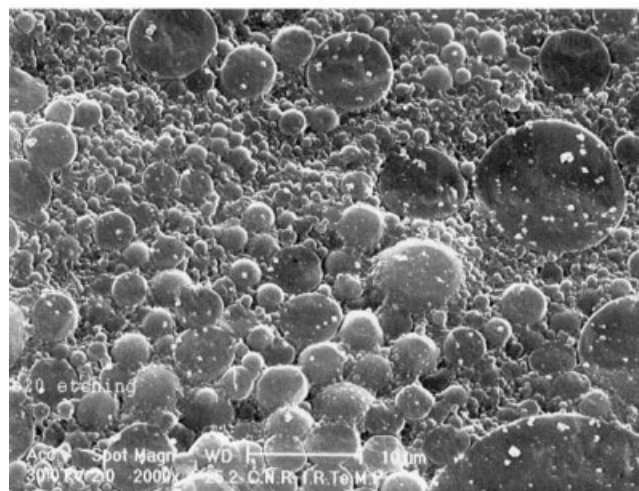
shown in Figure 2, where large domains constituted by a thin film of EVA, with subincluded PMMA particles, are evident. The dispersed phase appears well welded to the matrix. Such complex morphology is the result of a combination of parameters, such as the efficiency and time of stirring and the viscosity of the system. At the first stage, the system consists of an homogeneous solution of EVA in MMA monomer; as far as the polymerization of MMA proceeds, the system evolves to a situation in which the EVA is still the continuous phase while particles of PMMA precipitate as separate phase, until, when the amount of PMMA phase reaches a critical level, a phase-inversion process occurs, leading to the final morphology, in which the continuous phase is constituted by PMMA, while a thin film of EVA (dispersed phase) surrounds PMMA particles which remained entrapped inside. To allow the

phase inversion to occur, the stirring must be efficient and the viscosity at which the liquid reaction mixture is poured into the mold (static stage of polymerization) must be carefully controlled. In fact, as we already showed in our previous works, if the time or the efficiency of stirring is reduced, the PMMA remains as dispersed phase inside the EVA matrix. Analogous results were obtained for the MB80 blends.

SEM micrographs of MB80 blends crosslinked with 0.5% of BDDM are shown in Figure 3. It is evident that the acrylic phase formed discrete domains surrounded by a thin EVA film, indicating that the phase inversion process did not occur. This was attributed to the crosslinking of the acrylic phase, which had the effect of freezing the morphology of the system before the phase inversion process occurred.



(a)



(b)

Figure 3 SEM micrographs at different magnitude of a smoothed surface of MB80/0.5 blend after etching.

TABLE III
Glass Transition, Melting, and Crystallization
Temperatures, and molar enthalpy of crystallization as
obtained by DSC (rate: 10°/min)

Sample	T_g (°C)	T_m (°C)	T_c (°C)	ΔH (J/g)
PMMA*	115	—	—	—
M100	116	—	—	—
EVA	-28	85	63	59
M93	-28,105	83	55	30
EVA-g-PMMA	-28,120	85	57	20
M93/0.5	-28,106	84	60	32
M93/1	-28,110	86	61	32
MB80	-28,99	85	60	56
MB80/0.5	-28,99	85	60	40
MB80/1	-28,99	86	59	36

DSC analysis

Calorimetric analysis was performed on the homopolymers, on the blends and on the EVA-g-PMMA copolymer extracted from the M93 blend. For comparison, a commercial sample of PMMA was also analyzed. Thermal parameters are reported in Table III.

As far as the crystallinity of EVA is concerned, we can note a marked decrease of crystallinity parameters (T_c and ΔH_c) in all the blends, probably attributable to the intimate dispersion of EVA inside the PMMA matrix, which disturbs the crystallization process. Such effect is even more evident in the copolymer, indicating the occurrence of chemical bonds. Values of T_c and ΔH_c only slightly lower respect to plain EVA were observed, instead, in the case of MB80 blends. It is conceivable that the presence of the more flexible BMA component favors the crystalline organization of the EVA. The BMA is also responsible for the slightly lower T_g of the acrylic phase.

The thermogram relative to EVA-g-PMMA copolymer is shown in Figure 4. According to the hypothe-

sized structure, the DSC analysis revealed the presence of both the T_g (acrylic and rubber phases) in the copolymer.

Mechanical properties

Tensile testing was performed at a temperature of 110°C (which is close to the T_g of the PMMA acrylic matrix) to better study the influence of the addition of the rubbery phase and of the crosslinking agent. In the vicinity of the matrix glass transition, in fact, any modification of the structure is magnified. Results are reported in the diagrams of Figures 5 and 6.

It is evident that both crosslinked and uncrosslinked M93 blends showed a glassy behavior; the elastic modulus, E , increases from 260 to 380 MPa going from 0.5 to 1% of BDDM, according to an higher crosslinking degree. Instead, the MB80 blends (that contains 20% of BMA) showed a rubbery behavior; in fact, the BDDM allowed both a higher elongation and stress at break, as in typical crosslinked rubbery systems. For this blend, we found that the 1% BDDM curve showed a lower stress at low elongation values with respect to the 0.5% BDDM curve, but higher stress values at higher elongation, in agreement with the increased crosslinking degree, whose effect is more pronounced at high elongation.

Optical investigation

The blends exhibit an interesting optical behavior to be further investigated so as to understand the intrinsic properties of such a system, in regards to possible end-uses in thermooptical applications. Particularly, a deeper investigation was performed on the M93 blend.

This blend appears to be completely transparent at room temperature (RT), just as the acrylic PMMA

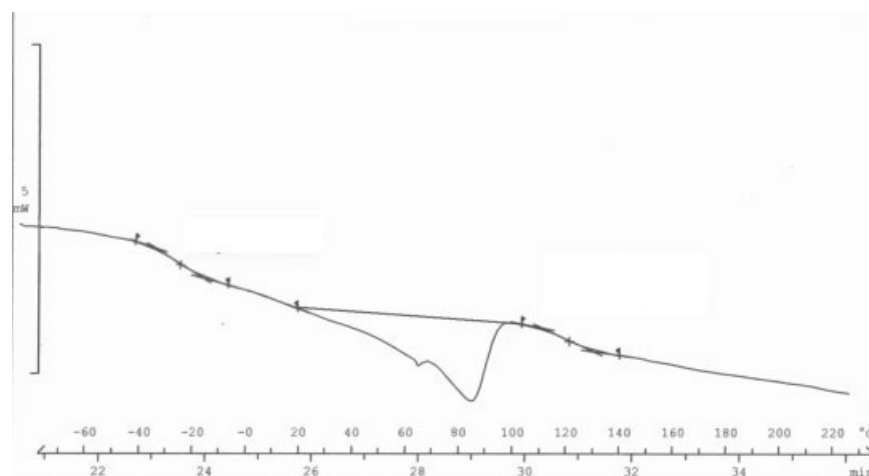


Figure 4 DSC curve of EVA-g-PMMA copolymer (2° heating run).

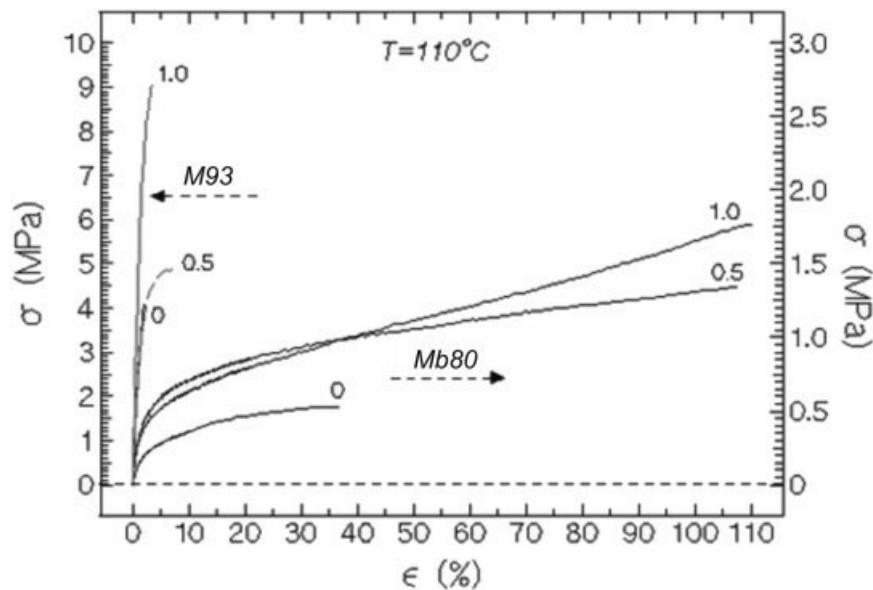


Figure 5 Stress-strain curves of M93 and Mb20 blends as a function of BDDM%.

matrix, whereas with increasing temperatures it becomes more and more opaque. The transparent-to-opaque transition depends on temperature and can be attributed to the light diffusing throughout its complex morphology. Transmittance measurements, as a function of temperature, have been performed by means of an optical microscope equipped with a device, which detects the quantity of the light transmitted across the specimens. The total quantity, Q , of light emitted from the halogen lamp and the film sensitivity are kept constant for all the specimens. The quantity of

light crossing the specimens, detected by the exposure meter, is given from the relationship:

$$Q = Lt \quad (1)$$

where L is the amount of light per unit time crossing the specimen and t is the exposure time in seconds. Since Q is constant for all the samples, L and t are inversely proportional. Therefore, the specimens transparency occurs at very low exposure times.

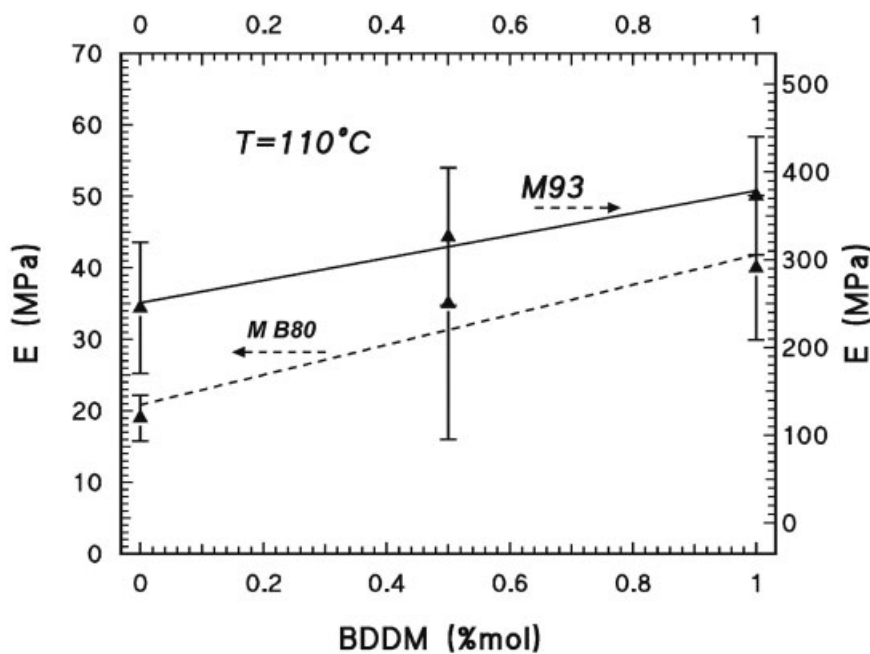


Figure 6 Young's elastic modulus versus BDDM% of M93 and Mb80 blends.

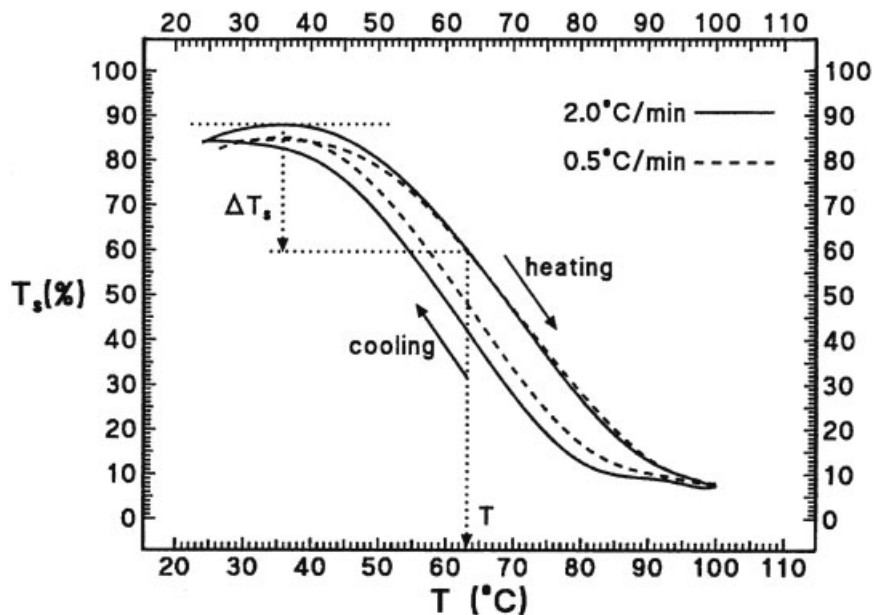


Figure 7 Transmittance versus temperature for the M93 blend. At the temperature T corresponds a degree of opacity, DTs calculated assuming proportionality between the DRI difference from the RI maximum reported in Figure 8.

The exposure meter used for such measurements is calibrated against a glass slab of the same average thickness of the specimens (about 2.7 mm). Assuming the glass transmittance equal to 100% from eq. (1):

$$Q = \text{const.} = L_g = t_s L_s \quad (2)$$

where the subscripts g and s stand for the glass (reference) and for the specimen, respectively. One can

therefore calculate the specimen transmittance by the following equation:

$$T_s = L_s = 100(t_g/t_s) \quad (3)$$

The transmittance, T_s as a function of temperature, is reported in Figure 7, where the data of both the aforementioned cycles are plotted (see arrows). The heating

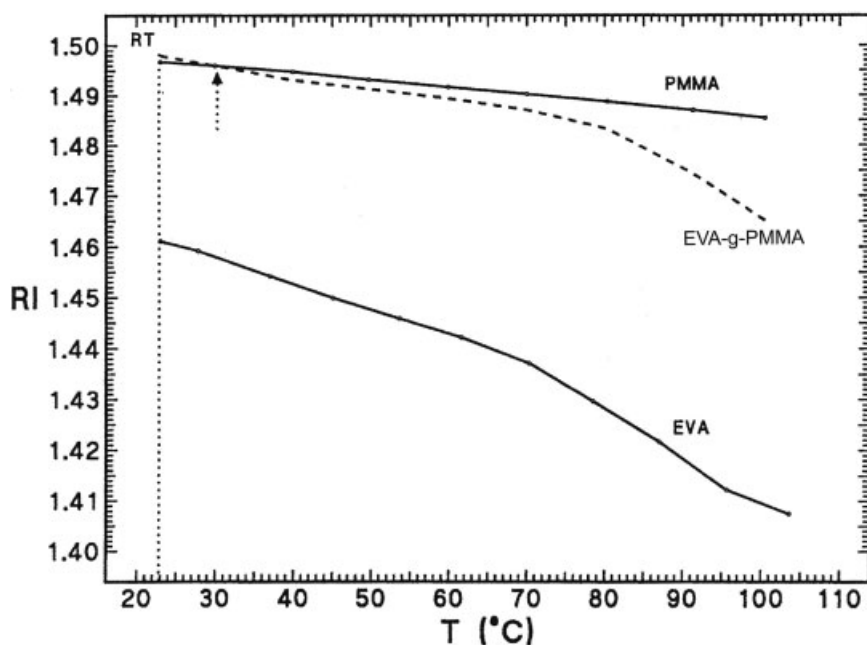


Figure 8 Refractive index versus temperature for PMMA and EVA, calculated from literature volume–temperature data, and EVA-g-PMMA copolymer, calculated from data of Figure 7.

and the cooling cycles T_s data exhibit a hysteresis because of the thermal inertia of the specimen with respect to the heat transfer into the hot stage.

The transparency at about 35°C is probably due to a refractive index matching between the PMMA matrix and the copolymer elastomeric domains. In comparison, the mechanical blend of same weight ratio, obtained by a melt-mixing, is completely opaque at RT and remains opaque at higher temperatures as well.

As previously shown by the morphological investigation, the system is made of a PMMA matrix in which large elastomeric domains are embedded. Such dispersed particles are in turn formed by a complex morphology made of an elastomeric cellular structure containing tiny PMMA particles inside the cells. The thin cellular walls are made mainly of EVA-g-PMMA graft copolymer chains.

These different behaviors can be explained by the RI curves versus temperature of EVA (with 18% of VA) and PMMA (solid lines) reported in Figure 8, whose data have been obtained by the Lorentz and Lorenz equation^{8,9}:

$$RI = \left(\frac{V + 2R_{LL}}{V - R_{LL}} \right)^{1/2}$$

where R_{LL} is the molar refractive index depending on the chemical structure and calculated by the method of the additive group contributions¹⁰ and V , the molar volume, taken from literature dilatometric experimental data as function of T .¹¹

The RI data of PMMA and EVA copolymer never intersect and match together all over the T investigated range; therefore, their simple blend, as the one obtained by melt mixing, must be always opaque at any temperature as it is the case.

The more complex behavior of the blend obtained by synthesis can be tentatively explained from the same figure: schematically one can calculate the EVA-g-PMMA graft copolymer curve from Figure 7. This is obtained imposing the same RI for PMMA matrix and the elastomeric domains of EVA-g-PMMA at about 30°C, where the transmittance is maximum. From this point on, one assumes for each temperature, T , ΔRI values with respect to the PMMA (for which $\Delta RI = 0$ at 30°C) proportional to the degree of opacity, ΔTs , of the graft copolymer (see Fig. 7), drawing the relative RI- T curve.

In this way at 30°C, the PMMA/EVA blend obtained by synthesis behaves, from the optical point of view, just like the isotropic and homogeneous PMMA matrix. When the temperature increases the copolymer RI diverges more and more from the one relative to the PMMA. Therefore, the difference ΔRI between the two components increases more and more until it reaches a constant value of opacity. Such an effect is

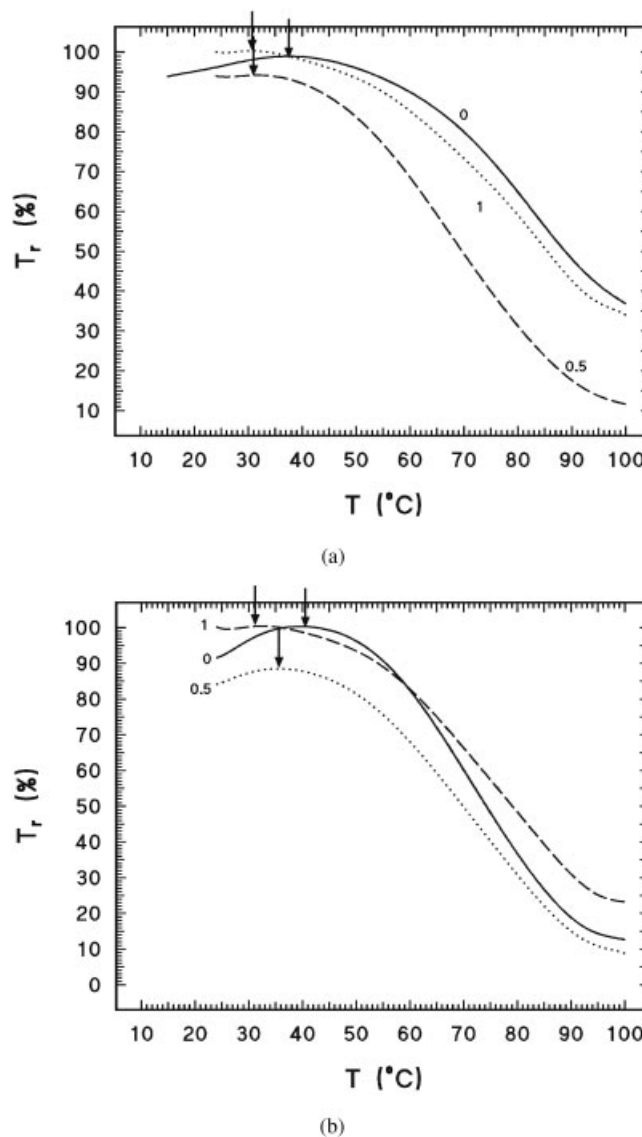


Figure 9 Transmittance versus temperature for M93 and MB80 blends at different % (0–0.5–1) of BDDM.

due to size of the dispersed particles, which, even though smaller than for the mechanical blend, are still higher than the light wavelength ($\lambda > 0.4 \mu\text{m}$), giving rise to a progressively increase of light diffusion scattering and hence to opacity.

For all the other blends, we performed just one experiment of heating, at a rate of 2°C/min. The corresponding curves are reported in Figures 9(a) and 9(b), where the arrows indicate the maxima of transparency, which are a function of the crosslinking agent concentration. The behavior of the crosslinked blends is very similar to that of uncrosslinked ones. It is interesting to note that the BDDM addition leads to a gradual shifting of the whole curve (and so of the maximum of transparency, also) towards lower temperatures, as a consequence of the higher density, which means higher refractive index too, of the crosslinked blends.

CONCLUSIONS

The reactive blending approach has been used to realize new acrylic glasses based on methacrylate polymers (either plain PMMA or its 20% copolymer with butylmethacrylate) and EVA rubbers with improved mechanical properties. The blends showed a typical multicore-shell morphology. The addition of a flexible dimethacrylate led to a semi-IPN structure, in which the acrylic phase formed discrete domains, while the continuous phase consisted of a thin film of EVA, as the occurrence of crosslinking hindered the phase-inversion process.

An EVA-g-PMMA graft copolymer was extracted by selective solvents, and its chemical structure was clearly determined through NMR spectroscopy. The formation of such interfacial agent during the reactive blending is responsible for the interesting morphological, mechanical, and optical properties of these materials.

The prepared blends and semi-IPN showed, in fact, a very interesting optical behavior, as they were transparent at room temperatures, while became opaque at higher T (about 50–60°C). Optical characterizations as a function of temperature showed that the T at which the transparent-to-opaque transition occurs was a function of the composition of the material. This effect was attributed to the complex morphology and to a matching of the refractive indices of the components,

as a consequence of the formation of an interfacial agent.

This peculiar behavior renders these materials attractive for several applications, as thermoselective glasses for rigid greenhouses coverings or as components in thermosensitive optical safety devices.

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