Recycling Polyethylene from Automotive Fuel Tanks

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ABSTRACT: Polyethylene (PE) from postuse automotive fuel tanks is considered a valuable material for mechanical recycling, and we assessed its properties, paying particular attention to transport properties and processability. The characterization included the study of the sorption–desorption isotherms, the rheological analysis of the molten materials and their processability. In particular, we obtained, sorption-–desorption isotherms using a model molecule (*n*-heptane) to simulate contact with the fuel. The measurements were carried out on films of PE blend for tanks and separately on the components of the blend. Rotational rheometry was carried out on scraps from used tanks and on virgin material for comparison. We performed some extrusion tests to evaluate the possibility of mechanical recycling of the postuse materials. In particular, we examined the melt-fracture incoming conditions by making use of a twin-screw extruder with a round die. Stress–strain measurements were carried out on films of virgin and used material, obtained with a press on a laboratory scale to evaluate the change of the mechanical properties of a manufacture obtained by reprocessing a polymer aged in contact with a mixture of liquids. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 347–351, 2002

Key words: polyethylene (PE); recycling; degradation

INTRODUCTION

In the last few years, there has been an increasing demand, in terms of ecology, from car producers to find new solutions to decrease the negative impact of vehicles on the surrounding environment.

The possibility of recycling the major part of vehicles at the end of their useful lives is one of the most discussed matters. Currently, much interest is focused on the possibility of recycling the plastic components, which represent about 15% of the vehicle.

The recycling of plastics used from cars, besides being important from an ecological point of view, provides many economical advantages. The recovery operations are not very difficult to carry out, principally because plastic components are easily recognized and separated from the other parts when the vehicle components are dismantled and also because they could be reprocessed to obtain the same manufactures they were in their "first lives," in a closed-loop recycling.

Polymeric materials are applied in dashboards, roof covers, and fuel tanks. Currently, there are some data about the possibility of recycling dashboards and roof covers, mainly regarding the rheology of the used material and the mechanical properties of the new manufactures,[1,2] whereas few data are available on fuel tanks.[3] The recycling operations, in the case of the fuel tanks, appear complicated by the fact that the plastic containers are used in contact with a mixture of liquids composing the fuel, and some solvent remains in the material even after many hours of drying under vacuum. This could cause problems and risks during the steps of regranulation and successive processing.

This investigation was a part of a wider project based on the possibility of recycling polymeric parts of civil and industrial vehicles. In this article, we present the results of absorption and desorption studies of a hydrocarbon molecule in a high-density polyethylene (HDPE) blend composing the fuel tanks.

We chose the hydrocarbon *n*-heptane as a model molecule to stimulate contact with the fuel. A simple molecule whose vapor activity (*a*) could be easily varied between 0.1 and 1 could help clarify many important aspects of the problem.

We also performed rheological and mechanical studies to analyze the behavior of the used material in the melt and also to investigate possible degradation phenomena that occurred in the material reprocessed after a prolonged contact with the liquids. We thus simulated mechanical recycling by extrusion tests performed on a laboratory scale to make a preliminary evaluation about the processability of tank scraps.

EXPERIMENTAL

All the materials were kindly supplied by FIAT (Torino, Italy).

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HDPE, free of any additives, was molded in a hot press into films of 0.15 mm thickness [polyethylene (PE) sample].

The virgin blend from unused fuel tanks, composed of HDPE and Carbon Black (CB; 0.2% w/w), was molded in a hot press into films of 0.15 mm thickness (PE–CB sample).

A blend of HDPE and CB obtained by granulation of fuel tanks from used cars was molded in a hot press into films of 0.15 mm thickness (Used (U)–PE–CB sample). CB powders were used as received.

Sorption–desorption curves were obtained by a microgravimetric method at different vapor activity (*a*) ($a = P/P_o$, where P is the actual pressure to which the sample was exposed and P_o is the saturation pressure at the test temperature), according to a previously reported procedure.[4] The model molecule used as a penetrant was *n*-heptane, and the experiments were conducted at 30°C.

Rheological tests were performed with a parallel plate rheometer (Rheometrics ARES, USA) on the materials from both used (U–PE–CB) and unused (PE–CB) fuel tank scraps. On the same materials, processability tests were carried out with a twin-screw extruder (Haake, Germany) at a temperature of 260°C.

Mechanical properties were tested for the PE–CB and U–PE–CB films with an Instron dynamometer (model 4301) (England) at room temperature. We obtained stress–strain curves by deforming the 10-mm specimens at an initial rate of 10 mm/min and detecting the stress on the initial section.

All the experimental measurements were averaged on 3 samples; for the mechanical properties, we used 10 samples.

RESULTS AND DISCUSSION

Sorption and desorption

Fuel tanks, during all of their lifetime, are in contact with a liquid mixture of solvents, and each of them has a specific interaction with the polymer. To simplify the study of the consequences of the contact of solvents with the tanks, we decided to perform a laboratory simulation using *n*-heptane as model molecule. We monitored the sorption–desorption behavior in a wide range of activity, $a = P/P_o$, between 0.2 and 1, to deeply investigate the solvent–polymer interactions at a controlled vapor pressure. In this way, it was possible to plot the complete isotherm of sorption–desorption, that could give useful information of any hysteretic phenomenon.

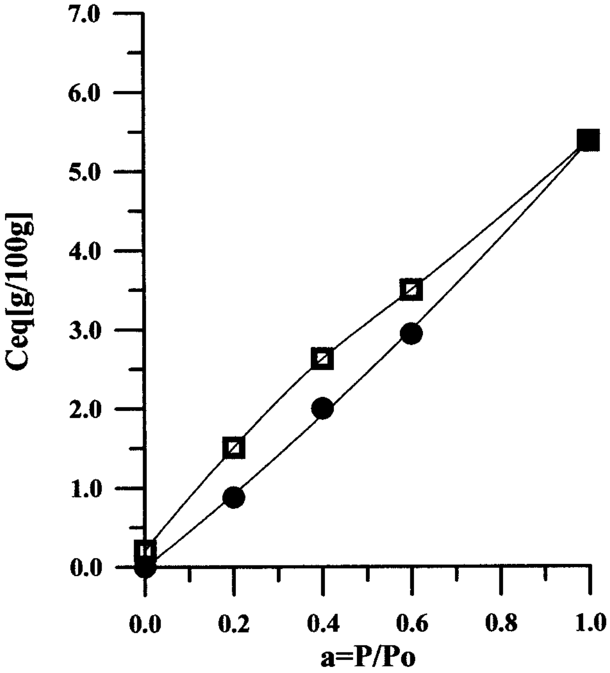

Figure 1 (●) Sorption and (□) desorption isotherms of *n*-heptane at 30°C for PE–CB.

Figure 1 shows the sorption–desorption isotherm of *n*-heptane at 30°C in PE–CB. The sorption of the hydrocarbon in the HDPE–CB blend was linear with *a* up to 0.6, and only at higher activities was a more than linear sorption, according to Flory–Huggins sorption behavior,[5] shown. The experimental desorption data showed hysteresis of solvent sorption into the polymer in the whole investigated range of activity. The hysteretic behavior was particularly relevant in the low range of *a*, between 0.2 and 0.4. This means that an amount of solvent remained entrapped into the structure after many hours of desorption under vacuum.

To separate the contribution of each component of the blend, that is, HDPE and CB, to the hysteresis phenomenon, we conducted separate experiments on the two components. In Figure 2, the sorption–desorption isotherm of *n*-heptane through PE is shown. It is evident that there was no hysteresis of sorption of the solvent into the pure polymer; as a matter of fact, the amount of sorbed solvent at each *a* was totally rejected (in the experimental error range) after drying in the vacuum. Figure 3 displays the sorption–desorption curve relative to CB powders with *n*-heptane. The shape of the plot calls for particular attention. The sorption curve of *n*-heptane into CB showed a different sorption behavior, that is, a Langmuir-type isotherm.[5] We interpreted this isotherm assuming that, for low *a*, the solvent was absorbed on preferential sites of the material, reaching a saturation level when all the specific sites were saturated. This behavior was already found for *n*-pentane in CB powders.[6]

During the desorption cycle, a significant hysteresis of sorption of the *n*-heptane molecules in the powders of CB was evident. This result is very important because it shows that a high amount of solvent remained entrapped into the CB structure on preferential physical sites, and these molecules, firmly absorbed, were

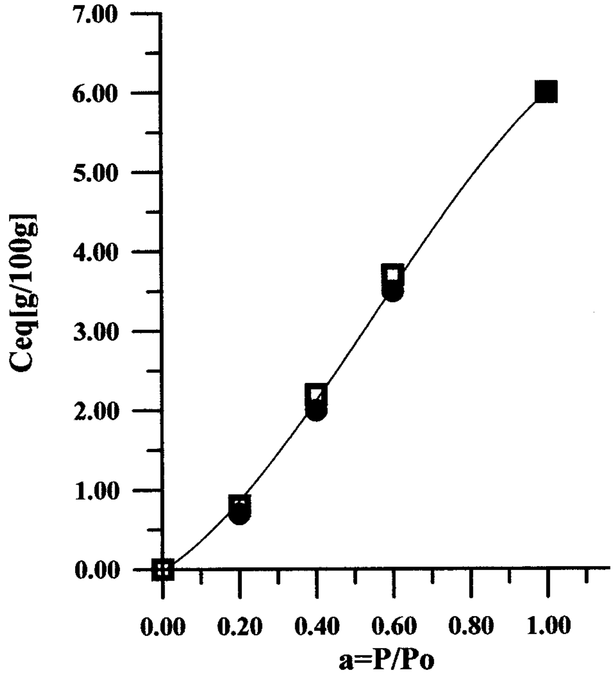

Figure 2 (●) Sorption and (□) desorption isotherms of *n*-heptane at 30°C; for PE.

unable to be rejected even after many hours of desorption under vacuum. With regard to the HDPE–CB blend this result could suggest that the observed hysteresis of sorption was principally due to the presence of CB in the PE matrix.

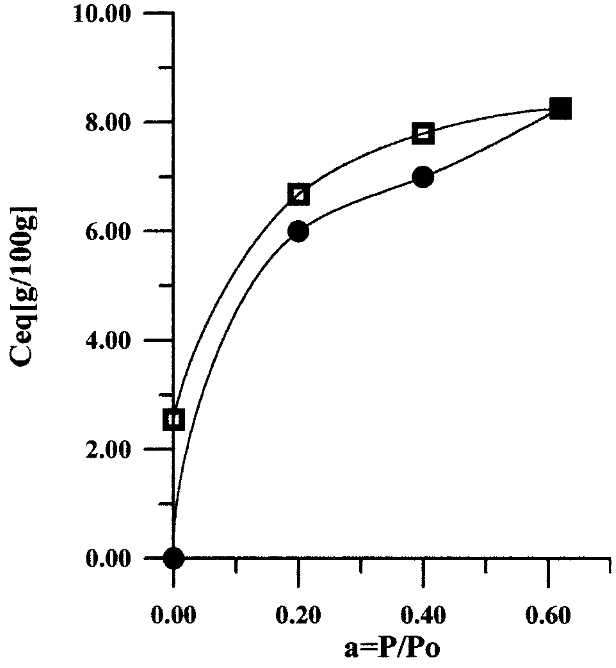

Figure 3 (●) Sorption and (□) desorption isotherms of *n*-heptane at 30°C for the CB powders.

TABLE I
Equilibrium Sorption of *n*-Heptane at Vapor Activity Equal to 0.2 and Successive Desorption Under Vacuum for PE–CB and the Blends with Different Percentages of CB

Sample	C_{eq}^{sorp} (%)	C_{eq}^{des} (%)
PE–CB	0.88	0.67
0.1% CB blend	0.47	0.34
0.2% CB blend	0.65	0.47
0.4% CB blend	0.50	0.12

To verify the suggestion that the sorption hysteresis in the HDPE–CB blend, especially at low activity, was due to the second component (CB), we prepared three blends of pure PE and CB powders, with different CB contents (w/w), 0.1, 0.2, and 0.4%, and investigated the sorption hysteresis. It is worth recalling that the percentage of CB present in the blend with HDPE for tanks was reported by FIAT to be 0.2%.

Table I shows the values of residual *n*-heptane concentrations in the three blends, after exposure to the vapor of *n*-heptane at $a = 0.2$ and subsequent desorption in vacuum. The residual solvent increased on increase of CB content. This result seems to confirm that the hysteresis of sorption of *n*-heptane, used as a model molecule, could be principally attributed to a specific interaction with CB. This was only a qualitative indication of the influence of CB added to PE. In fact, the preferential sorption on the surface of the inorganic particles depends on the particle dimensions, their interactions with the polymeric matrix, and their distribution inside the plastic matrix: in this preliminary study, we did not quantitatively investigate either of these characteristics.

Rheological behavior

The tests were performed with a rotational rheometer in dynamical mode in the range 0.01–10 Hz. Parallel plate geometry was used with plate diameters of 25 mm. The gap was fixed at 2 mm, and the strain amplitude was 20% at temperatures of 240 and 260°C. In Figure 4, the flow curves of the two types of materials are shown. The results clearly show that the flow properties of material from used tanks were quite different, in particular at low deformation rates. The used materials showed an evident increase of viscosity, which became less evident at higher deformation rates. Moreover, as highlighted from the flow curves at different temperatures, there was a major temperature effect on the rheological properties of U–PE–CB with respect to PE–CB. Probably such a stiffening of the melt could be ascribed to crosslinking induced both from the residual solvent and the thermomechanical processing at high temperatures that occurs during a rheological test. The effect of viscosity increasing during the process was highlighted by a temperature sweep test performed on scraps from used

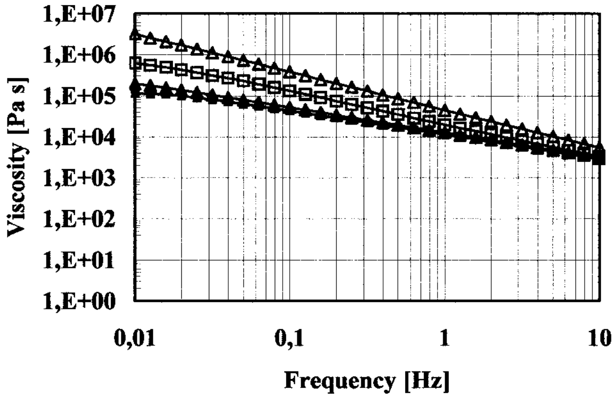

Figure 4 Flow curves of (▲) PE–CB and (△) U–PE–CB at 240°C and (■) PE–CB and (□) U–PE–CB at 260°C.

tanks. The experiment, whose results are reported in Figure 5, was carried out at 240°C and at a frequency of 10 Hz. In these conditions, the viscosity displayed a sensible increase, which was in agreement with the variation highlighted in Figure 4 between U–PE–CB and PE–CB at a given deformation rate.

Processability tests

To assess the suitability of tank scraps to be mechanically recycled, some extrusion tests were carried out at 240 and 260°C and at variable screw speeds. Our aim was to have some preliminary indications about the operating conditions and material behavior during the extrusion process. In particular, the screw speed at the onset of melt fracture and the required torque were recorded.

The results are reported in Table II. As expected, the material from used tanks (U–PE–CB) exhibited a lower speed for the beginning of melt fracture, and at a fixed screw speed, a higher torque was necessary to operate the extrusion. An increase in temperature, although not tested, could allow the operation at higher speed without the occurrence of melt fracture. However, a higher temperature could, in turn, also support major thermal degradative and/or crosslinking effects. These results again seem to indicate that although very slightly revealed from rheological tests, during the normal use of the material in contact with fuel, a structural modification takes place. In any case, extrusion is possible if one takes into account that a lower speed and a reduced output must be chosen for the operating conditions of the used material respect to the virgin one.

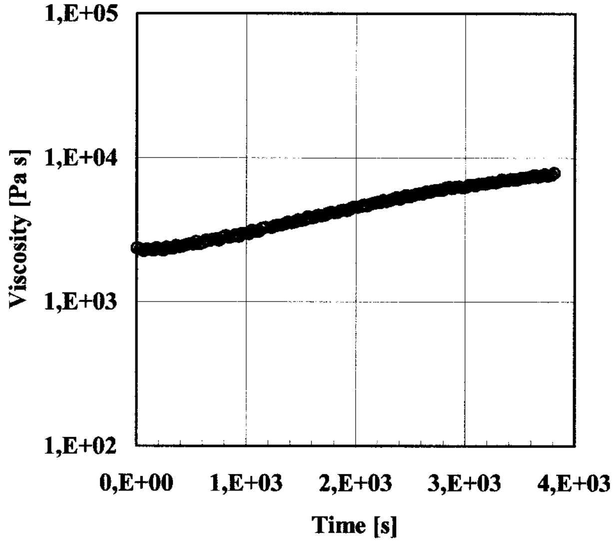

Figure 5 Viscosity of U–PE–CB as a function of time during a rheological test at 240°C and 10 Hz.

TABLE II
Extrusion Test Conditions for the Beginning of Melt Fracture

Material	Critical Screw Speed (rpm)	Torque (N m)
PE–CB	90	35
U–PE–CB	60	45

Mechanical behavior of films from virgin and recycled scraps

In Figure 6, the stress–strain curves of the PE–CB and U–PE–CB films are shown. The two materials were molded at 200°C on a laboratory scale. The two films showed the typical behavior of a semicrystalline system, which deformed with neck propagation. At the beginning, the stress was proportional to the deformation, according to Hook's law; after the yield point and the drop after the yield, there was an interval of almost constant stress, in which the neck, formed after the yield point, propagated to the whole sample. After the neck propagation, we observed a zone in which a bigger stress was needed for small deformations because now we were drawing an oriented fibrous structure, up to the breaking of the film. In Table III, we report the mechanical parameters: elastic modulus [E (MPa)], stress at the yield point [σ_y [MPa)], stress at the break point [σ_b (MPa)], the postyield stress drop [PYSD (MPa)], and the maximum elongation [ε_b (%)], derived by the stress–strain curves for both the samples. The drawing curves and the mechanical data reported in Table III show that the film of used material (U–PE–CB) broke before and exhibited mechanical properties worse than the virgin one. Anyway, such a worsening was limited, and we can affirm that from a polymer aged in contact with fuel does not undergo relevant degradation phenomena.

CONCLUSIONS

The recycling process of fuel tanks from used cars depends on the possibility of eliminating all the en-

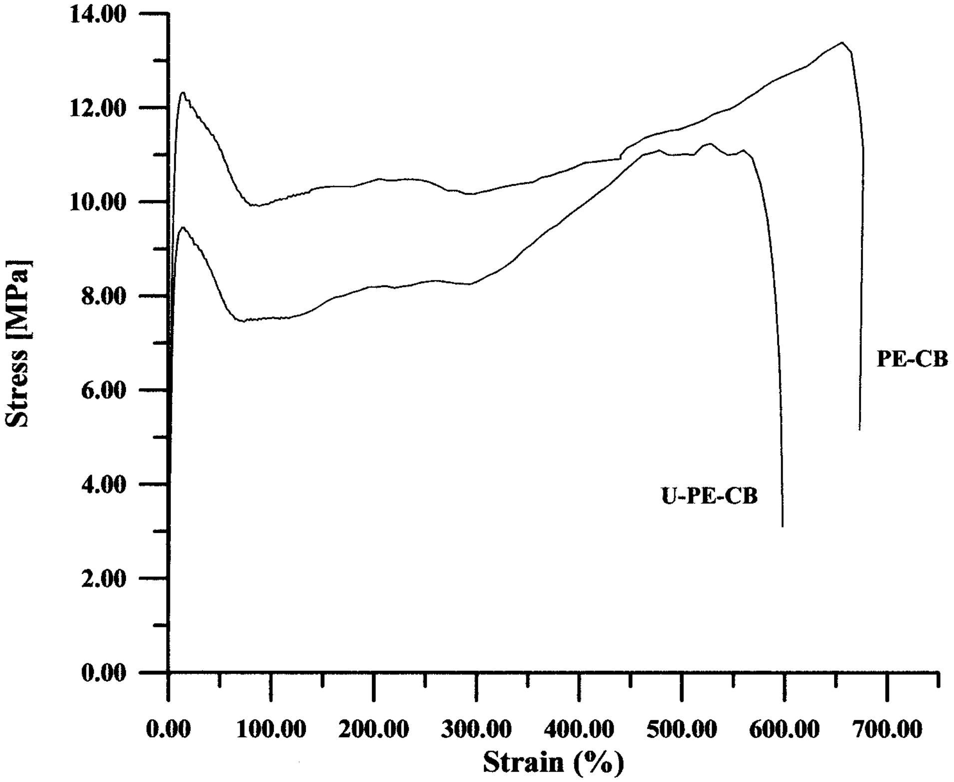

Figure 6 Stress–strain curves for PE–CB and U–PE–CB.

trapped solvent present, due to the prolonged contact with liquid fuel, and on a careful analysis of the mechanical behavior of the recycled materials.

Sorption–desorption investigations with a hydrocarbon model molecule showed that a possible source of sorption hysteresis can be considered as the preferential interaction of the solvent molecules on specific sites of the CB particles.

From rheological analysis, we found differences between used and unused materials in the molten state. In particular, it seemed that the presence of traces of fuel, which could desorb during the thermal processing operation (and thus also during the melt rheological tests), could promote some structural modifications of the polymer. Possible crosslinking between the chains could stiffen the melt. These, in turn, could make necessary the use of different working conditions to perform mechanical recycling. However, this operation was still possible. The films obtained after pressing the used material at 200°C on a laboratory scale showed mechanical properties slightly worse than the ones made of virgin polymer, which were, nevertheless, still acceptable.

TABLE III
Mechanical Parameters Obtained from the Stress–Strain Curves Reported in Figure 6

Sample	E (MPa)	σ_y (MPa)	σ_b (MPa)	PYSD (MPa)	ε_b (%)
PE–CB	297.73	10.25	13.30	2.40	6.70
U–PE–CB	263.18	7.95	11.10	2.00	5.60

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