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The Effect of Extrusion Reprocessing on Structure and Properties of Isotactic Poly(propylene)

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Summary: In this study, isotactic poly(propylene) (PP) and its nanocomposites reinforced with organic modified montmorillonite (OMMT) were subjected to five subsequent extrusion cycles, in order to simulate the effect of the processing involved with mechanical recycling on their properties. Additionally, tests were run in an attempt to explore whether the reprocessed polymers are appropriate as raw materials for several applications. It was concluded that repeated processing does not significantly affect the rheological and thermal properties, as well as the thermal stability of the above studied materials. Regarding mechanical properties, the tensile and flexural strength of the examined products remain almost unaffected. PP samples presented a decrease in tensile and flexural moduli, whereas in the case of OMMT/PP nanocomposites reprocessing improves these properties, probably due to better intercalation of clay platelets taking place upon melt mixing.

Keywords: degradation; extrusion; nanocomposites; poly(propylene) (PP); recycling

Introduction

Mechanical recycling of polymeric materials is a simple and versatile technique resulting in both, economic and environmental benefits, especially in the case of polymers with high production volume. However, recycling by melt reprocessing may give rise to thermal, thermo-oxidative or thermo-mechanical degradation that may affect the structural parameters of polymers and, subsequently, the end use properties of the products.[1,2] Poly(propylene) (PP) is an important commodity plastic, used extensively for packaging consumer goods. With increasing use, the amount of discarded packaging material in the waste stream is also increasing. Management of PP post consumer waste is therefore crucial and recycling is a viable option for waste management. The addition of reinforcing fillers tends to become a common practice for improving the final properties of recycled polymers and, thus, minimizing the possible negative effect of recycling on the characteristics of the obtained products. In recent years, polymer layered silicate (PLS) nanocomposites, especially those based on organic modified montmorillonite (OMMT) have received great attention, because they often induce excellent mechanical, thermal and barrier properties to the reinforced systems. However, melt processing, being one of the most convenient and attractive methods of producing polymer nanocomposites, may result in organoclay degradation through alkyl ammonium surfactants decomposition through a Hoffman elimination mechanism, starting at about 180 °C.[3] The above parameters dictate a careful experimental design for an efficient and reliable exploration of the related interactions.

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Experimental Part

Materials

Medium-high fluidity isotactic PP suitable for injection moulding, under the trade name Ecolen HN10P, was supplied by Hellenic Petroleum, Greece. Commercial montmorillonite clay, under the trade name Cloisite® 25A, was supplied by Rockwood Clay Additives GmbH. and used as reinforcing nanofiller at concentration 3 phr.

Sample Preparation

In an attempt to simulate the PP recycling process, the polymer was subjected to five repeated cycles of extrusion in a co-rotating twin screw extruder with L/D-25 and 16 mm diameter (Haake PTW 16), working at 200 rpm with a temperature profile ranging from 190–210 °C.

Characterization

Chemical characterization of the reprocessed PP was carried out by infra red spectroscopy (FTIR-ATR) (model Magna IR 750; DTGS detector; Nichrome source; beamsplitter; KBr). The thermal response of PP was recorded by differential scanning calorimetry (DSC) (DSC 1 model, Mettler Toledo), whereas the thermal stability of reprocessed samples was detected with thermogravimetric analysis (TGA) (model TGA-DTA, Mettler Toledo). Also, the rheological properties of the above compounds were investigated via melt flow rate (MFR) tests (model MP-E, Goettfert) according to ASTM 1238. Furthermore, the mechanical properties, such tensile (model 4466 Instron tensometer), flexural (model Z005/TH2A, Zwick) and impact (model 66 Charpy Izod I, Tinius Olsen) were investigated, according to ASTM D 638, ASTM D 790 and ASTM D256 specifications respectively.

Results and Discussion

In general, during extrusion reprocessing the macromolecules are exposed to high temperatures and intensive shearing, which promotes thermal, mechanical and oxidative degradation mechanisms or combinations of the above. The presence of tertiary carbons in the chemical structure of PP may induce rapid oxidation.[4] Figure 1 contains the FTIR spectrum of the virgin PP and the extruded material after five repeated cycles. The fact that the patterns presented in Figure 1 are almost identical, suggests that,

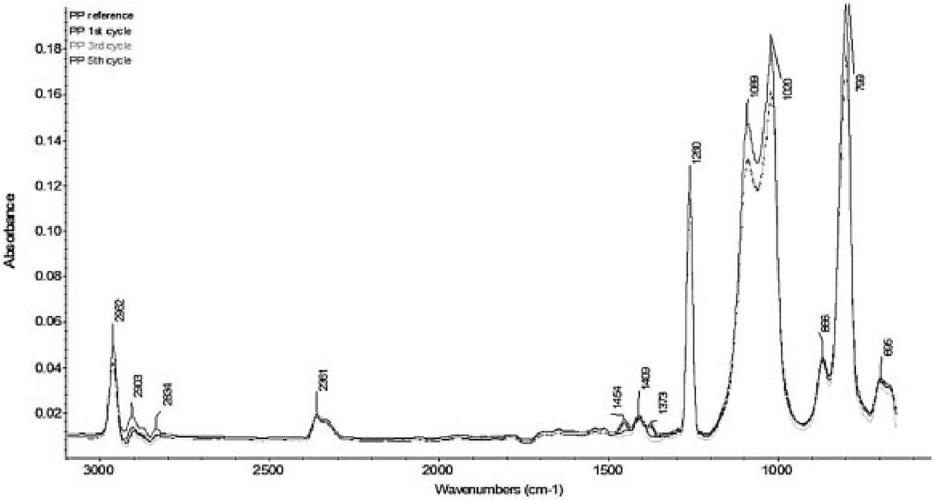

Figure 1.
FTIR spectrum of virgin PP (reference) and PP samples after 1, 3 and 5 extrusion cycles.

Table 1.
Total color change (ΔE) and MFR values of PP and PP nanocomposites (3 phr loading) during the repeated extrusion cycles.

Extrusion cycle	ΔE		MFR (g/10min)	
	PP	OMMT/PP	PP	OMMT/PP
Raw material	–	–	11,57 ± 0,63	–
1st cycle	1,859	9,300	11,43 ± 0,74	10,26 ± 0,32
2nd cycle	–	–	11,99 ± 0,81	10,16 ± 1,82
3rd cycle	2,852	10,424	11,76 ± 0,26	10,42 ± 0,24
4th cycle	–	–	11,59 ± 0,83	11,64 ± 1,08
5th cycle	4,859	11,78	12,58 ± 0,30	12,48 ± 1,12

practically, no oxidative reactions take place during the above described recycling process.

This behavior is probably due to the limited concentration of oxygen within the polymer melt, since the extruder machine is a closed system.

Visual inspection of the examined PP and OMMT/PP nanocomposites revealed a slight yellow color, which is more intense in the case of nanocomposites, especially after the 5th extrusion cycle. The total color change (ΔE) was measured by running tests with a laboratory colorimeter and the results are presented in Table 1. Under the combined action of high temperature and mechanical shear, the initiation of some chemical reactions between decomposition products of the surfactant and the polymer matrix, might lead to aging and colour changes of the PP hybrids. From Table 1 it is observed that, re-processing of PP in a twin screw extruder increases the MFR values (Table 1) after the fifth extrusion cycle. The retention of rheological properties of treated samples up to the forth extrusion cycle, is probably due to the presence of stabilizers. The fact that PP degradation starts at the fifth recycling step indicates that the stabilizer required to prevent degradation was probable consumed during the previous processing. The absence of changes in the chemical structure and the increase of the MFI in the 5th extrusion cycle suggest that β-chain scission reactions, rather than oxidation, is the dominant degradation mechanism under the above experimental conditions.[5]

As expected, the incorporation of montmorillonite in the PP matrix resulted in a slight decrease in MFR values. On the other hand, reprocessing of the prepared nanocomposites increases MFR values after the forth extrusion cycle.

Heating curves, obtained by DSC for all the examined PP samples, show a single peak around 164 °C, indicating that all samples have α-form structure. The absence of any β or γ phases suggest that PP can be reprocessed using a twin screw extruder and yet retain its crystalline structure.

From the DSC results of Table 2, it is observed that the melting temperature T_m of PP remains stable, whereas a decrease of crystallization temperature T_c after the

Table 2.
DSC results of PP and PP nanocomposites (3 phr loading) during the repeated extrusion cycles.

Extrusion cycle	PP		OMMT/PP	
	T_m (°C)	T_c (°C)	T_m (°C)	T_c (°C)
Virgin material	163,70 ± 1,08	105,98 ± 1,32	–	–
1st cycle	162,51 ± 0,21	114,15 ± 0,08	162,38 ± 0,47	110,48 ± 0,15
2nd cycle	163,35 ± 0,14	115,61 ± 0,5	162,41 ± 0,36	111,11 ± 0,22
3rd cycle	163,07 ± 0,42	113,86 ± 0,83	163,28 ± 0,59	114,16 ± 0,65
4th cycle	162,41 ± 0,16	110,40 ± 0,69	162,38 ± 0,12	112,80 ± 0,50
5th cycle	162,99 ± 0,31	110,44 ± 0,79	162,51 ± 0,06	113,55 ± 0,08

Table 3.
TGA results of PP and 3 phr OMMT/PP nanocomposite after extrusion reprocessing.

Extrusion cycle	PP		OMMT/PP	
	T_{onset} (°C)	T_{max} (°C)	T_{onset} (°C)	T_{max} (°C)
1st cycle	431,93 ± 1,36	451,12 ± 2,00	422,89 ± 1,7	429,34 ± 0,82
2nd cycle	432,61 ± 0,51	451,01 ± 1,79	423,88 ± 1,09	429,74 ± 0,65
3rd cycle	429,41 ± 1,09	450,02 ± 2,00	423,41 ± 2,03	429,94 ± 1,01
4th cycle	429,50 ± 0,24	449,29 ± 0,33	424,21 ± 1,62	430,59 ± 1,35
5th cycle	431,75 ± 1,69	452,02 ± 2,24	426,26 ± 1,60	432,21 ± 0,77

third cycle was recorded. On the other hand, in the case of OMMT/PP nanocomposites, T_c presents a tendency to increase after the third extrusion cycle. T_c indicates how the crystallization process is initiated during cooling of materials. The initiation of the crystallization process at higher temperatures indicated that a higher number of crystallite nuclei exist or that the polymer chain mobility was higher, which enabled them to move faster to the crystalline phase. The better intercalation of layered silicate platelets in the polymer matrix after reprocessing could reduce the free enthalpy of the formation of a critical nucleus. This can lower the critical size of nucleus and results in the formation of heterogeneous nuclei at higher apparent crystallization temperature.[6]

Regarding the thermal stability in inert atmosphere, reprocessed PP appears to have the same characteristics with those of virgin material (Table 3). In the case of OMMT/PP and nanocomposites, a shift of thermal degradation to lower temperatures was recorded, probably because of the presence of the lower molecular weight alkyl tails of the intercalation agent used for organic modification of MMT, which is more heat sensitive than pristine PP. However, after the first extrusion cycle OMMT/PP nanocomposites exhibited slightly higher thermal stability. This behavior can be attributed to better dispersion and intercalation by reprocessing of organoclay platelets in the polymer matrix, offering increased protection against the thermal degradation of the polymer. Furthermore, this might be the result of some interactions between the organoclay and the PP matrix, such as migration of OMMT to the surface, which forms a protecting barrier that impedes the release of gases from the decomposition.[7]

The mode of failure of tensile specimens started with stress-whitening up to the yield point followed by neck formation and fibrillar fracture (Figure 2).

As far as the mechanical properties of PP samples are concerned, as can be seen in Tables 4&5, no significant effect on the tensile strength, strain at yield and flexural tension at 1,2% elongation was found. However, the impact strength and both, tensile and flexural modulus, were decreased in comparison with specimens of virgin PP.

The addition of OMMT in PP improves the tensile and flexural properties of the material.

Reprocessing seems to further enhance the above properties and especially the modulus of elasticity, probably due to an

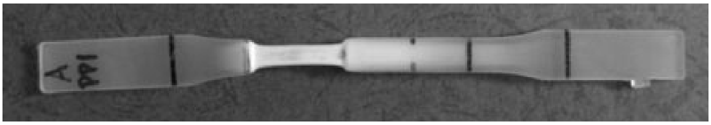

Figure 2.
Stress-whitening and necking formation during tensile test of PP.

Table 4.
Tensile test results of PP samples during the repeated extrusion cycles.

Extrusion cycle	Tensile strength at yield (N/mm^2)	Tensile Modulus (MPa)	Strain at yield (%)
		PP	
1st cycle	34,32 ± 0,07	1503,31 ± 50,53	10,21 ± 0,11
3rd cycle	34,12 ± 0,40	1509,64 ± 35,94	10,42 ± 0,17
5th cycle	33,64 ± 0,23	1523,17 ± 43,08	10,36 ± 0,19
		OMMT/PP	
1st cycle	34,66 ± 0,18	1608,93 ± 8,89	8,80 ± 0,12
3rd cycle	35,24 ± 0,29	1668,94 ± 7,24	8,79 ± 0,02
5th cycle	35,50 ± 0,06	1666,17 ± 36,9	8,86 ± 0,28

Table 5.
Flexure and impact test results of PP samples during the repeated extrusion cycles.

Extrusion cycle	Flexural strength at 1,2% strain (MPa)	Flexural modulus (MPa)	Izod Impact strength (J/m)
		PP	
1st cycle	14,68 ± 0,03	1443,74 ± 20,55	48,6 ± 2,67
3rd cycle	14,42 ± 0,05	1419,16 ± 16,53	48,85 ± 4,28
5th cycle	14,14 ± 0,07	1381,66 ± 8,80	47,98 ± 2,68
		OMMT/PP	
1st cycle	16,49 ± 0,07	1649,94 ± 8,98	36,38 ± 4,51
3rd cycle	16,85 ± 0,16	1693,19 ± 19,58	31,16 ± 0,35
5th cycle	16,87 ± 0,06	1713,94 ± 7,49	34,83 ± 5,13

improvement of intercalation/exfoliation of clay platelets in the polymer matrix, cause by the shear within the melt.

The impact strength of PP after reprocessing was decreased, in comparison with that of virgin PP. PP-OMMT nanocomposites presented lower impact strength, which became even worse upon extrusion reprocessing.

Conclusion

Based on the above results, we can conclude that mechanical recycling of PP through melt processing in a twin screw extruder is a simple recycling method that ensures stability of the processing characteristics and mechanical properties of the material up to five repeated extrusion cycles. This would probably allow the design of an easy and safe recycling process for large volume waste plastics, with the appropriate adjustment of processing parameters. The results obtained under the experimental set-up of this work, showed that improvement of some critical properties the recycled PP would be possible, by using organoclay reinforcement and the appropriate compatibilization system.

[1] E.-K. Karahaliou, P. A. Tarantili, *Polym. Engin. Sci.* **2009**, *49*, 2269.
[2] E. Vassiliadi, P. A. Tarantili, *J. Appli. Polym. Sci.* **2007**, *105*, 1713.
[3] R. K. Shah, D. R. Paul, *Polymer* **2006**, *47*, 4075.
[4] F. Catalina, *Rev. Plas. Mod.* **1998**, *75*, 391.
[5] J. Aurrekoetxea, M. A. Sarrionandia, I. Urrutibeascoa, *J. Mater. Sci.* **2001**, *36*, 2607.
[6] A. Galeskis, in: "*Polypropylene Structure, Blends and Composites'*, vol. 1, edited by Karger-Kocsis, (Chapmann & Hall, London **1995**,), Ch 4.
[7] E.-K. Karahaliou, P. A. Tarantili, *J. Appl. Piolym. Sci.* **2009**, *113*, 2271.