Macromol. Symp. ***135****, 157-165 (1998)*

The Role of Additives in the Recycling of Polymers

Francesco Paolo La Mantia

Dipartimento di Ingegneria Chimica dei Processi e dei Materiali,
Universita di Palermo, Viale delle Scienze, 90128 Palermo, Italy

Abstract: The main problems in post-consumer plastics recycling are due to the degradation undergone by the polymers during processing steps and by the products during their lifetime and, for heterogeneous recycling, to the incompatibility of different polymers. To reduce the negative effects of the recycling steps, two main ways can be adopted for homogeneous materials: *restabilization* during the recycling to avoid or at least to slow the degradation and addition of *fillers* and *modifiers* capable of improving the performance of thermoplastic polymers without increasing the final cost of the secondary material. In the case of mixed plastics, *compatibilization* is the necessary step to obtain secondary materials with acceptable properties.

INTRODUCTION

Additives play a very important role both in the processing of plastic materials and in their applications (Ref. 1). With the term additives, we mean all substances, inorganic and organic, that alter one or more properties of polymers. The most important classes of additives are:

- *processing aids:* improve polymer processability
- *antioxidants* and *stabilizers*: delay their degradative processes
- *mineral fillers:* can decrease their costs and enhance some of their properties
- *impact modifiers:* increase, in particular, the impact strength values
- *compatibilizers:* improve the compatibility between incompatible polymers

Other additives, like antistatic agents, flame retardants, antidrop, etc., are used for particular applications.

The additives in plastics recycling probably play the same role. In fact, one or more classes of additives of those cited can prevent some degradative phenomena, particularly dangerous in the reprocessing operations or in the use of recycled materials, and/or remarkably improve deteriorated properties of these secondary materials.

CCC 1022-1360/98/$ 17.50

In this work, the main additives that can be used in recycled plastics are briefly described and some examples of the effect of these substances on the properties of recycled plastics are reported.

MAIN PROBLEMS IN PLASTICS RECYCLING

Main problems in the homogeneous plastics recycling are only related to the degradative phenomena occurring during recycling processes (Ref. 2). These phenomena are generally much more dramatic than in virgin polymers since the oxygenated groups, formed during the processing or during the use, remarkably accelerate the degradation of plastic materials. This causes serious deterioration of end properties of secondary materials.

The same problems occur, of course, also in heterogeneous plastics recycling, but the presence of polymers having different chemical structures, and hence incompatible, gives rise to blends with poor properties, in some cases worse than those of neat polymers (Ref. 2). Therefore, in order to obtain secondary materials with acceptable properties, it is necessary:

- *to protect materials from thermomechanical degradation* occurring during recycling operations
- *to improve the properties of the secondary materials* by means of modifier agents or fillers
- *to compatibilize* the blends of mixed plastics

STABILIZING AGENTS

Some polymers, like PP and PVC, must be stabilized against thermomechanical degradation because of their limited thermal stability. The stabilization becomes necessary during reprocessing to stop, or at least to slow, the degradation phenomena of these polymers and the consequent deterioration of their rheological and mechanical properties (Ref. 3).

In order to investigate the change in the molecular structure of PP during repetitive reprocessing, the melt flow index, MFI, of a moulding-grade PP has been reported as a function of the number of injection-moulding steps (Fig. 1) (Ref. 4). In the same figure, the melt index of the same polymer in the presence of two stabilizers, added before each processing step, is shown. B900 (CIBA) is a mixture of Irganox 1076 and Irgafox 168, while P-EPQ (Sandoz) is a phosphite stabilizer (0 means virgin polymer, 1 first processing, 2 second processing and then first recycling step, etc.).

The dramatic increase in the MFI of the unstabilized sample suggests a drastic degradation of PP due to the thermomechanical stress acting during the processing. After the first recycling, the MFI value is about twice that of the virgin sample. The degradation is strongly reduced by adding the stabilizer before each injection-moulding step. In this case, MFI slightly increases indicating a small change in the molecular weight. The two stabilizers seem to act in a similar way.

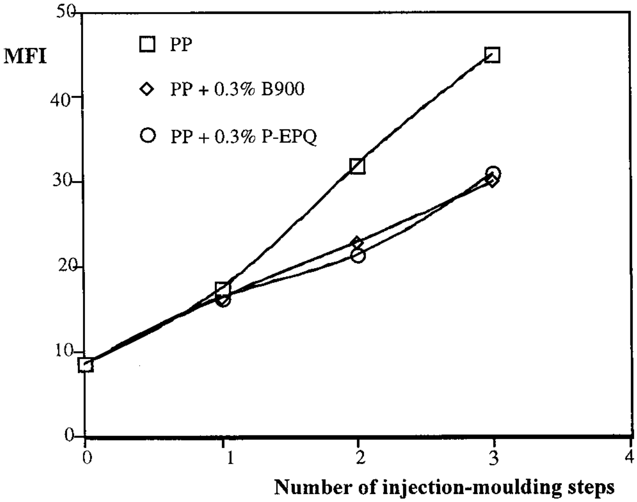

Fig. 1 Melt flow index vs number of the injection-moulding steps for stabilized and unstabilized PP

The stabilizer also allows to avoid dramatic deterioration of some mechanical properties. In Table 1, the elongation-at-break of an extrusion-grade PP (stabilized and not stabilized) after five extrusion steps is reported (Ref. 4). Without any stabilization, the PP sample shows a brittle fracture after five extrusion steps while the elongation-at-break value is very close to the virgin polymer if the stabilizer is added before each extrusion.

Table 1 Elongation-at-break of stabilized and unstabilized PP

Sample	Elongation-at-break, %
PP virgin	680
PP after five extrusions	20
PP + 0.3% B900 after five extrusions	520
PP + 0.3% P-EPQ after five extrusions	560

The poor thermal stability of PVC requires the addition of heat stabilizers to prevent a large extent of degradation. The stabilizer in the PVC products is consumed both during processing and sometimes during the lifetime; the thermal stability is remarkably reduced if PVC is subjected to the reprocessing steps.

The dynamic thermal stability time (DTST), the time at which the torque in a mixing test at constant temperature starts to rise, is a good index for evaluating thermal stability (Ref. 5). Degradation of PVC gives rise to loss of hydrogen chloride and the formation of unsaturated chains having high viscosity. This parameter is, of course, dependent on the processing conditions, in particular on temperature and time of processing, and on the applied mechanical stress.

The effect of temperature and mechanical stress is put in evidence in Fig. 2 (Ref. 6) where the DSDT values of a PVC sample recycled from bottles are reported as a function of temperature for three different rotational speeds. DTST decreases with increasing temperature and rotational speed. Of course, mechanical stress rises with rotational speed. However, a dramatic reduction in DTST is observed, however, when the temperature is equal or larger than 200 °C. The effect of mechanical stress is to increase the rate of formation of macroradicals and, in fact, it acts as a "catalyst" of thermal degradation.

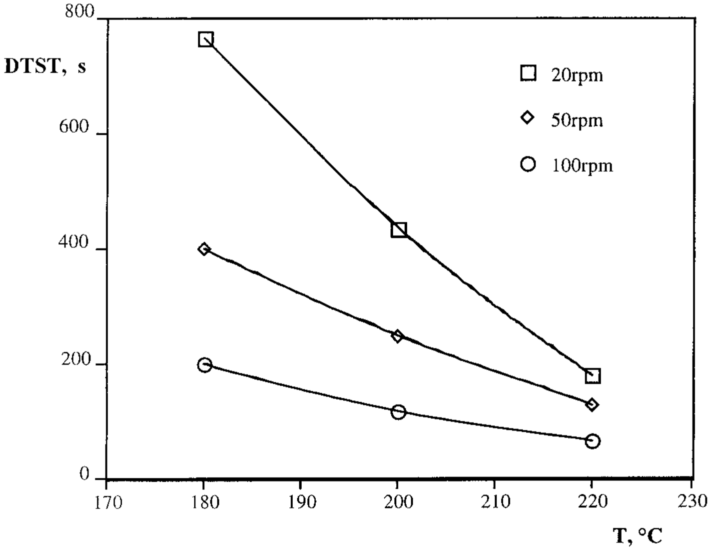

Fig. 2 DTST of PVC recycled from bottles as a function of temperature and rotational speed during processing

To enhance the processability, it is therefore necessary to increase the DTST value by adding suitable stabilizing systems which have been consumed during both processing and the lifetime of the PVC products.

The effect of a lead stabilizer on the processability of recycled PVC is evidenced in Fig. 3 (Ref. 6) where the DTST values in some processing conditions are reported as a function of the stabilizer content. The thermal stability of PVC is greatly enhanced by adding 1 phr of the stabilizer. Then the curve tends to flatten and the processability is not remarkably improved by increasing the concentration of the stabilizer. The stabilizer is particularly effective at high temperature and rotational speeds. Indeed, in these processing conditions, DTST increases about three times by adding 1 phr of the lead compound. On the contrary, the improvement is more limited when the processing is carried out in more soft conditions. At 180 °C and 20 rpm, the improvement of DTST is only about 50 %.

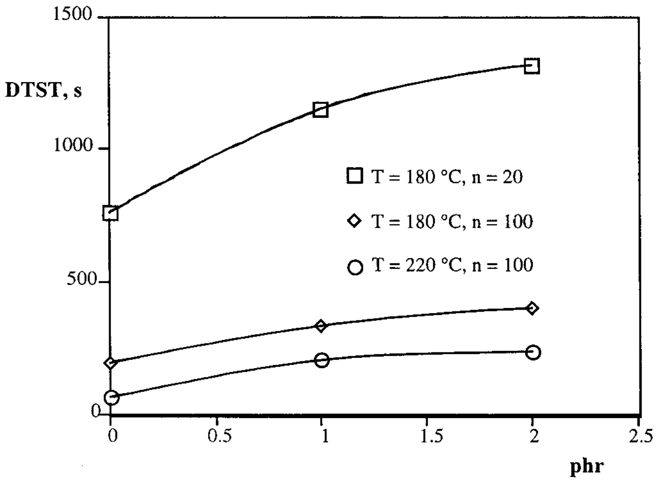

Fig. 3 DTST of PVC recycled from bottles as a function of the stabilizer content

FILLERS AND MODIFIERS

Fillers improve some mechanical properties, modulus and tensile strength, but worsen the processability and elongation-at-break. On the contrary, modifiers improve elongation-at-break and impact strength. As for the fillers, in many cases a beneficial effect on the cost of the material is also obtained.

By adding glass fibres, modulus, tensile strength, and impact strength of incompatible PET/HDPE blends are remarkably improved, while elongation-at-break is almost unchanged (Table 2) (Ref. 7).

Table 2 Mechanical properties of glass-fibre (GF)-filled PET/HDPE blends

Blend	Modulus GPa	Tensile strength MPa	Elongation-at-break %	Impact strength J/m	Heat distortion temperature °C
PET/HDPE	1.6	12	1.3	19	120
PET/HDPE + 10 % GF	1.95	21	1.4	28	158
PET/HDPE + 20 % GF	2.35	26	1.5	33	233
PET/HDPE + 40 % GF	3.1	30	1.4	39	239

The properties of the PET/HDPE blends reinforced with 20 % of glass fibres improve: the modulus by about 50 %, the impact strength by about 70 %, the tensile strength by about 110 % while the elongation-at-break remains almost unchanged. The mechanical properties of the blends are enhanced with increasing the glass fibre content, but for the elongation-at-break.

All the results show that by adding glass fibres, significant improvements of some mechanical properties are observed whereas the processability worsens because of the increase in viscosity (Ref. 7).

Glass fibres remarkably increase thermomechanical resistance of the polymers. The temperature at which the values of the modulus is 0.2 GPa has been considered as the heat distortion temperature (HDT) (Ref. 7) at a load of 66 MPa. The meaning of this value consists in that it is the maximum temperature at which the material can be used in industrial applications. The values of this parameter plotted vs the glass fibre content are also given in Table 2. The maximum working temperatures increase linearly with the fibre concentration up to 20 %, then the curve flattens and at 40 % of fibres, the increase is very small. It is evident that glass-fibre-filled recycled PET/PE blends can usefully work also at temperatures higher than those usually considered for neat PET.

Elongation-at-break and impact strength are mechanical properties more sensible to degradation and incompatibility; moreover, elongation-at-break cannot be improved by adding inert fillers. In this latter case, the use of small amounts of modifiers like elastomers can dramatically enhance both elongation-at-break and impact strength.

The effect of some elastomers on mechanical properties has been evidenced on an incompatible polymer mixture made of PET (~ 45 %), PE (~ 35 %) and PVC (~ 20 %) (Ref. 8) coming from a collection of plastic containers. The system is strongly incompatible; PVC is partly degraded during processing and mechanical properties, in particular elongation-at-break and impact strength, are very poor. In Table 3, modulus, tensile strength, elongation-at-break and impact strength are reported for this system and for the same material with 10 % of an elastomer (Ref. 8).

Table 3 Mechanical properties of PET/PE/PVC blends and effect of the addition of 10 % of an elastomer

Blend	Modulus GPa	Tensile strength MPa	Elongation-at-break %	Impact strength J/m
PET/PE/PVC	5.6	4.3	1.5	21
PET/PE/PVC + SEBS	4.2	7.3	3.4	69
PET/PE/PVC + MBS	3.2	4.2	3.1	32
PET/PE/PVC + EPDM	3.7	5.8	5.3	91

The elastic modulus decreases and this result is expected considering the low values of the modulus of the elastomers. The opposite reason can explain the improvement of the values of the other mechanical properties. These modifiers improve elongation-at-break and impact strength because of the inherent properties of the rubbery compounds. The EPDM rubber is very effective and, indeed, the elongation-at-break is more than three times, whereas the impact strength more than four times higher than the values of the non-modified blend.

COMPATIBILIZERS

The most appealing route for recycling plastic waste is the reprocessing of mixed plastics for obtaining secondary materials having good properties through the use of suitable compatibilizers. Unfortunately, only few pairs of polymer components can be at present compatibilized while plastic wastes are frequently composed of several polymers. Interesting results have been achieved by using modified copolymers

PET and PP are thermoplastics having different chemical nature and hence are strongly incompatible. Mechanical properties of the blends are very poor but a suitable compatibilizer can drastically change this picture: The thermoplastic rubber Kraton FG 1901X, a triblock copolymer consisting of polystyrene end blocks and a partly hydrogenated polybutadiene midblock grafted with maleic anhydride, can be considered a good candidate for compatibilizer for this system.

Elongation-at-break and impact strength are reported in Table 4 (Ref. 9) for the 1:1 PET/PP blends as a function of the concentration of Kraton. The blends with equal amounts of the two polymers have been prepared in an industrial corotating twin screw extruder.

Table 4 Elongation-at-break and impact strength of compatibilized PET/PP blends

Blend	Elongation- at-break, %	Impact strength, J/m
PET/PP	5	27
PET/PP + 2.5 % Kraton	140	54
PET/PP + 5 % Kraton	250	88
PET/PP + 7.5 % Kraton	285	108
PET/PP + 10 % Kraton	320	123

Elongation-at-break and impact strength increase in an impressive way with increasing the content of the functionalized rubber. It is worth noticing, however, that the enhancement of these properties mostly occurs at low contents of Kraton. The presence of the functionalized rubber induces, then, a brittle-ductile transition yielding a ductile material from a brittle one. The impressive increase in elongation-at-break and impact strength can be attributed to both the high values of these characteristics of the elastomer and the compatibilization induced by Kraton.

The morphology of the blend is remarkably modified by adding small amounts of the elastomer (Ref. 9). The two phases of the uncompatibilized blend show a very poor adhesion and the dispersed PET particles are completely separated by the continuous PP matrix. The pictures of the compatibilized blends show that the two phases adhere very well also at very low contents of Kraton and the dimensions of discrete particles are very small.

While at high contents of the elastomer, the high values of these properties of the rubber can be mainly considered responsible for the improvement of elongation-at-break and impact strength, their remarkable increase at low elastomer contents and the drastic change in the morphology confirm a compatibilizing action of the SEBS-*graft*-MA copolymer. The reactions between the anhydride groups and the OH end groups of PET which could form SEBS-*graft*-PET chains can be considered responsible for this compatibilization. The hydrocarbon block of these chains is miscible with the PP while their PET branches are miscible with the PET creating a bridge between the two phases. However, some tests carried with these blends do not confirm the occurrence of these reactions (Ref. 10). An interaction such as hydrogen bonding can be considered, then, as responsible for the compatibilizing action of SEBS-*graft*-MA copolymer.

ACKNOWLEDGEMENT

This work has been financially supported by MURST 60% and CNR Grant 96.02714.CT03

REFERENCES

(1) R. Gatcher, H. Muller, *Plastics Additives Handbook*, Hanser, Munich, 1990

(2) F.P. La Mantia, "Basic Problems in Plastic Recycling" in *Recycling of PVC and Mixed Plastics* (F.P. La Mantia, Ed), ChemTec Publishing, Toronto 1996

(3) P.P. Klemchuk, T. Thompson "Stabilization of Recycled Plastics" in *Emerging Technologies in Plastic Recycling* (G.D. Andrews and P.M. Subramanian, Eds), ACS Symp. Ser. **513** (1992)

(4) M. Marrone, F.P. La Mantia, Polym. Recycl. **2**, 17 (1996)

(5) W.G. Ma, F.P. La Mantia, J. Appl. Polym. Sci. **59**, 759 (1996)

(6) F.P. La Mantia, unpublished results

(7) W.G. Ma, F.P. La Mantia, Polym. Recycl. **2**, 69 (1994)

(8) F.P. La Mantia, "Recycling of Post-consumer Plastics Containers for Liquids", in *Recycling of PVC and Mixed Plastics* (F.P. La Mantia, Ed), ChemTec Publishing, Toronto 1996

(9) B. Ballauri, M. Trabuio, F.P. La Mantia, "Compatibilization of Recycled Poly(ethylene terephthalate) / Polypropylene Blends using a Functionalized Rubber" in *Recycling of PVC and Mixed Plastics* (F.P. La Mantia, Ed), ChemTec Publishing, Toronto 1996

(10) F.P. La Mantia, *Advanced Topics in Polymer Science 4, Chemical Modification of Polymers and Reactive Processing,* Gargnano (Italy), June 2-7, 1996