Influence of Recycling and Contamination on Structure and Transport Properties of Polypropylene

Loredana Incarnato,[1] Paola Scarfato,[1] Domenico Acierno,[2] Maria Rosaria Milana,[3] Roberta Feliciani[3]

[1]*Department of Chemical and Food Engineering, University of Salerno, Via Ponte Don Melillo, 84084 Fisciano (SA), Italy*
[2]*Department of Materials and Production Engineering, University of Naples Federico II, Piazzale Tecchio 80, 80125 Napoli, Italy*
[3]*Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Roma, Italy*

ABSTRACT: In this work the effect of three processing cycles on the physical properties of polypropylene (PP) was studied and related to the changes in the structure (molecular weight, molecular weight distribution, morphology) occurring during recycling. In order to simulate both the use and the recycling process of PP in the laboratory, PP pellets were contaminated with three model substances and submitted to three cycles of processing by injection molding. The bars for testing were produced from virgin and recycled polymers. The amount of degradation occurring during the reprocessing was estimated by means of viscosity and gel permeation chromatography measurements. Differential scanning calorimetry and scanning electron microscopy analyses were performed to investigate the crystallization behavior and the morphology of virgin and recycled PP. In order to obtain information on the structural organization and mobility of the amorphous phase, a dynamic mechanical thermal analysis and measurements of the transport properties were carried out. The results obtained were attributed to the different structural organization of the bars in relation to the number of processing cycles and contamination. Part of the work was focused on the recyclability of PP for food packaging applications, considering the residual contamination and migrational behavior after repeated processing cycles. In particular, the relationships existing between reprocessing, the residual amounts of contaminants, and the migrational behavior were investigated. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1768–1778, 2003

Key words: recycling; polypropylene; structure–property relations

INTRODUCTION

Environmental issues connected to packaging and packaging wastes have been the subject of discussion for a long time. Many strategies have been investigated worldwide to face these problems. In Europe, the Packaging Waste EEC Directive[1] was created to control the management of packaging and packaging waste in order to prevent or reduce any impact on the environment. To this end, Article 6(1) of the Directive specifies that quantified targets be achieved by Member States for the recovery and recycling of packaging waste. It goes without saying that plastic packaging manufacturers are fully involved in strategies that are being developed to fulfill the environmental requirements, and one of the most attractive fields is food packaging. Recovery and recycling of plastics for direct and/or indirect food packaging is a frequently debated topic from toxicological and technological points of view.[2,3] In fact, plastic packaging for foods must not endanger human health or cause organoleptic deterioration of packaged foods.[4] In addition, the articles produced by second-use materials must comply with technological requirements.

The possible scenario determined by migration of contaminants from recycled plastics to packaged foods and the possible technological solutions to solve this problem are a challenging field where the risks for consumer safety must always be considered. Moreover, while the U.S. Food and Drug Administration (FDA) adopts a case by case assessment and a specific authorization procedure,[5] European Union legislation does not allow the use of mechanically recycled plastics for direct contact with foods. A generally recognized reference procedure to monitor the hygienic safety of recycled plastics is not yet available. This is due to inconclusive and fragmented scientific knowledge; several international projects are ongoing to further investigate the topic.[6]

In order to consider the possibility of using recycled plastics in contact with foodstuffs, it is necessary to attain deep knowledge of the structural modifications

TABLE I
Physicochemical Characteristics of Migration Tracers

Surrogate contaminant	Molecular weight	Boiling point (°C)	Physicochemical character
Phenyl-cyclohexane	160	240	Nonvolatile, apolar
Benzophenone	182	305	Nonvolatile, polar
(di-*n*-butyl phthalate)	278	153	Nonvolatile, polar

that may occur when the polymer with potential contaminants and in contact with foods is submitted to repeated processing cycles. In fact, such structural changes (molecular weight, crystallinity, morphology) significantly modify the functional properties of a food grade polymer so that it could become unsuitable for food contact applications.

A number of studies report on the processability and performance of recycled polymers,[7–13] but few works are focused on the barrier properties of articles manufactured from postconsumer plastics. In our previous studies[14–16] we separately analyzed the influence of reprocessing (primary recycling) and food contamination (postconsumer recycling) on the structural, mechanical, and barrier properties and migrational behavior of polypropylene (PP). The results obtained from performing primary and secondary recycling experiments have shown that the structure, which is the number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (MWD) of the starting polymer is of primary importance to obtain first quality goods that are suitable for food packaging applications. In fact, during the reprocessing, PP undergoes degradation phenomena that modify its molecular structure parameters (decrease in M_w and MWD) and increase the oligomeric fraction. As a consequence, a worsening of the migration properties and a decrease in the mechanical parameters are observed. On the other hand, the narrowing of the MWD and the morphological changes produce a sensible improvement of the barrier properties, which have a very important role in food packaging applications.

However, the possibility of recycling refuse PP for food contact purposes must take into consideration the hygienic and toxicological safety of recycled PP. In fact, second-use materials can be contaminated by both foreign substances (processing-aid additives such as antioxidants and stabilizers, food, pesticides, detergents, metals, etc.) and degradation products from the previous life cycle of the material and reprocessing operations. Therefore, for recycled food contact materials, the study of migrational behavior is of primary importance to ensure the safety of consumers and the shelf life of foods.[17–20]

An attractive perspective for food safety can be seen in a multilayer process incorporating a layer of postconsumer polymer between two layers of virgin resin.

The layer of virgin polymer placed between the recycled material and the food is an impediment to migration into the food (functional barrier) of any impurities that might be present, even after cleaning of the recycled resin. This approach is particularly interesting for polymers such as polyolefins that, because of their high diffusivity, can easily uptake misused chemicals, thus constituting a potential risk for food contamination.

The aim of this study is to evaluate the recyclability of PP for food packaging by analyzing the influence of both recycling and contamination on the structure (molecular weight, MWD, morphology) and transport properties (sorption, diffusion, and migration) of PP. We performed a study on a food grade isotactic PP by adding three model substances as migration tracers and submitting it to three processing cycles. In order to simulate food contact of the polymer with fatty and nonfatty media during its normal life cycle, before each reprocessing step the polymer was put in contact with three simulant solvents, which were selected according to European directives.[21] After each processing cycle the PP samples were tested to analyze their structure (molecular weights, crystallinity, morphology), the residual amount (Q) of contaminants in the polymer, and the specific migration (SM) of the migrants.

Studies are in progress on multilayer PP films and their capability as functional barriers to prevent the migration of potential contaminants, and the results will be reported in future work.

EXPERIMENTAL

Materials

The study was conducted on a food grade homopolymer PP (PP SSF, Montell) with M_w and M_n values of 362,800 and 54,500, respectively.

The PP pellets were deliberately polluted with three surrogate contaminants, which were used as migration tracers. The contaminants and the procedure to contaminate PP were selected on the basis of the FDA and ILSI guidelines.[22–24] The selected substances and their physicochemical characteristics are reported in Table I.

A master batch was prepared by mixing 500 g of PP pellets in a toluenic mixture containing 1% (w/w)
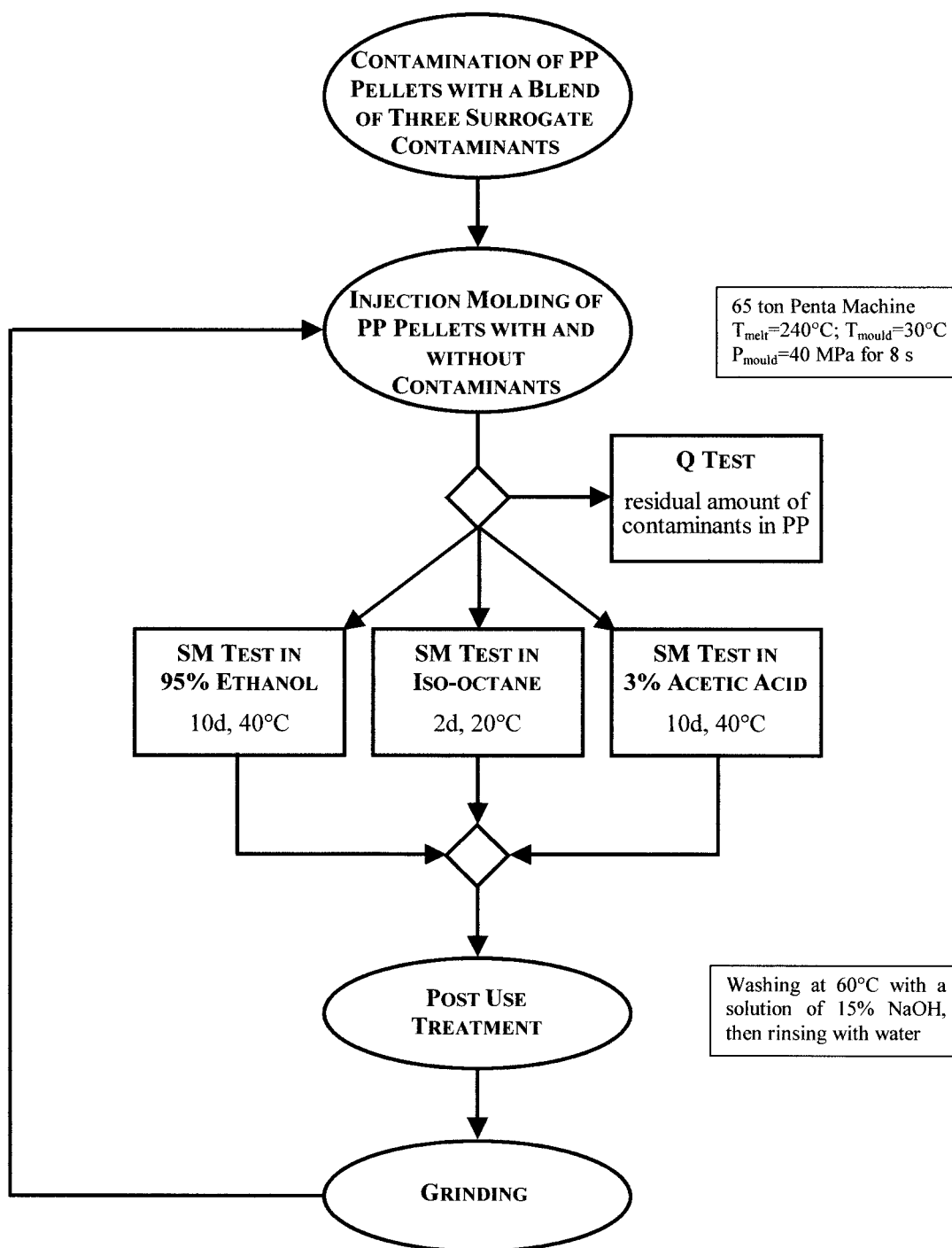
Figure 1 The scheme used to simulate a recycling process from postconsumer PP.

benzophenone (BP), 1% (w/w) di-n-butyl phthalate (DBP), and 1% (w/w) phenyl-cyclohexane (PCH) for 14 days at 40°C in a closed vessel. The pellets were dried for 12 h in a fume hood at room temperature to remove the solvent. Then they were mechanically mixed with 4500 g of PP pellets to attain a final amount of 0.1% (w/w) added substances. The obtained mixture was submitted to three processing cycles by injection molding (Fig. 1) in the conditions reported below. In order to simulate food contact of the polymer with fatty and nonfatty media during its normal life cycle, before each reprocessing step the PP samples were totally immersed in 100% iso-octane and 95% ethanol (substitute test media for fatty simulants); 3% acetic acid was used to simulate aqueous–acid food contact. All of the solvents and the test conditions were selected according to the EEC 97/48/EC directive.[21] At the end of the contact time, the PP samples

were reunited, submitted to a postuse treatment, and ground. Blank PP samples were obtained by processing uncontaminated PP pellets under the same conditions.

Methods

Gel permeation chromatography (GPC) was used to provide information about the M_w, M_n, z-average molecular weight (M_z), and the MWDs (M_w/M_n and M_z/M_w) of the samples. The GPC system used in this work was a Waters 150-C ALC/GPC (Millipore) equipped with four PL gel 20 μm mixed-4 columns with dimensions of 300×7.5 mm. The carrier solvent was 1,2,4-trichlorobenzene at 135°C at a flow rate of 1 mL/min and a pressure of 25 bar.

Calorimetric measurements were performed with a Mettler differential scanning calorimeter (DSC-30) calibrated for temperature and enthalpy with metallic standards (indium and zinc). In order to minimize thermooxidative degradation phenomena, all scans were run under a nitrogen gas purge. The samples were first heated at a rate of 10°C/min from 0 to 250°C and held at this temperature for 3 min to allow the complete melting of the crystallites; then they were cooled at 10°C/min from 250 to 0°C, and the crystallization temperature (T_c) and enthalpy (ΔH_c) were calculated.

Scanning electron micrographs were obtained using a Leo 420 apparatus (Leo Electron Microscopy Ltd.) on samples crystallized at 125°C from the melt state. The analysis was performed after etching the crystallized samples by immersion in a solution of sulfuric and *ortho*-phosphoric acid (10:4 v/v) at 1% (w/v) of KMnO$_4$ at room temperature for 4 h. All samples were coated with an AuPd alloy using a high vacuum sputter coater before analysis.

The dynamic mechanical properties were analyzed using a Polymer Laboratories dynamic mechanical thermal analyzer. The dynamic mechanical spectra were recorded in tensile mode (1.00-mm oscillation amplitude) at a frequency of 1.0 Hz and a heating rate of 5°C/min from −50 to 150°C.

The transport properties (sorption and diffusion) were measured by a microgravimetric method, using a quartz spring balance having an extension of 15 mm/mg. The penetrant used was dichloromethane (CH$_2$Cl$_2$). The experiments were conducted at 25°C. Sorption was measured as a function of the vapor activity (a), $a = P/P_0$, where P is the pressure to which the sample was exposed and P_0 is the saturation pressure at the temperature of the experiment.

The determination of the residual amount (Q) of contaminants in the PP samples was performed by Soxhlet extraction of cryoground PP and gas chromatography (GC)/flame ionization detector analysis. The instrument we used was a Perkin–Elmer GC Autosys-

tem equipped with a Dell workstation and Turbochrom Nt software. The test conditions were the following: column: PTE 5 tm (Supelco 2-4135-U) 30 m × 0.25 mm; df = 0.25 μm; temperature program: iso 80°C for 5 min, ramp 12°C/min to 280°C, hold 10 min; injection temperature: 250°C; detector temperature: 300°C; carrier gas: helium (1 mL/min flow); injection mode: splitless.

The determination of the SM of BP, DBP, and PCH was performed by direct GC/mass spectrometry with static ion mass (MS-SIM) analysis of contact solutions in the case of iso-octane and 95% ethanol. In the case of 3% acetic acid, the three migrants were extracted from the contact solutions by shaking with iso-octane.

The determinations were carried out by GC/MS-SIM analysis under the following conditions: instrument: HP5890A/HP5970B GC/MSD equipped with a Vectra Chemstation and Rev1034C software; column: DB-1 (J & W 122-1033) 30 m × 0.25 mm; df = 1 μm; temperature program: iso 70°C for 5 min, ramp 8°C/min to 260°C, hold 5 min; injection temperature: 250°C; transfer line temperature: 280°C; carrier gas: helium (1 mL/min flow); injection mode: splitless; energy: 70 eV; monitored ions: PCH (104, 160), BP (105, 182), DBP (149, 278).

Processing of test material

The samples for testing were produced from PP pellets by the injection molding process. Molding experiments were performed by a 65-ton PENTA injection molding machine with a rectangular cavity (120 × 30 × 2 mm). The injection flow rate was 23.5 cm^3/s; the melt and mold temperatures were 240 and 30°C, respectively. A holding pressure of 40 MPa was maintained for 8 s. The final artifacts were rectangular bars with a thickness of 2 mm.

RESULTS AND DISCUSSION

In order to obtain information about the effects of recycling operations and contamination on the molecular structural parameters of PP, GPC analysis and intrinsic viscosity measurements were performed on samples processed up to 3 times with and without contaminants; the average molecular weights (M_n, M_w, and M_z) and the MWDs (M_w/M_n and M_z/M_n) are reported in Tables II and III for the uncontaminated and contaminated PP samples, respectively. For the uncontaminated PP (Table II), it can be seen that after one recycling operation there is a slight increase in the MWDs that is essentially due to a broadening of the GPC curve toward lower molecular weights (M_n and M_w decreases). Then, after the second recycling process, all molecular structural parameters show a significant reduction with respect to those of the virgin polymer. In particular, the effect becomes more rele-

TABLE II
Average Molecular Weights (M_n, M_w, M_z.) and Molecular Weight Distributions
(M_w/M_n, M_z/M_n) for V_u, $R1_u$, and $R2_u$ PP Samples

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_z/M_w	M_w/M_n
V_u	54,552	362,788	1,034,669	2.85	6.65
$R1_u$	52,961	354,684	1,130,291	3.18	6.69
$R2_u$	50,220	331,311	922,343	2.78	6.59

vant passing from M_n to M_w and M_z (decreases of 7.9, 8.7, and 10.8%, respectively), indicating that the macromolecules with a high molecular weight are the most sensitive to thermomechanical degradation induced by reprocessing. On the other hand, in the case of contaminated PP (Table III), the GPC data in each step are lower than those of the uncontaminated PP. Moreover, all parameters are significantly decreased after each processing operation and the reduction is particularly marked after the second recycling. The parameters most affected by reprocessing are the M_z and M_w, which decrease 48 and 31%, respectively, after two cycles of processing. These results also reveal that in the contaminated PP the degradation phenomena are mainly in regard to the polymer chains with high molecular weight. Similar results were reported in our previous works conducted on the primary and secondary recycling of PP.[14,15] Moreover, the MWDs (M_z/M_w and M_w/M_n) calculated for the contaminated samples that are recycled twice ($R2_c$) are narrowed more than 20% with respect to the virgin contaminated (V_c) PP. All these results show that the presence of model contaminants at the percentages used in this work greatly intensifies the thermomechanical degradation phenomena during the PP recycling. The possible action of the contaminant molecules on the radical degradation of PP will be studied in detail in a future work.

Intrinsic viscosity measurements were also performed on virgin and recycled PP samples and the results are shown in Figure 2. These data, which agree with the GPC analysis, provide clear evidence that the decrease in the M_w after reprocessing becomes relevant after the second recycling step and is more pronounced for the contaminated PP samples.

Because the changes in the molecular structure parameters can significantly modify the crystallization behavior and consequently the crystalline morphology and properties of the polymer, differential scanning calorimetry (DSC) measurements and scanning electron microscopy (SEM) analysis were performed on virgin and recycled PP samples. In order to erase the thermal history of the molded PP samples, the polymer was heated at 250°C and held at this temperature for 3 min before the tests to allow the complete melting of the crystallites. The DSC traces obtained in the cooling scan from virgin and recycled samples of contaminated PP are reported in Figure 3. In comparing the curves it clearly appears that after two recycling operations the crystallization temperature of PP increases about 5°C. Both the decrease of the molecular weights (M_n, M_w, and M_z) and the narrowing of the MWDs (M_z/M_w and M_w/M_n) contribute to the determination of this result. The thermograms do not show significant differences in the crystallization enthalpy between virgin and recycled PP (ΔH_c = 96 and 97 J/g for the V_c and $R2_c$ samples, respectively), indicating a similar crystallinity content. Moreover, a higher and more sharpened melting peak temperature was also observed in the second heating scan of the recycled sample, suggesting that the crystalline morphology developed after recycling is different.

To achieve more information on the morphological changes induced by reprocessing, scanning electron micrographs were obtained on virgin and recycled contaminated PP samples crystallized at 125°C from the melt state. The SEM images reported in Figure 4(a,b) show that the two samples have a very different structural organization. In particular, in the virgin PP sample the amorphous and crystalline phases are not interconnected and the spherulites are well developed with a regular shape and diameter in the range of 50−65 μm. On the other hand, in the recycled PP sample the amorphous and crystalline phases are

TABLE III
Average Molecular Weights—(M_n, M_w, M_z) and Molecular Weight Distributions
(M_w/M_n, M_z/M_n) for V_c, $R1_c$ and $R2_c$ PP Samples.

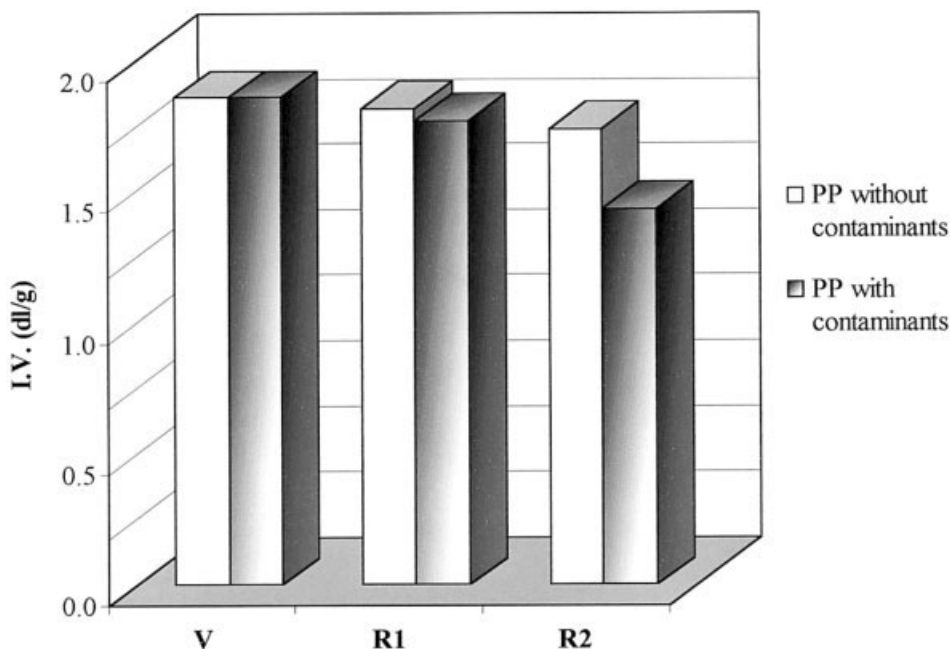| Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_z/M_w	M_w/M_n
V_c	49,127	350,737	1,061,824	3.02	7.13
$R1_c$	48,149	315,654	814,566	2.58	6.55
$R2_c$	42,549	240,791	548,944	2.27	5.66

Figure 2 The intrinsic viscosity of virgin and recycled PP samples.

strictly interconnected because a higher number of nuclei and a higher number of crystals with smaller sizes are observed (diameters = 15–25 μm). This result can be attributed to the narrowing of the MWDs after recycling and to the presence of contaminants and impurities that can act as nucleating agents.

Similar results in terms of the crystallization behavior (T_c, ΔH_c) and crystalline morphology are obtained for uncontaminated PP samples, even though in this case the changes after recycling are smaller, as a consequence of slighter degradation phenomena that are evidenced by GPC and intrinsic viscosity results previously discussed.
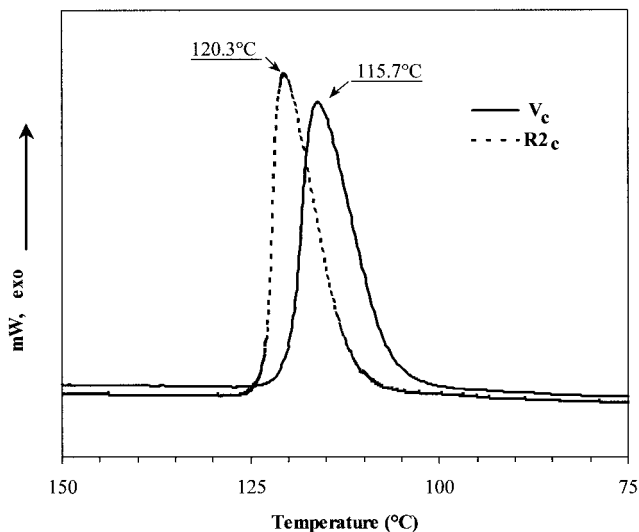
Figure 3 DSC traces obtained in the cooling scan from virgin and recycled samples of contaminated PP.

In order to further investigate the effect of the different structural organizations on the molecular mobility of the amorphous phase in the virgin and recycled PP, dynamic mechanical thermal analysis (DMTA) tests were carried out on the samples. In Figures 5 and 6 the storage (E') and loss (E'') moduli behavior are reported as a function of the temperature for the contaminated virgin (V_c) and twice recycled (R2$_c$) PP samples. The storage modulus curves (Fig. 5) show that the E' values are significantly higher for the R2$_c$ than for the virgin PP at temperatures ranging up to 60°C, but they become comparable for the two samples at higher temperatures. Moreover, the E' drop, which is related to relaxation processes of the amorphous fraction, has a different trend in the virgin and recycled samples. In particular, the decrease in the storage modulus curve begins at a slightly higher temperature for the R2$_c$ than for the V_c PP and takes place in two steps in a broader temperature range. This occurrence reveals that two amorphous regions with different mobility could be present in the recycled sample. Also, the E'' curve clearly shows different relaxation behavior of the amorphous fraction in virgin and recycled PP samples. In fact, comparing the E'' curves reported in Figure 6, it can be seen that after two recycling operations the peak loss modulus is slightly shifted (about 6°C) and broadened toward higher temperatures. All dynamic mechanical data show the reduced molecular mobility of the amorphous chains of recycled PP compared to the virgin sample.[25] In this regard, it is worthwhile to note that, as previously discussed, the SEM analysis pointed out the different morphology of the recycled PP, which
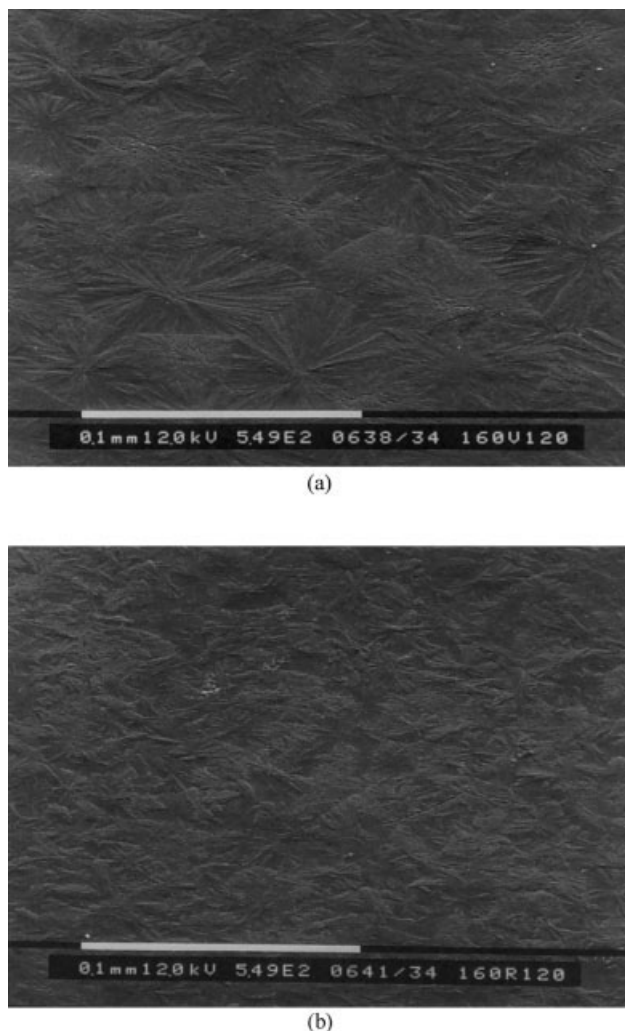
(a)

(b)

Figure 4 Scanning electron micrographs obtained on (a) virgin and (b) recycled contaminated PP samples crystallized at 125°C from the melt state.

results in a higher amount of interconnected amorphous chains between the crystals. It is known that tie chains have a lower molecular mobility compared to the bulk of the amorphous phase and do not necessarily assume liquid-like mobility above the glass-transition temperature (T_g).[26]

In order to investigate how the morphological changes observed in the recycled samples influence the transport properties of PP, sorption and diffusion experiments were performed on virgin and recycled samples using dicloromethane (CH_2Cl_2) as a penetrant solvent. Because for semicrystalline polymers the transport properties depend only on the mobility of the amorphous phase, significant differences were expected to exist between the V and $R2_c$ PP samples. Figure 7 reports the diffusion coefficient (D) as a function of the equilibrium concentration (C_{eq}) of CH_2Cl_2 in the polymer. It clearly appears that the diffusion coefficient of recycled PP is sensibly lower with respect to the virgin sample, confirming that the amor-
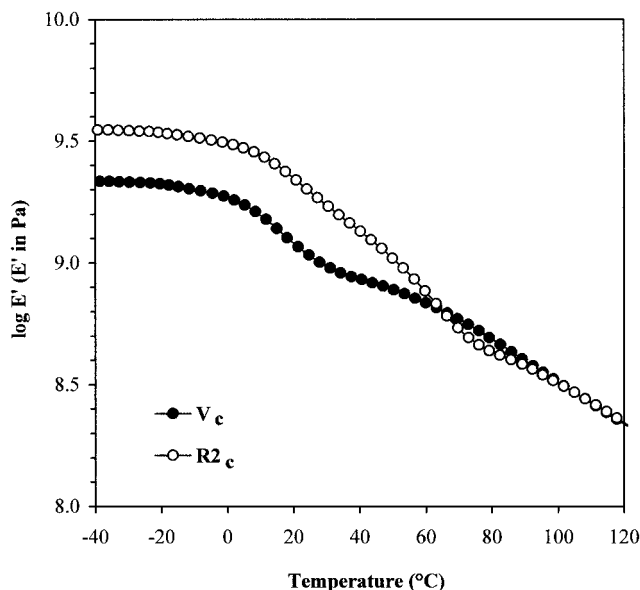

Figure 5 The elastic–dynamic modulus (E') behavior versus the temperature for the V_c and $R2_c$ PP samples.

phous phase becomes more rigid after recycling. Moreover, from the sorption isotherms of CH_2Cl_2 in PP (Fig. 8) it is clear that virgin and recycled samples show two different modes of sorption.[27] The V_c sample shows a positive deviation from Henry's law, whereas the $R2_c$ sample displays a region of negative curvature at low vapor activity and a positive deviation for activity greater than 0.3. The first mode of sorption represents a preference for penetrant–penetrant pairs to be formed, so that the solubility coefficient increases continuously with the pressure.[28] This behavior depends on the ability of the solvent to plas-
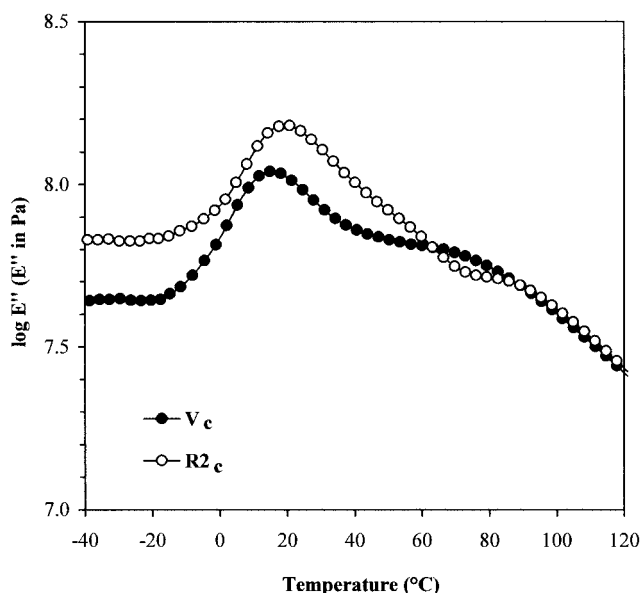

Figure 6 The loss–dynamic modulus (E'') behavior versus the temperature for the V_c and $R2_c$ PP samples.
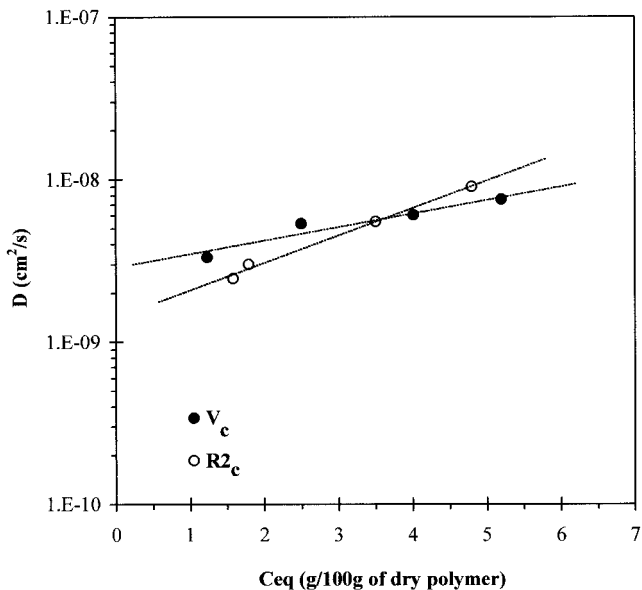
Figure 7 The diffusion coefficient at 25°C versus the equilibrium concentration (C_{eq}) of dichloromethane in the dry polymer for the V_c and $R2_c$ PP samples.

Figure 9 The residual amount (Q) of the surrogate contaminants in the V, R1, and R2 PP samples.

ticize the polymeric matrix and can be interpreted by the Flory–Huggins theory. Instead, the sorption mode of recycled PP can be explained as a process in which there are dual modes: either the penetrant molecules are normally dissolved and free to diffuse, or they are immobilized in particular sites of the polymeric matrix (dual sorption theory). The sorption mode observed for recycled samples indicates that higher vapor concentrations of CH_2Cl_2 are needed to plasticize the polymeric matrix. This is a consequence of a stiffening
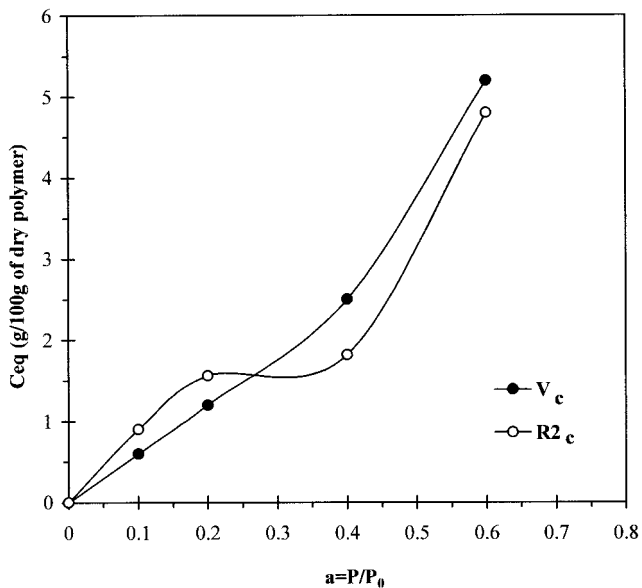

Figure 8 The equilibrium concentration (C_{eq}, g/100 g dry polymer) at 25°C of dichloromethane as a function of the vapor activity ($a = P/P_0$) for the V_c and R2$_c$ PP samples.
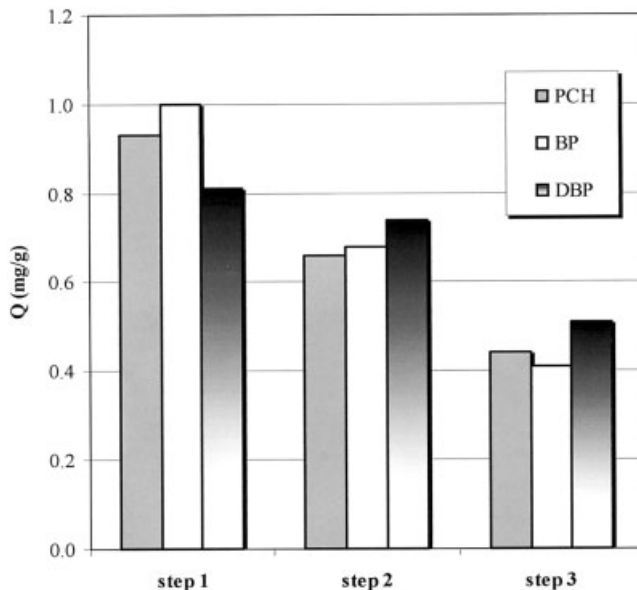
of the amorphous phase, as shown by DMTA tests, and it is related to the reduction of the M_w and MWD, which in turn influence the morphology of the samples.

Similar behaviors in the sorption modes and DMTA tests were obtained in a previous work, which was conducted on PP film samples recycled by extrusion without the use of contaminants.[16] However, in that case the rigidity of the amorphous phase was evident only after five processing cycles. Moreover, an improvement of the barrier properties in the recycled films was also observed by permeability tests to gases (CO_2, O_2, and N_2), where the interaction between the polymer and the gas molecules is very poor.

To investigate the migrational properties of surrogate contaminants from recycled PP, the residual amount (Q) of the three contaminants in the polymer and their SMs in food simulants were determined. The Q values measured for each contaminant in the virgin and recycled PP samples are reported in Figure 9. The histogram shows that the residual amounts of all surrogate contaminants after the first processing step are close to the amounts added before processing (0.1%, w/w). Then the Q values decrease after recycling, and there is a total average loss of contaminants that is equal to approximately 50% with respect to the initial values after the third processing cycle. This decrease could be attributed to several factors: migration of the contaminants from the material to the simulants, postuse washing procedures, and loss of contaminants during grinding and injection molding.

Figures 10, 11, and 12 report the SM data obtained for the three surrogate contaminants in 95% ethanol, iso-octane, and 3% acetic acid, respectively. In a com-
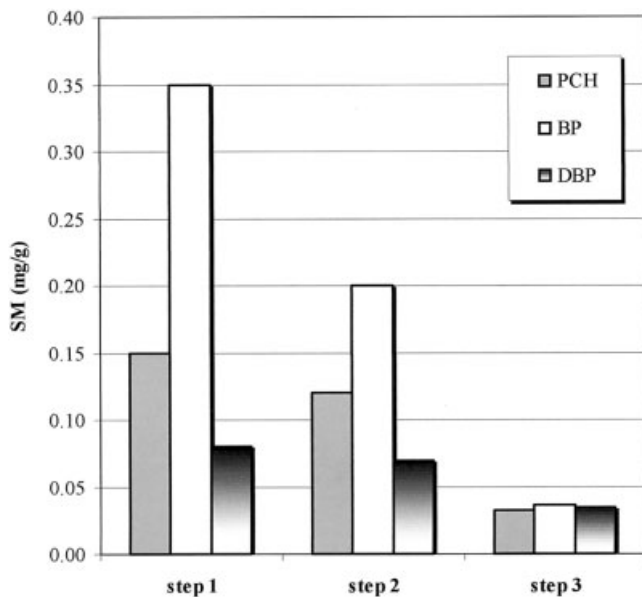
Figure 10 The specific migration (SM) of the surrogate contaminants in 95% ethanol for the *V*, R1, and R2 PP samples.

Figure 12 The specific migration (SM) of BP in 3% acetic acid for the *V*, R1, and R2 PP samples.

parison of the histograms it can be seen that the SM behavior is significantly different in the three food simulant solvents used. Because the migrants are soluble in all simulants (freely in iso-octane and 95% ethanol, less in 3% acetic acid), the final migration depends on the mobility of the migrant species across the polymeric matrix, which is strongly linked to the penetrant molecular size and shape and on the migrant–polymer–simulant interactions.

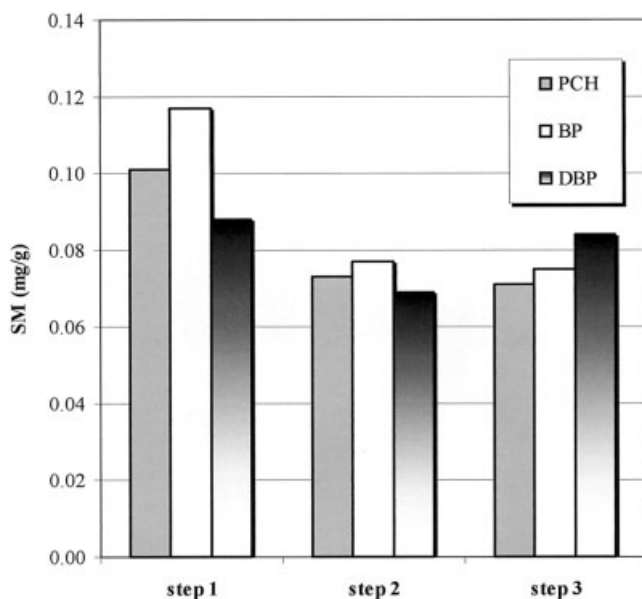An analysis of the results reported in Figure 10 for the 95% ethanol shows that the SM values are significantly different for the three surrogate contaminants. This result is a consequence of the differences in the structure and physicochemical character (molecular weight, polarity) of the migrant molecules. In fact, the highest SM values in each step are measured for BP, which, being the most planar molecule, has a more penetrating power with respect to the other contaminants. Moreover, for all migrants that were monitored the SM decreases significantly after each processing step. In this case both the reduction of the Q values after each reprocessing cycle and the stiffening of the PP amorphous phase due to recycling contribute to the decrease of SM data.

In the case of iso-octane (Fig. 11), different behavior is observed. The SM values are quite similar for the three surrogate contaminants after each step of processing. This result can be ascribed to the deep swelling action of this lipophilic simulant toward PP. In fact, because iso-octane opens up the structure of PP, the migration process is less influenced by the physicochemical character of the migrant but is governed essentially by the amount of migrants in the polymer and by the migrant–simulant interactions.[29,30] Moreover, comparing the SM of the migrants after each processing cycle, it can be observed that SM values significantly decrease from the first to the second processing cycle, then remain rather unchanged after the third processing cycle. Two factors can be taken into account to explain this behavior: the reduction of the Q values and the structural changes of PP after recycling. Up to the second processing step, where the changes in the PP structure are quite slight, the SM values decrease according to the reduction in the Q data. On the other hand, after the second reprocessing,

Figure 11 The specific migration (SM) of the surrogate contaminants in iso-octane for the *V*, R1, and R2 PP samples.
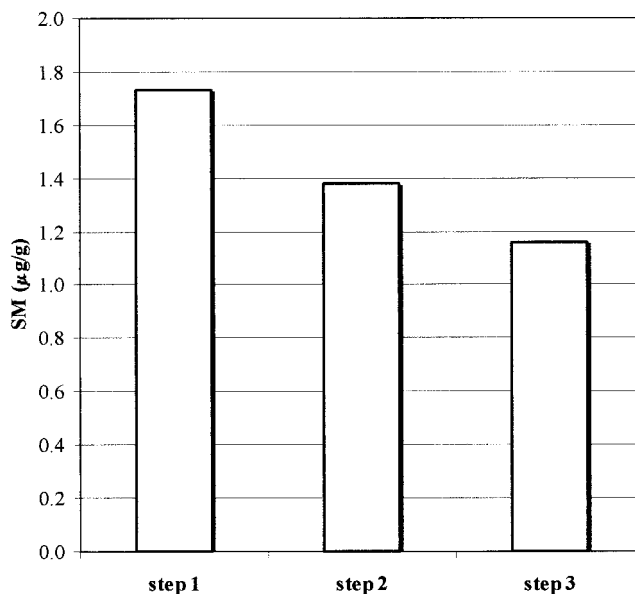
although the residual amount of contaminants decreases further, the iso-octane swelling action toward the recycled samples becomes more effective as a consequence of the reduction in the molecular structure parameters.

According to the SM data in the two fatty food simulants, the SM values measured in 95% ethanol after the first and the second processing steps are higher than those determined in iso-octane for PCH and BP. This phenomenon could be attributed to both the longer contact time and higher test temperature (10 days at 40°C) used for 95% ethanol with respect to iso-octane (2 days at 20°C), as recommended by the EEC Directive[21] to perform SM tests using alternative olive oil simulants.

In the case of 3% acetic acid (Fig. 12), which, on the basis of its polar character, has a poor interaction with PP, the amount of matter transferred through the polymeric material depends on the contaminant size and shape and the polymer structure more strongly than for the 95% ethanol. In fact BP, which has a more planar structure and low molecular weight, is the only surrogate contaminant showing detectable SM values in the acid simulant. The trend of its SM data is similar to that observed in 95% ethanol, but in this case the SM values are more than 100 times lower and their decrease after recycling is a lower percentage. Moreover, the SM values measured for PCH and DBP in the acid simulant can be neglected because they are near to the detection limit of the SM test; therefore, they are not reported in the graph.

To provide a more correct description of the performance of PP with respect to migration of the surrogate contaminants, it appears helpful to discuss the trend of the SM/Q ratios, because the SM values of the migrant species greatly depend on their concentration in the polymer. The SM/Q ratios calculated for BP after each processing step in the two fatty food test media are reported in Figure 13 as an example. The behavior of the other surrogate contaminants is omitted for clarity, because they show a similar trend of BP in each solvent with less marked changes; likewise, the SM/Q ratios in 3% acetic acid are not discussed because their trend has little significance, because the SM data are lower then the Q values by 6 magnitude orders. Comparing the SM/Q trends of BP in iso-octane and 95% ethanol, it clearly appears that the migrational behavior of BP in the two solvents is opposite. In particular, after the second reprocessing cycle the SM/Q ratios show a pronounced increase in iso-octane and a sharp drop in 95% ethanol. This is a combined result of several factors, such as the different penetrating and swelling power of the two simulants and the changes in the molecular structure parameters of PP, as discussed above.
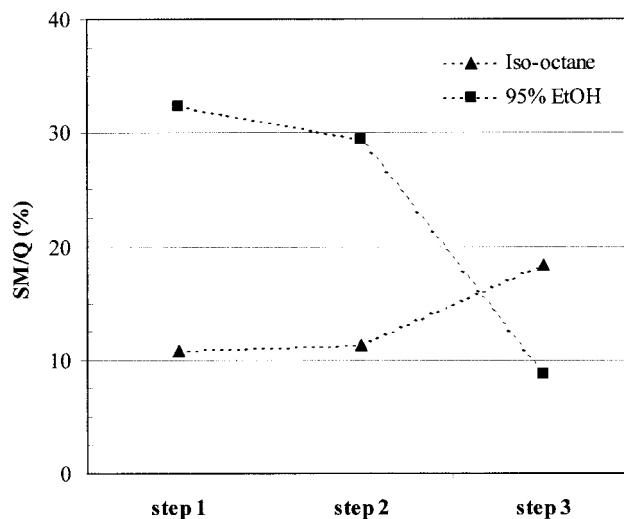

Figure 13 A comparison of the the specific migration (SM)/residual amount (Q) trends of BP in iso-octane and 95% ethanol for the V, R1, and R2 PP samples.

CONCLUSIONS

In this work a detailed study was performed on the structural modifications occurring during the recycling of PP with and without model contaminants and their effect on the migrational behavior of PP. Experimental measurements have shown that some effects of the degradation are

- a decrease of the M_n, M_w, and M_z;
- a narrowing of the MWD;
- some modifications of the crystal morphology.

All these changes strongly affect the structure and the molecular mobility of the amorphous phase. In particular, a reduction in the molecular mobility of the amorphous chains in the contaminated recycled samples was revealed by DMTA tests and transport properties.

The effects of these structural changes on the migrational behavior of PP depend upon the type of polymer–solvent interaction. Two different trends were observed in this study:

- In iso-octane, where swelling of PP occurs, the SM/Q ratios are comparable for all migrants in each step and increase after reprocessing.
- In 95% ethanol, where the swelling of the polymer is slighter, the SM/Q ratios decrease after recycling for all model contaminants. This result indicates that, in some cases, the transport properties (migration, permeability) of PP can be improved after recycling because of the structure modifications induced by reprocessing.

Similar results were found in samples recycled without contaminants. However, from the GPC data it was evident that the degradation phenomena are emphasized in the presence of contaminants.

A further important consideration in the possible use of recycled PP for food packaging is to assess the suitability of recycled PP for direct food contact use. It is not sufficient to test the composition of PP or the residual amount of contamination because migrational behavior, and thus potential contamination of the packaged food, is influenced by the structural changes determined during the processing.

References

1. European Economic Committee. Packaging Waste EEC Directive 94/62/EC of 20 December 1994 (Official Journal no. L365, 31. 12. 1994, p 10).
2. Piringer, O. G. Food Add. Cont. 1994, 11, 221.
3. Castle, L. Packaging Technol Sci 1994, 7, 291.
4. European Economic Committee. Packaging Waste EEC Directive 89/109/EC of 21 December 1988 (Official Journal No. L040, 11.2. 89, p. 38).
5. FDA. Center for Food Safety and Applied Nutrition, Office of Food Additive Safety. Recycled Plastics in Food Packaging; U.S. Food & Drug Administration: Washington, DC, 2001.
6. Raffael, B., Simoneau, C., Eds. Proceedings of the Final EU Project Workshop FAIR-CT-98-4318, Recyclability of food packaging materials with respect to food safety considerations: polyethylene terephthalate (PET), paper and board and plastics covered by functional barriers; EUR report 20249 EN (2002). Varese, Italy, February 10–11, 2002.
7. Andrews, G. D.; Subramanian, P. M., Eds. In Emerging Technologies in Plastic Recycling; ACS Symposium Series 513; American Chemical Society: Washington, DC, 1992.
8. Martínez, J. M.; Eguiazábal, J. I.; Nazábal, J. J Macromol Sci Phys 1995, B34, 171.
9. Bernardo, C. A.; Cunha, A. M.; Oliveira, J. Polym Eng Sci 1996, 36, 511.
10. Donnini Mancini, S.; Zanin, M. J Appl Polym Sci 2000, 76, 266.
11. Lozano-Gonzalez, M. A. J.; Rodriguez-Hernandez, M. A. T.; Gonzalez-De Los Santos, E. A.; Villalpando-Olmos, J. J Appl Polym Sci 2000, 76, 851.
12. Kartalis, C. N.; Papaspyrides, C. D.; Pfaender, R.; Hoffmann, K.; Herbst, H. J Appl Polym Sci 2000, 77, 1118.
13. Miguez Suarez, J. C.; Biasotto Mano, E.; Bruno Tavares, M. I. J Appl Polym Sci 2000, 78, 899.
14. Incarnato, L.; Di Maio, L.; Acierno, D.; Denaro, M.; Arrivabene, L. Food Add. Cont. 1998, 15, 195.
15. Incarnato, L.; Scarfato, P.; Acierno, D. Polym Eng Sci 1999, 39, 749.
16. Incarnato, L.; Scarfato, P.; Gorrasi, G.; Vittoria, V.; Acierno, D. Polym Eng Sci 1999, 39, 1661.
17. Figge, K. Progr Polym Sci 1980, 6, 187.
18. Crosby, N. T., Ed. In Food Packaging Materials; Applied Science Publishers Ltd.: London, 1981.
19. Feigenbaum, A. Packaging Technol Sci 1984, 7, 131.
20. Feigenbaum, A. E.; Bouquant, J.; Ducruet, V. J.; Ehret-Henry, J.; Marqué, D. L.; Riquet, A. M.; Scholler, D.; Wittmann, J. C. Food Add. Cont. 1994, 11, 141.
21. European Economic Committee. Packaging Waste EEC Directive 97/48/EC of 29 July 1997 (Official Journal No. L222, 12.8. 1997, p. 10).
22. FDA. Center for Food Safety and Applied Nutrition, Office of Food Additive Safety. Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations; U.S. Food & Drug Administration: Washington, DC, 2001.
23. ILSI Europe Packaging Material Task Force. Guidelines: Recycling of Plastics for Food Contact Use. ILSI Europe Report Series; Bruxelles, 1998 (ISBN 1-57881-035-3).
24. Nielsen, T.; Damant, A. P.; Castle, L. Food Add. Cont. 1997, 14, 685.
25. Turi, E. A, Ed. In Thermal Characterization of Polymeric Materials, 2nd ed.; Academic: New York, 1996.
26. Iannace, S.; Nicolais, L. J Appl Polym Sci 1997, 64, 911.
27. Vieth, W. R., Ed. In Diffusion in and Through Polymers; Hanser: New York, 1991.
28. Rogers, C. E., Ed. In Physics and Chemistry of the Organic State; Wiley: New York, 1965.
29. Feigenbaum, A. E.; Hamdani, M.; Ducruet, V. J.; Riquet, A.-M. J Polym Eng 1996, 15, 47.
30. De Kruijf, N.; Rijk, M. A. Food Add. Cont. 1998, 5, 467.