Expanding the Application Field of Post-Consumer Poly(ethylene terephthalate) Through Structural Modification by Reactive Blending

Patrizio Raffa,[1,2] Maria-Beatrice Coltelli,[3,4] Valter Castelvetro[1,4]

[1]Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy
[2]Department of Chemical Engineering – Product Technology, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands
[3]Dipartimento di Ingegneria Civile e Industriale, Università di Pisa, Largo Lucio Lazzarino 2, 56124 Pisa, Italy
[4]SPIN-PET s.r.l., Viale Rinaldo Piaggio 32, 56025 Pontedera (PI), Italy
Correspondence to: P. Raffa (E-mail: p.raffa@rug.nl)

ABSTRACT: With the aim of up-grading the material properties of post-consumer PET, making them suitable for extrusion of thermoformable thick sheets, a series of polyepoxy chain extenders have been comparatively evaluated as melt viscosity modifiers for a toughened compatibilized blend containing up to 80 wt % of bottle-grade post-consumer recycled poly(ethylene terephtalate) (r-PET). Combinations of a commercial modifier with pentaerythritol were also successfully employed to cause simultaneous hyperbranching and controlled chain scission, thereby modifying the melt rheology of the material without excessively increasing the molecular weight, as highlighted by common technological melt viscosity measurements such as online torque and off-line melt flow rate (MFR). Since the high melt fluidity of PET plays a critical role on its flame resistance, the combined effect of chain extenders and halogen-free phosphorated additives on the fire resistance of the modified toughened blends was also investigated. Preliminary results indicate that the chemical reactions among polymer and additives must be taken into careful account to prevent unfavorable effects on the ultimate melt rheology and mechanical properties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40881.

INTRODUCTION

Thermoforming of extruded sheets is typically suited for low-volume production of large parts, when injection molding is less convenient due to its high fixed costs and lower versatility. The low-cost issue is also strictly related to availability and cost of the base material, which can be reduced by using recycled polymers.

In previous studies high impact injection molding grade blends based on recycled PET (r-PET) were developed by using proper combinations of toughening reactive agents, such as functional polyolefins and compatibilizers (Figure 1).[1–4] Adapting a toughened r-PET blend to the requirements for sheet extrusion and thermoforming involves at the outset adjustment of its rheological behavior, and particularly of its melt fluidity.[5,6] This can be achieved by proper addition of chain extenders and chain branching agents to modify in a controlled way the structure of the polyester without negatively affecting its compatibilized interface with the toughening polyolefin.

Typically, a chain extender for a polyester must have two or more reactive groups for bridging the carboxyl or hydroxyl terminals of the polymer, thus increasing its average molecular weight. The use of chain extenders in r-PET was recently reviewed by Dimonie et al.[7] They evidenced that the reactive groups of these polyfunctional molecules may be epoxy, anhydride, phosphites/phosphates, oxazoline, phosphazene, lactam, isocyanate, hydroxyl and carboxylic acid.

In the case of epoxy-based chain extenders both the esterification of carboxyl terminals and etherification of hydroxyl ones may occur (Figure 2). In both cases, secondary hydroxyls are formed that can further react with the carboxyl or epoxy groups, leading to the formation of branched or cross-linked structures.[8]

Polyepoxides are among the most effective chain extenders for PET,[9,10] thus multifunctional molecular and oligomeric reactive additives bearing different number of epoxy groups can be used to modify even drastically the melt viscosity of PET or PET blends. Further tuning of melt viscosity and enhanced nonlinearity of the rheological behavior may be achieved through a balanced combination of chain branching and chain scission, as obtained by concurrent transesterification and chain extension with polyol and polyepoxy additives, respectively. This approach has been scarcely investigated, as treatment of PET with polyols
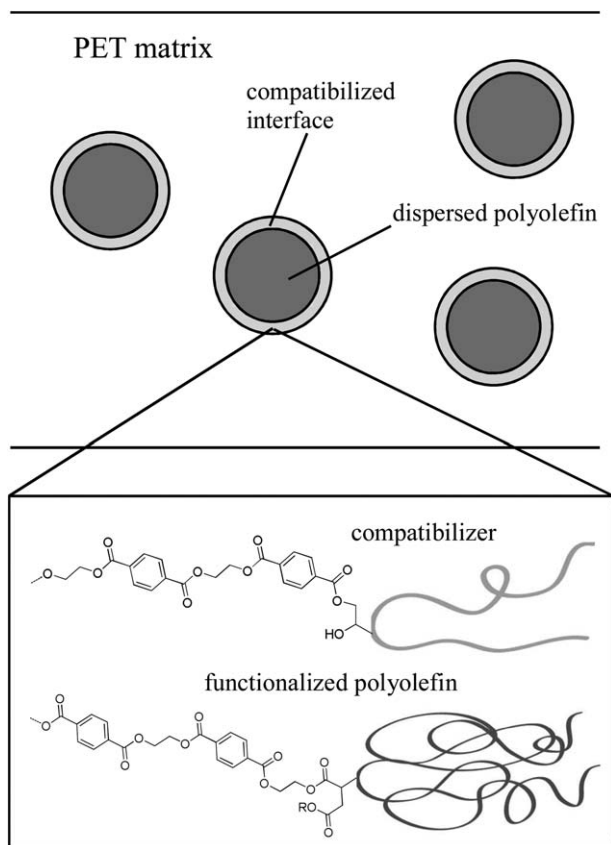
Figure 1. Representation of a PET/polyolefin compatibilized blend.

was usually performed in solution rather than in the melt, with the aim of obtaining chemicals or regenerate the monomers according to a chemical recycling approach.[11–14] Among the few reports on melt processing, Campanelli et al.[15] studied the reactive blending of PET with ethylene glycol, resulting in efficient PET chain scission. Pardal et al. compared different glycols and observed that a mixture of dipropylene glycol and glycerol was the most efficient in determining a significant decrease in PET molecular weight.[16] Mendes et al.[17] used pentaerythritol and zinc acetate as transesterification catalyst in the melt blending of PET, where the multicomponent additive promoted simultaneous alcoholysis and esterification. In the latter case, the extent of each type of reaction depended on the composition. The esterification reaction was predominant at molar ratios in which PET was the main component, leading to the formation of star-type branched macromolecules. Conversely, the alcoholysis reaction took over

when the compositions were richer in pentaerythritol. Incidentally, the latter behavior is somewhat similar to the general behavior of r-PET upon melt processing, in which the presence of residual moisture or of chemical species with hydroxyl groups is known to promote polyesters degradation through chain scission [9–10]. Devising new tools to regulate the melt viscosity behavior of r-PET based blends and upgrade the mechanical properties of the resulting materials is a key issue when dealing with recycled polymers that are typically characterized by variability of the bulk properties caused by the heterogeneous origin of polymers, by the effect on them of the primary industrial cycle, by the effect of aging and, due the ever increasing fraction of plastics reclaiming from post-consumer urban waste, by the presence of heterogeneous and often incompatible polymers.[18,19] Further to that, the need to expand the market for recycled polymers calls for the possibility to adapt their melt viscosity behavior to different processing technologies, such as, e.g., injection molding, sheet extrusion and thermoforming, and their mechanical properties to a variety of applications.

In the case of PET based material an additional critical issue limiting the range of its potential applications (e.g. in the automotive, construction, electric and electronic sectors) is its poor flame extinguishing behavior, emphasized by the typical sagging of smoldering PET[20,21] and the persistent lack of effective halogen-free flame retardant additives.[22] The resulting flame propagation may effectively be inhibited by appropriate modifications of the macromolecular structure leading to increased melt viscosity, in contrast to the viscosity reduction often caused by the hydrolytic activity of phosphorus-based flame retardants often used for polyesters.[23–29]

In the present paper, a series of polyepoxy chain extenders differing both in structure and in the number of reactive epoxy groups have been comparatively evaluated as melt viscosity modifiers for a toughened r-PET compatibilized blend, containing up to 80 wt % of bottle-grade r-PET. The addition of a polyol/polyepoxy mixture was also explored as a tool to expand the melt viscosity range of the blend, owing to the somewhat competing structural modifications caused by such combination. Finally, the possible synergistic effect of the addition of either red phosphorus-based or inorganic hypophopsphite flame retardant additives on the fire resistance of the modified toughened blends was also preliminarily investigated, with the aim of estimating the effectiveness of these halogen-free flame retardants and the influence of the preparation procedure on the final mechanical properties and fire resistance of the material.
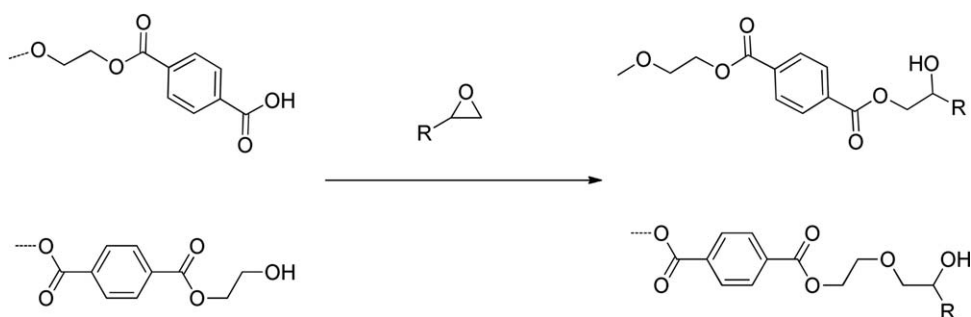

Figure 2. Reaction of PET terminal groups with a generic epoxide.

MATERIALS AND METHODS

Colored PET flakes (r-PET, intrinsic viscosity $\eta = 0.75$ dL/g, $\overline{M_n} = 22{,}000$ Da, determined from viscosity with Uglea equation[30]), reclaimed mainly from post-consumer beverage bottles, was purchased from Seriplast s.r.l. (Firenze, Italy). The material was dried in an oven at 150°C for at least 15 h and stored in a desiccator over anhydrous silica gel before use.

A low density polyethylene functionalized with 1.5 wt % maleic anhydride (POFD1.5, Auserpolimeri s.r.l., Italy) was used as the rubbery polyolefin component of the blend. A terpolymer of ethylene/methyl acrylate/glycidyl acrylate (Lotader AX8900[TM], Arkema, hereafter simply Lotader) was used as the compatibilizer. Joncryl ADR-4368[TM] (hereafter simply Joncryl), a styrene-acrylic copolymer with $\overline{M_n} \sim 6800$ g/mol and 23.8 epoxy groups per molecule (as glycidyl acrylate units) was purchased from BASF A.G., Germany. Poly[(glycidyl-o-cresyl)-co-formaldehyde)] (PGCF) with two different molecular weights ($\overline{M_n} \sim 870$ and 1080 g/mol, respectively) were purchased from Aldrich. Red phosphorous masterbatches 50 wt % in polyamide (PAP) and 60 wt % in polyethylene (PEP), respectively, as well as two hypophosphites of aluminum (IPA) and calcium (IPC) were a kind gift from Italmatch S.p.A., Italy. Melamine cyanurate (MC) was purchased from Sigma–Aldrich. The antioxidant Irganox B-225[®] (a 1:1 blend of the phenolic Irganox1010[®] and the phosphite Irgafos168[®]) was purchased from CIBA.

Tetraglycidylpentaerythritol (TEGPE) was synthesized as described below from pentaerythritol and epichlorhydrine according to a slightly modified literature procedure.[31]

Reactive blending of r-PET was performed with a 50 mL internal chamber Brabender mixer operating at 270°C and 90 rpm, using a standard mixing time of 10 min on feed compositions that were always added with 0.5 wt % of the antioxidant Irganox B-225[®] to prevent polymer degradation induced by thermo-mechanical stress during processing. Different amounts of the given chain extender were added into the pre-heated mixing chamber 2–4 min after the simultaneous introduction of r-PET flakes and the other additives (polyolefin, compatibilizer, flame retardants and antioxidant), for a total amount of 55 g. The time evolution of the torque was recorded during the reactive blending experiment. The melt flow rate (MFR), expressed as g of material per 10 min, was determined using a CEAST melt flow module PIN 7026 equipped with "VisualMELT" software which provides melt volume rate (MVR) data. The melt flow rate was measured at 260°C with an overhead weight of 2.16 kg (ASTM D1238), following an ISO1133A standard procedure. The samples were dried for 2 h at 150°C in an oven before the MFR measurement.

Attenuated Total Reflectance FT-IR (ATR-IR) analyses were performed with a Perkin Elmer Spectrum 400 instrument equipped with a germanium crystal ATR accessory. Cryogenically fractured films were examined with Jeol JSM model T-300 scanning electron microscope.

The mechanical properties were evaluated using a Tinius Olsen H10KT dynamometer equipped with a 500 N HTE charge cell. Tensile test specimens were obtained with a dinking machine from 0.2 to 0.5 mm thick compression molded films according to ASTM D638 and analyzed at room temperature at a stretching rate of 10 mm/min. Each measurement is the average from at least 10 tested specimens. The films were prepared using a Collin PM20/200 press equipped with a water cooling system. Each sample was pre-heated to 270°C for 2 min, then compressed at 5 MPa for 1 min and finally quenched under pressure for 3 min. Fire tests were performed according to the UL94 standard onto 1 mm thick specimens obtained by compression molding with a COLLIN P200M press. Both horizontal and vertical test configuration were used to classify samples; ranking from the least to the most effective flame retardant behavior a material is classified as: HB (horizontal burning), V2 (burning stops within 30 s on a vertical specimen; drips of flaming particles are present); V1 (burning stops within 30 s on a vertical specimen; drips of particles allowed as long as they are not aflame); V0 (burning stops within 10 s on a vertical specimen; drips of particles is allowed as long as they are not aflame).

Synthesis of TEPGE

A total of 5 g of KOH pellets (90 mmol) were ground under nitrogen and suspended in 20 mL of DMSO. The suspension was transferred into a 100 mL round-bottomed flask and stirred under nitrogen for 5 min, then added with pentaerythritol (1.36 g, 10 mmol) and stirred for an additional 30 min at 40°C. After removal of the heating bath epichloridrine (10 mL, 100 mmol) was added dropwise over 1 h to the stirred mixture at room temperature, causing the suspension to become less turbid and turn slowly from colorless to yellow. After another 5 h of stirring at 40°C the reaction mixture was allowed to cool down to room temperature, added with 50 mL of CH_2Cl_2, filtered and washed with saturated aqueous NaCl. After extracting the aqueous phase washings twice with CH_2Cl_2, the organic phases were united, dried over anhydrous Na_2SO_4 and concentrated with a rotary evaporator. Purification of the crude product by column chromatography on silica (eluent hexane/acetone 7:3 v/v) gave 2.6 g of a viscous pale yellow oil in a 70–80% yield.

RESULTS AND DISCUSSION

Preliminary test performed on r-PET based blends had shown that a composition containing 80 wt % r-PET, 15 wt % POFD1.5 and 5 wt % Lotader (hereafter referred to as PET80155), once modified with 0.5% Joncryl (PET80155 + 0.5J trial) results in a material suitable for the extrusion into thermoforming grade sheets.[9,32] The internal morphology of a sheet produced by reactive extrusion of PET80155 + 0.5J was thus investigated and compared with the product obtained from the same composition but through reactive blending in a discontinuous mixer. In both the cases, a similar pattern of dispersion of the rubbery polyolefin phase in the PET matrix can be observed in the SEM micrographs of Figure 3, taken from the respective cryogenically fractured surfaces.

While such chain-extended r-PET blend composition was directly suitable for sheet extrusion and thermoforming, it is to be expected that a feedstock based on a recycled polymer from post-consumer or even a post-industrial reclaiming would not ensure the consistency of the melt viscosity and mechanical
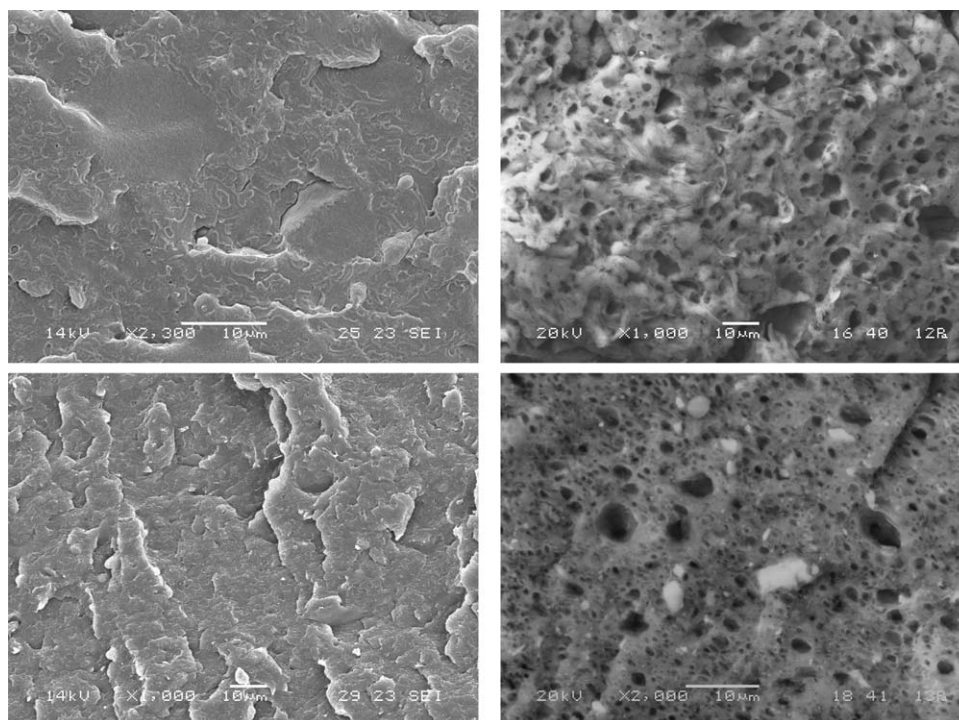
Figure 3. SEM images of the PET80155 + 0.5J blend prepared by either a two-step processing using a twin screw extruder followed by sheet extrusion (above) or a one-step reactive blending in a discontinuous mixer (below). On the left, the cryogenically fractured surfaces; on the right, the same surface after etching with hot toluene to remove the rubbery polyolefin phase.

properties as required by specific industrial applications. It is thus apparent that a better understanding of the effect of different structural modifications of the PET matrix on the rheology of its compatibilized blends would be quite a valuable tool for devising practical criteria to adapt the formulation of r-PET based materials to specific processing conditions and target mechanical properties. Based on these considerations, the effect of Joncryl and of other structurally different branching polyepoxy chain extenders on the melt viscosity and tensile mechanical properties of the PET80155 blend was further investigated

Melt Viscosity Regulation with Joncryl

The melt viscosity of r-PET and PET80155 blends with Joncryl under different dynamic conditions was evaluated by recording the torque during reactive processing and measuring the MFR of the resulting modified blend. The dependence from the Joncryl concentration (in the 0–1.0 wt % range) of the torque recorded after 600 s processing (end of the processing) and of the MFR is illustrated in Figure 4.

In the case of r-PET, the final torque value, related to the melt viscosity at high shear, increases almost linearly with the concentration of Joncryl, rising short of three times at 1 wt % additive content. On the other hand, the MFR value, which is an indicator of melt viscosity at low shear, is much more heavily affected by the addition of the branching agent, being lowered by a factor of around 50 at 1 wt % Joncryl. This can be reasonably explained if we consider that Joncryl reacts with PET terminations leading to highly branched structures (Figure 5).

Such structural modifications have a stronger impact on the behavior of the material at low shear rate, when the effect of chain entanglements on the polymer motion is more pronounced. In other words, by increasing the fraction of highly branched structures the shear-thinning behavior is enhanced, as it is often observed for condensation polymers.[33]

The behavior of the PET80155 blend is quite peculiar, as low amounts of Joncryl cause a sharp increase in final torque; however, the chain extender effectiveness becomes less pronounced at higher concentrations, as one would expect in case of substantial depletion of the available reactive macromolecular chain ends. Moreover, the absolute values of final torque for the unmodified r-PET and PET80155 are comparable while the MFR values are markedly different, indicating that the unmodified materials behave more similarly at high shear stress. These results may be tentatively explained by pointing out that the concentration of the PET chain ends is lowered in PET80155 by partial consumption through reaction with the carboxyanhydride and epoxy groups of the two compatibilizers POFD1.5 and Lotader, respectively; such reactions result in branched structures responsible for the observed shear-thinning behavior of the unmodified blend. Upon addition of the Joncryl chain extender, competition with the blend compatibilizers could result in early depletion of the reactive macromolecular chain ends as noted before.

On the other hand the MFR of PET80155 is less affected by the addition of Joncryl at low additive concentrations, and becomes
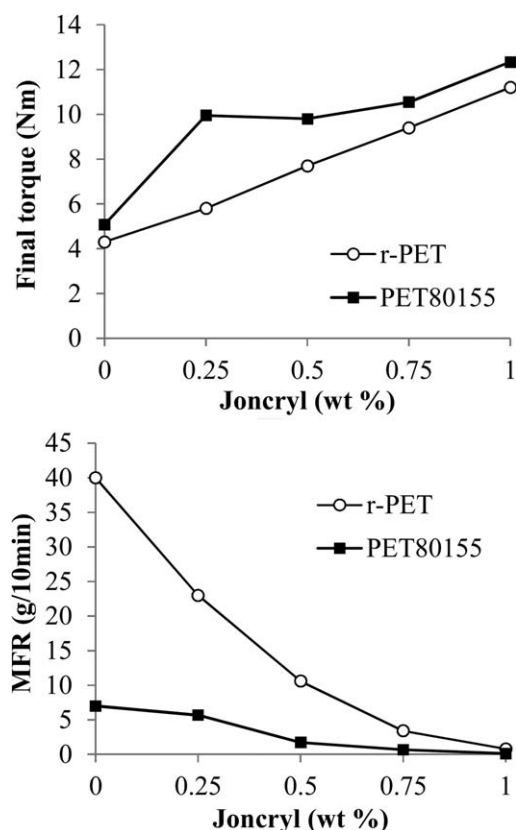
Figure 4. Variation of final torque (above) and MFR (below) with the Joncryl amount for r-PET and PET80155.

nearly superimposed to that of r-PET at higher concentrations. This is better highlighted in Figure 6, in which MFR is normalized to the initial value for the two systems, respectively.

Given the complexity of the PET80155 blend, a straightforward rationalization of the above results is out of question. Nevertheless, a better understanding of how different types (as discussed later) and amounts of these polyfunctional chain extenders may affect the melt viscosity of r-PET or r-PET based reactive blends, albeit based on a semi-empirical approach, could provide valuable predictive tools for selecting proper processing conditions, e.g. for extrusion and thermoforming.

Effect of Joncryl on the Tensile Properties of PET80155

Tensile test were performed on specimens of PET80155 modified with various amounts of Joncryl. The main results, sum-
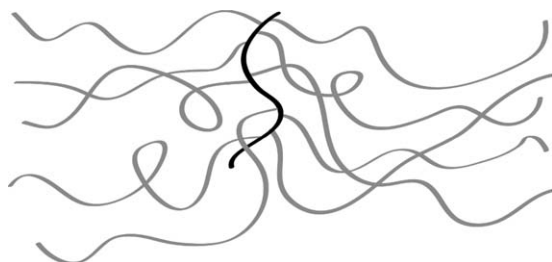

Figure 5. Schematic representation of r-PET (longer grey branches) after reaction with Joncryl (black central strand).

marized in Table I, show that within the explored range of Joncryl concentration and the scattering of experimental data intrinsic of this heterogeneous system (as shown by the standard deviation even in the measurements on the unmodified blend) the mechanical properties are only slightly influenced by the structural modifications caused by this branching chain extender. A slight increase of the Young's modulus at intermediate Joncryl content ($0.25 \leq C_J \leq 0.75$) is the main noticeable effect, while the poor reproducibility of the Elongation at break measurements, as indicated by the highly scattered experimental data, may be ascribed to the persistent residual heterogeneity of the compatibilized blend. In any case, the overall toughened character of PET80155 blend is not affected by the addition of Joncryl, as the integrals of the stress strain curves, accounting for the tenacity of the material, that is, its capability of absorbing and thermally dissipating mechanical energy, were found to be nearly unaffected by the addition of the chain extender within the explored concentration range.

A semi-quantitative estimation of the effect of branching on the crystallinity of PET can be obtained through infrared spectroscopy analysis.[34,35] In particular, IR-ATR measurements performed on mechanically stretched specimens provided useful information on the variations in crystallinity under high deformation. The degree of crystallinity was determined from the relative intensity of the peaks at 1340 and 1370 cm^{-1}, corresponding to methylene wagging vibrational modes of the oxyethylene moieties in the *trans* and in the *gauche* conformation,
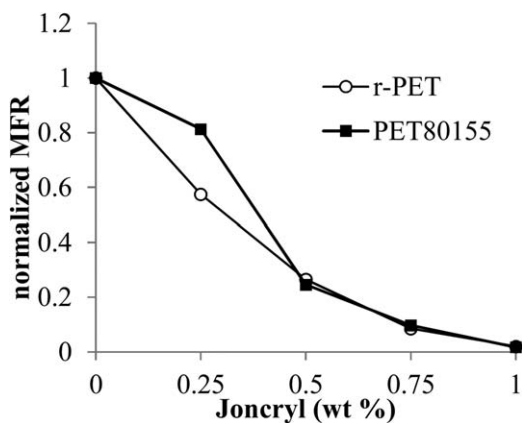
Figure 6. Normalized value of MFR in r-PET and PET80155 as a function of Joncryl content.
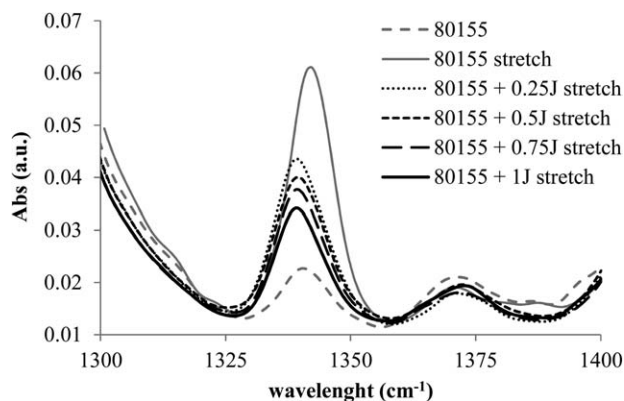

Figure 7. Methylene wagging absorption recorded from the normalized ATR-IR spectra of stretched and unstretched PET80155 blends modified with different amounts of Joncryl.

respectively.[35] The correlation is based on the fact that in the crystalline regions the PET chains are in an extended *all-trans* conformation; since the *gauche* conformers are only located in the amorphous regions, the *trans/gauche* ratio correlates with the degree of crystallinity.

In Figure 7, the superimposed IR spectra recorded from the plastic deformation zone of specimens undergone tensile tests are reported for the variously modified toughened r-PET blend (the spectrum for the unstretched and unmodified PET80155 blend is also reported for comparison).

The intensity of the *trans* peak is much higher for all the stretched samples than for the unstretched material, indicating that the polymer undergoes, as expected, strain-induced crystallization. However, the *trans/gauche* ratio decreases with increasing Joncryl content, suggesting that the macromolecular structural disorder and the reduced conformational freedom caused by the correspondingly increasing density of branching of PET macromolecules hinders the chain rearrangement induced by stretching, and thus crystallization. At these additive loadings, however, strain-induced crystallization is still largely allowed.

TEPGE as Viscosity Modifier for r-PET and the Toughened r-PET Blend

Since Joncryl contains a large number of epoxy groups (about 24) per molecule, its effect on the molecular structure of PET, and consequently on its properties, was expected and observed to be quite significant already at relatively low concentrations. To inves-

Table I. Tensile Properties of PET80155 Modified by Joncryl, at Different Chain Extender Concentrations, C_J

C_J (Joncryl wt %)	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)
0	1200 ± 100	27 ± 2	90 ± 30
0.25	1390 ± 50	25 ± 2	60 ± 40
0.5	1370 ± 80	27 ± 1	100 ± 30
0.75	1300 ± 100	27 ± 2	100 ± 40
1.0	1200 ± 200	29 ± 1	90 ± 30

tigate the role of the absolute number and structural density of reactive epoxy groups in the chain extender, the tetraglycidyl derivative of pentaerythritol, tetraglycidylpentaerythritol (TEGPE, Figure 8), was synthesized and used as branching agent for r-PET and the r-PET based toughened blend. The centrosymmetric structure of this tetraepoxide and its equivalent molecular weight as low as 82 g·mol^{-1} per epoxy group compares with the linear, oligomeric structure of Joncryl with its less dense concentration of epoxy groups (although six times larger in terms of absolute number of functional groups per molecule), corresponding to an epoxy equivalent molecular weight of 285 g·mol^{-1}.

First, the effect of the use of TEGPE as a chain extender of r-PET was investigated by preparing binary mixtures of the two components and by performing on-line (torque) and off-line (MFR) melt viscosity as well as mechanical (tensile) measurements. Two oligomeric PGCF polyepoxides (Figure 9) bearing a comparable number of epoxy (five and six functional groups per molecule, respectively, corresponding to an epoxy equivalent molecular weight of about 176 g·mol^{-1}) were also tested, as these would result in non-centrosymmetric branched PET structures as those expected when using Joncryl. A previous investigation on a diepoxy chain extender had shown that at such low functionality the molecule is practically ineffective.[9]

While r-PET is a simpler and possibly less interesting matrix than the PET80155 blend, it is also more suitable as a reference material since the competitive reactions with the different functional groups of the various compatibilizers in the PET80155 blend would make it very difficult to draw any straightforward and meaningful conclusion from a simple set of standard rheological and mechanical data. As shown in Figure 10, the effect of TEGPE on r-PET is less pronounced than that of Joncryl and comparable to that of the two PGCF oligomers.

It is worth pointing out that the MFR and torque data from the various blends are compared in Figure 10 by considering the equivalent number of epoxy groups introduced with the chain extender rather than the weight fraction, as a means to emphasize the role of the different structural modifications induced by the various chain extenders and neglect the effects deriving from the different density of functional groups (the higher the
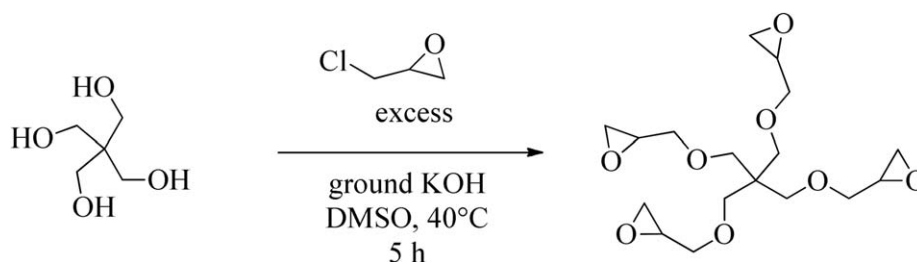
Figure 8. Schematic representation of the synthesis of TEGPE.

density, the lower the monoepoxy equivalent molecular weight). Given the similar effectiveness of TEGPE and the oligomeric PGCF chain extenders as modifiers of the r-PET melt viscosity, both types resulting in nearly star-like rather than comb-like branching of the polyester, only the former was further investigated as a modifier of the toughened r-PET blend.

In Table II, the melt viscosity and tensile properties of PET80155 modified with different amounts of TEGPE are summarized. The MFR and torque data show that TEGPE increases the viscosity of the r-PET blend, although less effectively than Joncryl. However, even from these simple technological measurements it is apparent that the blends modified with the two chain extenders display a different dependence of the melt viscosity on the shearing regime. In particular, achieving a final torque value comparable with that of the PET80155+0.5J blend (taken as the reference material) requires the addition of nearly 4 wt % TEGPE (corresponding to an epoxy equivalent ratio TEGPE/Joncryl ≈ 25). On the other hand, an MFR value similar to that of PET80155 + 0.5J is reached only slightly above 1.5 wt % TEGPE (epoxy equivalent ratio TEGPE/Joncryl ≈ 10), a clear indication that while the melt viscosity at low shear is somehow related to the total concentration of epoxy groups, it is the number of epoxy groups per molecule of chain extender, and hence the molecular architecture of the resulting chain-extended polymer, that affects more specifically the shear sensitivity of the polymer melt. The above results also indicate that TEGPE is better suited than Joncryl for fine tuning of the rheological behavior, since its concentration can be varied within a larger range before reaching the critical threshold corresponding to gel formation due to extensive branching and crosslinking. As in the case of the addition of Joncryl, the addition of TEGPE and J + PE did not result in a significant change of tensile properties with respect to the unmodified PET80155 blend.
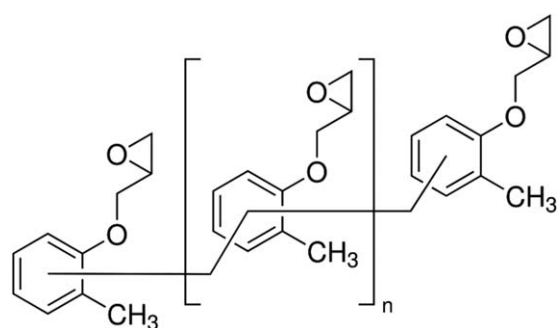
Competitive Branching and Chain Scission for Regulating Melt Fluidity

As a further way to modify the melt viscosity behavior of r-PET based blends, and thus adapt it to the requirements of different applications and processing conditions (e.g. sheet extrusion and thermoforming), the simultaneous use of Joncryl as a branching agent and pentaerythritol as a chain scission agent was evaluated. Pentaerythritol may participate in transesterification reactions with the internal ester groups of PET, leading to chain scission and branching with an overall effect on the molecular weight that is predictably dependent on the feed ratio of the two additives (Figure 11).

At low concentration (0.5 wt %) pentaerythritol does not cause significant changes in the melt viscosity of the PET80155 blend
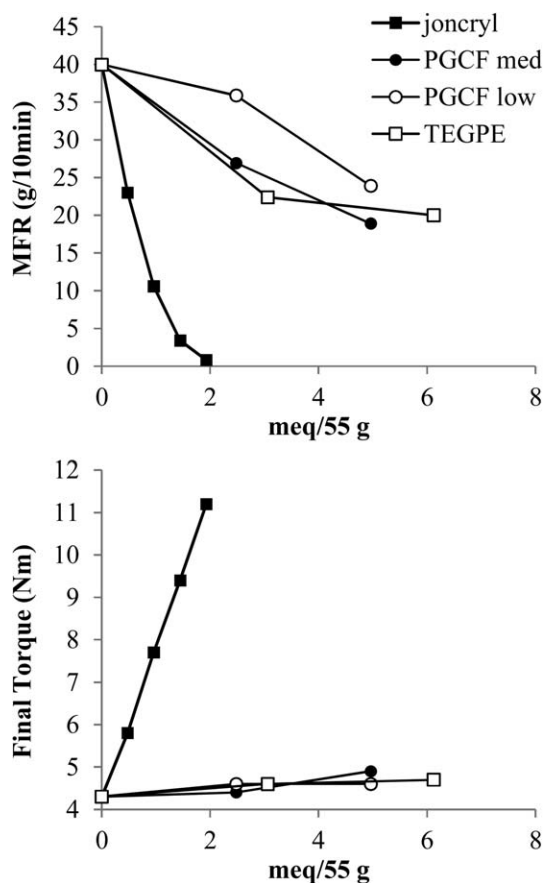

Figure 9. Structure of PGCF low ($n = 3$) and PGCF med ($n = 4$).

Figure 10. Variation of MFR (above) and final torque (below) as a function of the amount of chain extender (as meq of epoxy groups) added to 55 g of r-PET.

Table II. Melt Viscosity Data and Tensile Properties of the Chain-Extended PET80155 Blends

Chain extender	Additive concentration (wt %)	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Final torque (Nm)	MFR (g/10 min)
TEGPE	0.5	1100 ± 100	28 ± 2	110 ± 50	6.6	8.8
TEGPE	1.5	1200 ± 100	26 ± 2	130 ± 20	7.7	3.7
TEGPE	4.0	1200 ± 100	26 ± 2	120 ± 30	9.6	∼0
J + PE[a]	2.0	1200 ± 100	27 ± 1	90 ± 40	8.6	1.2

[a] Total amount of Joncryl and pentaerithritol 1/1 (by weight) mixture, as discussed in the paragraph: "TEPGE as Viscosity Modifier for r-PET and the Toughened r-PET Blend".

(final torque = 4.2 Nm), while at high concentration (5 wt %) polymer chain scission is extensive. In an experiment performed by adding in a discontinuous mixer under the usual conditions (270°C, 90 rpm) 5 wt % pentaerythritol and 0.5 wt % Joncryl to PET80155 a sharp drop in viscosity was observed (PET80155 + 0.5J + 5PE, Figure 12) and the final product was very brittle, as expected for a very low molecular weight material. Much better results were obtained by decreasing the amount of pentaerythritol (1 wt %) and increasing that of Joncryl (1 wt %), corresponding to the addition of 16.2 eq of hydroxy groups and 1.9 eq of epoxy ones (per 55 g of material). The values of MFR and final torque as well as the mechanical properties of the obtained material (last line of Table II) are comparable with those of the reference toughened blend PET80155 + 0.5J (see Table I), even though very different topologies of the final macromolecular structures (and therefore nonlinear rheological properties) are expected in the two cases.

Flame Retardation Through Combined Action of Phosphorus-Based Flame Retardants and Viscosity Reduction in a Chain-Extended r-PET Toughened Blend

Due to the increasingly severe restrictions on the use of halogenated flame retardant additives, the formulation of flame resistant PET based materials has become an open issue. This is mainly due to the tendency of PET to drip and propagate the flame as a result of low melt viscosity, which may even be enhanced by the acid- and base-catalyzed chain scissions caused at high temperature even by the less catalytically active phosphor-, sulphur-, and nitrogen-containing flame retardants. Increasing the melt viscosity is thus an effective way for improving the fire resistance and self-extinguishing behavior of flame-retarded PET formulations. In addition, chain extenders and chain branching additives with tunable effectiveness may be used to offset the deterioration of mechanical properties caused by the high load of additive often required when using less toxic but also less effective inorganic flame retardants.

In order to evaluate the suitability of the toughened PET80155 blend for applications requiring a given minimum level of fire resistance, the effect of the incorporation of various phosphorus based and inorganic phosphorated flame retardant additives on its fire resistance and the tensile strength was investigated. The simple addition of PAP (6 wt %; PAP = 50 wt % red phosphorus in a polyamide masterbatch), PEP (5 wt %; PEP = 50 wt % red phosphorus in an LDPE masterbatch), IPA (10 wt %; IPA = Al hypophosphite) or IPC (10 wt %; IPC = Ca hypophosphite) during the reactive blending of PET80155 + 0.5J gave materials with at best comparable or, in case of the
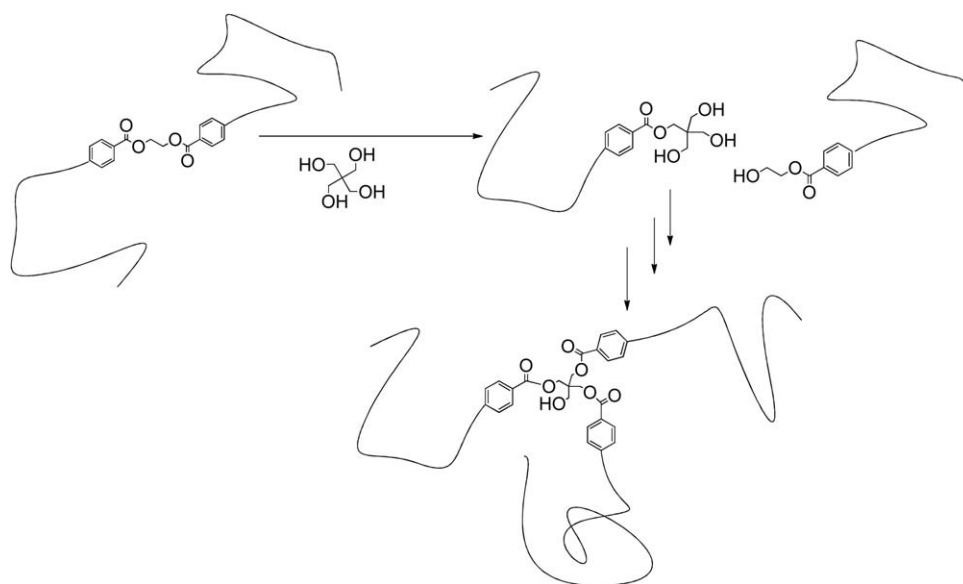
Figure 11. Transesterification reaction between pentaerythritol and PET.
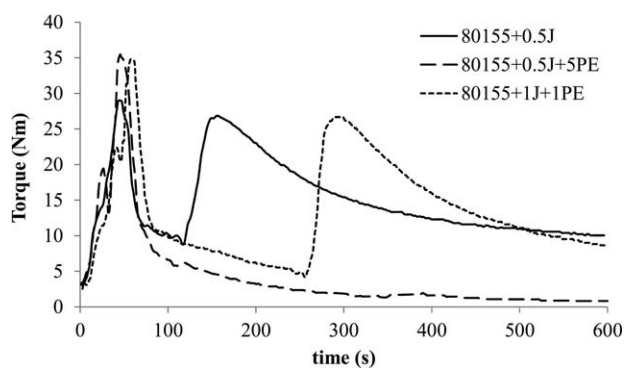
Figure 12. Torque vs. time trend during reactive blending of PET80155 + 0.5J, PET80155 + 0.5J + 5PE and PET80155 + 1J + 1PE.

hypophosphites, poorer mechanical properties than the parent polymer blend, while the fire resistance was not significantly improved (see Table III). In fact the HB class according to UL94 indicates a performance below the minimum threshold acceptable for most of the applications in which fire resistance is required. Since red phosphorous masterbatches (PAP and PEP) are a generally less preferred or altogether undesired choice because of their intense coloration, which is transferred to the final material posing severe limitations to the range of possible applications, further investigations were focused on the two hypophosphites, IPA and IPC.

By replacing the powdery pure inorganic additive with its masterbatch in a POFD1.5 matrix (m-IPA and m-IPC, respectively, containing 40 wt % hypophosphite in the masterbatch) both the melt viscosity and the extensibility of the filled r-PET blend could be significantly improved with respect to the material obtained from the same overall feed composition (the total amount of POFD1.5, including the fraction from the masterbatch, was kept at 15 wt % of the total polymers in the feed), but with direct addition of the hypophosphites in the feed of the melt mixer together with the other components of

the reactive polymer blend. The actual role played by the masterbatch could hardly be limited to a better dispersion of the hypophosphite during reactive blending. A more sensible although purely descriptive explanation would be that by embedding the hypophosphites in a reactive POFD1.5 matrix prior to blending with the other components of the r-PET based feed, the direct contact between additive particles and PET is either prevented or delayed by the rubbery component sheathing the inorganic particles, and thus the possibility of PET chain cleavage catalyzed by the hypophosphite is effectively hindered. Inspection of the SEM images obtained from the cryogenically fractured blend surfaces before and after solvent etching to remove the phase-separated rubbery domains (Figure 13) confirms that at least a fraction of the hypophosphite particles are still within the polyolefin domains; in fact they are removed more efficiently from the blends prepared with m-IPA rather than from those prepared with the raw hypophosphite particles.

While the mechanical properties of the r-PET toughened blend could be preserved by using the hypophosphite masterbatches, their flame resistance was still unsatisfactory. Clearly, a higher concentration of the hypophosphite or a combination of flame retardant additives was required to improve the fire resistance of the toughened blend. This could not be done with m-IPC since the sharp reduction of melt viscosity at low shear caused by this additive did not allow to increase its concentration above 10 wt %. On the other hand, when the m-IPA content was raised to 20 wt % the fire resistance could be improved to the V2 class while the mechanical and rheological properties remained still acceptable. The same improvement of fire resistance could be achieved at 10 wt % IPA if a synergistic additive was used (5 wt % melamine cyanurate, MC), although at the cost of a significant increase of brittleness as evidenced by the reduction from 110% down to 55% of the elongation at break. Replacement of Joncryl with a fourfold amount of TEGPE had a minor effect on the mechanical properties and flame

Table III. Properties of PET80155 + 0.5J Modified with Flame Retardant Additives

Additive	Young's modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Final torque (Nm)	MFR (g/10 min)	UL94 class
None	1370 ± 80	27 ± 1	100 ± 30	9.8	1.7	–[c]
PAP 6%	1180 ± 90	26 ± 1	108 ± 17	10.9	1.3	HB
PEP 5%	920 ± 180	25 ± 2	127 ± 28	11	2.4	HB
IPA 10%	1230 ± 130	26 ± 2	50 ± 20	7.9	8.8	HB
IPC 10%	1170 ± 80	26 ± 1	70 ± 30	10.3	1.3	HB
m-IPA 10%	1130 ± 80	25 ± 1	110 ± 40	9.7	2.4	HB
m-IPC 10%	1100 ± 50	26 ± 2	90 ± 50	10.3	0.3	HB
m-IPA 10% + MC[a]	1100 ± 70	26 ± 1	55 ± 15	7.3	1.0	V2
m-IPA 20%	1090 ± 90	24 ± 1	73 ± 15	7.7	2.4	V2
m-IPA 20%+TEGPE[b]	1030 ± 50	23 ± 1	70 ± 20	7.7	5.2	V2

[a] Melamine cyanurate (MC) added to the m-IPA masterbatch (5 wt % MC in the final blend, 25 wt % MC in the masterbatch).
[b] Joncryl (0.5 wt %) replaced with TEGPE (2 wt %).
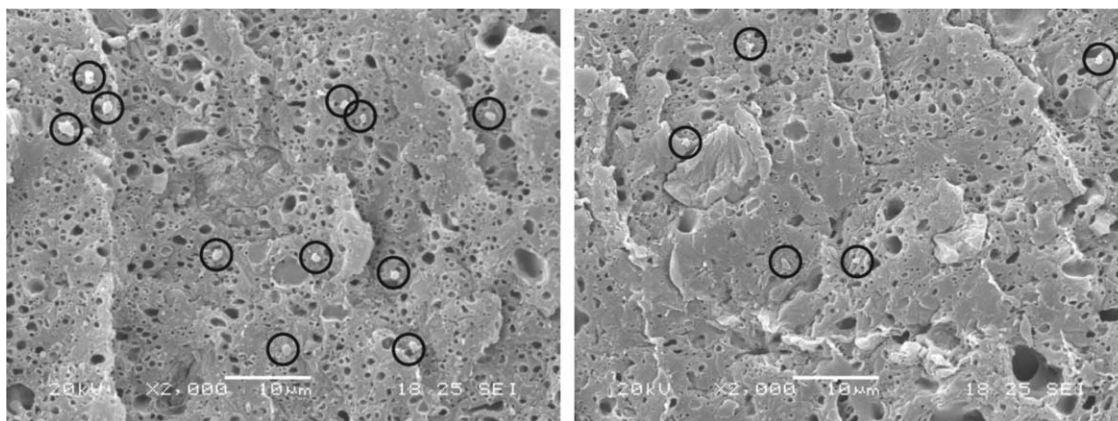[c] Not flame extinguishing: HB grade not achieved

Figure 13. SEM picture on cryogenic fractures of IPA 10 (left) and M-IPA 10 (right). Samples etched with hot toluene.

resistance of the PET80155 blend loaded with 20 wt % IPA. On the other hand, the unaffected final torque and higher MFR values indicate less extensive branching of PET, possibly associated with a lower reactivity of this chain extender (lower conversion of the epoxy groups due to steric hindrance and/or to poorer miscibility of TEGPE with the polymer matrix). In fact, as discussed before, a high density of branching affects the melt viscosity more heavily at high shear than at low shear; therefore a highly branched, high MW polymer as obtained with Joncryl may display a high shear viscosity (as determined by the final torque) similar to that of a less branched but lower MW analogous as obtained with TEGPE, even though the latter may show a significantly lower viscosity at low shear (as determined by MFR).

CONCLUSIONS

Various polyepoxy chain extenders, either commercially available or prepared by a simple synthetic procedure, were used as viscosity modifiers for new thermoforming grade r-PET based formulations, and their effect on the melt viscosity and mechanical properties of both r-PET and a toughened r-PET blend were investigated. In particular, by using 1.5 wt % of the commercial oligomeric Joncryl a material with sufficiently high melt viscosity and elongation at break could be obtained. Compared to Joncryl, that was observed to cause a sharp increase of melt viscosity with increasing chain extender concentration, both the low MW tetrafunctional TEGPE and a combination of a tetra-ol (pentaerythritol) and Joncryl allowed to expand the range of achievable melt fluidity without markedly downgrading the tensile properties of the polymer blend. It is worth remarking that using the latter combination of additives, promoting concurrent chain scission and hyperbranching of PET macromolecules, is a potentially powerful tool to enhance rheological non-linearity.

Various phosphorus-containing flame retardant additives were performed to assess their effect on the fire resistance as well as the ultimate melt fluidity and tensile properties of the resulting compounds. All the investigated blend compositions reached the HB class of fire resistance at additive loadings low enough to prevent any significant downgrading of melt rheology and mechanical

properties of the blend, providing that the respective masterbatch rather than the pure additive was used. In particular, with the IPA hypophosphite masterbatch the UL94-V2 class could be reached either by increasing the amount of additive from 10 wt % up to 20% or by addition of the synergistic melamine cyanurate.

While the achieved flame retardation effect is still below the threshold required for most practical uses, the results of the present investigation clearly indicate that by adopting a comprehensive approach including a proper choice of both chain extenders and flame retardant additives, leading to suitable modifications of the PET macromolecular structure and preventing the possible side reactions between flame retardant additive and polymer matrix, even a challenging material such as r-PET can be successfully turned into a high performing fire resistant material. In the specific case of a toughened r-PET blend investigated in this work, the preparation of a masterbatch of aluminum hypophosphite in the same reactive polyolefin used as the toughening component proved to be a promising strategy to prevent polymer chain scission during processing, preserve the mechanical properties of the material, and improve its ultimate fire resistance.

The obtained results demonstrated that a selection of the proper structural features of PET chain extenders is required to achieve a comprehensive control of processability, in particular when the presence of reactive polymer modifiers and other additives may result in complex reactivity patterns with the PET matrix and among the additives themselves. This is especially important when aiming at up-grading the melt viscosity behavior of r-PET not only to adapt it to different melt processing requirements, but also to overcome potential problems arising from the specific reactivity of flame retardants. The successful preparation of r-PET based materials suitable for extrusion of thermoformable thick sheets opens up the perspectives for using recycled PET in a wide variety of products in the transportation, construction and furniture sectors.

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