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Effect of Fillers on the Properties of Recycled Polymers

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Summary: The main problems in post-consumer plastics recycling are due to the degradation undergone during lifetime and during processing steps. Moreover, for heterogeneous recycling, the incompatibility among the different polymeric phases give rise to secondary materials with low mechanical and thermomechanical properties. The properties-reprocessing relationships are an important tool for determining not only the properties of the recycled polymers but also the strategies to apply (processing conditions, stabilisers, fillers, compatibilizers, etc) in order to obtain recycled polymers with good mechanical properties.
In this work the effect of adding inert fillers and modifier agents to recycled post-consumer plastic materials is discussed. The addition of inert fillers of different nature can strongly improve the rigidity and thermomechanical resistance of these secondary materials. The addition of modifier agents improves the deformability and the impact strength of the recycled plastics. The beneficial effect of inert fillers and modifier agents is particularly important in the case of commingled post-consumer plastics.

Introduction

Polymers undergo, during recycling operations, changes of the structure and, in some cases, of the morphology [1]. Changes of structure mean decrease of the chain length - but also formation of cross-linked structures - formation of chain branching and of functional groups. As for the changes of morphology, the cristallinity of semicrystalline polymers can vary according with the changes of molecular weight. The thermomechanical stress, the presence of oxygen and, for the polycondensation polymers, the presence of water or of other small molecules during the melt reprocessing, are responsible for these modifications. Both changes of structure and morphology induce drastic changes of many properties, and in particular of the rheological and mechanical properties, of the outdoor resistance and of the thermal stability. Of course, the level of degradation and then the deterioration of the properties

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depend on the amount of "stress", on the number of reprocessing operations and on the initial state of the structure of the post-consumer polymer.

Different strategies are usually adopted - or are under study - in order to reduce or to avoid the dangerous effect of the reprocessing or, better, to try to improve the final mechanical properties of the reprocessed plastic materials. Adding stabilisers is a typical way to avoid - or at least to decrease - the thermomechanical degradation, while adding fillers and modifier agents leads to improve some specific properties of the plastic secondary materials. The improvement of these properties can lead to secondary materials with characteristics similar to those of the virgin polymer and even better to those of the post-consumer material.

In this work the effect of fillers on the mechanical and thermomechanical properties and on the processability of recycled plastic materials is discussed. Moreover, the recycling of filler plastic materials is discussed.

Fillers in plastic recycling

Mineral Fillers

To improve the mechanical properties and the thermal resistance of the polymers - both virgin and recycled - inorganic fillers or polymeric impact modifiers can be used. Inorganic fillers - like calcium carbonate, glass fibres, etc.- enhance the elastic modulus, the dimensional stability and the thermal resistance, while a reduction of the elongation at break is in general observed. Impact modifiers - like elastomers - improve elongation at break and impact strength, whereas the elastic modulus and the thermal resistance are reduced.

Table 1, taken from [2], reports the heat distortion temperature (HDT) of recycled PP and of recycled PP samples in presence of different contents of glass fibres (GF) and wollastonite (W). HDT - the maximum working temperature the polymer can sustain - is drastically enhanced by adding the two fillers and the short glass fibres are more efficient than wollastonite. Indeed, the HDT value is more than two times that of the unfilled polymer by adding 20% of glass fibres.

Table 1. HDT values of recycled PP with glass fibres (GF) and wollastonite (W)

filler content, %	HDT, °C (GF)	HDT, °C (W)
0	55	55
20	125	95
40	138	108

Similar features have been reported for some other polymers with other inorganic fillers like calcium carbonate, mica, etc. [3]. At the same time, however, a decrease of the elongation at break and of the processability is observed. This means that adding inert fillers increases the viscosity with a consequent worsening of the processability.

In Table 2 the values of the torque, T, for an unfilled sample of recycled PP and for the same sample with 35% wt/wt of W and GF are reported (4). The values of the elongation at break, EB, are also reported [4].

Table 2. Torque and elongation at break values of unfilled recycled PP and filled with 35% of glass fibres (GF) and wollastonite (W)

filler	T, N*m	EB, %
none	33	155
GF	44	12
W	36	36

The torque is proportional to the power necessary to extrude the molten polymer, is directly related to the viscosity of the melt and is a measure of the processability of the polymer.

Both fillers decrease the elongation at break and, increasing the torque value, worsen the processability of the polymer. The glass fibres show a larger effect. This fact has been correlated with the larger length-to-diameter ratio of the particles.

An interesting way to add fillers in recycled plastics is to use post-consumer filler reinforced polymers. The environmental and economical beneficial effect is in this case well evident. In Figure 1, adapted from [5], tensile strength, TS, impact strength, IS, and modulus, E, of a recycled PP/EPDM blend are reported as a function of the content of recycled glass-mat PP (GMT). Both the materials are used for automotive bumpers. In the same figure the content of the glass fibres is also reported. Increasing the GMT, and then the GF concentration, the rigidity of the material and then modulus and tensile strength rise, while the impact strength decrease.

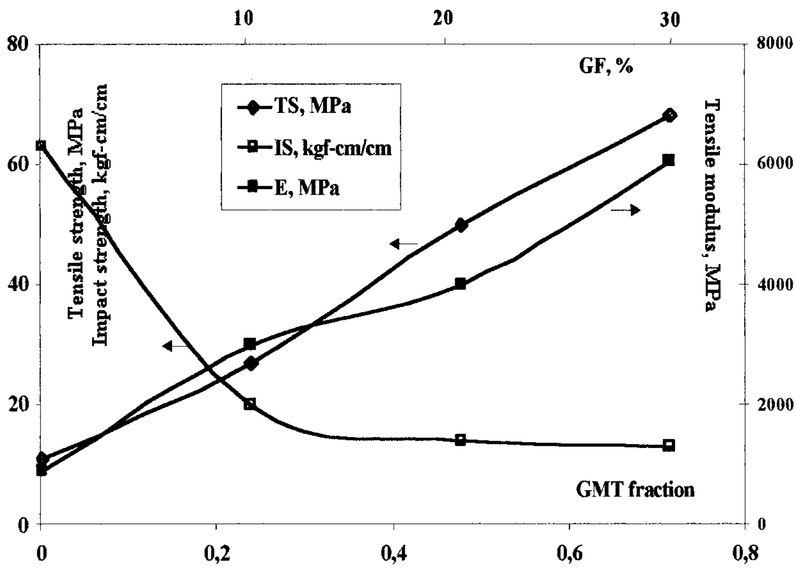

Figure 1. Tensile strength, elastic modulus and impact strength of a PP blend as a function of the GMT and GF content

The effect of mineral fillers can be more important for recycled commingled plastics [6,7]. Indeed, these systems are incompatible and their properties are very poor. Modulus, E, tensile strength, TS, impact strength, IS, and elongation at break of incompatible PET/HDPE bends are reported in Table 3 [6] as a function of the content of added glass fibres.

Table 3. Mechanical properties and HDT values of glass fibres filled PET/HDPE blends

Sample	E, GPa	TS, MPa	EB, %	IS, J/m	HDT, °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% GF increase by about 50% for the modulus, by about 70% for the impact strength, by about 110% for the tensile strength while the elongation at break is almost unchanged. The mechanical properties of the blends rise with increasing the GF content, but for the elongation at break. AS already said, the glass fibres increase remarkably also the thermomechanical resistance of the polymers. In the same Table 3 the temperature at which the value of the modulus is 0.2 GPa - considered as the heat distortion temperature (HDT) [6] at a load of 66 MPa – is reported. The maximum working temperature increase linearly with the GF concentration up to 20%, then the curve flattens and at 40% of GF, the increase is very small. It is evident that GF filled recycled PET/PE blends can usefully work also at temperatures higher than those usually considered for pure PET.

Wood Fillers

Wood fillers are a new filler type that continuously rises the interest of scientists and industry [8-14]. Wood fibres, very cheap and "environment friendly", can be used with the same scope of other fibres and with similar results. In Figure 2 the values of elastic modulus, E, tensile strength, TS, impact strength, IS, and elongation at break, EB, of a sample of recycled post-consumer mixture (LF) of PE (about 80%) and PP in presence of different types of fillers are compared [14].

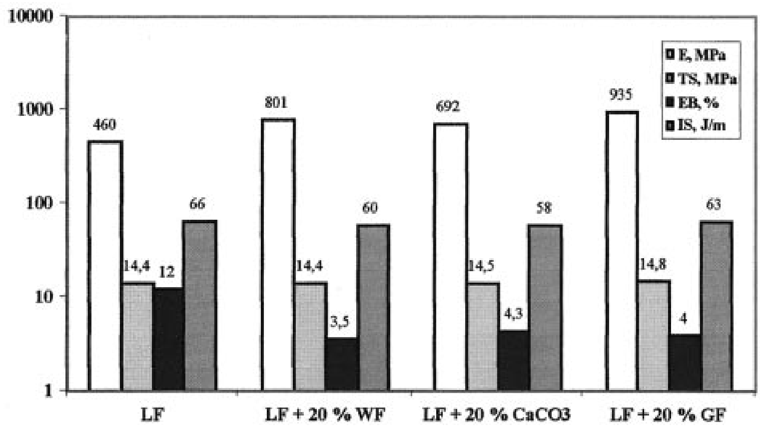

Figure 2. Mechanical properties of the unfilled and filled PE/PP recycled blends

The effect of the three fillers is quite similar for tensile strength, elongation at break and impact strength. In particular tensile strength and impact strength show values similar to those of the unfilled material, whereas the elongation at break is lower. On the contrary, the elastic modulus increases with the filler and wood fibres and glass fibres show the best results. The addition of inert fillers strongly improves the rigidity of this plastic waste mixture, whereas the reduction of the elongation at break does not infirm the possible applications of this system in injection moulding. The thermomechanical resistance and the creep behaviour of filled polymer are also enhanced by adding the fillers. Also for these tests, the best result is shown by the systems with wood and glass fibres.

These results can be interpreted both on the basis of the intrinsic properties of the inert fillers and considering the geometry of the three fillers.

Calcium carbonate is in the form of small spherical particles, whereas the other two fillers are in the form of fibres.

It is well known that the longer is the length-to-diameter ratio of the particles the higher is the improvement of the mechanical properties.

The efficiency of the wood fibres is less than that expected on the basis of the properties of this material and this is mainly due to the scarce adhesion between the polar filler and the apolar matrix. The efficiency can be than enhanced by using adhesion promoters. In Table 4 the values of elastic modulus and impact strength of the previous system with 40% of wood fibres are reported when 2% of two functionalized polypropylenes (acrylic, PPAA, and maleic, PPMA, grafted PP) are added [13]. The addition of these additives at very low concentration improves the performances of the wood fibres and indeed the mechanical properties show a significant improvement.

Table 4. Effect on modulus and impact strength of PE/PP blend of adding functionalized PP

Modified PP	E, MPa	IS. J/m
none	760	48
PPAA	1100	62
PPMA	1050	64

Recycling of filled plastics

As alreadv said, the presence of fillers increases the viscosity of the melt filled polymers. The higher viscosity implies that during melt reprocessing operation a larger amount of mechanical stress is applied on the melt and this means that the degradation of the material is larger. On the other hand, fibres can be broken during reprocessing and this leads to a further deterioration of the mechanical properties. This does not happen when the filler is in other form or cannot be change its geometry. Only a relatively few works dealt with the recycling of filler plastic materials [15].

The dimensionless melt flow index (MFIad) of a polycarbonate (PC) sample and of the same sample reinforced with 20% glass fibres is reported in Figure 3[16] as a function of the number of reprocessing steps. Dimensionless MFI is calculated as the ratio between the value of MFI after any recycling step and that of the virgin sample. The faster rise of the reinforced polymer with respect that of the unfilled material is due to the higher viscosity of the filled polymer and then to the higher mechanical stress acting on the polycarbonate.

The contemporary reduction of the length of the glass fibres increases the deterioration of the mechanical properties, see Table 5 adapted from [16], where the dimensionless tensile strength, TSad, and elongation at break, EBad, are reported. Both propertied strongly decrease with the number of recycling cycles, while the tensile modulus, here not reported, is almost unchanged. The decrease of the two properties is, however, much more pronounced for the reinforced polymer. As hypothesised above, this is due to the decrease of molecular weight of the polymer matrix and to the reduction of the length-to-diameter ratio of the glass fibres.

Conclusion

Fillers can play an important role in the plastic recycling because they can strongly enhance the rigidity of the secondary materials. The reduction of elongation at break and impact strength - that occurs with some fillers and, in particular, with glass fibres - does not play a significant influence in many applications. Among the fillers, wood fibres – cheap and "environment friendly" - seem a good candidate for a large use in the plastic recycling industry.

The recycling of filled plastic materials leads to secondary materials with worse properties than that of the same unfilled polymer because the increased viscosity gives rise to a larger amount of polymer degradation.

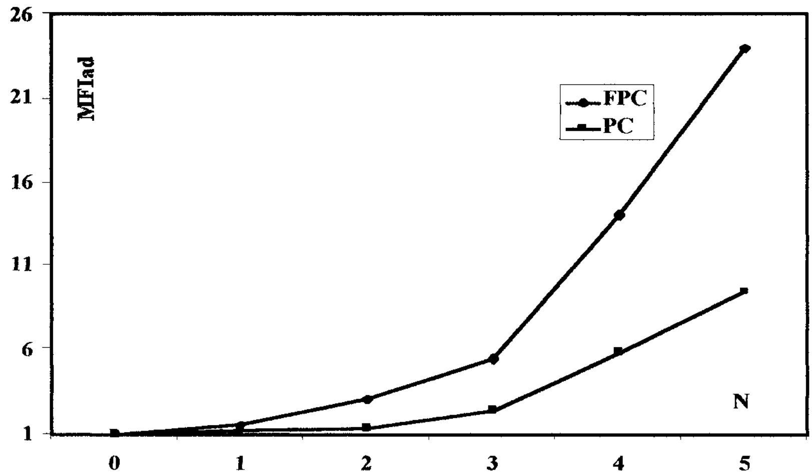

Figure 3. Dimensionless melt flow index (MFI) of a polycarbonate (PC) sample and of the same sample reinforced with 20% glass fibres as a function of the number of reprocessing steps

Table 5. Dimensionless change of some mechanical properties of the same samples of Figure 3 as a function of the number of reprocessing steps

Recycling steps	TSad		EBad	
	PC	FPC	PC	FPC
0	1	1	1	1
1	0,99	0,97	0,97	0,97
2	0,99	0,84	0,86	0,93
3	0,98	0,79	0,77	1
4	0,99	0,60	0,17	0,73
5	0,58	0,42	0,02	0,33
6	0,38		0,012	

Acknowledgement

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