Gamma Radiation of EVA-AA/MMA Swollen Systems to Obtain Mechanically Improved Blends

G. Spadaro[1], C. Dispenza[1], A. M. Visco[2], A. Valenza[2]

[1] Dipartimento di Ingegneria Chimica dei Processi e dei Materiali University of Palermo, Viale delle Scienze, 90128 Palermo, Italy
[2] Dipartimento di Chimica Industriale e Ingegneria dei Materiali, University of Messina, Salita Sperone 31, 98166 S. Agata, Messina, Italy

Summary: In this work a "new" way to obtain "compatibilised" blends of rubber-glassy thermoplastic components is presented. Polyethylen-vinyl acetate acrylic acid terpolymer is swollen by methylmetacrylate and the system is irradiated through gamma rays in order to induce polymerisation of the monomer. Solubility and dynamic mechanical tests indicate the formation of a two phase system, even though in presence of strong interactions between the two components. Mechanical tensile behaviour is that of a ductile material with appreciable modulus values.

Introduction

Blending of elastomers with brittle termoplastics can be considered a way to produce "new" materials with improved mechanical behaviour. In designing these materials the main problems arise from their thermodinamic incompatibility, better performances can be obtained inducing interactions between the polymer components, giving rise to the formation of "compatibilised" blends. Several compatibilisation procedures are reported in literature [1-4].

It is known that the interaction of ionising radiation with matter causes the formation, through intermediate exited species, of neutral and charged free radicals, which can undergo to further evolution with significant modification of the final molecular structure of the irradiated material [5, 6].

In previous papers[7,8] the use of both gamma rays and elctron beam to produce polymethylmetacrylate-rubber "compatibilised" blends has been suggested. The rubber was dissolved in methylmetacrylate and the monomer was polymerised by

 CCC 1022-1360/00/$ 17.50+.50/0

ionising radiation. During polymerisation rubber phase separation occurred, and the presence of strong interactions between the two phases cuased significant improvement of some mechanical properties.

In this work a new way to improve the thoughness of polymethylmetacrylate or, in turn, the stiffness of a rubber, is presented. Methylmetacrylate is swollen in ethylen-vinyl acetate-acrylic acid terpolymer and polymerised through gamma rays. Solubility tests, mechanical tensile and dynamic thermal mechanical analysis show the presence of strong interactions between the two polymer components.

Experimental

Materials

- Methylmetacrylate (MMA) inhibited with 100 ppm of hydroquinone (Merck). MMA was freed from inhibitor by distillation under the pressure of 1 Pa at about 40°C.
- Ethylene-vinylacetate-acrylic acid terpolymer (EVA-AA), ELVAX 4355 by Dupont, containing the 25% of vinyl acetate and 0.8% of acrylic acid (MFI=6.0).

Sample preparation

Sheets of EVA-AA rubber were swollen in methylmethacrylate under vacuum for 24 h. Before irradiation samples were put in a cylindrical reactor without air and saturated with MMA vapors.

Irradiation was done in the I.G.S.-3, a panoramic ^{60}Co irradiator at the Nuclear Engineering Department of the University of Palermo, having an activity of about 1400 Ci. The absorbed doses were 8, 15, 30 and 60 KGy. After irradiation, the samples were kept under dynamic vacuum at 40°C until not polymerized MMA was totally eliminated. As a rule, during the time between irradiation and tests, all samples were kept at a temperature of about -18°C to inhibit further radical reactions.

Pure PMMA was obtained irradiating MMA, in absence of air, at the same total absorbed doses. Also pure EVA-AA samples were irradiated, under vacuum, at the same total doses.

MMA loading and insoluble fractions determination

MMA loading after gamma-rays polymerisation was determined by the weight difference of rubber sheets before MMA swelling and after irradiation. In order to extract loaded MMA, irradiated samples were subjected to soxhlet extraction using acetone as solvent, typical solvent for pure PMMA and non-solvent for pure EVA-AA. Solubility tests were done in soxhelet using toluene, which is solvent for both EVA-AA and PMMA copolymers. The extraction time was always about 48 hours.

Mechanical tests

Mechanical tensile tests were done by an Instron machine mod 1122. Compression moulded specimens with a gauge length of 4 cm were strained at a initial strain rate of 0.05 s^{-1}. Young modulus (E) and elongation at break (ε_b) were reported as average values for at least five samples.

Transparency tests

Trasmittance measurements, in the visible region, was performed with a Perkin-Elmer Lambda 2 UV/VIS Spectrophotometer.

Dynamic mechanical analysis

Dynamic-mechanical thermal analysis was performed, for all prepared blends and for pure omopolymers, through a DMTA by Rheometrics. The frequency was 31.4 Hz and the temperature range was between -60°C and 150°C. The heating rate was 1.5°C/min. A rectangular geometry was used (width 13 mm, length 15-25 mm, thickness 1 mm) at a strain amplitude of 0.2%.

Scanning electron microscopy

Micrographs were obtained using a Jeol-JSM 5600 LU Scanning Electron Microscope. The samples, fractured under liquid nitrogen, were coated with gold under vacuum to make them electrically conductive.

Results and Discussion

In Table 1 the weight percentage of MMA loaded in the rubber after irradiation is reported. It can be observed that the total absorbed irradiation dose does not affect significantly the loaded amount.

Table 1. Weight percentage of MMA loaded in the rubber after irradiation

Dose (KGy)	MMA in EVA-AA (wt %)
8	39
15	40
30	41
60	40

All irradiated samples were subjected to soxhlet extraction using acetone, typical solvent for PMMA and non-solvent for EVA-AA; the results are reported in Table 2. The experimental results indicate that almost all MMA loaded in the rubber though irradiation remains trapped in the matrix and this amount does not depend on the irradiation dose.

Table 2. Weight percentage of MMA not extracted from the rubber after irradiation

Dose (KGy)	MMA not extracted (wt %)
8	96
15	97
30	94
60	98

In Table 3 solubility data for blends and pure polymers subjected to similar irradiation procedures are reported. For blends large amounts of insoluble fractions are detected, while pure PMMA and rubber are completely soluble. It is noticeable that the total insoluble fractions are greater than the corresponding fractions relative to MMA component, reported in table 1, thus indicating the formation of a strongly interacting structure which hinders the solubility of the rubber component.

Table 3. Solubility data for blends and pure polymers

Dose (KGy)	EVA-AA (wt %)	PMMA (wt %)	EVA-AA+PMMA (wt %)
8	Soluble	Soluble	38
15	"	"	49
30	"	"	43
60	"	"	48

Mechanical tensile results for blends are reported in Table 4, together with data relative to pure unirradiated polymers. With respect to unirradiated rubber, all blends present a significant increase of elastic modulus, while even though in presence of a decrease of the elongation at break, the material maintains its ductile behaviour. Consequently a generalised significant increase of tensile strength, with respect to pure unirradiated rubber is also achieved. For the effect of the irradiation dose, the trend is a generalised, not dramatic, decrease of elongation at break and an increase of modulus and tensile strength with the dose until 30 kGy. The decrease of modulus value for the material irradiated at 60 kGy can be attributed to the incoming occurrence of degradation phenomena.

Table 4. Mechanical tensile results for blends and pure polymers

SAMPLE	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
EVA-AA unirradiated	18	9.5	875
EVA-AA+MMA 8 KGy	290	17.89	300
EVA-AA+MMA 15 KGy	332	19.43	275
EVA-AA+MMA 30 KGy	380	21	258
EVA-AA+MMA 60 KGy	243	19.63	217
PMMA unirradiated	1728	50.5	4

In fig. 1 the transmittance in the UV-visible wavelength range for blends and pure polymers is shown. It is worth to notice that the transparency of EVA-AA MMA blends is slightly lower than the corresponding values of pure PMMA, and significantly higher with respect to pure rubber.

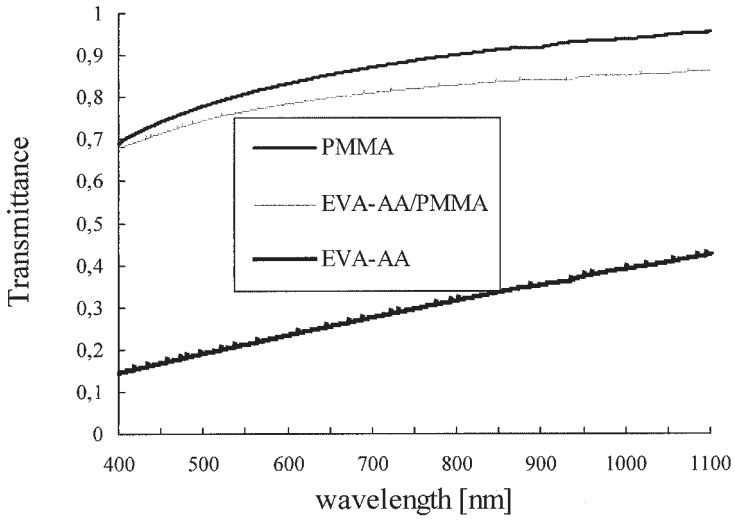

Fig. 1. Transmittance in the UV-visible wavelength range for the blend and pure polymers

Information about the blend structure have been obtained by dynamic mechanical analysis and scanning electron microscopy. In fig. 2 dissipation factor, tan δ, is reported as a function of temperature. Two relaxations can be clearly observed; indicating of the presence of two incompatible components. On the basis of the temperature values of both relaxation, we can hypotize that the polymer components are radiation modified EVA-AA rubber and polymethylmethacrylate formed by the irradiation of MMA monomer entrapped in the rubber. The presence of two distinct peaks is an indication of the absence of compatibilization phenomena; but if we compare the transition temperatures of both components with the pure corresponding polymers, see fig. 3, we can observe the presence of interactions that affect each other. In fact glass transition of both rubber and

PMMA components increases with respect to pure polymers, further indication of the presence of strong interactions between the two components.

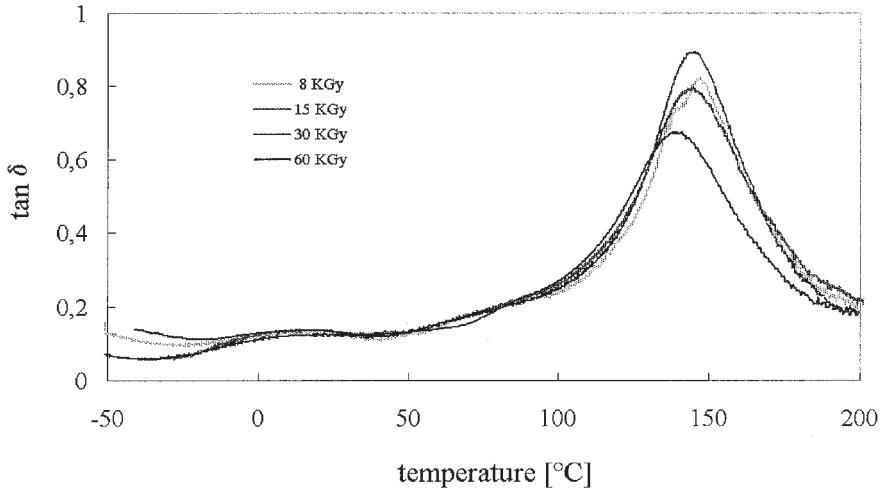

Fig. 2. Dissipation factor, tan δ, versus temperature.

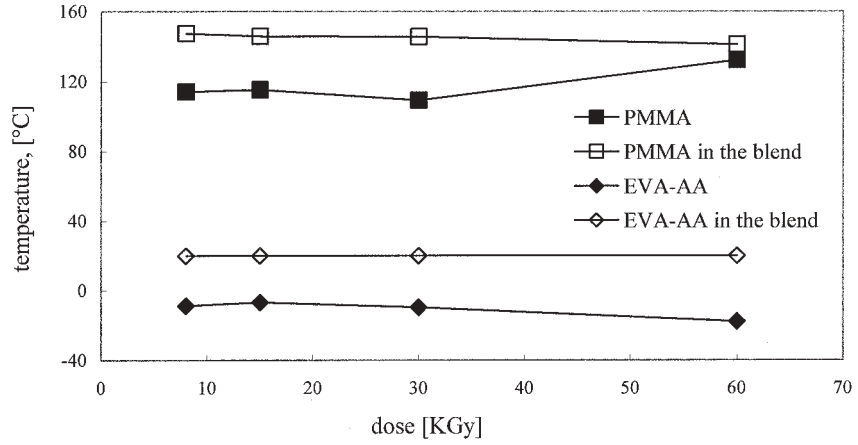

Fig. 3. Transition temperatures of both blend components and of the pure polymers versus the dose.

All these results are well in agreement with morphologycal analysis, shown by micrographs in fig. 4a-b, where scanning electron microscopy of just fractured and formic acid etched surfaces of EVA-AA/MMA blend is reported. Not etched surface does not allow to distinguish the presence of separated phases, while etching evidences the presence of very small voids indication of a very distributed PMMA phase inside the rubber matrix.

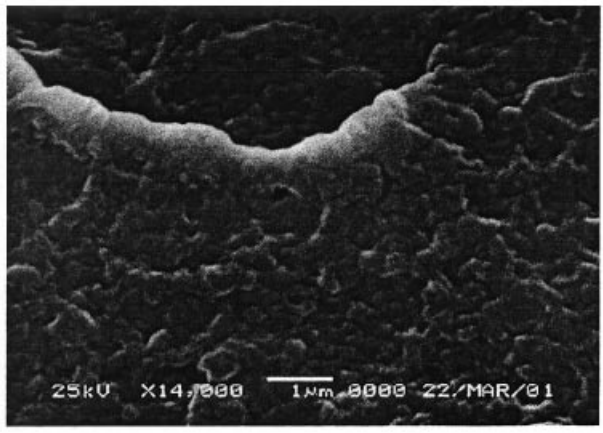

Fig. 4a. SEM micrographs of just fractured of EVA-AA/MMA blend.

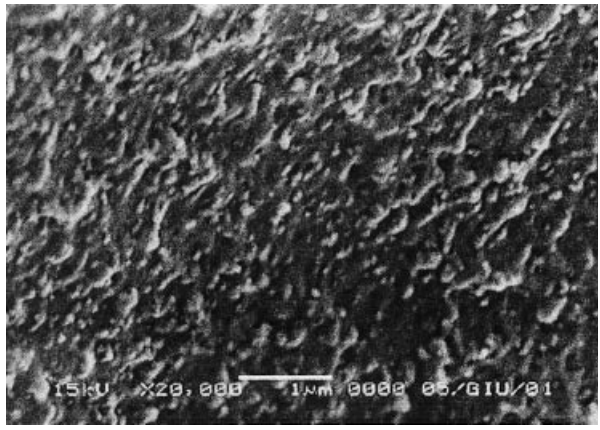

Fig. 4b. SEM micrographs of formic acid etched surfaces of EVA-AA/MMA blend.

Conclusions

In this work EVA-AA based blends are obtained through gamma radiation of MMA swollen rubber matrices. The aim is to obtain a strongly "compatibilised" system favouring the interaction of polymerising MMA with rubber.

Solubility tests indicate that the irradiated rubber-MMA swollen systems have significant insoluble fractions, despite the complete solubility of both pure polymers subjected to the same irradiation procedures. Mechanical tensile results are in between the properties of EVA-AA and PMMA polymers, with a good ductility even though in presence of significant increase of modulus value, with respect to rubber. Dynamic mechanical behaviour are typical of incompatible systems with two distinct relaxation for both components; however the temperature values indicate the presence of strong interactions between the two components, in line with solubility and mechanical behaviour.

Acknowledgement

This work has been financially supported by the CNR grant n 99.01205.CT03

[1] Z. Oommen, G. Groeninckx, S. Thomas, *Journal of Polymer Science Part B: Polym. Phy.* **2000**, 38, 525
[2] M. Akay, S.N. Rollins, *Polymer*, **1993**, 34, 1865
[3] V. Mishra, F.E. Du Prez, E.J. Goethals, L.H. Sperling, *J. Appl. Pol. Sci.* **1999**, 58, 347
[4] P. M. Remiro, C. C. Riccardi, M. A. Corcuera, I. Mondragon, *J. Appl. Pol. Sci.*, **1999**, 74, 772
[5] D. W. Clegg, A. A. Collyer "*Irradiation Effects on Polymer*" Elsevier, London 1991
[6] J. W. T. Spinks, R. J. Woods "*Introduction to radiation Chemistry*" John Wiley, New York 1990
[7] C. Cangialosi, C. Lindsay, P. T. McGrail, G. Spadaro, *European Polymer Journal*, **2001**, 37, 535
[8] D. Cangialosi, P. Fuochi, M. Lavalle, P.T. McGrail, G. Emmerson, G. Spadaro *Radiat. Phys. Chem*, in press.