



## Effects of reprocessing on the structure and properties of polyamide 6 nanocomposites

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### ABSTRACT

PA6 based nanocomposites (NCs) were reprocessed by repeated injection moulding to find out whether reprocessing is possible in these materials by means of the observation of the changes in the structure and mechanical properties. The studied variables were (a) the number of cycles (1–5), (b) the origin of the NC: either laboratory mixed or commercial and (c) the processing temperature (230 °C and 270 °C). Neat PA6 was also reprocessed as a reference material. In spite of the colour change, the Young's modulus, the solid state characteristics and the dispersion level were preserved upon reprocessing. The lack of change of chemical nature observed by FTIR, and the observed decreases in viscosity indicated that the main effect of reprocessing was a decrease in the molecular weight. At 230 °C the decreases in viscosity were smaller after reprocessing, and almost no change was seen in the structural parameters and properties. The decrease in the molecular weight after reprocessing at 270 °C leads to lower ductility and mainly to a decrease in the ability of the nPA6 matrix to cold draw. However, no change of the interphase conditions or agglomeration of the OMMT was detected and the NCs remained clearly ductile; thus, revealing a lack of deterioration of the interface and the ability of the NCs for recycling.

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### 1. Introduction

It is known that polymer recycling [1,2] is increasingly common for two main reasons. The first is economic, mainly in the case of high performance polymers, and leads to the reprocessing of scrap material from transformation processes, such as faulty parts, sprues, runners. The second reason for recycling is environmental, and is due to the increasing amount of post-consumer plastic materials in the waste stream.

Polymer recycling is carried out mainly by reprocessing. This involves several high temperature shearing cycles that make easier (i) the occurrence of thermal and/or mechanical degradation, (ii) the consequent chemical and physical changes, and (iii) a detriment of final properties. Therefore, knowledge of the nature and intensity of the degradation is of interest either to choose a stabilizer or to determine the maximum amount of recycled material that may be added to the virgin material without significant losses in the final properties.

Studies on reprocessing and its effects on properties have been conducted for a large number of polymers, such as polyolefins [3,4], polycarbonate (PC) [5], poly(alkylene terephthalates) [6],

polyamides (PAs) [7–11]. Reprocessing of polymer blends such as PC/ABS [12], PA6/polypropylene (PP) [13] and polypropylene–(ethylene–propylene) copolymer (PP–EP)/poly(ethylene–co–vinyl acetate) (EVA) [14] has been studied as well as that of reinforced materials with matrices like polyolefins [15,16], styrene–maleic anhydride resin [17] and PA6 [18]. Reprocessing of polymer nanocomposites has been studied to our knowledge only in the case of PA6 [19,20], PA12 [21] and a thermoplastic olefin elastomer (TPO) [22] matrices.

Nanocomposites (NCs) composed of a polymer matrix and an organically modified layered clay (OMMT) are today one of the most promising ways for the development of new polymeric materials because of their mechanical, barrier and fire properties, transparency and density that give them a high potential for many applications [23]. Studies on polymer blends being one of the phases a nanocomposite material are also increasingly common; they use the nanocomposite as the matrix [24], as a master-batch [25,26] and so on. The possibility of degradation is of clear importance here, since two mixing cycles are needed to produce these ternary materials. Further, the best processing conditions of the components of a polymer blend may not overlap. The same may occur in the case of the processing conditions to disperse the organoclay and those of the polymeric components of the nanocomposite. Both possibilities lead to harsh processing conditions for at least one of the components.

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Besides the possible degradation processes associated with the matrix, the possible degradation processes typical of NCs are related to (i) an additional degradation of the matrix induced by the presence of OMMT as it can work as a catalyser [27], (ii) degradation by modification of the polymer/clay interface or (iii) degradation by collapsing and agglomeration of the clay particles. Provided that any of the aforementioned processes takes place to a significant extent, it should influence the mechanical properties.

PA6 NCs are increasingly studied as components of polymer blends. This is probably due to the possibility of obtaining almost full exfoliation of the OMMT in PA6 [28], and to the resulting substantial increase in mechanical properties, fire resistance and so on [29]. However, despite their already high and increasingly applied and scientific interest, only two studies on reprocessing of nanocomposites based on PA6 [19,20] extruded up to three times, have been published to our knowledge.

This work examines the impact of reprocessing on the structure and mechanical properties of PA6 based NCs, by means of repeated injection moulding cycles. The studied variables were (a) the number of cycles (1–5), (b) the processing temperature (230 °C and 270 °C) and (c) the origin of the NC: either commercial or compounded in the laboratory. Neat PA6 was also reprocessed as a reference material. The possible variations in either the chemical structure or the molecular weight were tested by Fourier transform infrared spectroscopy (FTIR) and rheological measurements, respectively. Dynamic-mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to analyse possible changes in the physical structure. The nanostructure of the NCs was studied by wide-angle X-ray diffraction (WAXS) and transmission electron microscopy (TEM). The effects of structural changes on the mechanical properties were determined by tensile tests.

## 2. Experimental

The commercial PA6 NC (nPA6-c) used in this work (Durethan® KU2-2601 from Lanxess) was synthesised by in situ polymerization. The PA6 NC obtained in the laboratory (nPA6-lab) was obtained by mixing a widely used PA6 (Durethan® B 30 S from Lanxess) with a montmorillonite modified with octadecylammonium (OMMT) (Nanomer® I30TC from Nanocor Inc.). This PA6 was also reprocessed under the same conditions as a reference material. No PA6 that could be used as a reference for the nPA6-c was found. The nPA6-lab was obtained in a Collin ZK25 co-rotating twin-screw extruder-kneader. The screw diameter and the  $L/D$  ratio were 25 mm and 30, respectively. The rotation speed was 200 rpm, and the melt temperature was 240 °C. The extrudates were cooled in a water bath and pelletised.

The amount of MMT in nPA6-c (1.6%) and nPA6-lab (1.35%) was measured after calcination of dry pellets of the nanocomposites at 900 °C for 45 min and weighing the remaining MMT ash. A correction for the loss of structural water was made in the calculation [30]. According to the recommendations of the manufacturer, the materials were dried before each processing cycle for 12 h at 80 °C in a vacuum oven to minimize degradation reactions caused by moisture.

Injection moulding of the NCs and of the reference PA6 was carried out in a Battenfeld BA-230E reciprocating screw injection moulding machine to obtain tensile (ASTM D638, type IV, thickness 3.19 mm) and impact (ASTM D256, thickness 3.1 mm) specimens. The screw of the plasticization unit was a standard screw with a diameter of 18 mm,  $L/D$  ratio of 17.8 and compression ratio of 4. The melt temperatures were 230 °C and 270 °C, and the mould temperature 15 °C. The screw rotation speed was 250 rpm. The injection speed and pressure were 10 cm<sup>3</sup>/s and 2750 bar, respectively. The specimens were left to condition for 24 h in a desiccator before analysis or testing.

The infrared analysis of the reprocessed samples was performed in a Nicolet Magna-IR 560 spectrophotometer with an attenuated total reflectance (ATR) objective. The samples were obtained from the injection moulded tensile specimens.

Continuous flow measurements of pure PA6 and the NCs after 1, 3 and 5 injection moulding cycles at 230 °C and 270 °C were performed in plate–plate mode (diameter 2.5 cm), using an ARES Rheometric Scientific rheometer at 230 °C.

Dynamic-mechanical tests (DMA) were carried out using a TA Instruments DMA Q800 apparatus, that provided the loss tangent ( $\tan \delta$ ) and the storage modulus ( $E'$ ) against temperature. A frequency of 1 Hz and a constant heating rate of 4 °C/min from –10 °C to 80 °C were used. The melting behaviour was studied by DSC using a Perkin–Elmer DSC-7 calorimeter, calibrated with an Indium standard. The samples were heated from 30 °C to 260 °C at 20 °C/min. The melting enthalpy ( $\Delta H_m$ ) was determined in the heating scan from the melting peak area, and the crystallinity was calculated assuming a melting enthalpy of 190.6 J/g [31] for 100% crystalline PA6. Then, the samples were cooled to 30 °C at 20 °C/min and the crystallization temperature ( $T_c$ ) was determined. Finally, a second heating scan was done under the same conditions as the first one and the melting temperature ( $T_m$ ) was determined from the peak maximum.

TGA measurements were carried out using a TA Instruments thermobalance, TGA Q500, under an oxygen atmosphere and at a heating rate of 10 °C/min.

X-ray diffraction patterns were recorded on a Philips PW 1729 GXR D X-ray diffractometer, operating at 45 kV and 50 mA, using a Ni-filtered Cu K $\alpha$  radiation source. The scan speed was 2.7°/min. The transmission electron microscopy (TEM) samples were ultra-thin-sectioned at 30–40 nm using an ultramicrotome. The micrographs were obtained in a Philips Tecnai 20 at an accelerating voltage of 200 kV.

Tensile testing was carried out with an Instron 4301 machine, at a crosshead speed of 10 mm/min and at 23 ± 2 °C and 50 ± 5% relative humidity. The mechanical properties (Young's modulus, yield stress and ductility measured both as the elongation and the reduction of the cross-section at break) were determined from the load–displacement curves. A minimum of five tensile specimens were tested for each reported value.

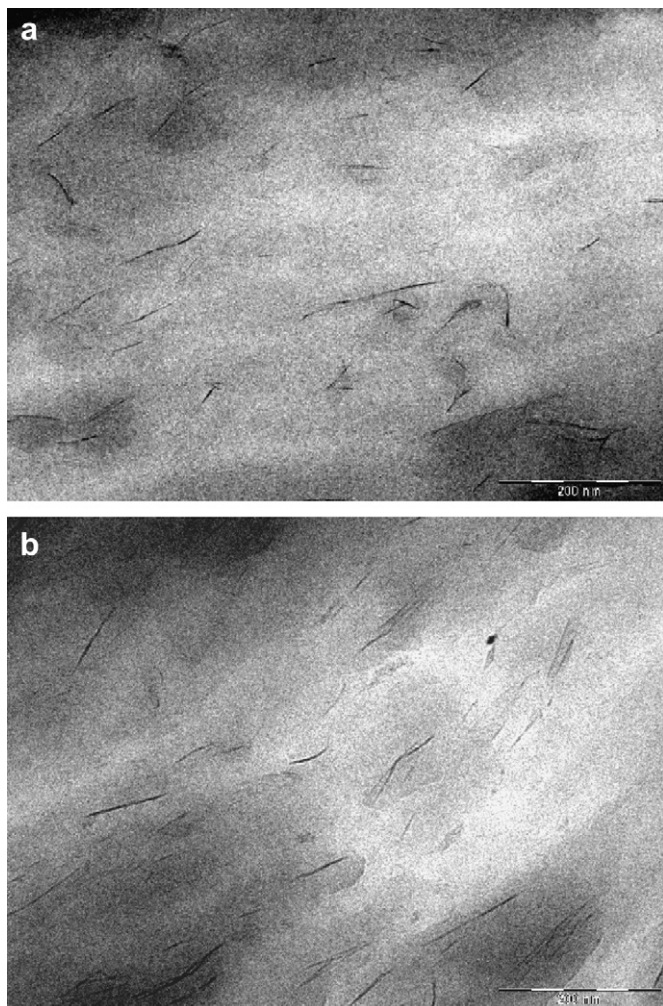
## 3. Results and discussion

### 3.1. Colour

During reprocessing, the slightly brown colour of the nPA6-lab and nPA6-c increased slightly and independently of the processing temperature. These colour changes are a first indication of degradation. To find out whether this colouration was due to either the PA6 matrix or due to the OMMT, the colour of the reprocessed neat PA6 references was observed. The original white colour of the reference PA6 also darkened progressively due to the formation of pyrroles [9], reaching a different colour, but an opacity level similar with the naked eye to that observed in the NCs after 5 reprocessing cycles. Therefore, as colouration occurred at a similar extent in the NCs and in the neat PA6, it was attributed mainly to the PA6 matrix degradation.

### 3.2. Nanostructure

The nanostructure of the NCs was studied by both WAXS and TEM. The WAXS patterns did not show any diffraction peak even after 5 reprocessing cycles which is an indication of exfoliation. Fig. 1a and b shows the TEM images of the nPA6-lab after 1 and 5 cycles at 270 °C, respectively. The images of the nPA6-c and those of the NCs processed at 230 °C showed the same characteristics. As



**Fig. 1.** TEM images of the nPA6-lab after 1 (a) and 5 (b) injection moulding cycles at 270 °C.

can be seen, the morphologies of Fig. 1a and b are very similar, indicating that the exfoliation level remained the same after reprocessing and that agglomeration did not occur.

Reprocessing may help dispersion, due to the longer exposition to the shear stresses. This occurred in the case of polyolefins [22] because exfoliation and dispersion are difficult to attain. In the case of polyamides where exfoliation is easier, when reprocessing was made by single screw extrusion [19], agglomeration occurred. However, when reprocessing was made in the twin-screw extruder [19], dispersion was preserved, in agreement with the larger shear stresses proper of this configuration. Thus, the lack of dispersion change and agglomeration upon reprocessing by injection moulding of this study that resembles the result of the twin-screw extruder, is attributed to the high screw speed in the injection machine that favours dispersion.

### 3.3. Physical structure

The structure of the crystalline phases was studied by differential scanning calorimetry (DSC) and the results of the neat PA6 and the NCs processed at 270 °C are tabulated in Table 1. Similar values were obtained after reprocessing at 230 °C. As can be seen, the crystalline content did not significantly change and maintained at 34% in the neat PA6, 32% in the nPA6-lab and 30% in the nPA6-c. This disagrees with the observed decrease of PA6 reprocessed in

**Table 1**

Crystalline content and transitions of the NCs and neat PA6 reprocessed at 270 °C, measured by DSC

Cycles	Crystalline content (%)		$T_m$ (°C)		$T_c$ (°C)	
	1	5	1	5	1	5
PA6	35	33	221	221	183	185
nPA6-lab	32	33	223	220	184	183
nPA6-c	30	30	221	222	177	180

a twin-screw extruder [19]. The similar crystalline contents of the NCs and the neat PA6 indicated that no nucleation effect or remarkable hindering of crystallization took place in the presence of the organoclay.

No significant change of either  $T_m$  or  $T_c$  was observed, indicating that reprocessing did not modify the main characteristics of the crystalline phase in this study. However, when neat PA6 was reprocessed, an increase in the  $T_c$  and in the crystallization rate occurred [9,11] as well as in the crystallinity [7]. The results were attributed to a decrease in the molecular weight [7,11] or to unmelted particles acting as a nucleation agent and decreasing the spherulite size [9].

The nature of the amorphous phase was studied by DMA and the correspondent  $T_g$ s are reported in Table 2. The reference PA6 showed slightly higher values, although the behaviour with the reprocessing cycles was similar. Similar values were seen after reprocessing at 230 °C. As can be seen, the  $T_g$  decrease was not significant, as it was close to the standard deviation of the measurement. Additionally, possible effects leading to a decrease in  $T_g$  did not occur: the crystalline content did not change and the slight  $T_g$  change was not consistent with the OMMT content and therefore with a possible migration and plasticization induced by the clay surfactant.

### 3.4. Chemical structure

FTIR was used to detect possible changes in the chemical nature of the NCs. The FTIR spectra of the nPA6-lab after 1 and 5 reprocessing cycles at the highest temperature, where degradation is more probable, are shown in Fig. 2. The spectra of the nPA6-c were very similar. If we look at the spectra after 1 cycle, the characteristic bands of PA6 [32,33] are present, plus a small difference in the region between 1000  $\text{cm}^{-1}$  and 1100  $\text{cm}^{-1}$  which is due to the Si–O stretching vibration of the structure of the montmorillonite [32,33]. If we compare the spectra after 1 and 5 cycles, no significant change is observed indicating that any possible change of the chemical structure must be slight. This is because either the organoclay may obscure the peak being sought, or the extent of the degradation was too low and thus the concentration of the functionalities was simply below the sensitivity of the instrument. Similar results were obtained after reprocessing of both PA6 [11] at a lower melt temperature (235 °C), and of an NC based on an olefin elastomer [22].

Possible changes in the molecular weight were tested by measuring the Newtonian viscosity of the NCs which is directly related to the molecular weight. In the case of nanocomposites, rheological analysis is the most sensitive measure of changes of the

**Table 2**

$T_g$  values of the NCs reprocessed at 270 °C, measured by DMA

Material	Cycles		
	1	3	5
nPA6-lab	60.2 ± 0.5	58.3 ± 1.7	58.2 ± 1.2
nPA6-c	64.1 ± 0.8	63.9 ± 0.9	62.9 ± 0.2

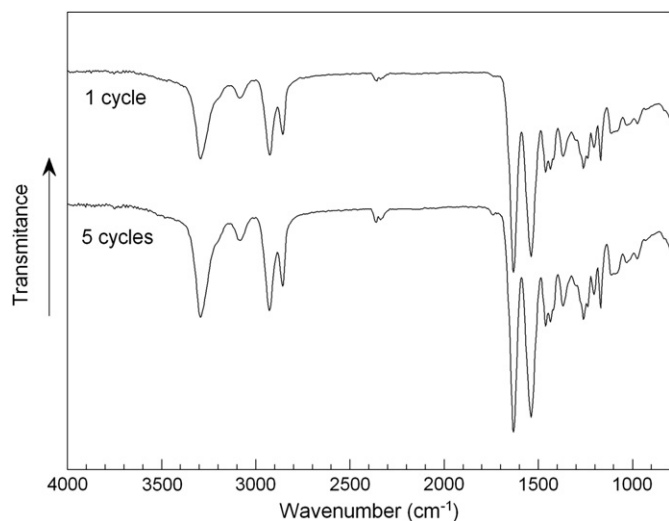


Fig. 2. FTIR spectra of the nPA6-lab reprocessed at 270 °C.

molecular weight as gel permeation chromatography is almost infeasible due to the presence of the inorganic nanoparticles. The Newtonian viscosity at 230 °C of the two NCs reprocessed at 270 °C and of the reference PA6 is shown in Fig. 3 as a function of the number of injection cycles. The plots after reprocessing at 230 °C showed similar characteristics, although with smaller decreases in viscosity. As can be seen, the viscosity of the two NCs decreased as a consequence of reprocessing. The molecular weight decrease of the nPA6-lab was smaller than that of the nPA6-c. This is a somewhat unexpected result, since no stabilizer was added to the nPA6-lab. It is known that in injection moulding, besides shear flow, some elongational flow is involved, but its effect on degradation is comparatively negligible. In the literature, reprocessing of PA6 NCs by injection moulding has not been studied to our knowledge but, regarding single or twin extruders, decreases in the complex viscosity after 3 cycles in a single screw extruder [19] and increases and decreases in the case of twin-screw extruder [19] have been observed.

With respect to the origin of the degradation in Fig. 3, the initial viscosity of the nPA6-c was clearly higher than that of the nPA6-lab. This will lead to higher shear stresses on the melt and to stronger mechanical degradation in the nPA6-c. However, if mechanical

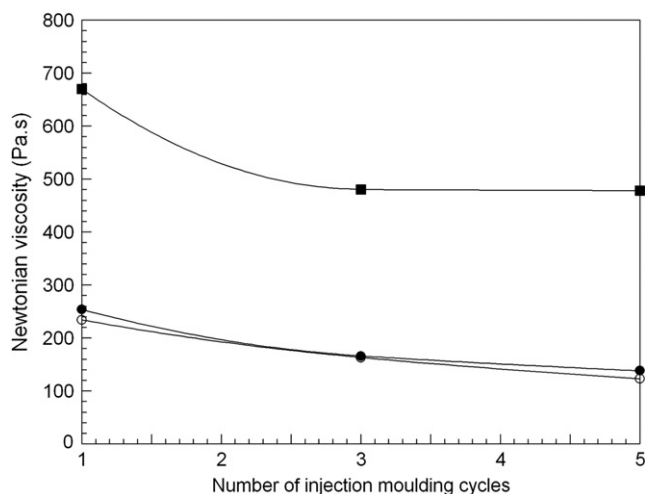


Fig. 3. Newtonian viscosity at 230 °C as a function of the number of injection moulding cycles of the nPA6-lab (●), of the reference material (○) and of the nPA6-c (■) reprocessed at 270 °C.

degradation was important, at 230 °C degradation and viscosity decrease upon reprocessing should be higher, as the melt viscosity and shear stress are higher at lower temperatures. This did not occur. Consequently mechanical degradation is scarcely significant and degradation is seen as mostly thermal in nature.

With respect to the reasons for the decrease in viscosity, it is possible that a progressive surfactant migration upon reprocessing of the NCs occurs. This might lead to plasticization [34,35] and to a decrease in viscosity. However, as previously seen, the  $T_g$  did not decrease, so surfactant migration and plasticization must be discarded. Additionally, no new products were observed by FTIR; hence the viscosity decrease in Fig. 3 is attributed to a molecular weight decrease [7,19] by chain scission. In reprocessed neat PA6, both chain scission and recombination (through cross-linking, for instance) occurred. The competition between the two processes lead to molecular weight decreases [7,8,18], increases [9], and also combined behaviours [11,19].

Water absorbed in the clay could promote chain scission in polyamides [27,36], but the severe drying conditions of this study rule out this possibility. Other possible degradation reactions in NCs, not observed in this study, are thermo-oxidative degradation [37] and inter-chain reactions [38,39] through recombination of the degrading polymer chains trapped in the gallery space of the clay.

In Fig. 4 the TGA curve of the organoclay is reported with the derivative of the weight loss to better appreciate the critical degradation temperatures of the Nanomer I30 used in nPA6-lab. As can be seen, a small secondary peak centred at roughly 200 °C indicates the decomposition of some surfactant; however, this temperature is below the  $T_m$  and the usual processing temperature of PA6 [40], so the peak is probably due to the free or excess surfactant. The first significant weight loss peak is centred at 330 °C, i.e., far from the experimental processing temperatures (230 and 270 °C). This agrees with the fair degree of stability observed for the two nPA6 after reprocessing, which leads to a small decrease in mechanical properties after reprocessing.

### 3.5. Mechanical properties

The modulus of elasticity of the two NCs is shown in Fig. 5. The moduli after reprocessing at 230 °C were the same, and the plots of the yield stress showed similar characteristics. As can be seen, the modulus values did not significantly change upon reprocessing. This agrees with the TEM results where no change in the degree of dispersion was seen, and also with the unchanged crystalline content. Fig. 5 is also an experimental evidence of a lack of reprocessing induced compaction of the OMMT layers, as the modulus should decrease in this case.

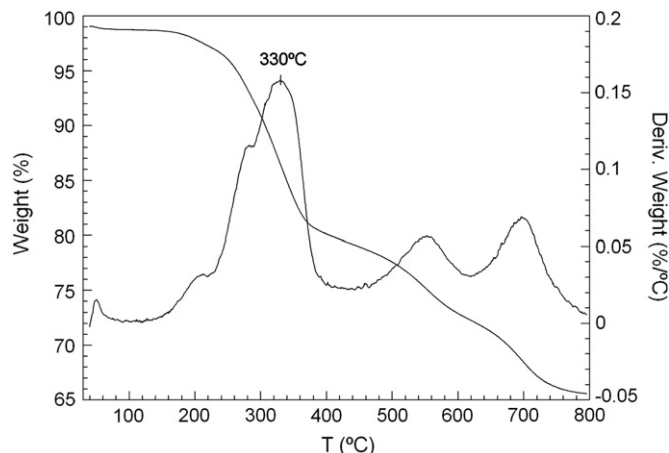


Fig. 4. TGA curves and loss weight derivate of the Nanomer I30 used in nPA6-lab.

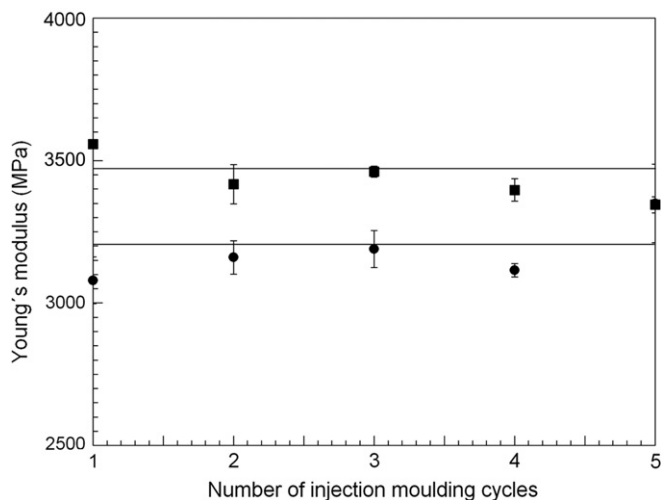


Fig. 5. Young's modulus of the nPA6-c (■) and nPA6-lab (●) reprocessed at 270 °C as a function of the number of injection moulding cycles.

It has been seen [41] that compaction of layers may take place after harsh processing conditions. The almost fully exfoliated state of the OMMT in these NCs will most probably account for the difference in behaviour. The lack of change of the modulus values after reprocessing agrees with previous results on reprocessing of PA6 by injection moulding up to 7 cycles [9], and of TPO based NCs [22]. Increases in the modulus of elasticity were claimed upon reprocessing of nPA6 by extrusion [19,20], and were attributed to an increase in the dispersion due to the larger exposure to the shear stresses in the melt. However, this possibility implies that full dispersion in the PA6 matrix was not achieved after the first cycle, contrary to what we observed in this study.

The ductility values measured as the elongation at break, are shown in Fig. 6. When reprocessing was carried out at 230 °C, ductility remained unchanged in the nPA6-lab and only slightly decreased in the nPA6-c. These facts agree with the smaller viscosity decrease (and consequently, molecular weight decrease) observed after reprocessing at 230 °C. As can be seen in Fig. 6, the overall behaviour after reprocessing at 270 °C is a decrease in the elongation at break. However, both nPA6 remained ductile indicating that the interfacial characteristics did not significantly deteriorate. A decrease in the elongation at break is the usual consequence of reprocessing of NCs [20,22], polyamides [7,9,18]

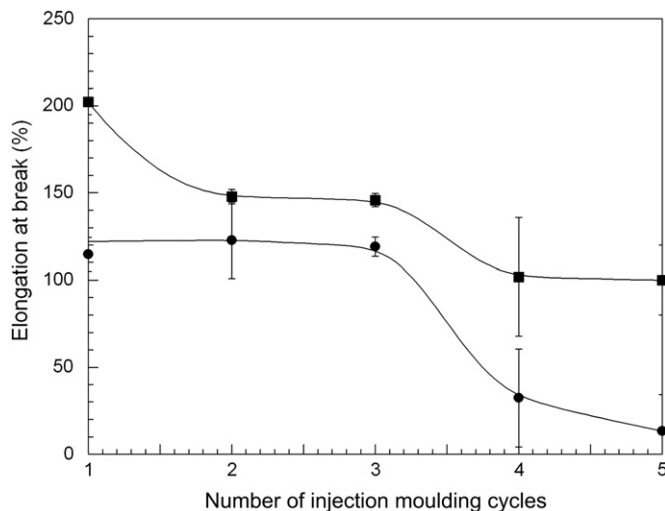


Fig. 6. Elongation at break values. Symbols as in Fig. 5.

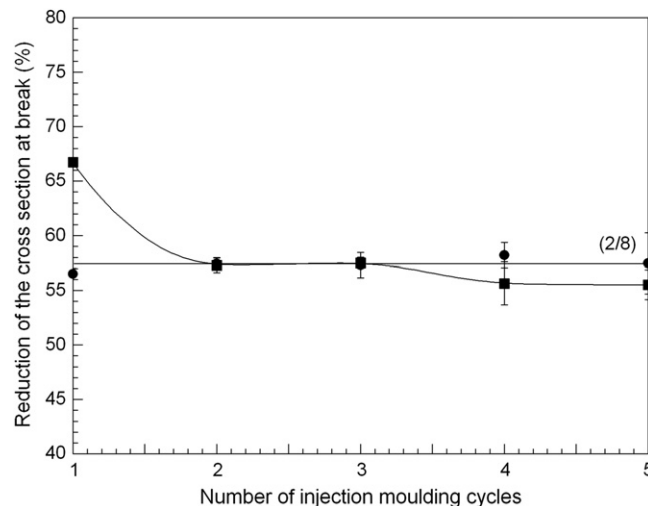


Fig. 7. Reduction of the cross-section at break values. Symbols as in Fig. 5. The number inside parenthesis indicates the amount of specimens that yielded.

and other polymers [4] as all degradation processes have negative influence on the break properties. Ductility did not decrease after reprocessing of neat PA6 [11] but at a lower reprocessing temperature (235 °C). Reprocessing of nPA6 by extrusion [19] leads to a ductility increase, when appropriate dispersion was not reached in the first cycle, by means of an improved dispersion that ameliorated the fracture properties.

Upon inspection of the stress/strain curves, it is clear that the elongation at break values in Fig. 6 are a consequence of a single cold drawing process in the nPA6-lab and of a triple cold drawing process in the nPA6-c. As can be seen in the case of the nPA6-lab, ductility was mostly preserved up to three processing cycles, and then decreased as a consequence of the suppression of the single cold drawing ability. In the case of the nPA6-c the decrease after one cycle was a consequence of the suppression of one of the three cold drawing processes and the decrease after three cycles of the suppression of a second cold drawing process. Thus, reprocessing and the consequent degradation in the nanocomposites lead to a decrease in the drawing ability and the elongation at break of both NCs. The greater decreases observed in the nPA6-c are attributed to its also clearly greater molecular weight decrease.

As most of the specimens broke during cold drawing leading to important differences in elongation at break which do not correspond to the same difference in ductility, ductility was measured more properly by means of the reduction of the cross-section at break. These ductility data are shown in Fig. 7. The reference PA6 showed similar values to those of the nPA6-lab. As can be seen for the nPA6-lab, the reduction of the cross-section at break did not change upon reprocessing, in agreement with the small decrease in molecular weight observed. In the case of the nPA6-c, the decrease in cross-section after the second cycle appears as a consequence of the concomitant decrease in the Newtonian viscosity (and consequently molecular weight) in Fig. 3. The smaller decrease in cross-section after 5 cycles is not accompanied by an observable viscosity decrease. Thus, the decrease in the molecular weight of nPA6-lab and nPA6-c by degradation has the only effect of decreasing the elongation at break; more specifically, it causes a decrease in their ability to cold draw.

#### 4. Conclusions

Both the nPA6-lab and the nPA6-c are basically stable after five injection cycles at 230 °C, and only slightly degraded after reprocessing at 270 °C. Despite the observed darkening, the main solid

state characteristics of the matrices did not change. In opposition with that observed in other NCs, **no compaction of the clay layers was observed after reprocessing, probably because of the widely exfoliated nanostructure.**

**Upon reprocessing at 270 °C mainly, viscosity decreased, but no chemical modification was observed by FTIR, indicating a molecular weight decrease. As this was the only structural change observed, it is proposed as the reason for the observed ductility decrease as observed mainly by the reduction of the ability of the two nPA6 to cold draw. The lack of change of the Young's modulus, and the ductile nature of the two nPA6 after reprocessing both at 230 and 270 °C testified to a lack of change of the interface conditions upon reprocessing, and to the ability of the two nPA6 for mechanical recycling.**

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## References

- [1] Scheirs J. Polymer recycling. Science, technology and applications. England: John Wiley & Sons Ltd; 1998.
- [2] La Mantia F. Handbook of plastics recycling. Shrewsbury, UK: Rapra Technology Limited; 2002.
- [3] Kostadinova M, Proietto M, Jilov N, La Mantia FP. Recycling of high density polyethylene containers. *Polym Degrad Stab* 1997;57:77–81.
- [4] Ahmed N, Khan JH, Hussain I, Hamid SH. Thermal, chemical and mechanical property evaluation of recycled–reprocessed high density polyethylene. *J Polym Mater* 1999;16:341–5.
- [5] Liu ZQ, Cunha AM, Yi XS, Bernardo AC. Key properties to understand the performance of polycarbonate reprocessed by injection molding. *J Appl Polym Sci* 2000;77:1393–400.
- [6] Silva Spinacé MA, De Paoli MA. Characterization of poly(ethylene terephthalate) after multiple processing cycles. *J Appl Polym Sci* 2001;80:20–5.
- [7] La Mantia FP, Curto D, Scaffaro R. Recycling of dry and wet polyamide 6. *J Appl Polym Sci* 2002;86:1899–903.
- [8] Scaffaro R, La Mantia FP. Characterization of monopolymer blend of virgin and recycled polyamide 6. *Polym Eng Sci* 2002;42(12):2412–7.
- [9] Lozano-Gonzalez MAJ, Rodríguez-Hernandez MAT, Gonzalez-De los Santos EA, Villalpando-Olmos J. Physical–mechanical properties and morphological study in nylon-6 recycling by injection molding. *J Appl Polym Sci* 2000;76:851–8.
- [10] Groning M, Hakkarainen M. Headspace solid-phase microextraction with gas chromatography/mass spectrometry reveals a correlation between the degradation product pattern and changes in the mechanical properties during the thermooxidation of in-plant recycled polyamide 6,6. *J Appl Polym Sci* 2002;86(13):3396–407.
- [11] Su KH, Lin JH, Lin CC. Influence of reprocessing on the mechanical properties and structure of polyamide 6. *J Mater Process Technol* 2007;192–193:532–8.
- [12] Eguiazábal JI, Nazábal J. Reprocessing polycarbonate/acrylonitrile–butadiene–styrene blends: influence on physical properties. *Polym Eng Sci* 1990;30(9):527–31.
- [13] La Mantia FP, Capizzi L. Recycling of compatibilized and uncompatibilized nylon/polypropylene blends. *Polym Degrad Stab* 2001;71:285–91.
- [14] Ramírez-Vargas E, Navarro-Rodríguez D, Blanqueto-Menchaca AI, Huerta-Martínez BM, Palacios-Mezta M. Degradation effects on the rheological and mechanical properties of multi-extruded blends of impact-modified polypropylene and poly(ethylene-co-vinyl acetate). *Polym Degrad Stab* 2004;86(2):301–7.
- [15] Guerrica-Echevarría G, Eguiazábal JI, Nazábal J. Effects of reprocessing conditions on the properties of unfilled and talc-filled polypropylene. *Polym Degrad Stab* 1996;53(1):1–8.
- [16] Balatinez JJ, Sain MM. The influence of recycling on the properties of wood fibre–plastic composites. *Macromol Symp* 1998;135:167–73.
- [17] Chrysostomou A, Hashemi S. Effect of reprocessing on mechanical properties of short glass fiber reinforced styrene maleic anhydride. *Plast Rubber Comp* 2000;29(5):235–42.
- [18] Maspoch ML, Ferrando HE, Velasco JI. Characterisation of filled and recycled PA6. *Macromol Symp* 2003;194:295–303.
- [19] Russo GM, Nicolais V, Di Maio L, Montesano S, Incarnato L. Rheological and mechanical properties of nylon 6 nanocomposites submitted to reprocessing with single and twin screw extruders. *Polym Degrad Stab* 2007;92:1925–33.
- [20] Acierno D, Scarfato P, Incarnato L, Di Maio L. Mechanical recycling of polymer–clay nanocomposites prepared by melt compounding. *Wiss Ber FZKA* 2004;7005:A3/1–3/7.
- [21] Lew CY, Murphy WR, McNally GM. Recyclability of polymer–clay nanocomposites: part 1. The influence of multiple-extrusions on structure and mechanical properties. *Ann Tech Conf – Soc Plast Eng* 2004;62(1):299–303.
- [22] Thompson MR, Yeung KK. Recyclability of a layered silicate–thermoplastic olefin elastomer nanocomposite. *Polym Degrad Stab* 2006;91(10):2396–407.
- [23] Zeng QH, Yu AB, Lu GQ, Paul DR. Clay-based polymer nanocomposites: research and commercial development. *J Nanosci Nanotechnol* 2005;5:1574–92.
- [24] Li Y, Shimizu H. Novel morphologies of poly(phenylene oxide) (PPO)/polyamide 6 (PA6) blend nanocomposites. *Polymer* 2004;45(22):7381–8.
- [25] Shah RK, Paul DR. Nylon 6 nanocomposites prepared by a melt mixing masterbatch process. *Polymer* 2004;45(9):2991–3000.
- [26] González I, Eguiazábal JI, Nazábal J. Exfoliated PA6,6 nanocomposites by modification with PA6. *Polymer* 2005;46(9):2978–85.
- [27] Davis RD, Gilman JW, VanderHart DL. Processing degradation of polyamide 6/montmorillonite clay nanocomposites and clay organic modifier. *Polym Degrad Stab* 2003;79(1):111–21.
- [28] Fornes TD, Hunter DL, Paul DR. Effect of sodium montmorillonite source on nylon 6/clay nanocomposites. *Polymer* 2004;45(7):2321–31.
- [29] Alexandre M, Dubois P. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. *Mater Sci Eng R-Rep* 2000;28(1–2):1–63.
- [30] Fornes TD, Yoon PJ, Keskkula H, Paul DR. Nylon 6 nanocomposites: the effect of matrix molecular weight. *Polymer* 2001;42(25):9929–40.
- [31] Russo P, Acierno D, Di Maio L, Demma G. Thermal and mechanical characterisation of films from nylon 6/EVOH blends. *Eur Polym J* 1999;35(7):1261–8.
- [32] Pramoda KP, Liu T, Liu Z, He C, Sue HJ. Thermal degradation behaviour of polyamide 6/clay nanocomposites. *Polym Degrad Stab* 2003;81(1):47–56.
- [33] Loo LS, Gleason KK. Fourier transform infrared investigation of the deformation behavior of montmorillonite in nylon-6/nanoclay nanocomposite. *Macromolecules* 2003;36(8):2587–90.
- [34] González I, Eguiazábal JI, Nazábal J. New clay-reinforced nanocomposites based on a polycarbonate/polycaprolactone blend. *Polym Eng Sci* 2006;46(7):864–73.
- [35] Morgan AB, Harris JD. Effects of organoclay Soxhlet extraction on mechanical properties, flammability properties and organoclay dispersion of polypropylene nanocomposites. *Polymer* 2003;44(8):2313–20.
- [36] Fornes TD, Yoon PJ, Paul DR. Polymer matrix degradation and color formation in melt processed nylon 6/clay nanocomposites. *Polymer* 2003;44(24):7545–56.
- [37] Zong R, Hu Y, Liu N, Li S, Liao G. Investigation of thermal degradation and flammability of polyamide-6 and polyamide-6 nanocomposites. *J Appl Polym Sci* 2007;104(4):2297–303.
- [38] Jang BN, Wilkie CA. The effect of clay on the thermal degradation of polyamide 6 in polyamide 6/clay nanocomposites. *Polymer* 2005;46(10):3264–74.
- [39] Jang BN, Wilkie CA. The thermal degradation of polystyrene nanocomposite. *Polymer* 2005;46(9):2933–42.
- [40] <<http://techcenter.lanxess.com>>.
- [41] Shah RK, Paul DR. Organoclay degradation in melt processed polyethylene nanocomposites. *Polymer* 2006;47(11):4075–84.