

# POST-CONSUMER POLY(ETHYLENE TEREPHTHALATE) IN COMPOSITES AND BLENDS FOR AUTOMOTIVE APPLICATIONS

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## SUMMARY

The possibility of employing materials based on post-consumer PET for injection moulded external and internal body parts in automotive and other applications requires passing mechanical properties, processability, weather resistance, surface stability. Different strategies pursued in our laboratory to improve the properties and broaden the application range of r-PET are shortly reviewed.

*Keywords: PET, toughness; flame resistance, reactive processing, polymer blends*

## INTRODUCTION

Polyethylene terephthalate (PET) is extensively used for the production of fibers, films, and bottles for water and other beverages (especially carbonated drinks) as well as containers for other edible products because of its combination of unique physical, mechanical, and permeability properties, as well as processability. As an engineering thermoplastic material it offers, among others, excellent high-temperature mechanical performance, creep behaviour, and solvent resistance. Besides, the case of PET is particularly fortunate because it is easily separable from other urban waste, usually through mechanical sorting processes assisted by optical sensor and/or by flotation fractionation. This allows an economically viable recovery when properly complemented by the education of citizens and regulation.

In Italy the selective collection of post-consumer plastics is essentially limited to packaging materials, dominated by polyethylene and PET. In particular, the PET main stream comes from post-consumer beverage bottles. Although the reclaiming of PET as flakes with an adequate purity for mechanical recycling requires a complex multi-step treatment (washing, grinding, flotation, etc.), the final product – PET flakes - shows only slightly downgraded properties with respect to those of virgin PET, but at a decidedly lower cost. This, together with increasing environmental pressure and demanding regulations, is pushing industry towards its reuse. However, the success of PET recycling depends on the possibility of developing strategies leading to materials and products with high technical value.

In the automotive industry the necessity of using recyclable materials is becoming more and more stringent because of environmental regulations, which are promoting the reuse and recycling of all the materials deriving from end-of-life vehicles (ELV).

Every year, in the EU between 8 and 9 million tonnes of waste are generated by ELV, which should be managed in a more environmentally and economically viable fashion. The EU Regulation 2000/53/CE aims at making vehicle dismantling and recycling more environmentally friendly, sets clear quantified targets for reuse, recycling and recovery of vehicles and their components and pushes producers to manufacturing new vehicles also with a view to their recyclability.

In this context, post-consumer materials based on PET are suitable for automotive applications not only because they are recyclable (downstream perspective), but also because they may be produced from recycled PET (upstream perspective), resulting in an overall energetically and economically favourable lifecycle extension.

The possibility of upgrading the recycled PET (r-PET) to new engineering materials has been largely investigated in the last decade. Toughened materials have been obtained by blending r-PET with various olefin copolymers or functionalized polyolefins (1, 2). The high solvent resistance of PET based materials can allow their use in the parts of the vehicles close to the fuel tank, where polyolefin based or ABS based materials, not much suitable for this application, are usually employed. Depending on the specific function, the possibility of employing materials based on post-consumer r-PET for external and internal injection moulded parts in automotive and other applications may require the optimization not only of mechanical properties (toughness or stiffness), but also of surface stability and flame retardancy.

The toughness of PET-based materials can be improved by blending with elastomeric polyolefins. However, as the compatibility between PET and polyolefins is poor, reactive compatibilization methods are usually adopted (1-7). Maleic anhydride (1) or glycidyl methacrylate (8) modified polymers, bearing anhydride or epoxy groups reactive towards PET terminal hydroxyl or carboxylic groups, respectively, showed the best efficiency. In particular, fine tuning of the reactivity by appropriate formulation and processing conditions was shown to result in correspondingly improved phase morphology and final properties of such blends (1, 4, 9).

The stiffness of PET-based materials can be improved by adding proper micro or nano fillers or reinforcing additives. Some authors have recently reported on the preparation and properties of PET-montmorillonite nanocomposites (10-13). According to their results, as the thickness of the layered silicate falls in the nanometre scale addition of just a small amount (lower than 5% by weight) of the filler is sufficient to significantly improve the stiffness. Moreover, improved gas barrier properties and increased degradation temperatures were also observed for these composites.

When using post-consumer recycled polymers the addition of melt viscosity regulators in the formulation is generally required to adjust the rheology and match the specifications for e.g. injection moulding or thermoforming processing. In the case of r-PET based compounds upgrading of the polymer melt rheology is achieved by addition of chain extenders or branching agents (14).

As an example, in injection moulded objects produced with compounds based on post-consumer r-PET the occurrence of surface instability due to delayed crystallization

induced by thermal aging may be critical, as it can negatively affect the appearance of injection moulded pieces and impair the adhesion of coatings or paints, e.g. for the external body in the automotive and household appliance sectors.

Flame retardancy is also critical for PET-based materials, particularly if they have to be approved for the fabrication of components of inner part of vehicles. Due to the ban of halogenated flame retardants, phosphorous based organic and inorganic additives are gaining increasing attention, as evidenced by Wang (15), Liu (16) and Chen (17).

In the present paper the strategies adopted for the control of toughness, stiffness, processability, surface properties and flame retardant properties of post-consumer r-PET based compounds is described with a particular emphasis on possible applications of these compounds.

### **Toughness of compounds based on post-consumer r-PET**

The toughening of pseudo-ductile materials can be attained by incorporating rubber as the minor phase. The rubber should therefore be present in the form of dispersed domains within the brittle polymer matrix and the dimensions of the dispersed phase be smaller than a critical value. This general rule about polymer blends was applied to r-PET/r-LDPE (recycled low density polyethylene) blends. The composition of the not compatibilized blend A (table 1) was 70 wt.% of r-PET and 30 wt.% of r-LDPE. As expected, this blend showed deterioration of the mechanical properties with respect to pure PET (typical values for injection blow-moulding grade PET are 1-3 % elongation at break and < 20 J/m Izod).

Table 1: Composition and morphologic features of the PET/LDPE blends

Blends	LDPE [% by weight]	POF ( MAH content in POF) [% by weight]	d (μm)
A	30	-	12 ± 6
B	20	10 (0.3)	3.8 ± 2.7
C	20	10 (1.0)	0.9 ± 0.5
D	20	10 (1.5)	0.7 ± 0.4

When maleic anhydride (MAH) functionalized rubber (POF) was added to post-consumer r-PET/r-LDPE blends as a compatibilizer and a phase morphology regulator, the average diameter of the dispersed phase domains decreased along with the increase of MAH content in the rubber. The compatibilized blends were prepared by keeping constant the composition PET/LDPE/POF 70/20/10 whereas the content of maleic anhydride grafted in the rubber was varied.

The tensile properties (figure 1) showed a corresponding improvement with increasing elongation at break. Moreover the Izod Impact Strength tests (Figure 1) showed that the compound with POF had properties similar to toughened virgin poly(butylene terephthalate), widely used for household appliances and in automotive applications.

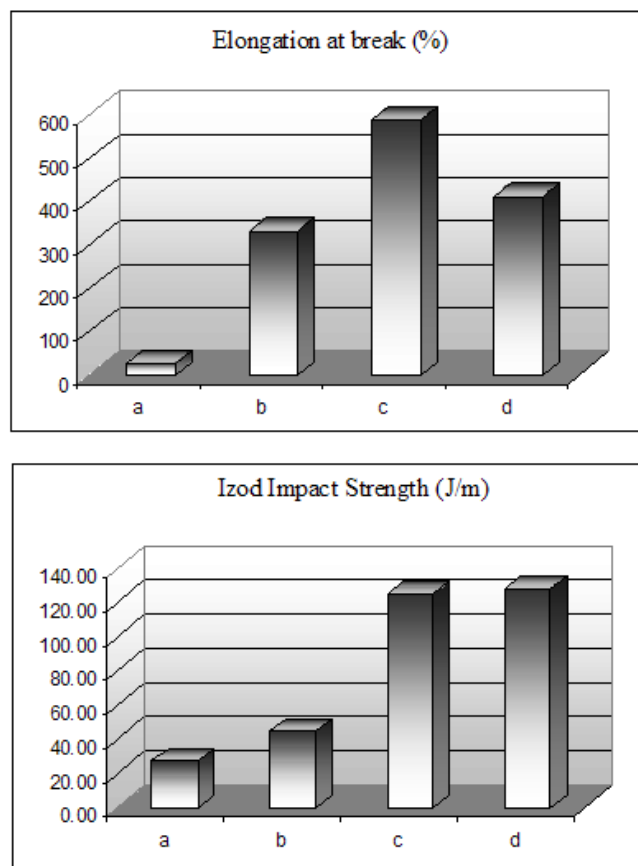


Figure 1. Elongation at break and Izod Impact Strength

These preliminary results gave the first indications on a promising route to attain toughened r-PET through simple and cheap processes. The subsequent expansion of the field of investigation involved using chain extenders and nucleating additives in pure r-PET or in its blends with polyolefins or POF. At the same time the properties of these materials were studied with the purpose of identifying and defining the optimal conditions for processing by injection moulding and thermoforming, thus providing additional perspective for the industrial development of post-consumer PET based products.

The initial stage of the investigation was aimed at developing formulations providing materials with improved toughness, and to define a compound composition suitable for processing through injection moulding. The excellent impact properties are exemplified by the successful preparation of ski helmet prototypes passing the crash tests.



Figure 2. Ski helmet prototype made by injection moulding of a toughened r-PET.

### Stiffness of compounds based on post-consumer r-PET

Post-consumer r-PET based nanocomposites were prepared by melt-mixing r-PET flakes with either a Na-montmorillonite or a modified organophilic montmorillonite (HPS and D43B, respectively, a kind gift of Laviosa Chimica Mineraria, Leghorn, Italy).

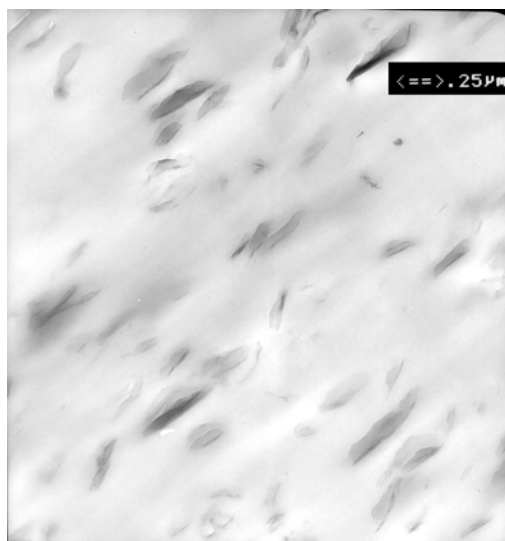
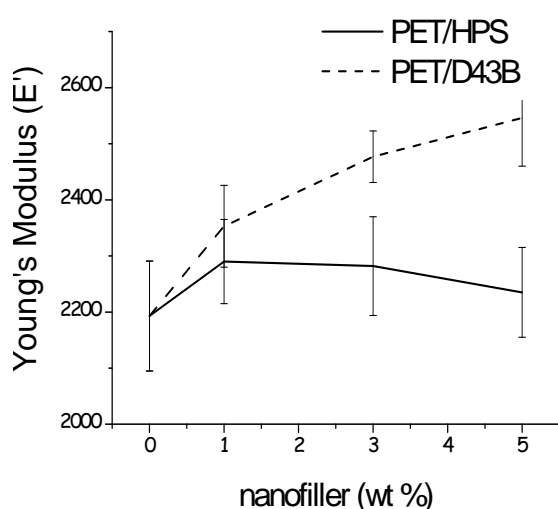


Figure 3. (left) Young's Modulus as a function of nanofiller content; (right) TEM micrograph of r-PET containing 3 wt% organophilic modified montmorillonite (D43B).

The introduction of the layered silicate results in increased stiffness of the r-PET nanocomposite already at very low nanoclay content. In particular, as shown by the results of the tensile data, the Young's Modulus progressively increased with increasing content of the organophilic nanofiller D43B. On the other hand, addition of HPS results in a slight increase in stiffness at very low loading, but the reinforcing action is not maintained upon increasing the amount of nanoclay.

The reason of this difference is due to the better dispersion of D43B than HPS. In fact, as confirmed by the WAXD spectra (not shown), in the former case stronger matrix-filler interactions cause the nearly complete disappearance of the interlayer reflections from the lamellar structure of the nanoclay, indicating the generation of a larger polymer-silicate interface. The formation of a true nanocomposite morphology is confirmed by the TEM analysis, showing the presence of stacks and lamellae of nanometric dimensions (figure 3). On the other hand the dispersion of HPS in the r-PET matrix is comparatively poor, and consequently the WAXD diffractogram presents still the reflections characteristics of large silicate staks. Hence the organophilic modification of the montmorillonite was essential.

### Processability of compounds based on post-consumer r-PET

Thermoforming processing of a compound based on r-PET mainly reclaimed from injection-moulding grade virgin PET requires a significant adjustment of its rheology. In fact the production of sheets through extrusion requires a higher viscosity than that typical of post-consumer r-PET.

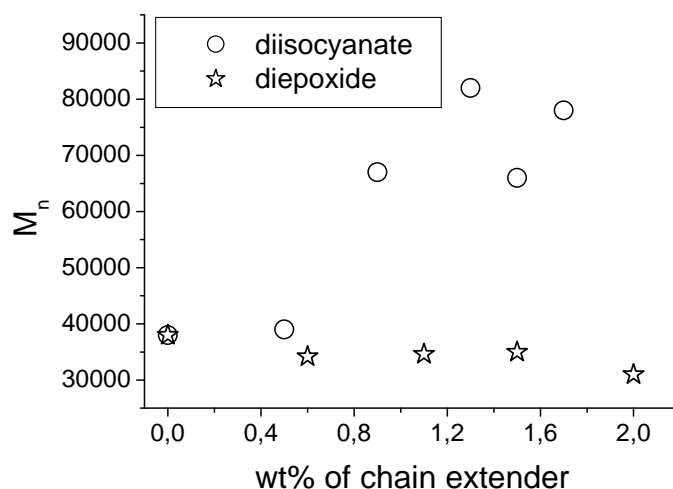


Figure 4. Average molecular weight of r-PET as a function of wt% of chain extender

For this purpose different reactive modifiers were tested as melt viscosity regulators. Preliminary tests carried out using 1,6-diisocyanato-hexane (hexamethylene diisocyanate, HMDI) and 1,4-butanediol diglycidyl ether were carried out in order to understand which reactive group was more retractive toward PET terminals. In fact the scientific literature does not provide unambiguous information on the most effective reactive groups for the chemical modification of the polyester chain ends of PET. On the basis of molecular weight determinations made by SEC analysis, the diisocyanate resulted more reactive than diepoxide.

In fact, while in both cases an increase of viscosity was observed, the diisocyanate chain extender leads to a more marked shear thinning behaviour, suggesting the generation a more highly branched structure of modified PET chains. The values of fluidity index obtained by the use of these chain regulators could be adjusted within the range suitable for the extrusion of sheets.

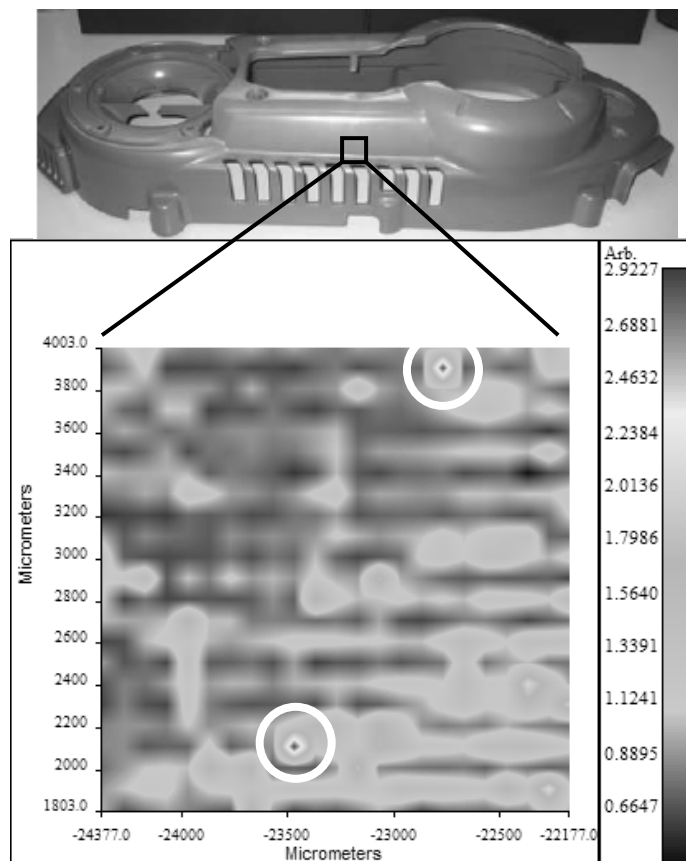


Figure 5. Above: injection moulded engine cover prototype for a motorvehicle. Below: infrared microscope micrograph mapping of its surface after a 70 h immersion in water at 50 °C (the encircled spots correspond to the highest spots generated by crystal growth).

### Surface properties of compounds based on post-consumer r-PET

The compound based on r-PET was injection moulded into a prototype motorcycle engine cover. The moulded piece was artificially aged by a 70 h immersion in water at 50 °C. Subsequent surface analysis by infrared microscopy revealed the generation of surface inhomogeneities associated with the presence of regions of higher crystallinity of PET. As a result the micro-roughness of the material increased and the scattered presence of sharp protrusions could be observed (the two red points in figure 5). The surface modifications occurring upon hydrothermal ageing resulted in a marked instability of the water-based paint layer prepared with a WB product currently used for other polymer surfaces. By selecting a more hydrophobic WB coating product this disadvantage was overcome. The painted surface resulted quite stable, matching the strict requirements of a major motorvehicle manufacturer.

### Flame retardant properties of post-consumer PET based compounds

After testing several poorly effective inorganic additives based on B, Mg, and Zn derivatives, different percentages by weight of an Al hypophosphite (IPA) were added

to a r-PET blend in different amounts. The materials thus prepared were tested for flame resistance (FR) according to UL-94. Addition of 20 % and 10 % by weight of IPA, respectively, resulted in appreciable FR properties, as determined from the time necessary to achieve the self-extinction of the flame ( $t_{\text{ext}}$ ). However, due to the presence of large agglomerates of the inorganic additive (figure 6) the material became quite brittle. In fact the strain at break under tensile testing decreased significantly already upon addition of small amounts of IPA. Other phosphorous-containing flame retardant additives were also tested. In particular, polyamide- and polyolefin-based masterbatches containing red phosphorous allowed to obtain good flame retardant properties for the r-PET based blends, without the negative implications given by IPA. The specific role of the type of polymer in the masterbatch, and particularly the influence of the uniformity of distribution of the active component (red phosphorous) within the r-PET compound on the FR behaviour of the compound, are currently investigated..

Table 2. Content of IPA and corresponding time elapsed before extinction of the flame ( $t_{\text{ext}}$ )

Sample	IPA (wt-%)	$t_{\text{ext}}$ (s)
IPA20	20	21
IPA10	10	12
IPA5	5	73
IPA3	3	59
IPA1.5	1.5	$\infty$
r-PET blend	0	$\infty$

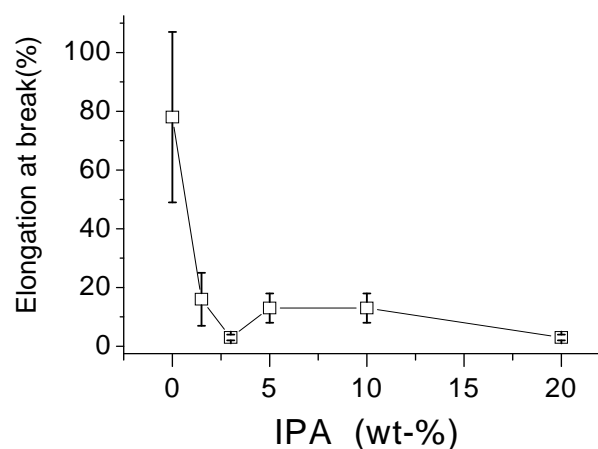
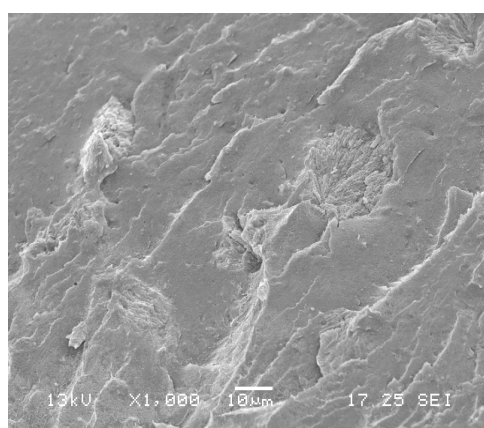


Figure 6. SEM micrograph (left) and results of tensile tests as a function of wt % of IPA.



## CONCLUSIONS

New post-consumer compounds and composites based on r-PET with tunable toughness, stiffness, processability, surface and flame retardant properties can be obtained by appropriate choice of formulations and reactive processing conditions. The successful preparation of high-performance materials is the results of an interdisciplinary approach to explore the potential for high added value applications of post-consumer PET, and thus for favouring its recycling.

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## References

1. Aglietto M, Coltelli M-B, Savi S, Lochiatto F, Ciardelli F, Giani M. Postconsumer polyethylene terephthalate (PET)/polyolefin blends through reactive processing. *J. Mater. Cycles and Waste Management* 2004;6:13-19.
2. Coltelli M-B, Harrats C, Aglietto M, Groeninckx G. Influence of compatibilizer precursor structure on the phase distribution of low density poly(ethylene) in a poly(ethylene terephthalate) matrix. *Polym. Eng. Sci.* 2008;48:1424-1433.
3. Coltelli M-B, Aglietto M, Ciardelli F. Influence of the transesterification catalyst structure on the reactive compatibilization and properties of poly(ethylene terephthalate) (PET)/dibutyl succinate functionalized poly(ethylene) blends. *Eur. Polym. J.* 2008;44:1512-1524.
4. Coltelli M-B, Bianchi S, Aglietto M. Poly(ethylene terephthalate) (PET) degradation during the Zn catalyzed transesterification with dibutyl maleate functionalized polyolefins. *Polymer* 2007;48:1276-1286.
5. Coltelli M-B, Bianchi S, Savi S, Liuzzo V, Aglietto M. Metal catalysis to improve compatibility at PO/PET blends interfaces. *Macromol. Symp.* 2003;204:227-236.
6. Coltelli M-B, Della Maggiore I, Savi S, Aglietto M, Ciardelli F. Modified styrene-butadiene-styrene block copolymer as compatibiliser precursor in polyethylene/poly(ethylene terephthalate) blends. *Polym. Degrad. Stab.* 2005;90:211-223.
7. Coltelli M-B, Savi S, Della Maggiore I, Liuzzo V, Aglietto M, Ciardelli F. A model study of  $Ti(OBu)_4$  catalyzed reactions during reactive blending of polyethylene (PE) and poly(ethylene terephthalate) (PET). *Macromol. Mater. Eng.* 2004;289:400-412.
8. Loyens W, Groeninckx G. Phase morphology development in reactively compatibilized polyethylene terephthalate/elastomer blends. *Macromol. Chem. Phys.* 2002;203:1702-1714.

9. Coltelli M-B, Coiai S, Bronco S, Passaglia E. Nanocomposites based on phyllosilicates: from petrochemicals to renewable thermoplastic matrices. in *Advanced Nanomaterials* K. E. Geckeler Ed., Wiley, in press, 2009.
10. Hwang SY, Lee WD, Lim JS, Park KH, Im SS. Dispersibility of clay and crystallization kinetics for in situ polymerized PET/pristine and modified montmorillonite nanocomposites. *J. Polym. Sci., Part B: Polym. Phys.* 2008;46:1022-1035.
11. Lee S-S, Ma YT, Rhee H-W, Kim J. Exfoliation of layered silicate facilitated by ring-opening reaction of cyclic oligomers in PET-clay nanocomposites. *Polymer* 2005;46:2201-2210.
12. Chung JW, Son S-B, Chun S-W, Kang TJ, Kwak S-Y. Nonisothermal crystallization behavior of exfoliated poly(ethylene terephthalate)-layered silicate nanocomposites in the presence and absence of organic modifier. *Journal of Polymer Science, Part B: Polym. Phys.* 2008;46:989-999.
13. Calcagno CIW, Mariani CM, Teixeira SR, Mauler RS. The effect of organic modifier of the clay on morphology and crystallization properties of PET nanocomposites. *Polymer* 2007;48:966-974.
14. Awaja F, Daver F, Kosior E. Recycled poly(ethylene terephthalate) chain extension by a reactive extrusion process. *Polym. Eng. Sci.* 2004;44:1579-1587.
15. Wang L-S, Kang H-B, Wang S-B, Liu Y, Wang R. Solubilities, thermostabilities and flame retardance behaviour of phosphorus-containing flame retardants and copolymers. *Fluid Phase Equilib.* 2007;258:99-107.
16. Liu W, Chen D-Q, Wang Y-Z, Wang D-Y, Qu M-H. Char-forming mechanism of a novel polymeric flame retardant with char agent. *Polym. Degrad. Stab.* 2007;92:1046-1052.
17. Chen D-Q, Wang Y-Z, Hu X-P, Wang D-Y, Qu M-H, Yang B. Flame-retardant and anti-dripping effects of a novel char-forming flame retardant for the treatment of poly(ethylene terephthalate) fabrics. *Polym. Degrad. Stab.* 2005;88:349-356.