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Study of Different Mixing Sequences in Polymer Blends Reinforced with Nano-Clays

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Summary: Different polymer blends reinforced with nano-clay were prepared by melt compounding. The influence of four different sequences on the microstructural and thermomechanical properties has been analyzed. Polyamide 6–ethylene-propylene-diene monomer (PA6/EPDM) blends were the most thermally stable of all showing that nano-clay dispersion in the continuous phase (NB1) produced the best balanced properties. On the other hand, in polycarbonate–(acrylonitrile-butadiene-styrene) (PC/ABS) blends the nano-clay addition on the dispersed phase (NB2) led to an increase in stiffness and HDT with a low value of toughness. Finally, the best properties (impact strength and HDT) in poly (lactic acid)–low density polyethylene (PLA/LDPE) blends were obtained when all the materials were blended in one step (NB3).

Keywords: extrusion process; mechanical properties; nanoclays; order of mixing; polyblends

Introduction

Polymer blends, both mixtures of traditional matrix as PA, PC or ABS,[1] or biodegradable polymers as PLA,[2] offer a wide field of applications to the automotive industry, such as automobile parts: bumpers, instrument panels, air-bag covers, consoles, door handles, mirror housings and new applications as biodegradable hubcaps made of PLA. The combination of the best properties of polymeric phases has resulted in the development of commercially available blends. In addition, the incorporation of a relatively low content (less than 5% by weight) of nanodispersed clays into the polymeric matrix can result in significant improvements in a range of properties when compared to their bulk polymer constituents and conventional macrocomposite counterparts.[3]

When polymers and clays are mixed to develop nanocomposite blends, three structures could be achieved: clays are dispersed in one phase, in both phases or at the interphase. It is well-known that the order of this mixing plays a fundamental role in these distributions, affecting the final properties of the material.[4–6] Thus, the aim of this work is to study the viability of the different ways of processing and its relationship with the morphology and mechanical properties on three polymer blends reinforced with nanoclays:

1. Polyamide 6–ethylene-propylene-diene monomer (PA6/EPDM),
2. Polycarbonate – (acrylonitrile-butadiene-styrene) (PC/ABS) and
3. Poly (lactic acid) – low density polyethylene (PLA/LDPE).

Additionally, in the case of PA6 and PLA, compatibilizers such as EPDM-g-MAH (C1) and SBS-g-MAH (C2) respectively, were incorporated to the blend in order to improve the matrix interactions with the no polar phase (polyolefins).

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Experimental Part

Materials

In this work, different polymeric blends were elaborated: in the first blend (PA6/EPDM), the PA6 (Akulon F130C) was a commercial product from DSM, and the suppliers of EPDM (Nordel IP3722P) and EPDM-g-MAH (Royaltuf 498) were Dupont and Crompton respectively; in the blend of PC/ABS, PC (LEXAN 223R) and ABS (HI-100H) were supplied by SABIC and LG Chem, respectively; in the last blend (PLA/LDPE), PLA (2002D) was supplied by Cargill-Dow, LDPE by Polinter and a commercial styrene/ethylene-butylene/styrene rubber functionalized with maleic anhydride (SBS-g-MAH, Kraton FG-1901) was supplied by Shell Chemical.

Two types of sepiolite were supplied by Tolsa S. A.: modified with a quaternary ammonium salt (SEP1) and unmodified (SEP2). Additionally, a montmorillonite (Nanofil 8) named MMT was supplied by Süd-Chemie. An antioxidant (Irganox B1171) was employed in the fabrication of the blends and it was supplied by Ciba.

Preparation

Melt compounding of the PA6/EPDM and PC/ABS blends were obtained using a Leistritz 27 GL corrotating twin-screw extruder, operating at 250 °C, and screw speeds of 145 and 200 rpm respectively. On the other hand, the PLA/LDPE blends were prepared in a Berstorff (ECS-2E25) corrotating intermeshing twin-screw extruder at 200 °C and 100 rpm. To obtain the thermo-mechanical experiment bars, the materials were pelletized, dried and injected using injection moulding machine. In case of PLA blends, the test specimens were compression moulded for 2.5 minutes at 200 °C.

These blends were obtained according to four different sequences of mixing in order to demonstrate that processing conditions are the main issue to take into account when nanocomposite blends are designed:

1. NB1: (Polymer 1 + Clay) + Polymer 2, means Polymer 1/Clay nanocomposite was prepared and then mixed with polymer 2 in a second step.
2. NB2: (Polymer 2 + Clay) + Polymer 1, means Polymer 2/Clay compound was first prepared and then mixed with Polymer 1.
3. NB3: Polymer 1 + Polymer 2 + Clay, means Polymer 1, Polymer 2 and Clay were blended in one step.
4. NB4: (Polymer 1 + Polymer 2) + Clay, means Polymer 1/Polymer 2 blend was prepared and then mixed with the Clay.

Polymer 1 is referred to matrix while Polymer 2 is referred to disperse phase.

Characterisation

Characterisation of microstructural properties of nanocomposites has been carried out by means of microscopic techniques such as scanning electron microscopy (SEM). The morphology was related to thermo-mechanical properties: Young's modulus, notched Izod impact strength at room temperature and heat deflection temperature (HDT). Thermogravimetric analysis (TGA) has been done in order to know the thermal stability and the real percentage of clay in the nanocomposites.

Results

The goal of this work was the evaluation of the blending sequence and how the mechanical properties are affected in different polymer blends. As it was explained above, four different sequences could be carried out in order to process the materials.

In PA6/EPDM blends, there were no problems in the mixing procedure, all blending sequences proposed could be performed. Nevertheless, in the blends of PC/ABS and PLA/LDPE, the processing methods NB1 and NB4 seem to have a significant effect in the initial temperature of decomposition of the blends, as it can be seen from T5% in the Table 1 and in the

Table 1.
Thermo-mechanical properties of blends and nanocomposites.

Blends	Composition %wt	$T_{5\%}$[b]	Clay[c]	Processing method	Modulus	Izod	HDT
	(M/DF/C/NC)[a]	(°C)	%		(MPa)	(kJ/m^2)	(°C)
PA6/mEPDM/C1	(80/10/10/0)	413	–	–	1439 ± 10	49.6 ± 1.2	49.9 ± 0.3
(PA6 + MMT) + (EPDM + C1)	(75/10/10/5)	400	4.9	NB1	2900 ± 23	12.6 ± 0.5	81.3 ± 2.2
(EPDM + MMT + C1) + PA6	(75/10/10/5)	395	4.9	NB2	2820 ± 39	15.1 ± 0.6	80.6 ± 3.9
(PA6 + mEPDM + C1 + MMT)	(75/10/10/5)	388	5.1	NB3	2870 ± 11	11.2 ± 0.6	88.9 ± 3.9
(PA6 + mEPDM + C1) + MMT	(75/10/10/5)	395	5.0	NB4	2777 ± 44	14.5 ± 3.1	88.4 ± 2.0
PC/ABS	(70/30/0/0)	367	–	–	2470 ± 27	2.2 ± 0.7	96.1 ± 0.3
(PC + SEP1) + ABS	(65/30/0/5)	341	3.7	NB1	n.m[d].	n.m.	n.m.
(ABS + SEP1) + PC	(65/30/0/5)	372	3.7	NB2	3220 ± 27	2.9 ± 0.5	101.0 ± 0.4
(PC + ABS + SEP1)	(65/30/0/5)	404	3.9	NB3	3140 ± 25	3.4 ± 0.8	100.0 ± 0.2
(PC + ABS) + SEP1	(65/30/0/5)	348	4.3	NB4	n.m.	n.m.	n.m.
PLA/LDPE/C2	(75/20/5/0)	346	–	–	2893 ± 46	0.48 ± 0.04	49.2 ± 1.2
(PLA + SEP2) + (C2 + LDPE)	(70/20/5/5)	308	4.3	NB1	n.m	n.m	n.m
(LDPE + SEP2 + C2) + PLA	(70/20/5/5)	353	4.1	NB2	1532 ± 30	1.4 ± 0.7	50.0 ± 1.0
(PLA + LDPE + C2 + SEP2)	(70/20/5/5)	358	4.1	NB3	2381 ± 45	5.2 ± 0.1	56.1 ± 3.2
(PLA + LDPE + C2) + SEP2	(70/20/5/5)	323	4.5	NB4	n.m	n.m	n.m

[a](M/DF/C/NC) is referred to (Matrix/Dispersed phase/Compatibilizer/Nanoclay). In this blends the PA6, PC and PLA corresponding to the matrix, respectively.[b]$T_{5\%}$ is referred to temperature at 5%of weight loss.[c]By TGA method at 900°C.[d]Not measured because these blends could not be fabricated due to the degradation of matrix.

TGA curves of the Figure 1. In these cases, it was no possible to process the matrix twice because of the high thermal sensitivity and the possible hydrolysis of carboxylic groups in PC and PLA polymers produced by the silanol groups attached to the surface of the sepiolite.

Regarding PA6/EPDM blends, the best balanced mechanical properties were achieved in those blends fabricated by the first and fourth blending sequence, NB1 and NB4 respectively (Table 1). As it can be seen in this table, modulus and HDT were increased around 90 and 65% respectively in both reinforced blends, while the impact strength was decreased around 70%. However, better values were achieved with the first sequence due to an easier exfoliation and optimal rubber particle size (Figure 2(a)) which led to a higher stiffness.

For PC/ABS nanoblends, only the second and third blending sequences were carried out. The resulting properties of these materials were summarized in Table 1. Due to the reinforcing effect of sepiolite, the stiffness was increased around 30% in comparison with the (70/30) blend, and the HDT values were slightly

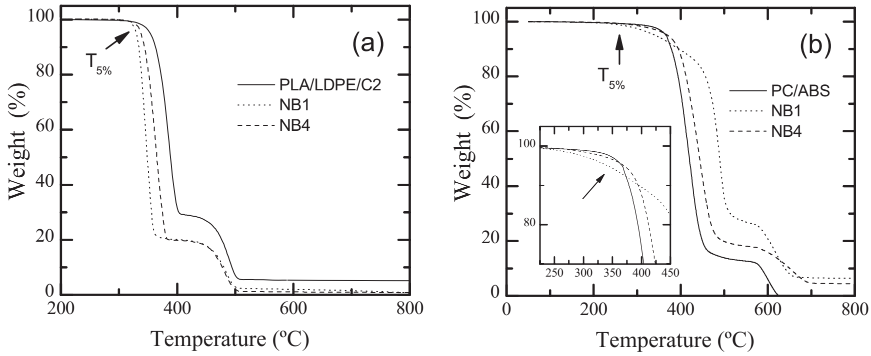

Figure 1.
TGA curves: (a) PLA blends and their nanocomposites and (b) PC blends obtained by NB1 and NB4.

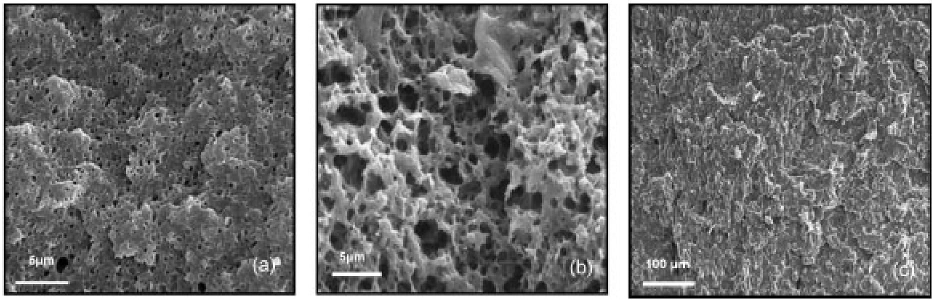

Figure 2.
SEM micrographics of nanocomposites of (a) PA6/EPDM, (b) PC/ABS and (c) PLA/LDPE.

enhanced. The low value of the toughness obtained for this blend is probably related to the phase inversion, maintaining the value of impact strength with the addition of sepiolite. In Figure 2(b), where ABS phase was etched, the dispersion of the nano-clay in PC phase could be appreciated. The good dispersion of sepiolite fibres led to an enhancement in the stiffness of the blend keeping the values of toughness.

Finally, the PLA is a biodegradable polyester with poor thermal stability in its processing, and low tensile ductility. Blending PLA with low-cost commodity PEs as dispersed phase could be an alternative to find the desired requirements for different applications. Similarly, the NB1 and NB4 blending sequences could no be used in these nanocomposites. On the other hand, to avoid thermal degradation of PLA in the blends, all polymer components were fed through the first port of the extruder, being the sepiolite fed through the second port (one step, NB3).[7] This sequence was the best way to increase toughness in the impact strength test (1000%) and heat deflection temperature (15%) with a reduction of the rigidity of PLA (15%), due to the incorporation of the elastomeric phase (LDPE). Beside, blend NB2 has increased the impact strength in a 192% and the modulus has decrease in a 47% but the highest improvement of the toughness was achieved in the method NB3.

In addition, it was found that the microstructure in ternary nanocomposites (PLA/LDPE/C2) was significantly influenced by the blending sequence which influenced their mechanical properties (Table 1). The blend obtained by NB3 method presented the smallest particle size (Figure 2(c)) in comparison with the ones of PLA blends. This may be the reason why the NB3 method achieved the best interaction between the components of these PLA blends, and consequently the best mechanical properties.

Conclusion

In general, the mechanical properties of polymer blends reinforced with nano-clays are highly dependent on the processing conditions whatever the composition.

For PA6/EPDM blends, processing the clay with the continuous phase (NB1) offers the best way of compounding; however, for PC/ABS blends, processing the clay with the dispersed phase (NB2) resulted as the best order of mixing. Furthermore, the process carried out in the extrusion of PLA/LDPE blends (NB3) requires half screw speed than the one applied in the other blends leading to the best final properties.

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