

Studying the Degradation of Polyhydroxybutyrate-co-valerate during Processing with Clay-Based Nanofillers

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ABSTRACT: Polyhydroxybutyrate-co-valerate (PHBV) is attracting interest as a new material for packaging applications and nanoparticulate layered silicates are being increasingly explored as a way to improve PHBV film properties. In this context, it is essential to understand how different types of nanofillers could influence polymer properties. PHBV was processed with three-layered clay types using different mixing methods, and we examined the effect of processing time, clay type, and clay content on polymer molecular weight and composite morphology. PHBV molecular weight (M_w) decreased by 38% after extrusion processing and was further reduced in the presence of montmorillonite (MMT). However, when PHBV was processed with kaolinite as the additive, no further reduction in polymer molecular weight was observed. Molecular weight also decreased as the MMT clay content

increased from 1 to 5 wt %. The results suggest that release of tightly bound water from clay surfaces at elevated temperature may be responsible for PHBV degradation during processing. Evidence also points to the possibility that the surface modifier present in organically modified MMT may catalyze PHBV degradation in some way. X-ray diffraction studies indicated an intercalated morphology in the presence of modified montmorillonite but good dispersion was also achieved when unmodified kaolinite was blended with PHBV. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3669–3676, 2009

Key words: poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV); nanocomposites; degradation; processing; montmorillonite; kaolinite

INTRODUCTION

Interest in bioplastics for commodity markets, especially packaging, has grown at a rapid rate over the past several years. There are considerable advantages from an industry and societal viewpoint in using renewable polymers derived from non-petroleum sources and biodegradability is also an important factor in light of growing concerns about plastic wastes in the environment.¹ The latter is particularly the case in developing countries where non-degradable plastic bags can litter the landscape and contribute to flooding problems in major urban centers because of drain blocking.

Poly lactide (PLA) is the bioplastic that has achieved the greatest market penetration in the packaging sector. PLA is a polyester obtained in several steps from corn starch or other carbohydrates. There are a growing number of PLA production plants either operating or under construction around

the world. In addition to PLA, there is also considerable interest in polyhydroxyalkanoates (PHAs) obtained in high yield as energy storage materials from certain bacteria grown under nutrient-limited conditions. These bacteria can produce a wide range of PHAs depending on the nutrient medium on which they are grown. Polyhydroxybutyrate (PHB) and polyhydroxybutyrate-co-valerate (PHBV) have drawn the most commercial attention to date. Development of PHBV has been driven by the need for improvements in the mechanical properties and processability of PHB. PHBV is considered an interesting material for use in packaging because of its barrier properties^{2–4} and also its compostability.⁵ Cava et al.⁴ compared the properties of PET with those of biodegradable polymers such as PLA, PCL and PHBV and their nanocomposites. Their research showed that PHBV could withstand thermal retorting but that its oxygen and aroma barriers were not as good as those of PET.

To further improve key properties of polymers and to make them more suitable for applications in the packaging market, nanocomposites incorporating laminar clays have been developed. The gas barrier properties of some polymers can be increased to a large extent by including low contents of laminar

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nanofillers in the composition. This effect has been attained by an increase in the tortuosity of the diffusion path generated by the impermeable platelets.⁶ Several articles can be found in the literature reporting a decrease in the oxygen permeability of poly (lactic acid) when nanoclays are incorporated^{7,8}: Cheng et al.⁹ found that the oxygen permeability can be lowered from 777 to 340 cc/m²/day by adding 10 wt % of Cloisite[®] 25A (Rockwood Additives Ltd.) to pure PLA. In previous work,¹⁰ a decrease in the oxygen permeability of 43% was reported for an amorphous PLA containing 4 wt % of modified kaolinite. Regarding PHBV, an improvement in the gas barrier properties through addition of clay has already been demonstrated.^{3,4}

Wang et al.⁵ prepared PHBV/organically modified montmorillonite (OMMT) composites by a solution intercalation method. These authors found that polymer biodegradability was reduced but the range of processing temperatures increased when OMMT was incorporated. It was also suggested that the addition of OMMT to PHBV could improve the application potential while reducing costs. Chen et al.¹¹ also used solution intercalation and examined the influence of an organophilic clay on the crystallization of PHBV. The temperature of crystallization of PHBV from the melt was increased and the addition of organophilic clay caused an increase in the overall crystallization rate but did not change the mechanism of nucleation. Mechanical tests revealed that the tensile strength of PHBV was increased by 32% with the incorporation of 3% clay and that the modulus was also increased. In an earlier publication,¹² the same authors investigated the mechanical properties of PHBV-clay nanocomposites.

Sánchez-García et al.¹³ observed a substantial drop in the thermal and mechanical performance of PHB homopolymer and PHB homopolymer blends with PCL when processing with MMT clays; however, the use of organomodified kaolinite led to stable nanocomposites with enhanced barrier properties. The lack of performance with the use of MMT was attributed to a high level of polymer degradation taking place during processing as suggested by DSC and ATR-FTIR spectroscopy results. The research described in this article was aimed at a better understanding of how clay addition influences the degradation of PHBV during melt processing. The effect of the clay type, clay content and processing conditions on the degree of PHBV degradation was analyzed.

EXPERIMENTAL

Materials

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), otherwise known as PHBV, containing 12 mol % of valer-

ate, was a commercial grade supplied by Goodfellow Cambridge Ltd. (Huntingdon, UK). Polyethylene glycol ($M_w = 600$ g/mol) was purchased from Aldrich.

The three commercial nanoclays for this work were two MMTs, Cloisite[®] 20A from Southern Clay Products (Gonzales, TX) and Nanoter[®] NaMMT from NanoBioMatters Ltd. (Paterna, Spain), and Nanoter K, a kaolinite-based product from NanoBioMatters Ltd. Cloisite 20A (hereafter referred to as C) is an organically modified MMT. Among the different grades of Cloisite available, 20A was chosen due to its relatively low polarity. The chemical modification of this clay consists of replacing the sodium cations of the original clay by quaternary ammonium salts (dimethyl-dihydrogenated tallow ammonium chloride), thereby conferring an organophilic character to the clay layers. The sodium montmorillonite (hereafter referred to as NaMMT) and the kaolinite (hereafter referred to as K) are unmodified precursors of the organomodified Nanoter[®] grades.

Nanocomposite processing

Three different routes for processing PHBV and clays into composites were studied, namely: solvent casting, extrusion and melt mixing.

Solvent casting involved dissolving dry PHBV in chloroform (10 mg/mL) at room temperature. In a different beaker, clay was suspended in the same solvent under similar conditions. The solution of PHBV and the suspension of clay in chloroform were then subjected to magnetic stirring for 14 h. The mix was subsequently poured into a glass Petri dish and allowed to dry gently. The resulting film was dried at 60°C under vacuum for 24 h to remove any residual solvent.

Extrusion processing was undertaken using a Haake MiniLab bench-top twin screw extruder with counter-rotating screws at a temperature of 180°C and screw speed of 100 rpm. This equipment allows quantities of material as low as 5–6 g to be processed. Before blending, clay was dried at 120°C under vacuum for over an hour to remove weakly bound water. The polymer pellets and the clay powder were mixed in the dry state before feeding into the extruder. To minimize the loss of clay during the addition, 4 mg of PEG 600 was added to the solid mixture so that the clay would stick to the PHBV pellets. It has been seen by means of GPC experiments that the addition of such a small amount of PEG does not have any effect on the degradation of the PHBV during processing. Different processing times and clay contents were studied. Processing under inert gas was possible by injecting a flow of nitrogen into the extrusion chamber, thereby

TABLE I
Nomenclature of the Samples

Sample	Processing method	Clay type	Clay content (%)	Processing time (min)	Atmosphere
C-PHBV	Solvent cast				
C-PHBV5C	Solvent cast	Cloisite20A	5		
M-PHBV	Internal mixer			5	Air
M-PHBV5C	Internal mixer	Cloisite20A	5	5	Air
N-PHBV	Mini-extruder			5	Nitrogen
A-PHBV	Mini-extruder			5	Air
N-PHBV1C	Mini-extruder	Cloisite20A	1	5	Nitrogen
N-PHBV2C	Mini-extruder	Cloisite20A	2	5	Nitrogen
N-PHBV5C	Mini-extruder	Cloisite20A	3	5	Nitrogen
A-PHBV5C_2min	Mini-extruder	Cloisite20A	5	2	Air
A-PHBV5C_5min	Mini-extruder	Cloisite20A	5	5	Air
A-PHBV5C_6min	Mini-extruder	Cloisite20A	5	6	Air
A-PHBV5C_30min	Mini-extruder	Cloisite20A	5	30	Air
A-PHBV5NaMMT	Mini-extruder	Nanoter NaMMT	5	5	Air
A-PHBV5K	Mini-extruder	Nanoter K	5	5	Air

allowing the effect of atmosphere on degradation of the polymer during processing to be studied.

Melt mixing was performed using a Brabender mixer or a ThermoHaake Rheomix PolyLab for 5 min at 180°C and a rotor speed of 100 rpm. Each batch was then extracted from the mixing chamber manually and allowed to cool to room temperature in air. As in the extrusion processing, clay was fed together with the polymer using a small quantity of PEG 600 as a polymer granulate wetting agent. The material generated in the mixing processes was then hot pressed at 180°C for 2 min so as to produce films for wide angle x-ray scattering analysis (WAXS).

Table I summarizes the nomenclature of the samples produced and the conditions under which they were obtained.

Characterization techniques

WAXS experiments were performed using a Siemens D5000 instrument. Radial scans of intensity versus scattering angle (2θ) were recorded at room temperature in the range 2–30° (2θ). The step size was 0.02° (2θ) and the scanning rate was 8 s/step with identical settings of the instrument using filtered Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$), an operating voltage of 40 kV, and a filament current of 30 mA. The clay basal spacing was calculated using Bragg's law ($\lambda = 2d\sin\theta$).

Selected samples of PHBV compounded with clay were examined using field emission scanning electron microscopy (FE-SEM). The instrument used was a Zeiss Supra 35 FE-SEM equipped with an HKL Technology Channel 5.6 electron back-scattering diffraction detector and a Noran System Six Model 300

EDS detector. Compounded PHBV-clay composite material surfaces were examined without coating.

PHBV molecular weights were calculated from gel permeation chromatography (GPC) results. The PHBV samples (typically 55 mg) were dissolved in 10 mL of chloroform over 4 h at room temperature. Before injection in the GPC equipment, all the samples were filtered through a PTFE 0.45 μm filter to remove any insoluble fractions or clay additive. GPC experiments were conducted in a Shimadzu SIL-10AD using a pre-column PL gel 5- μm Guard (50 \times 7.5 mm) and two combined columns, PL gel 5- μm Mixed-C and PL gel 5- μm Mixed-D, from Polymer Laboratories, UK. The column eluent was THF at a flow rate of 1.0 mL/min and this was monitored using a Model 200 differential refractive index detector (Viscotek Corp., Houston, TX). Calculation and processing of the data was performed using Trisec[®] software from Viscotek. All samples were analyzed in duplicate. PHBV molecular weight and molecular weight distribution was determined relative to a polystyrene-based calibration curve.

Thermogravimetric analysis (TGA) was performed using a TG-STDA Mettler Toledo model TGA/SDTA851e/LF/1600 at a heating rate of 10°C/min from room temperature to 900°C under argon flow. The initial weight of the samples was typically about 15 mg.

RESULTS AND DISCUSSION

Morphology of PHBV/clay nanocomposites

Figure 1 shows the WAXS patterns of pure Cloisite20A organoclay and PHBV5C nanocomposites as obtained by the three different processing methods. The presence of the peak associated with the basal

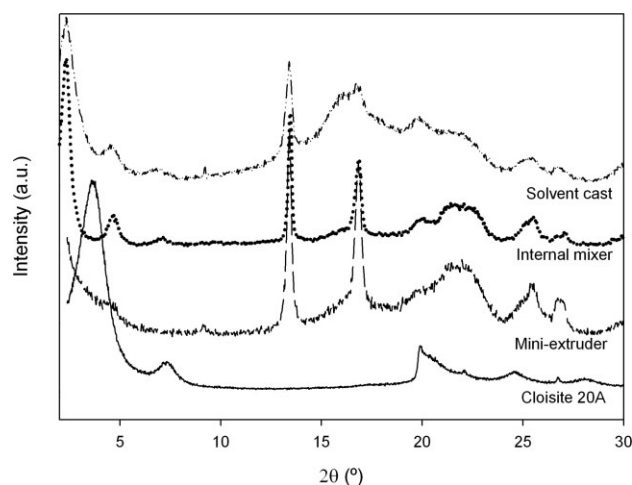


Figure 1 WAXS patterns of the Cloisite20A and PHBV/5C nanocomposites obtained by three different processing methods.

reflection of the clay is visible in all patterns, indicating the presence of some degree of order in the clay platelets in each case. From this observation it can be said that complete exfoliation has not been achieved during any of the processing routes. However, the position of the basal peak of the nanocomposites has shifted towards lower angles relative to the basal peak of the as-received organoclay. According to Bragg's law, this decrease in the angle at which the reflection takes place indicates an increase in the distance of the diffraction planes (i.e., an increase in the basal spacing). This enlargement of the gallery is generally correlated with intercalated morphology. Cloisite20A presents basal 001 (first order) and 002 (second order) reflections at

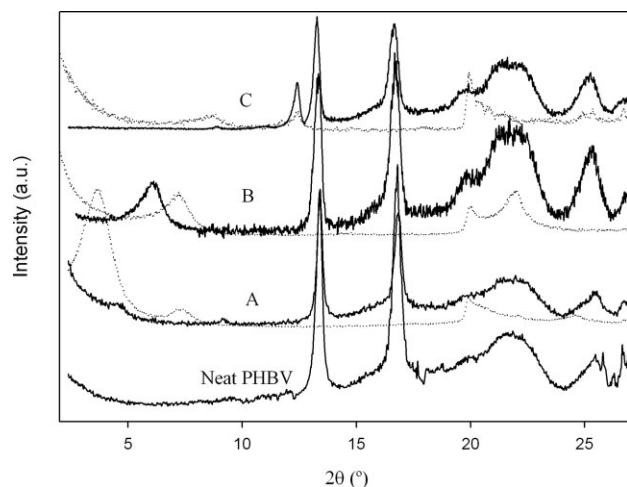


Figure 2 WAXS patterns of the neat PHBV and the PHBV nanocomposite samples produced using the mini-extruder and containing 5 wt % of: A) Cloisite 20A, B) NanoterNaMMT, C) NanoterK. WAXS patterns for the nanocomposites are shown as solid lines and patterns for the clays are shown as dotted lines.

3.58° (2θ) and 7.16° (2θ) respectively, showing a single population of modified clay with a d-spacing of 2.42 nm. The patterns of nanocomposites processed by solvent casting and internal mixing show basal reflections at 2.34° (2θ) and 4.64° (2θ), indicating a basal spacing of 3.8 nm. In the case of the sample obtained from the mini-extruder, only the 002 reflection is visible, because the 001 reflection cannot be clearly differentiated from the direct incoming radiation (beam stop). In this case, the basal distance is 3.97 nm as derived from the position of the 002 reflection. The broadness (high degree of imperfection) of this peak reveals either a poor stacking of the clay or a low concentration of aggregates.

Figure 2 shows the WAXS patterns of the pure PHBV and the PHBV nanocomposite samples containing 5 wt % of different natural clays obtained in the mini-extruder. The Nanoter NaMMT shows a single basal peak at 7.24° (2θ), corresponding to a d-spacing of 1.22 nm, which is the basal space distance of the natural clay. The nanocomposite sample obtained with this clay shows an enlargement of 0.23 nm in the d-spacing, revealing that some inter-gallery expansion has taken place. As in the sample with Cloisite20A, no clay peak can be observed at the natural position and, therefore, it can be assumed that the clay is somewhat intercalated in the polymer matrix. Figure 3 shows a FE-SEM micrograph of the nanocomposite sample containing Nanoter NaMMT; although good dispersion can be seen in the image, the presence of small clay aggregates (white bright dots) can be noticed in agreement with the WAXS patterns. On the other hand, the composite with NanoterK shows no increase in the basal spacing of the clay when blended with PHBV. Nevertheless, the size of the clay tactoids

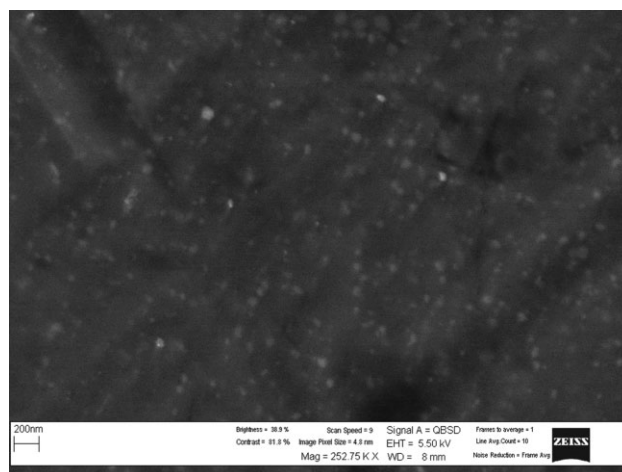


Figure 3 FE-SEM micrograph of the PHBV nanocomposite obtained in the mini-extruder with the NaMMT clay (A-PHBV5NaMMT).

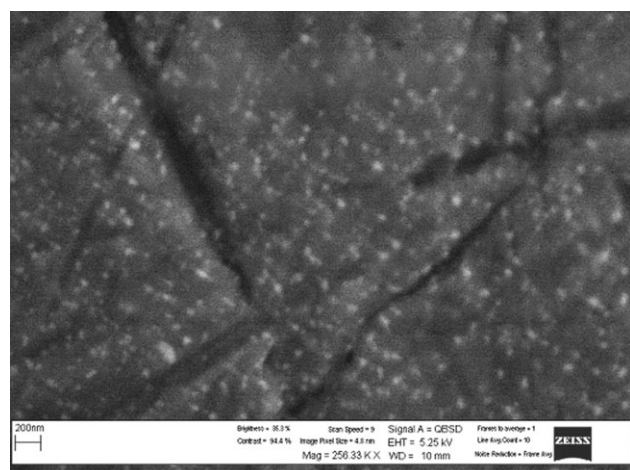


Figure 4 FE-SEM micrograph of the PHBV nanocomposite obtained in the mini-extruder with the kaolinite clay (A-PHBV5K).

decreased during mixing and reached nanometric values as illustrated by FE-SEM (Fig. 4).

Effect of processing method and conditions on the degradation of PHBV/clay nanocomposites

The effect of processing method and conditions on the molecular weight of the neat PHBV and the PHBV containing 5 wt % of Cloisite20A was studied by means of GPC. Results of GPC analyses are shown in Table II in terms of number-average molecular weight (M_n), the ratio between M_n for each sample and M_n for unprocessed PHBV (M_n/M_{n_i}), polydispersity (Pd) and the molar fraction (%) with M_w above 300,000 g/mol or below 50,000 g/mol.

Figure 5 depicts the GPC chromatographs of the neat PHBV in the original state and after processing by the three different methods. As can be seen, a mono-modal distribution is observed in all cases with a peak that moves towards higher retention

volumes as molecular weight decreases. In Figure 5, only the range between 10 and 17 mL in retention volume is shown, because low-molecular weight species were not detected in any of the samples.

As expected, the samples obtained by solvent casting do not show any significant reduction in PHBV molecular weight. The slight increase in molecular weight relative to neat PHBV indicated in Table II is considered to be within the margin of experimental error. The addition of clay does not influence PHBV molecular weight when solvent casting under ambient conditions.

Processing pure PHBV in an internal mixer in the presence of air caused a minor decrease in the molecular weight of the polymer with an 8% reduction in M_n relative to unprocessed PHBV. This behavior changed when organoclay was added to the polymer, resulting in a very significant decrease in molecular weight (from M_n of $93,900 \pm 1300$ g/mol for the starting material to M_n of $19,330 \pm 210$ g/mol in the nanocomposite sample). The fraction of polymer chains in which molecular weight exceeds 300,000 Da also changed from 25.21% in the raw PHBV to 21.92% in the PHBV processed in the internal mixer and to 0.06% in PHBV processed with Cloisite20A in the internal mixer.

Greater degradation of PHBV was observed when processing in the mini-extruder than when processing by means of the internal mixer. For example, the M_n of PHBV was reduced to 68% of the value for the starting polymer when processing in the mini-extruder but only to 92% of this value when processing in the internal mixer. This finding may be due to the higher thermal impact on the polymer when processing in the mini-extruder.¹⁴ Changing from air to a flow of nitrogen in the mini-extruder did not significantly influence PHBV degradation when processing without clay. However, when blending with Cloisite20A, PHBV degradation was to some extent determined by whether processing occurred under air or nitrogen. For example, the molecular

TABLE II
GPC Results of the Pure PHBV and PHBV Nanocomposites for the Different Processing Routes

Sample	M_n (Da)	M_n/M_{n_i} (%)	M_w (Da)	Pd	Fraction (%)	
					>300,000 Da	<500,00 Da
Raw PHBV	$93,900 \pm 1300$	100	$218,900 \pm 4400$	2.33 ± 0.01	25.21	11.89
C-PHBV	$95,200 \pm 1900$	101	$222,300 \pm 1900$	2.34 ± 0.02	25.90	11.80
C-PHBV5C	$95,800 \pm 2800$	102	$225,650 \pm 2300$	2.36 ± 0.05	26.53	11.48
M-PHBV	$86,800 \pm 2200$	92	$201,500 \pm 4100$	2.32 ± 0.01	21.92	13.18
M-PHBV5C	$19,330 \pm 210$	21	$37,480 \pm 350$	1.94 ± 0.003	0.06	74.72
N-PHBV	$63,700 \pm 1300$	68	$135,200 \pm 1500$	2.12 ± 0.02	8.78	21.03
N-PHBV5C	$46,950 \pm 920$	50	$93,050 \pm 630$	2.00 ± 0.03	2.65	32.80
A-PHBV	$64,150 \pm 350$	68	$136,900 \pm 1100$	2.13 ± 0.005	9.09	20.68
A-PHBV5C	$22,850 \pm 70$	24	$41,950 \pm 210$	1.84 ± 0.003	0.0045	69.13

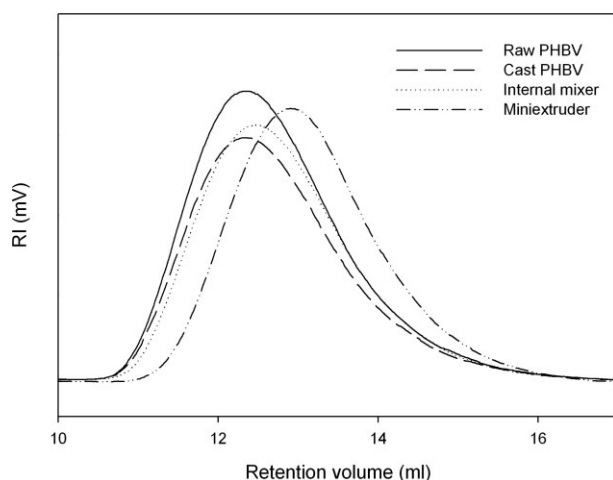


Figure 5 GPC chromatographs for neat PHBV and PHBV processed by the three different methods.

weight (M_w) of PHBV5C processed under nitrogen decreased to $93,050 \pm 630$ g/mol, whereas processing in air resulted in a value of $41,950 \pm 210$ g/mol, corresponding to reductions of 57.5 and 80.1%, respectively in the M_w relative to the original PHBV. This difference in the effect of the nitrogen flux observed with and without clay cannot be explained by the chemical inertness of nitrogen or lack of moisture because the sample processed without clay in air (A-PHBV) gives a virtually identical PHBV M_w to the sample processed under nitrogen (N-PHBV). Although the experimental set-up used in our work did not allow this to be proven, it is possible that volatiles generated during processing with clays could catalyze PHBV degradation and that these volatiles would be flushed away under nitrogen flow but not when processing under a normal air atmosphere.

Effect of clay content and processing time on the degradation of PHBV/clay nanocomposites

In the case of PHBV/Cloisite20A combinations, different clay contents and processing times were studied when using the mini-extruder. Polymer degradation in the resulting samples was determined by GPC (Table III).

Figure 6 shows the weight-average molecular weight (M_w), polydispersity (Pd) values and the polymer chain fraction in which M_w is below 50,000 Da for the raw PHBV starting material as well as for the PHBV and PHBV/Cloisite20A nanocomposites processed in the mini-extruder under nitrogen flow with different clay contents (1, 2, and 5%). As can be seen, the clay clearly contributed to the degradation of the polymer matrix with a significant decrease of PHBV molecular weight at 1% clay content and an increasing effect as clay content increases (e.g., decrease of M_w to 12.25% of value for PHBV processed without clay).

The effect of processing time in the mini-extruder on the molecular weight of PHBV in PHBV/Cloisite20A nanocomposites can be seen in Figure 7, revealing a clear increase in degradation with processing time. For example, when processing pure PHBV in air for 5 min, the M_n of PHBV decreases to 6890 of the value for raw PHBV (Table III), whereas for the sample containing clay (A-PHBV/5C_5min), it drops to a value of 24% with regard to the unprocessed pure polymer. The decrease in M_n is more than an order of magnitude for processing times close to 30 minutes.

Effect of clay type on the degradation of PHBV/clay nanocomposites

The effect of clay type on the degradation of PHBV can be seen in Figure 8. This figure shows the GPC

TABLE III
GPC Results of the Nanocomposite Samples as a Function of the Clay Content, Processing Time and Clay Type

Sample	M_n (Da)	M_n/M_n (%)	M_w (Da)	Pd	Fraction (%)	
					>300000 Da	<50000 Da
Raw PHBV	$93,900 \pm 1300$	100	$218,900 \pm 4400$	2.33 ± 0.01	25.21	11.88
N-PHBV	$63,700 \pm 1300$	68	$135,200 \pm 1500$	2.12 ± 0.02	8.78	21.03
N-PHBV1C	$55,900 \pm 1200$	60	$114,800 \pm 1300$	2.06 ± 0.02	5.35	25.31
N-PHBV2C	$53,000 \pm 1100$	56	$107,800 \pm 1400$	2.03 ± 0.02	4.31	27.25
N-PHBV5C	$46,950 \pm 920$	50	$93,050 \pm 630$	2.00 ± 0.03	2.65	32.90
A-PHBV	$64,150 \pm 350$	68	$136,900 \pm 1100$	2.13 ± 0.005	9.09	20.68
A-PHBV5C_2min	$35,200 \pm 140$	38	$67,600 \pm 420$	1.92 ± 0.005	0.60	45.92
A-PHBV5C_5min	$22,850 \pm 70$	24	$41,950 \pm 210$	1.84 ± 0.003	0.0045	69.13
A-PHBV5C_6min	$24,700 \pm 100$	26	$45,300 \pm 150$	1.83 ± 0.007	0.087	66.08
A-PHBV5C_30min	5325 ± 150	5.7	7370 ± 200	1.38 ± 0.00	0	100
A-PHBV5NaMMT	$46,000 \pm 2200$	49	$88,800 \pm 2900$	1.93 ± 0.03	2.03	33.94
A-PHBV5K	$69,600 \pm 1300$	74	$159,100 \pm 0$	2.29 ± 0.004	13.79	18.07

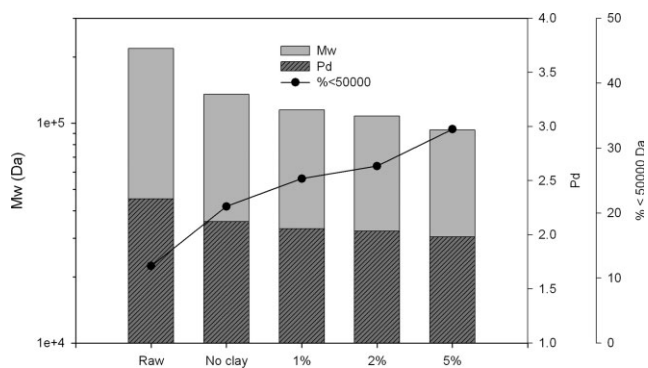


Figure 6 GPC results for neat PHBV as well as PHBV and PHBV/Cloisite20A nanocomposites processed in the mini-extruder under nitrogen flow with different clay contents (1, 2, and 5%).

curves of the raw PHBV, A-PHBV, A-PHBV5C, A-PHBV5NaMMT and A-PHBV5K and therefore shows analytical results for nanocomposites containing 5% nanoadditive processed by melt mixing under air for 5 min. The sample containing Cloisite20A exhibited the most PHBV degradation, with a value of M_n only 24% of the original PHBV (i.e., about 35% when compared with the pure PHBV processed under the same conditions). The sample containing 5% NanoterNaMMT showed a decrease in M_n of almost 50%. This drop in the molecular weight correlates with a decrease in the polydispersity to 1.93 ± 0.03 from 2.33 ± 0.01 . In contrast, the nanocomposite containing kaolinite does not degrade further with the addition of the clay, but retains almost the same molecular weight as the pure PHBV after processing.

The variation in PHBV degradation when processing with different clays may be explained by the fact that MMT clays are very hydrophilic and can potentially release tightly bound water when heated at the PHBV processing temperature, whereas kaolinite

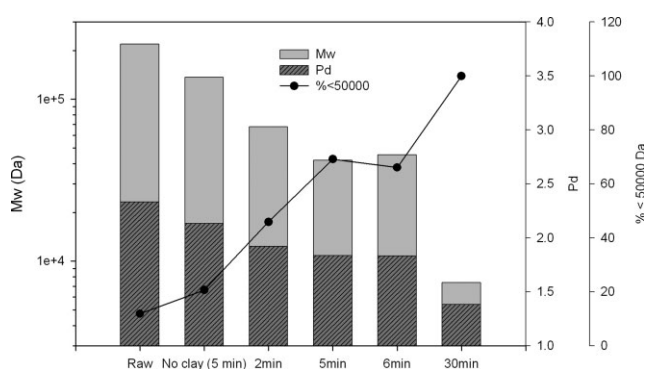


Figure 7 GPC results for neat PHBV as well as PHBV and PHBV/5C nanocomposites processed in the mini-extruder under air flow at different processing times.

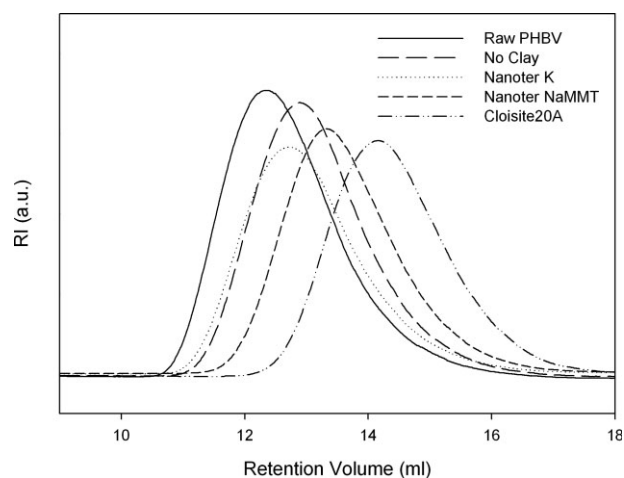


Figure 8 GPC chromatographs for neat PHBV as well as PHBV and PHBV/clay nanocomposites containing 5% loading of the different clays and processed in the mini-extruder under air using a mixing time of 5 min.

clays do not release water until temperatures above 450°C have been reached.¹⁵ This phenomenon can be seen in the TGA analytical results depicted in Figure 9, in which the weight loss curve of MMT shows a decrease near 200°C related to the release of tightly bound water (point B). The weight change in MMT between 100 and 200°C (point A) can be attributed to the loss of surface water, which for practical purposes in our processing experiments was removed during drying at 120°C and before processing with PHBV. The weight loss observed in both clays at temperatures above 400°C is due to dehydroxylation of the aluminium hydroxide layer (points C and D). Tightly bound water released by

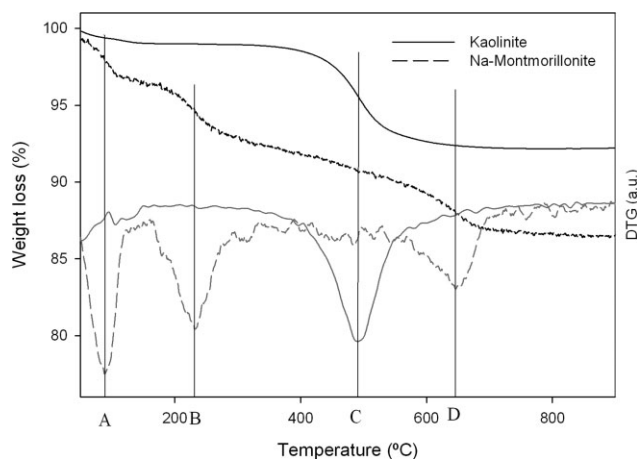


Figure 9 TGA curves of kaolinite and Na-montmorillonite under air. The curves depict: A) Desorption of surface water, B) Desorption of tightly bond water, C and D) Dehydroxylation of the aluminium hydroxide layer.

MMT clays could therefore contribute to hydrolysis of the ester groups present in PHBV during processing at elevated temperature. Although the nanocomposite samples obtained with Cloisite20A contain less phyllosilicate on a weight basis than those produced using pure NaMMT, the extent of PHBV degradation appears to be less in the latter case. This finding indicates that the surface modifier present in Cloisite20A increases the degradation rate of the polymer.¹⁶

CONCLUSIONS

Intercalated morphology was found to be predominant when PHBV/MMT clay nanocomposites were obtained either by solvent casting or melt mixing. Sub-micron aggregates were obtained when melt blending with unmodified kaolinite.

Nanocomposite processing degrades PHBV when heat is applied during the mixing. Significant degradation of the PHBV matrix takes place when melt mixing with MMT clays and this behavior seems to be enhanced by the presence of an organomodifier in the clay. The extent of PHBV degradation depends on the clay content and processing time. The injection of a nitrogen flow in the mixing chamber decreases the extent of PHBV degradation during nanocomposite compounding. Unlike MMT, kaolinite, does not appear to catalyze the degradation of PHBV.

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