

STUDY OF THE PROCESSING CONDITIONS OF PCL/CLAY NANOCOMPOSITES: molecular weight degradation, thermal and mechanical properties

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ABSTRACT: The effect of processing conditions on the thermal and mechanical properties of the pure polycaprolactone (PCL) and 5wt.% PCL/organo-modified clay nanocomposites was studied. The possibility of molecular weight degradation of the matrix was also analyzed. The different materials were prepared by double-screw micro-extruder changing barrel temperatures, screw rotation speed and resident time. It was demonstrated that the extrusion parameters have negligible effect on the molecular weight of the matrix and on the final thermal and mechanical properties of the matrix and the nanocomposites.

KEYWORDS: Biodegradable, Clay, Nanocomposite, Processing Conditions, Twin-Screw Micro-Compounder, Thermal Properties, Mechanical Properties.

INTRODUCTION

Packaging is the biggest industry of polymer processing. Food industry is its principal customer. Despite environmental problems, polymer packaging European market is increasing in about millions of tons per year. Foreseeing future laws about reducing the weight and volume of these products, cheap and biodegradable polymeric products are receiving growing attention [1]. Polycaprolactone (PCL) belongs to this class of synthetic biodegradable polymers. PCL is linear, hydrophobic and partially crystalline polyester that can be slowly consumed by micro-organisms [2]. The performance of PCL can be greatly enhanced by the dispersion of nanometer-size particles. This kind of materials are called nanocomposites and have the interesting characteristic that the mechanical properties [3]; the barrier properties [4]; the thermal properties [5], and some others such as the flammability [6] and water adsorption [7], can be greatly enhanced with the addition of a small amount of filler (usually less than 10wt.%). One kind of the nanometer-size reinforcement is the montmorillonite, which is a layered silicate whose interlayer ions can be changed by organ-ions in order to produce an increment in the interlayer spacing and to improve the polymer/clay compatibility. These improvements allow the dispersion of clay platelets to be easier. As far as totally dispersion of the clay platelets (exfoliation) is achieved, more effective the reinforcement phase is [8]. Instead of fully exfoliated structures, intercalated structures (the silicate layers are intercalated between polymer chains) or a mixture of both, are

generally achieved [9]. From previous works it was found that 5 wt. % of montmorillonite modified with dimethyl, dehydrogenated tallow, quaternary ammonium (C20A) leads to the best dispersion degree of the reinforcement inside the PCL matrix comparing between several organo-modified montmorillonites.

EXPERIMENTAL

Materials

The matrix used in this work was a commercial polycaprolactone (Mn 80000), provided by Sigma Aldrich. The clay named Cloisite 20A (C20A) was purchased from Southern Clay Products Inc., USA. The characteristics of the clay are shown in Table 1.

Table 1 Characteristics of the clay used as nanofiller

Material	Organic modifier	Modifier Concentration (meq/100 g clay)	Interlayer Spacing d_{001} (Å)
C20A	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N}^+ - \text{HT} \\ \\ \text{HT} \end{array}$	95	24.2

HT is hydrogenated tallow (~65% C18; ~30% C16; ~5% C14)

Composite preparation and characterization methods

Nanocomposites with 5 wt.% of C20A (5C20A) were prepared by melt-intercalation in a micro-double-screw extruder DSM Xplore. The effect of processing conditions on the final properties of the materials was analyzed by changing the resident time (2, 3 and 4 minutes), the temperature profile along the compounder barrel ([60,80,100]°C; [60,90,120]°C; [70,100,130]°C) and the screw rotation speed (50, 100 and 150 rpm) from the reference processing condition (2 min; [60,90,120]°C; 100rpm). The as extruded materials were characterized by differential scanning calorimetry to find differences in the crystallinity and fusion temperature of the matrix and by gas permeation chromatography to study the possibility of polymer molecular weight degradation by severe processing conditions. Then, films 0.5mm thick were prepared by compression molded to be mechanically characterized by static tensile tests.

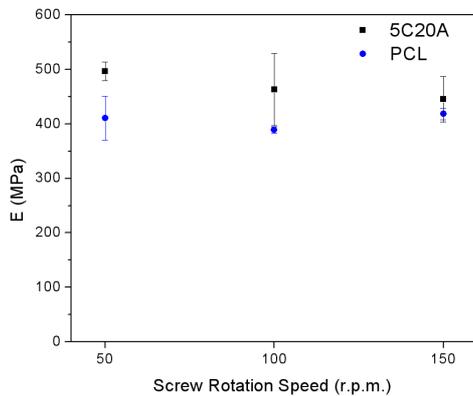
RESULTS

Table 2 shows the effect of the processing parameters on the fusion temperature and the crystallinity degree of the as extruded pure matrix and nanocomposites. From this table it can be concluded that extrusion conditions (in the processing window analyzed) have negligible effect on the fusion temperature and the crystallinity of the neat matrix and 5C20A nanocomposites.

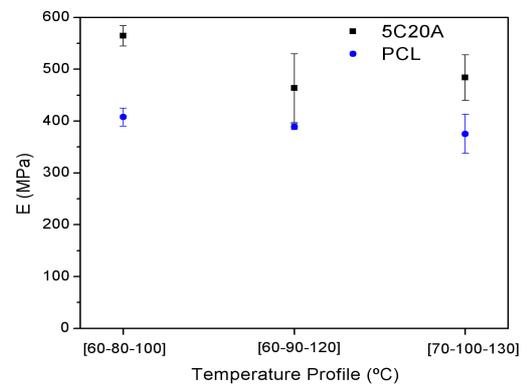
Table 2 Effect of processing parameters on the thermal properties of neat PCL and 5C20A nanocomposites

Material	T _f (°C)	X _{cr} (%)
PCL (2 min;[60,90,120°C];100rpm)	63	51
PCL (2 min;[60-80-100°C];100rpm)	64	50
PCL (2 min;[70-100-130 °C];100rpm)	63	50
PCL (2 min;[60,90,120°C];50rpm)	67	54
PCL (2 min;[60,90,120°C];150rpm)	68	54
PCL (3 min;[60,90,120°C];100rpm)	69	55
PCL (4 min;[60,90,120°C];100rpm)	68	53
5C20A (2 min;[60-90-120°C];100rpm)	66	51
5C20A (2 min;[60-80-100°C];100rpm)	62	49
5C20A (2 min;[70-100-130°C];100rpm)	61	48
5C20A (2 min;[60-90-120°C];50rpm)	66	49
5C20A (2 min;[60-90-120°C];150rpm)	62	48
5C20A (3 min;[60-90-120°C];100rpm)	68	49
5C20A (4 min;[60-90-120°C];100rpm)	65	48

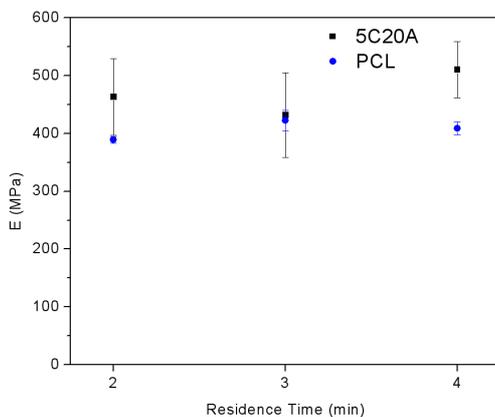
Fig. 1(a-c) shows the Young's modulus as a function of the processing parameters. Similar plots were obtained for the tensile strength and the deformation at break.



(a)



(b)



(c)

Figure 1. Young's modulus of the PCL and 5C20A as a function of processing parameters: (a) Screw rotation speed, (b) Temperature profile, (c) Residence time.

The Young's modulus of PCL and 5C20A, as well as the tensile strength and the deformation at break, were not substantially changed by the processing conditions. Homminga et. al. [10] found that shear forces in the melt-preparation of polymer layered mineral nanocomposites facilitate the brake-up of large sized agglomerates, whereas the extent of further exfoliation of the mineral layers is determined by the compatibility between the polymer matrix and the mineral layers rather than by shear forces. As was earlier mentioned, from previous works it was found that C20A has the best compatibility with PCL between several organo-modified clays analyzed, thus, in our case, the final extent of clay dispersion degree is being dominated by the polymer/clay compatibility rather than the processing conditions.

Fig. 2 shows the effect of processing parameters on the molecular weight of PCL obtained from gas permeation chromatography.

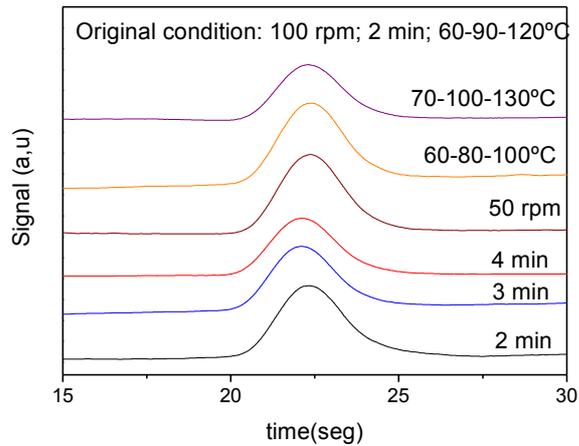


Figure 2. Elution times of PCL processed at different conditions

Low melt temperature and high screw rotation speed and residence time become the effect of shear forces on the polymer melt more severe. Shear forces developed in the extruder barrel may degrade the molecular weight of the matrix. In this case, we would have found strong differences on the thermal and mechanical properties of the materials by changing extrusion parameters. As was expected from previous results, it can be concluded from Fig. 2 that the processing conditions had negligible effect on the molecular weight of the neat matrix.

CONCLUSIONS

The effect of extrusion parameters on the preparation of PCL/Clay nanocomposites was evaluated. The final thermal and mechanical properties of the nanocomposites will be strongly dependent of the clay dispersion degree achieved inside the polymer matrix which can be governing by two phenomena depending on the polymer/clay compatibility. Once good compatibility between the polymer and the clay is achieved, intense shear forces during processing (avoiding polymer matrix degradation) may accelerate the formation of the final clay morphology by breaking up large sized agglomerates but changing processing parameters will not modify the extent of clay dispersion of the nanocomposite.

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