

Recycling of Inside Upholstery of End-of-Life Cars

A. Correnti,¹ M. Bocchino,² S. Filippi,² P. L. Magagnini,² G. Polacco,² F. P. La Mantia¹

¹Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, University of Palermo, viale delle Scienze, 90128 Palermo, Italy

²Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, University of Pisa, via Diotisalvi, 2, 56126 Pisa, Italy

Received 19 April 2004; accepted 4 August 2004

DOI 10.1002/app.21638

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A model study for the recycling of the interior upholstery plastic parts of end-of-life cars has been carried out by reprocessing the homogenized scraps of an upholstery farm in the presence of different compatibilizer precursors, such as an ethylene-glycidylmethacrylate copolymer (EGMA), a maleic anhydride functionalized thermoplastic elastomer (SEBS-MA), etc. The investigated scraps contained recycled polyethylene (from agricultural uses) and poly(ethylene terephthalate), as the main components, plus minor proportions of polypropylene, polyamide-6, and other additives, including an ethylene copolymer (EC), probably an ethylene-acrylic acid copolymer, which is used to compatibilize the carpets' backing and increase their flexibility. The reactive blending experiments were carried out using a Brabender Plasticorder static mixer and a Brabender twin-screw compounder, and the products were characterized by rheometry, differential scanning calorimetry, scan-

ning electron microscopy, stress-strain measurements, etc. It was shown that EGMA was most effective for the reactive compatibilization of the polyolefin and poly(ethylene terephthalate) components of the scraps. It was also found, however, that the EC contained in the upholstery backing neutralizes in part the functional epoxy groups of EGMA, thus reducing its compatibilizing efficiency. The results suggest that substitution of EC with an inert flexibilizing agent, such as an ethylene-propylene copolymer, and use of small amounts (~ 5%) of an EGMA compatibilizer, might allow recycling of used upholstery into injection moldable plastic articles. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1716–1728, 2005

Key words: recycling; compatibilization; reactive processing; morphology; mechanical properties

INTRODUCTION

The automobile industry is presently facing the challenging problem of devising economically viable routes for recycling the plastic components of end-of-life cars.^{1,2} This practice might perhaps be expected to be relatively less troublesome than that of recycling the plastic materials from other industry or civil wastes, because car components are probably easier to collect and select.² It should be considered, however, that many of these articles are made up of more than one polymeric material, and that the same components of different makes of cars may have quite different composition. Thus, very often, designing a reprocessing strategy for postconsumer car components involves solving the problems connected with the incompatibility of the polymers they are made of. This is particularly so for the end-of-life car upholstery, including carpets, mats, hood and trunk linings, etc. In fact, though some new monomaterial (polyester) products are being put on the market, most of the

articles presently in circulation are multimaterial systems made up of a plastic layer (backing) carrying an upper fiber mat. These two components are generally coupled by direct extrusion of a molten polyolefin-based layer onto the polyester (PET) or polyamide (PA) mat and, therefore, they cannot be recycled separately. On the other hand, the backing itself is commonly a polymer blend, made up of a low-density polyethylene (LDPE) grade to which other polymers, such as high-density polyethylene (HDPE), polypropylene (PP), or ethylene copolymers (EPR, EVA, etc.), may be added, for example, to confer the appropriate rigidity or flexibility to the product. Moreover, very often, the backing composition also includes some PET and/or PA, because the remnants of the operation by which the upholstery articles are cut out of the bilayer ribbon coming from the extruder are normally minced and fed back to it, together with the polyolefin pellets. Thus, end-of-life car upholstery articles are complex mixtures of polymers and polymer blends containing LDPE and PET (or, less frequently, PA), as the main components, and minor proportions of a large number of different polymers that are used as modifiers, compatibilizers, processing aids, etc.

The compatibilization of blends of polyolefins, especially PE and PP, with condensation polymers, es-

Correspondence to: F. P. La Mantia (lamantia@dicpm.unipa.it).

pecially PET,³⁻⁸ PBT,^{9,10} and polyamides (PA6 or PA66),^{9,11-25} has been studied extensively during the last decades, and a great variety of polymeric compatibilizers, either preformed or produced *in situ* by a reactive processing procedure involving the use of appropriate compatibilizer precursors (CPs), have been employed and their effectiveness has been discussed. Particular attention has been devoted to the investigation of the CP efficiency of different functionalized polyethylenes, polypropylenes, and thermoplastic elastomers. The functional groups of these CPs, such as the anhydride, oxazoline, and epoxide rings or the free carboxyl groups, etc., have been shown to react, during blending, with the end groups, or the inner bonds, of the polar polymers to produce block or graft copolymers that migrate to the blend interface, lower the interfacial tension, and enhance the adhesion between the phases. In particular, the polyolefins and the polystyrene-*block*-poly(ethylene-*stat*-butylene)-*block*-polystyrene copolymers (SEBS), modified by grafting with maleic anhydride (MA),^{11,13} have been found to be particularly efficient for polyolefin/polyamide blends, whereas those grafted with glycidylmethacrylate (GMA) have shown good compatibilizing effectiveness especially for polyolefin/polyester blends.^{3-7,12} However, these literature results, which were generally obtained from compatibilization experiments carried out on blends of pure polymers, cannot be applied directly to the case of such complex polymer mixtures as those composing the car upholstery articles because some of the minor components of the latter mixtures might adversely interact with the employed CPs, thus reducing severely their effectiveness.

In this article, we describe the results of an investigation in which commercial samples of new car upholstery articles or their cutting remnants were melt blended in the presence of different compatibilizer precursors (CPs) to model a possible recycling procedure for similar postconsumer articles to produce plastic objects, either mat backings or something else, for use in the automobile industry.

EXPERIMENTAL

Materials

The main material used in this work consisted of pellets prepared from the scraps of the upholstery articles produced by ROI, Automotive Technology s.r.l., Italy.

Four samples of different lots of scrap pellets were provided by ROI and were analyzed separately. Successively, as their composition and characteristics were found not to differ considerably, the four samples were dry blended so as to avail a sufficient amount of material (about 50 Kg), referred to in the

following as SCR, which was used for our investigation.

Other materials employed in this work, all provided by ROI, Automotive Technology s.r.l., were:

1. A sample of recycled PE (from agricultural films), referred to herein as R-PE.
2. A sample of an ethylene copolymer of unknown composition, used together with R-PE for the backing extrusion, referred to as EC.
3. Several cuts of PET and PA fiber mats.
4. Several samples of upholstery articles of different types.

Commercial samples of LDPE, LLDPE, HDPE, i-PP, PET, and PA6 were also used for the production of model blends and for comparative analytical determinations.

The compatibilizer precursors (CPs) used in this work were:

1. Escor 5001 (Exxon-Mobil Chemical Mediterranean), referred to as EAA: an ethylene-acrylic acid copolymer with 6.2 wt % acrylic acid (AA) and melt flow index (MFI) = 2.0 g/10 min (190°C/2.16 Kg).
2. Iotek 4200 (Exxon-Mobil Chemical Mediterranean), referred to as IOT: an ethylene-AA copolymer partially neutralized with zinc, with MFI = 3.0 g/10 min (190°C/2.16 Kg). IOT was analyzed as described elsewhere²³; the content of AA was found to be 6.7 wt % and the degree of neutralization about 20%.
3. Lotader GMA AX8840 (Elf-Atochem), referred to as EGMA: an ethylene-glycidylmethacrylate copolymer with 8 wt % GMA and MFI = 5.0 g/10 min (190°C/2.16 Kg).
4. Kraton FG 1901X (Kraton Polymers), referred to as SEBS-MA: a polystyrene-*block*-poly(ethylene-*stat*-butylene)-*block*-polystyrene copolymer with 28 wt % styrene, functionalized with 1.7 wt % MA.
5. Polybond 3009 (Uniroyal Chemical), referred to as PE-MA: an HDPE functionalized with 1.0 wt % MA, with a density of 950 Kg m⁻³ and MFI = 5.0 g/10 min (190°C/2.16 Kg).

Irganox B 215 and Irganox HP 2215, antioxidant blends by Ciba Specialty Chemicals, or Sandostab P-EPQ, a phosphorous based antioxidant processing stabilizer by Clariant, were also occasionally used for the blend preparations.

Common chemicals and solvents were Aldrich products.

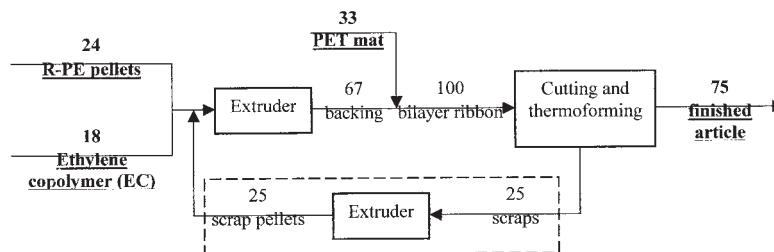


Figure 1 Typical flow sheet of the production of an upholstery bilayer mat by ROI Automotive Technology s.r.l., Italy.

Procedures

The composition of the scrap samples was determined as follows: A weighed sample of the pellets was cooled in liquid nitrogen and powdered in a Fritsch “pulverisette 14” mill operating at 8000 rpm. It was then treated with boiling cresol for 5 h to dissolve the condensation polymers. The cooled suspension was separated with a sintered glass filter and the residue was carefully washed on the filter with fresh cresol, dried, weighed, and analyzed by differential scanning calorimetry (DSC). The cresol solution was poured into excess methanol, and the resulting fine suspension was centrifuged; the clear supernatant solution was separated and replaced with fresh methanol and the operation was repeated 10 times; the solid powder was finally separated by centrifugation, dried, weighed, transformed in a thin film with a laboratory press at 270°C and 4 bar, and analyzed by FTIR spectroscopy. The cresol soluble fraction was also treated with formic acid with the aim of dissolving and separating the PA from the PET. However, this attempt failed both because the concentration of PA was too small and because the solid PET particles were too fine to be reliably separated from the formic acid solution. The concentration of PA was roughly estimated through elemental analysis and FTIR spectroscopy.

The blends were prepared under nitrogen either with a Brabender Plasticorder internal mixer, at $T = 270^\circ\text{C}$, speed = 50 rpm, and $t = 8$ min, or with a Brabender twin-screw compounder, using a temperature profile of 180–270–270°C.

Before processing, the polymers were dried under vacuum for at least 12 h at 80°C and 2 h at 110°C, unless otherwise stated.

The DSC measurements were carried out under nitrogen, on samples of 5–8 mg, using a Pyris Perkin–Elmer apparatus calibrated with indium and tin standards. The scanning rate was 10 K min^{-1} .

Scanning electron microscopic analyses (SEM) were made with a Jeol JSM-5600 apparatus on specimens fractured under liquid nitrogen and coated with gold. In some cases, the cryofractured samples were treated with selective solvents before being observed by SEM. In particular, a prolonged (about 15 h) treatment with warm (about 100°C) cresol was used to dissolve the

PET phase. The use of higher temperatures (and shorter times) led to softening of the polyolefin phase and to modification of its morphology. Boiling toluene was used to extract the polyolefin.

The tensile properties were determined with an Instron universal testing machine, mod. 4443, on specimens ~ 2 mm thick and 10 mm wide, prepared by compression molding with a Carver laboratory press. The crosshead speed was 5 mm min^{-1} and the initial length was 30 mm.

RESULTS AND DISCUSSION

Characterization of the upholstery scraps and of their components

In the commercial practice, the scraps left after cutting out the different upholstery articles from the appropriate bilayer mats are stored and sent to another farm of the group, where they are extruded and pelletized. This procedure allows limiting the scraps’ composition differences resulting from the different production cycles adopted at any time. Actually, depending on the type of product needed, a PA, rather than PET, fiber can be used for the exterior mat, and HDPE or PP, rather than an ethylene copolymer, may be employed together with LDPE as the main backing components. Thus, the average composition of the scrap pellets is expected to include varying amounts of a great number of components, although LDPE and PET are normally predominant in the ROI production. The scrap pellets are then commingled in appropriate proportions with those of the polyolefin and the additive, and sent to the backing extrusion.

The scheme in Figure 1 illustrates an example of a typical flow sheet adopted for the production of a particular bilayer mat. The numbers represent the approximate amounts of the different materials with respect to 100 parts of extruded bilayer ribbon. If the above flow sheet is taken as representative of an ideally continuous production process, a simple mass balance demonstrates that the scraps’ composition would be: PET ≈ 44 wt %, R-PE ≈ 32 wt %, and EC ≈ 24 wt %. Notice that the average amount of scraps actually rerun to the backing production is of the order of 25%. This is probably not far from the maxi-

TABLE I
Composition of the Scrap Pellets (wt %)

Component material	Polyethylene phase (PE + E copolymer)			
	PP	PET	PA	
Scrap sample 1	53.2	1.7	44.3	0.8
Scrap sample 2	50.6	2.9	46.5	0.2
Scrap sample 3	51.1	2.4	45.9	0.6
Scrap sample 4	51.7	2.6	44.1	1.6
Dry blend-SCR	51.5	2.5	44.8	1.2

mum amount that, on condition that a sufficient proportion of a compatibilizing additive is employed, can be tolerated in the backing composition without impairing its properties unacceptably. Thus, a recycling of plastic upholstery of end-of-life cars involving its use as an additional component of the backing composition is only conceivable in the hypothesis that the amount of material to be recycled is very small. More realistic appears a recycling procedure by which the postconsumer car upholstery is employed, in the automotive industry itself, for the production of other plastic parts for which fairly modest mechanical characteristics, coupled with sufficient impact strength, may be acceptable.

As already stated, we used the upholstery scraps as a model for end-of-life upholstery. The composition of the four lots of scrap pellets provided by ROI, determined as described in the experimental section, is reported in Table I, together with that (calculated) of their dry blend (SCR), which was used as a raw material in this work.

Typical DSC cooling and second heating scans of SCR, R-PE, and EC are shown in Figure 2. The heating traces of both SCR and R-PE show a weak endotherm in the temperature region close to 160°C, which can be attributed to the presence of small amounts of PP. Some PP is, therefore, already present as a minor phase in the R-PE. That the latter is not a single-phase material is confirmed by the SEM micrograph shown in Figure 3. The enthalpy change associated with the fusion of the PP phase is slightly higher for the SCR sample, and this suggests that part of the PP contained in the latter material comes from carpet scraps with polypropylene backing. The crystallization of the PP phase is affected by considerable undercooling, and the relevant exothermic peak is masked by the much stronger one connected with the crystallization of the polyethylene phase in the cooling scans of both SCR and R-PE.

The twin peak endotherm in the 250°C region of the heating scan of SCR and the exothermic peak at about 215°C in the relevant cooling trace are due to the fusion and crystallization of the PET phase. The first order transitions associated with the very small amounts of PA revealed by elemental analysis and FTIR spectroscopy are not visible in the DSC scans.

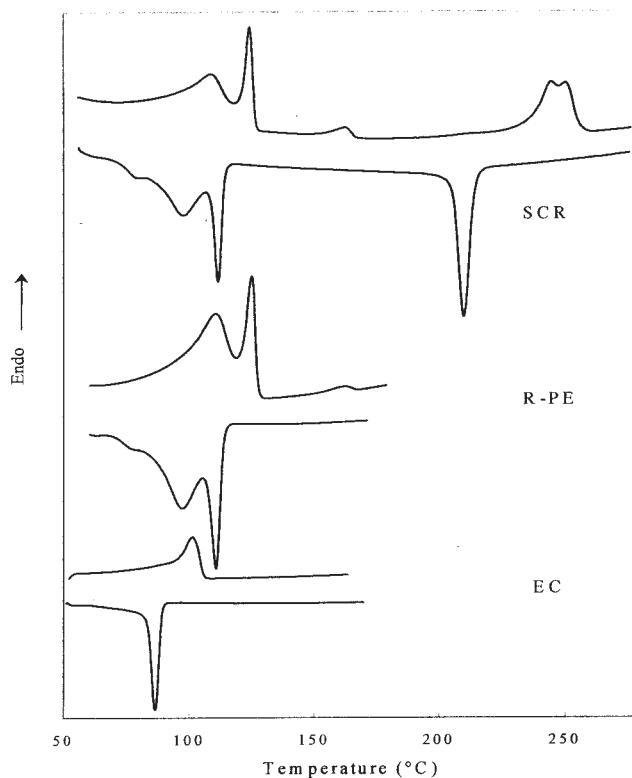


Figure 2 DSC second heating and cooling scans of SCR, R-PE, and EC.

The endothermic/exothermic multiple peaks seen in the 80–130°C region in the thermograms of SCR are very similar to those present in the DSC traces of R-PE. They can be associated with the fusion/crystallization of the different PE grades contained in this recycled material. From the thermograms of SCR and R-PE, it was found that the ratio of the enthalpy changes associated with the lower temperature broad peaks and the higher temperature sharp ones ascribed to the polyethylene phase is somewhat higher for SCR. This suggests that the EC, which is contained in the SCR

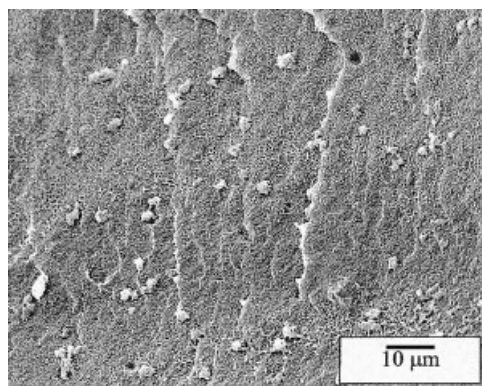


Figure 3 SEM micrograph of the fracture surface of an R-PE pellet.

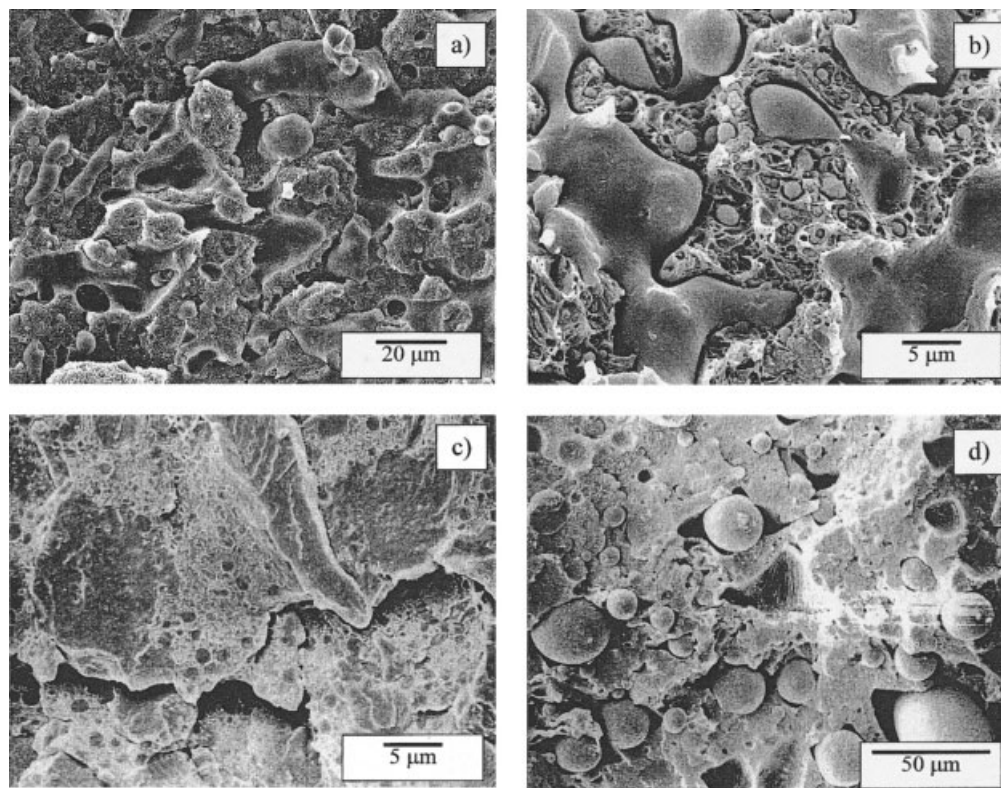


Figure 4 SEM micrographs of the fracture surfaces of: a) and b) as received SCR; c) Brabender kneaded SCR; d) 72/28 SCR/R-PE blend.

blend, is probably miscible with the LDPE phase, which is responsible for the lower temperature peaks. On the other hand, this assumption is consistent with the DSC response of pure EC, shown in Figure 2.

The different pelletized scrap samples provided by ROI were found to have rather coarse biphasic morphology. A representative example is illustrated by the SEM micrographs shown in Figures 4a and b. The morphology is typical for a biphasic system with a composition close to phase inversion, and this might be expected on the basis of the analytical data in Table I. The PET phase consists of very large, quasi-continuous domains of irregular shape, and of smaller (about 0.1–3.0 μm) spherical droplets dispersed within the polyolefin phase. The interfacial adhesion is extremely poor. A micrograph taken on the same SCR sample, after further kneading in the Brabender mixer (Fig. 4c), was found to have rather different aspect, thus indicating that the morphology of this material is highly unstable and strongly dependent on the thermomechanical history (shear rate during the melt processing, cooling rate, etc.). On the other hand, prolonged high temperature annealing was shown to induce important coalescence and phase separation effects. In the particular case of the micrograph shown in Figure 4c, the interfacial adhesion appeared to be quite good, probably because the material had been cooled slowly and under no shear from the melt, and

it was even difficult to distinguish the two phases from each other. The latter problem became particularly important when compatibilized SCR samples had to be analyzed. For this reason, the subsequent studies on the effect of SCR compatibilization were carried out using SEM micrographs taken on cryofractured samples, after dissolution of one of the phases with selective solvents.

The micrograph in Figure 4d was taken on a sample that was prepared in the Brabender mixer by blending appropriate amounts of SCR and R-PE (72/28 wt/wt) so as to increase the polyolefin content to about 65 wt %. It is apparent that the PET is now well dispersed within the polyolefin matrix as spherical or slightly elongated droplets with diameters ranging from ~ 0.1 to ~ 100 μm. Here also, the interfacial adhesion appears to be very poor.

Compatibilization of the upholstery scraps

The effect of the addition of the different CPs to SCR was studied by a number of techniques, as indicated in the experimental section. It was decided to start this investigation by using fairly high concentrations of the CPs, to be able to record any macroscopic difference in their behavior. In Figure 5, the plots of the torque applied to the Brabender rotors while blending SCR with 10 phr of the different CPs are shown. During the

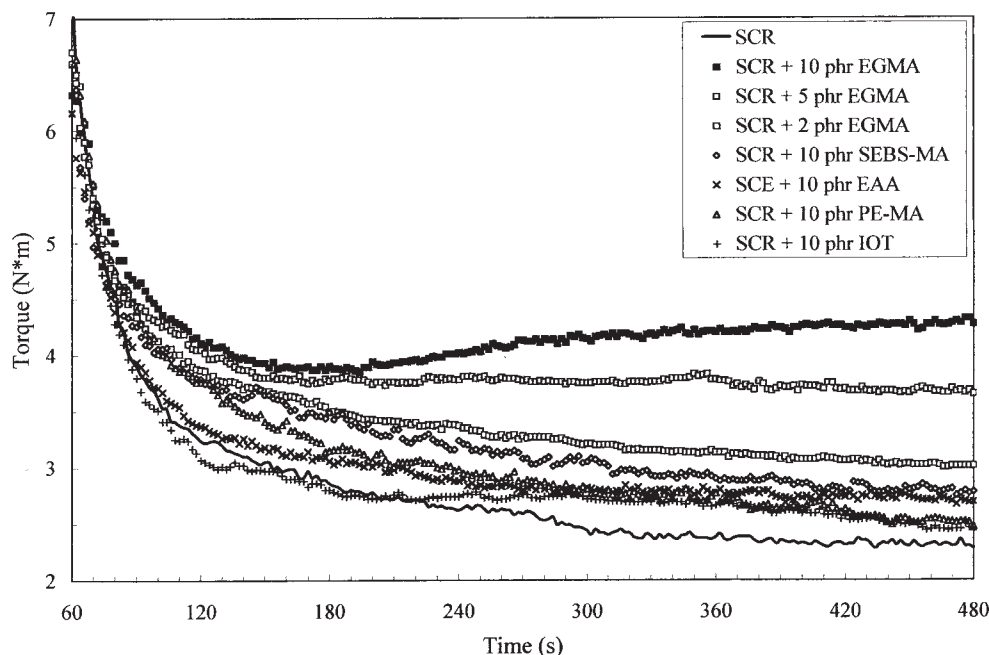


Figure 5 Brabender torque versus time curves recorded while kneading SCR and the blends of SCR with different CPs.

first two minutes of kneading, after addition of the polymer pellets into the Brabender mixing bowl, the torque goes through a maximum and then tends to decrease down to a fairly constant value, as the pellets melt and the selected temperature is again approached. The plots in Figure 5 demonstrate that the addition of all the CPs except EGMA into SCR fails to change the shape of the torque/time curve dramatically, although a modest increase of the final torque is observed for all of them. The behavior of EGMA is quite different. In fact, with this CP, a progressive departure of the torque/time curve toward higher torque values can be observed during the whole mixing period investigated. An increase of viscosity of a molten blend is generally considered as an indication that chemical interactions are occurring among the blend components. In this case, a clear viscosity in-

crease is only observed when EGMA is added into the SCR melt, and this may be considered as an indirect, yet definite, evidence that the chemical reactions taking place in the system involve the epoxy groups of this CP.

The effect of changes of the EGMA concentration, within the range 0–10 phr, on the torque/time curves recorded while blending SCR with this CP is also illustrated in Figure 5. This confirms that an increase of the amount of added EGMA leads to a larger increase of the viscosity of molten SCR.

The results of the calorimetric analysis of the products of the attempted compatibilization of the SCR blend by addition of the different CPs are collected in Table II. It should be pointed out that the CPs used in this work, unless they are amorphous as SEBS-MA, are characterized, in the pure state, by first order transitions appear-

TABLE II
Thermal Properties of the Scrap Pellets Without and With Different CPs

Material (CP phr)	PE + EC phase						PP phase		PET phase			
	T _c ¹ (°C)	T _c ² (°C)	ΔH _c (cal/g)	T _m ¹ (°C)	T _m ² (°C)	ΔH _m (cal/g)	T _m (°C)	ΔH _m (cal/g)	T _c (°C)	ΔH _c (cal/g)	T _m (°C)	ΔH _m (cal/g)
SCR	99.0	112.8	20.9	108.2	123.9	22.9	162.4	25.0	211.4	10.8	250.5	10.3
SCR + EAA (10)	98.6	111.2	19.5	101.1	123.7	22.1	162.2	23.8	210.8	10.6	250.6	10.6
SCR + IOT (10)	96.7	111.1	18.6	110.3	125.0	20.9	163.2	24.3	210.2	11.2	251.8	10.6
SCR + SEBS – MA (10)	97.9	111.4	16.3	108.6	124.1	18.1	162.6	23.3	212.1	10.3	250.7	10.4
SCR + PE – MA (10)	98.0	113.5	25.2	108.6	125.6	26.4	163.0	25.3	212.7	10.9	248.9	11.0
SCR + EGMA (2)	96.8	111.0	22.1	107.9	123.6	22.2	162.1	23.8	210.7	10.2	250.1	10.6
SCR + EGMA (5)	95.7	109.1	22.1	108.0	124.1	21.7	162.9	23.7	208.8	10.0	250.5	10.6
SCR + EGMA (10)	96.6	110.0	19.0	107.2	123.3	21.8	162.3	26.6	205.2	6.8	250.4	9.6

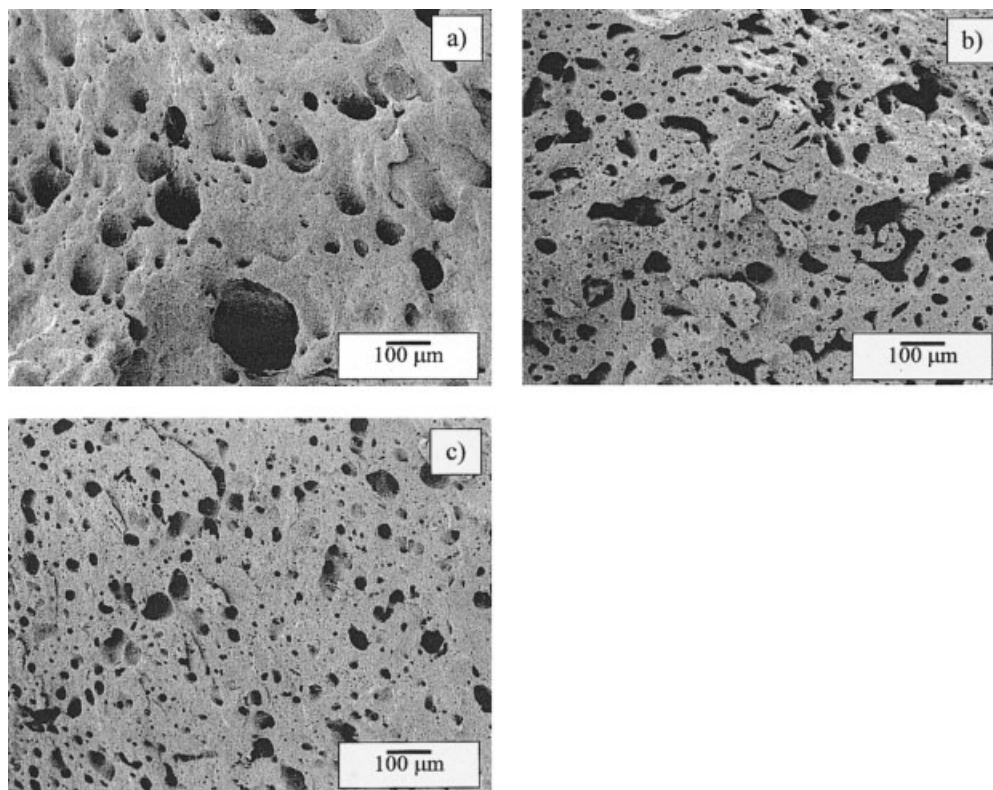


Figure 6 SEM micrographs of the fracture surfaces, etched with warm cresol, of: a) SCR; b) SCR + 2 phr EGMA; c) SCR + 5 phr EGMA.

ing in the same temperature region of the transitions of the LDPE and HDPE components of SCR. Moreover, independent of this, they are expected to be miscible or, at least, physically compatible with the polyolefin phase. Thus, small alterations of the temperatures and/or of the enthalpy changes of the DSC peaks associated with this phase should not be considered as a definite proof of a compatibilizing efficiency of these CPs. On the contrary, as their effectiveness is expected to rest on their ability to chemically interact with the PET functional groups and to produce CP-g-PET copolymers, any change of the thermal behavior of the PET phase, if any, would certainly be more meaningful. The data in Table II demonstrate that the addition of increasing amounts of EGMA into SCR does actually cause a progressive lowering of the PET crystallization temperature and enthalpy. Thus, the results of the calorimetric analysis are in agreement with the conclusion drawn from the preliminary rheological investigation, that EGMA appears to be the best candidate for the compatibilization of SCR. Such a conclusion, on the other hand, finds strong support in a number of papers available in the scientific literature,³⁻⁷ confirming that, for blends comprising a polyolefin and a polyester, the compounds containing epoxy functional groups display the best CP effectiveness. For this reason, in the prosecution of the present study, we focused our attention on EGMA and used the other CPs only for occasional comparative experiments.

The morphological analysis of the SCR/EGMA blends with 2 and 5 phr EGMA was carried out on cryofractured samples that were preliminarily etched with warm cresol to dissolve the PET phase. The relevant micrographs are shown in Figure 6, together with that of an SCR sample with the same history (kneading in the Brabender mixer and treatment with warm cresol). The effect of compatibilization is clearly manifested by the reduction of the average size of the holes left by the PET dissolution. Even more important, a strong increase of the population of the small PET droplets is observed already for a CP concentration of 2 phr. However, the morphology of both compatibilized blends is still very coarse, and a comparison of the present results with those found by others³⁻⁷ for the compatibilization of blends of PET (or recycled PET) and HDPE (or recycled polyethylene) with EGMA demonstrates that the effectiveness of this copolymer is considerably lower when it is used as a CP for SCR.

The mechanical characterization of the SCR/CP blends confirmed that the compatibilization achieved by addition of 5 phr of any of the investigated CPs, including EGMA, is rather modest. The blends were prepared both without and with accurate predrying of the components and/or with the occasional use of the antioxidant additives Irganox B 215, Irganox HP 2215, or P-EPQ. Some of the results of the mechanical characterization are shown in Table III. It can be observed

TABLE III
Mechanical Properties of Some SCR/CP Blends

Material (CP phr and/or additive phr)	State	TS _{max} (MPa)	ε _{max} (%)	TS _B (MPa)	ε _B (%)	E (MPa)
SCR	Humid	4.0	2.4	3.4	3.2	250
	Dry	4.2	2.4	3.6	3.0	261
SCR + P-EPQ (0.2)	Humid	5.0	2.9	4.6	3.4	273
	Dry	4.9	3.3	4.3	4.2	242
SCR + SEBS-MA (5)	Humid	6.0	5.7	5.9	5.8	216
	Dry	7.2	7.0	6.5	7.7	252
SCR + SEBS-MA + P-EPQ (5/0.2)	Humid	6.4	6.9	6.2	6.9	230
	Dry	6.7	7.5	6.7	7.5	221
SCR + EGMA (5)	Humid	8.0	5.8	7.7	6.2	266
	Dry	9.2	4.6	9.1	4.6	291
SCR + EGMA + P-EPQ (5/0.2)	Humid	7.4	6.6	7.3	6.6	245
	Dry	9.4	7.2	9.1	7.3	290

that: (1) the tensile strength and the elongation at break of the samples is almost doubled as a result of compatibilization; (2) the elastomeric CP (SEBS-MA) causes (expectedly) a slight reduction of the elastic modulus; (3) the predrying treatment leads to an increase of both modulus and strength, whereas its effect on the elongation at break is practically none; and (4) the effect of the antioxidant additives is negligible. Although the effect of the CP addition may appear appreciable on a relative ground, the absolute values of the mechanical properties, particularly the elongation at break, demonstrate that the compatibilized blends are still too weak and brittle. Again, a comparison with the results found by others³⁻⁷ for PET/HDPE or PET/PP blends compatibilized with EGMA seems to indicate that this CP is considerably less effective when used with SCR.

Compatibilization of model blends miming the scraps composition

The above conclusions led us to speculate that some of the minor components of SCR might interact with the epoxy groups of EGMA and neutralize them. Quite obviously, the search for the disturbing component started from EC. In fact, the FTIR spectrum of this material (Fig. 7) was found to contain the typical absorbance signals ascribable to the presence of free carboxyl groups, and it is known that these groups can react with the epoxy rings of EGMA. To prove this, we prepared a number of EGMA/EC blends with various compositions, at 200°C and 50 rpm, and recorded the torque applied to the Brabender rotors during blending. Examples of the torque versus time curves are shown in Figure 8 for three of these blends. As usual,

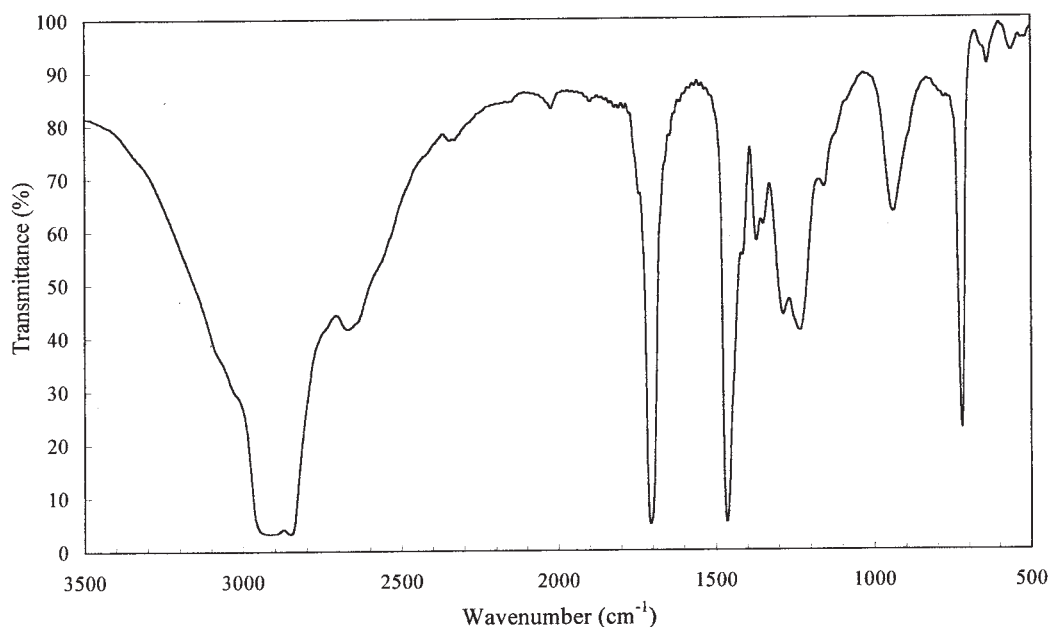


Figure 7 FTIR spectrum of EC.

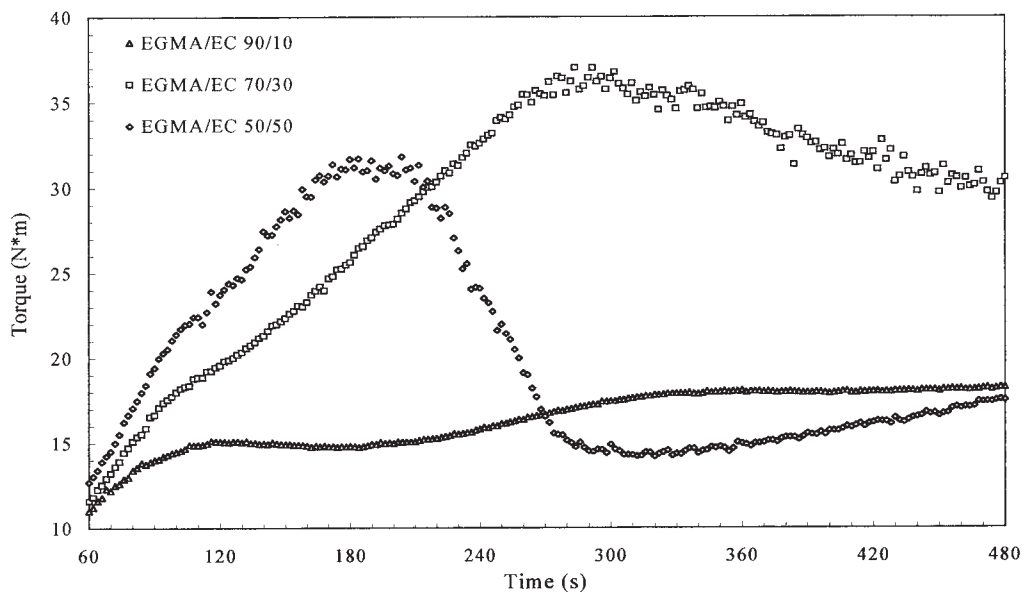


Figure 8 Brabender torque versus time curves recorded for the 90/10, 70/30, and 50/50 EGMA/EC blends.

the initial part of the curves, not shown, is characterized by a rapid decrease of the torque resulting from the fusion of the polymer pellets. Thereafter, in the absence of chemical reactions, the torque would be expected to reach a stationary value corresponding to the viscosity of the molten mixture.

For all the EGMA/EC blends studied, on the contrary, the torque reached a minimum value of about 10 N m in 40–50 s and then started growing. The torque increase was particularly strong and rapid for the 70/30 and 50/50 blends and was then followed by a more or less rapid decrease. At the end of the blend-

ing period, the blends were extracted from the mixer and were found to consist of an incoherent aggregate of gel-like granules. It could be concluded, therefore, that the increase of torque recorded during blending is due to the chemical reactions between the carboxyl groups of EC and the epoxy rings of EGMA, whereas its subsequent decrease can be ascribed to cohesive failure and granulation of the gel-like, crosslinked mass produced by these reactions. Thus, the EC, which is used as one of the backing components either to improve the flexibility and to help compatibilize the R-PE with the scraps, does in fact adversely interact

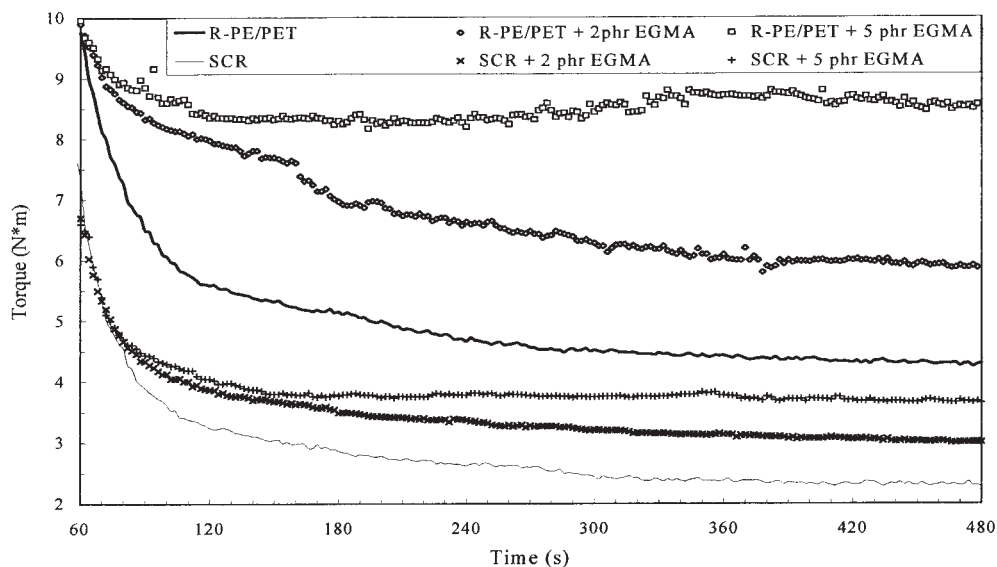


Figure 9 Brabender torque versus time curves recorded while kneading SCR or the 55/45 R-PE/PET blend, with 0, 2, and 5 phr EGMA.

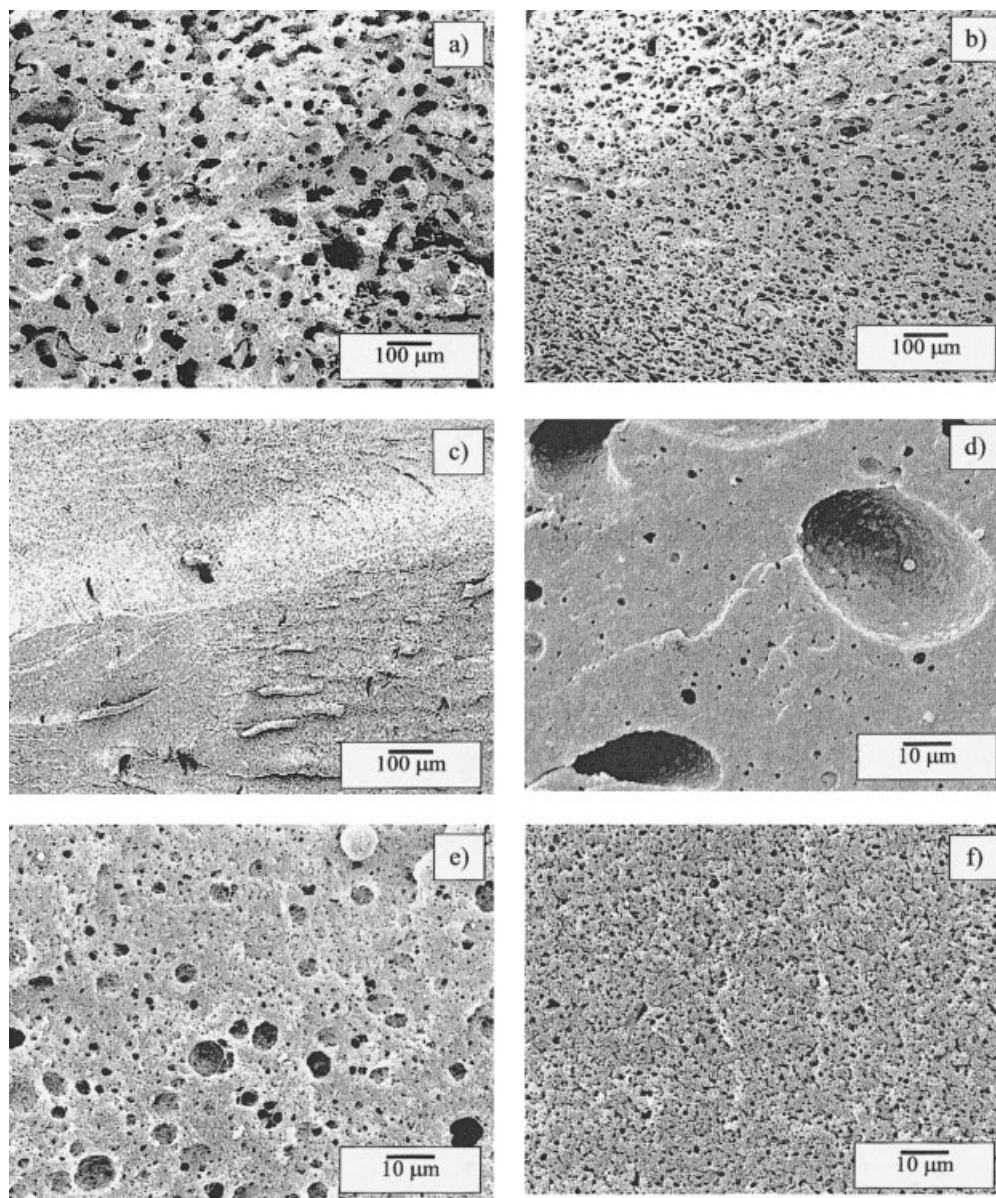


Figure 10 SEM micrographs of the fracture surfaces, etched with warm cresol, of: a) and d) 55/45 R-PE/PET; b) 55/45 R-PE/PET + 5 phr EC; c) and f) 55/45 R-PE/PET + 5 phr EGMA; e) 55/45 R-PE/PET + 2 phr EGMA.

with the CP that, on the basis of both the literature data and the results of the present study, appears to be the most promising one for the reactive compatibilization of the two main components of car upholstery, namely, polyolefin and polyester. On the other hand, as the compatibilizing effectiveness of EC was shown to be extremely modest (see below), we thought that a viable route for the recycling of end-of-life car carpets might involve the substitution of EC with a chemically inert elastomer to adjust the blend flexibility and the use of EGMA as a compatibilizing agent.

To test this possibility, we decided to further our investigation by studying the reactive compatibilization of a model blend with a composition similar to that of SCR, yet free of EC. This new model blend,

referred to as R-PE/PET, was prepared by blending appropriate amounts of PET fiber mat (45 wt %) with R-PE (55 wt %). In other words, the EC component of SCR was substituted with an equivalent amount of R-PE. The reactive compatibilization of R-PE/PET was then studied with the usual techniques by addition of appropriate amounts (usually 2 and 5 phr) of the different CPs listed in the experimental section. The CP effectiveness of EC was also investigated in these compatibilization experiments.

The torque applied to the mixer rotors while blending R-PE and PET, either without or with the CPs, was recorded. The torque/time curves found for the R-PE/PET/EGMA blends are shown in Figure 9, together with those previously found for the corresponding

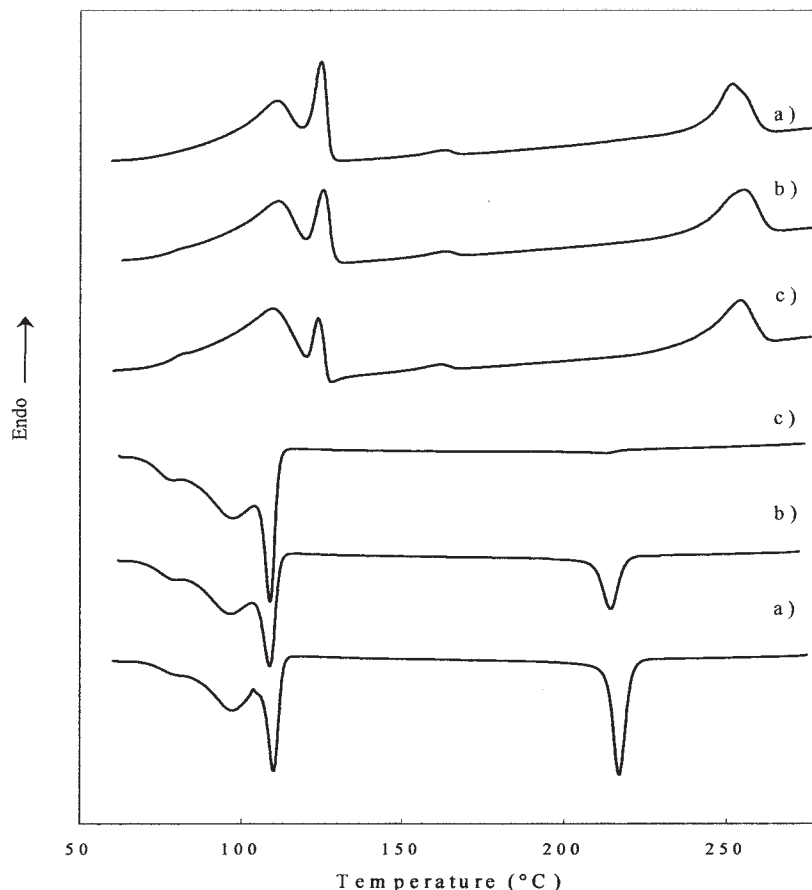


Figure 11 DSC second heating and cooling traces of the 55/45 *R*-PE/PET blend with: a) 0; b) 2; c) 5 phr EGMA.

SCR/EGMA blends. The uncompatibilized *R*-PE/PET blend is considerably more viscous than SCR, probably because the viscosity of *R*-PE is higher than that of EC. Except for this, the torque behavior found for the *R*-PE/PET/CP blends is very similar to that, already discussed before with reference to Figure 5, of the SCR/CP blends. The torque/time curves recorded in the presence of 2 and 5 phr of EC, or of one of the CPs listed in the experimental section, except EGMA (not shown), were close to that of the uncompatibilized blend. However, the addition of EGMA caused a considerable increase of the blend viscosity, thus confirming that the epoxy groups of this CP do actually react with the functional groups of the PET.

The morphology of the *R*-PE/PET blend is illustrated by the SEM micrograph, taken on the fracture surface etched with hot cresol, shown in Figure 10a. A comparison with the morphology of SCR, shown in Figure 6a, demonstrates that the substitution of EC with *R*-PE has led to a much finer dispersion of the PET droplets within the polyolefin matrix, most probably due to the increased viscosity of the latter phase. On the other hand, EC was found to behave as a (moderately effective) CP for the *R*-PE/PET blend, when used in small amounts, as demonstrated by the

micrograph shown in Figure 10b. The morphology of the 55/45 *R*-PE/PET blend compatibilized by addition of 5 phr of EGMA is shown in Figure 10c. The morphology of the blends prepared in the presence of the other CPs listed in the experimental section (not shown) was very similar to that in Figure 10b. The micrographs shown in Figures 10d–f, taken with higher magnification, confirm that EGMA does indeed possess a considerable efficiency for the reactive compatibilization of polyolefin/polyester blends and, in particular, for the blends of the *R*-PE and the PET fiber mats used by ROI srl. In fact, the maximum size of the dispersed PET droplets, which is tens of microns for the *R*-PE/PET blend, is lowered to less than 10 μm and to about 1 μm after addition of 2 and, respectively, 5 phr of EGMA.

The CP effectiveness of EGMA was confirmed by the DSC analysis, as demonstrated by the traces of the *R*-PE/PET blends containing 0, 2, and 5 phr EGMA, shown in Figure 11. The traces of the 55/45 uncompatibilized *R*-PE/PET blend is very similar to those of SCR shown in Figure 2. Upon addition of 2 or 5 phr EGMA, however, appreciable changes of the thermal behavior of this blend are found, especially with respect to the crystallization of the PET phase. In fact,

TABLE IV
Mechanical Properties of Some 55/45 R-PE/PET/CP
Blends Tested in the Humid State

Material (CP phr)	TS _{max} (MPa)	ε _{max} (%)	TS _B (MPa)	ε _B (%)	E (MPa)
R-PE/PET	4.5	3.4	4.0	3.9	232
R-PE/PET + EC (5)	5.4	4.4	5.1	4.6	194
R-PE/PET + EGMA (2)	10.1	10.7	10.0	11.5	216
R-PE/PET + EGMA (5)	11.6	23.6	11.4	23.9	199

the PET crystallization peak undergoes a strong reduction of intensity in the blend with 2 phr EGMA, qualitatively similar to that found for SCR with 10 phr EGMA (cf. curve d in Fig. 6), and almost disappears when the concentration of the CP is increased to 5 phr. The corresponding heating traces, on the other hand, display only minor changes of the intensity and the shape of the PET fusion peak, thus suggesting that, for the compatibilized blends, the crystallization of the PET phase takes place at lower temperatures, together with that of the HDPE component of R-PE. The behavior is very similar to that found for many compatibilized polyolefin/polyamide blends^{20–25} and can be interpreted in terms of a fractionated crystallization caused by the very fine dispersion of the polymer droplets, where the crystallization cannot occur any more with the usual heterogeneous nucleation mechanism. In conclusion, the DSC analysis provides further definite evidence in favor of the occurrence of chemical interactions, involving the CP and the PET, and leading to formation of EGMA-g-PET copolymers.

The mechanical properties of the R-PE/PET/CP blends were measured with the procedure already used for the SCR/CP blends (cf. Table III). However, no predrying was used for the present measurements. Some of the results are collected in Table IV. It can be observed that the compatibilizing effect of EC is rather modest, as is that of the other investigated CPs except EGMA. On the contrary, the addition of EGMA into the R-PE/PET blends brings about an appreciable increase of both the tensile strength and the elongation at break. The latter, though not very high, should be considered satisfactory on the basis of the composition of the investigated blend. Experiments are in progress to address the possibility of using these EGMA compatibilized R-PE/PET blends for the production of injection molded articles to be used in the automobile industry.

CONCLUSIONS

The scraps of a car upholstery farm have been used for a model investigation of the recycling possibili-

ties of the interior upholstery of end-of-life cars. As the two main components of these materials are a recycled polyethylene and poly(ethylene terephthalate), several commercial functionalized polymers commonly used for the reactive compatibilization of polyolefins with polyesters or polyamides were employed as additives for scraps reprocessing. Among them, an ethylene-glycidylmethacrylate copolymer (EGMA) was found to be the most efficient compatibilizer precursor (CP). However, the very complex composition of the scraps and, in particular, the presence of additives capable of reacting with the epoxy groups of EGMA, was found to limit the effectiveness of this CP, with respect to that displayed toward the reactive compatibilization of virgin polyethylene and poly(ethylene terephthalate) as described in the literature. The rheological, calorimetric, microscopic, and mechanical characterizations carried out on polymer samples prepared from the scraps and from a R-PE/PET blend miming the scraps composition showed that the ethylene-acrylic acid component, which is used commercially to compatibilize and flexibilize the carpets' backing, does in fact possess poor compatibilizing efficiency and, in addition, it interacts negatively with EGMA under the processing conditions. The results of this work suggest that replacing this EC component with a different flexibilizing agent, such as an ethylene-propylene copolymer, which is expected not to react with the epoxy groups, and using EGMA as a CP, might offer a viable route for recycling the upholstery articles of end-of-life cars.

This work was carried out with the financial contribution of CNR (PF MST A II). The authors express their gratitude to Dr. E. Zoppo, director of the ROI Automotive Technology s.r.l., Montanaro, Turin, for providing the materials used in this work, and to Dr. V. Nepote of Turin University who was very helpful in planning the research and discussing the results.

References

- Brandrup, J.; Bittner, M.; Michaeli, W.; Menges, G. *Recycling and Recovery of Plastics*; Hanser Gardner: Cincinnati, 1996.
- Various Authors. In "Car Recycling," *Proceedings of the Round Table*; Simeone, G., Ed.; Pisa University Offset Grafica: Pisa, 1999.
- Pazzagli, F.; Pracella, M. *Macromol Symp* 2000, 149, 225.
- Pluta, M.; Bartczak, Z.; Pawlak, A.; Galeski, A.; Pracella, M. *J Appl Polym Sci* 2001, 82, 1423.
- Pracella, M.; Pazzagli, F.; Galeski, A. *Polym Bull* 2002, 48, 67.
- Pracella, M.; Rolla, L.; Chionna, D.; Galeski, A. *Macromol Chem Phys* 2002, 203, 1473.
- Pawlak, A.; Morawiec, J.; Pazzagli, F.; Pracella, M.; Galeski, A. *J Appl Polym Sci* 2002, 86, 1473.
- La Mantia, F. P.; Scaffaro, R.; Colletti, C.; Dimitrova, T.; Magagnini, P. L.; Paci, M.; Filippi, S. *Macromol Symp* 2001, 176, 265.
- Xanthos, M.; Dagli, S. S. *Polym Eng Sci* 1991, 31, 929.

10. Martin, P.; Gallez, C.; Devaux, J.; Legras, R.; Leemans, L.; van Gurp, M.; van Duin, M. *Polymer* 2003, 44, 5251.
11. Jiang, C.; Filippi, S.; Magagnini, P. *Polymer* 2003, 44, 2411.
12. Chiono, V.; Filippi, S.; Yordanov, Hr.; Minkova, L.; Magagnini, P. *Polymer* 2003, 44, 2413.
13. Filippi, S.; Yordanov, Hr.; Minkova, L.; Polacco, G.; Talarico, M. *Macromol Mat Eng* 2004, 289, 512.
14. Scaffaro, R.; La Mantia, F. P.; Canfora, L.; Polacco, G.; Filippi, S.; Magagnini, P. *Polymer* 2003, 44, 6951.
15. Vocke, C.; Anttila, U.; Heino, M.; Hietaoja, P.; Seppälä, J. *J Appl Polym Sci* 1998, 70, 70.
16. Anttila, U.; Vocke, C.; Seppälä, J. *J Appl Polym Sci* 1999, 72, 877.
17. Vocke, C.; Anttila, U.; Seppälä, J. *J Appl Polym Sci* 1999, 72, 1443.
18. La Mantia, F. P.; Scaffaro, R.; Valenza, A.; Marchetti, A.; Filippi, S. *Macromol Symp* 2003, 198, 173.
19. Pompe, G.; Pötschke, P.; Piontek, J. *J Appl Polym Sci* 2002, 86, 3445.
20. Tang, T.; Huang, B. *J Appl Polym Sci* 1994, 53, 355.
21. Moon, H.-S.; Ryoo, B.-K.; Park, J.-K. *J Polym Sci, Polym Phys Ed* 1994, 32, 1427.
22. Morales, R. A.; Arnal, M. L.; Müller, A. *Polym Bull* 1995, 35, 379.
23. Jannasch, P.; Wesslén, B. *J Appl Polym Sci* 1995, 58, 753.
24. Ohlsson, B.; Hassander, H.; Törnell, B. *Polymer* 1994, 39, 6705.
25. Filippi, S.; Chiono, V.; Polacco, G.; Paci, M.; Minkova, L.; Magagnini, P. *Macromol Chem Phys* 2003, 203, 1512.