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Full Length Research Paper

Effects of Preparation Methods of Organoclays with Polyvinyl Alcohol in their Compatibility with HDPE. Thermal Stability

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In this paper, the effect of polyvinyl alcohol addition on organoclay obtained by in situ polymerization and subsequent alcoholysis of polyvinyl acetate is studied. The incorporation of the monomer is carried out following two procedures. The first is the incorporation of the monomer by direct contact between the monomer and the organoclay. The second procedure involves a first step of impregnating the organoclay with propyl alcohol and the subsequent incorporation of the monomer. Both procedures consist of the polymerization in situ via a free radical mechanism. PVA modified clays showed substantial improvements in thermal properties with respect to the organoclay (MMT_{HDTMA}), corresponding to the greater stability to clay obtained by direct contact with the monomer, $PVA_{MMT/HDTMA}$ (VA). The clays prepared by both methods were incorporated into a HDPE matrix by melt blending, to study the effect of the method of preparing the organoclay with PVA in the polymer/clay compatibility and the effect on their thermal properties. The material characterization techniques were performed using X-ray diffraction (XRD), infrared spectroscopy (FTIR), thermal analysis (TG, DTG, DSC) and transmission electron microscopy (TEM). The results show a clear improvement in the HDPE thermal properties with the addition of organoclays containing PVA and allow a discussion of effect of preparation on compatibility and improved thermal properties.

Keywords: polyvinyl alcohol, montmorillonite, organoclay, HDPE, nanocomposites.

INTRODUCTION

The thermal resistance is one of the most dominant properties in polymers because it governs other properties such mechanical properties, durability, stability and life cycle of the same (Cho et al, 2003, Jin & Smith, 2003, Peng et al, 2006, Xia et al, 2005). The addition of clay in the polymer matrix improves the thermal stability of polymer acting as a superior insulation and barrier transport of volatile products generated during decomposition (Ray & Bousmina, 2005).

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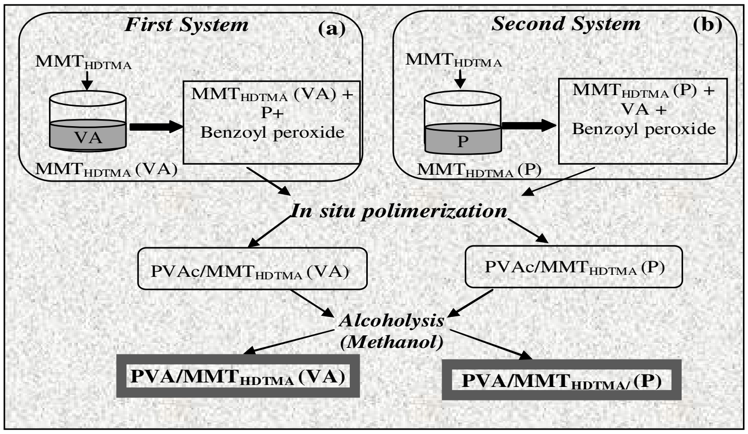


Scheme 1. Preparation of clay modified with PVA by two systems: First system (a) and Second system (b).

One of the most commonly used clay is montmorillonite (MMT), which is a 2:1 phyllosilicate clay type that has interesting properties (Strawhecker & Manias, 2000), such as high water absorption, ease of performing ion exchange, high surface area, high availability and low cost.

For these features, the clay most commonly used in the study is the MMT which obtains nanocomposite polymer materials (Ray & Okamoto, 2003). Because they present high hydrophilicity, the MMT is widely used for the preparation of nanocomposites with hydrophilic polymers such as polyvinyl alcohol (PVA), poly (N-isopropylacrylamide), polylactic acid, among others (Ray & Bousmina, 2005). The nanocomposite materials can be defined as compounds containing more than one solid phase in which the inorganic dispersed phase has at least one dimension in nanoscale (Roy et al, 1984).

In this paper sodium montmorillonite was organically modified with hexadecyltrimethylammonium chloride and subsequently treated with vinyl acetate (VA), aimed at in situ polymerization and subsequently alcoholysis to obtain organoclay modified with polyvinyl alcohol (PVA). Incorporating propanol is required for dissolution of polyvinylacetate and clay avoiding the formation of crosslinks in the polymer, which would hinder subsequent handling in alcoholysis to obtain the polyvinyl alcohol / organophilic clay to be used in the formation of nanocomposite with HDPE. For this reason there is the need to find the way to obtain organophilic clay modified by incorporating the propanol at the beginning or end of the procedure. For this the preparation was carried out through two paths, one for direct impregnation of the organoclay with the monomer, and the other by prior treatment of the organoclay with a solvent and subsequent impregnation with the monomer. The *first* variant: organic vinyl acetate monomer was intercalated into the interlayer regions of organoclay hosts and followed by one-step free radical polymerization. The *second* variant: propyl alcohol (P) was intercalated into clay and later was mixed with the monomer to continue the polymerization in situ.

The structure, morphology and thermal properties of the modified clays were characterized using X-ray diffraction (XRD), infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Finally these organoclays, modified with PVA, were incorporated in a polymeric olefin (HDPE). Was analyzed if the method of obtaining the modified clays influences the thermal properties of the polymer/clay material through of TGA and DSC. For the verification of the dispersion grade, morphological analyses were performed using transmission electron microscopy (TEM).

MATERIALS AND METHODS

Materials

The type of clay used in this study was sodium montmorillonite (MMT) provided by MINARMCO S.A. and exchanged with hexadecyltrimethylammonium chloride (Merck) and was obtained the clay called MMT$_{\text{HDTMA}}$.

The monomer used for the in situ polymerization was vinyl acetate (VA) (M = 86.09 Veteco. Boiling point: 73°C. I: 1.394 to 1.396). Was stabilized previously with hydroquinone (Reagen-Industry $C_6H_6O_2$ M = 110.11 g / mol) and was purified by distillation.

Preparation of organoclay

MMT was interchanged with hexadecyltrimethylammonium ions following the modified technique of Yeh et al., 2006. MMT was placed in water,

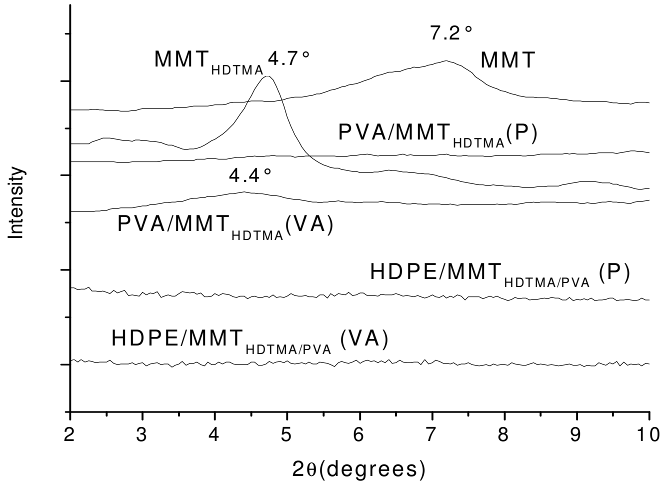


Figure 1. XRD of: MMT, MMTHDTMA, PVA/MMTHDTMA (VA) and PVA/MMTHDTMA (P) (5 wt %) and HDPE with modified organoclay.

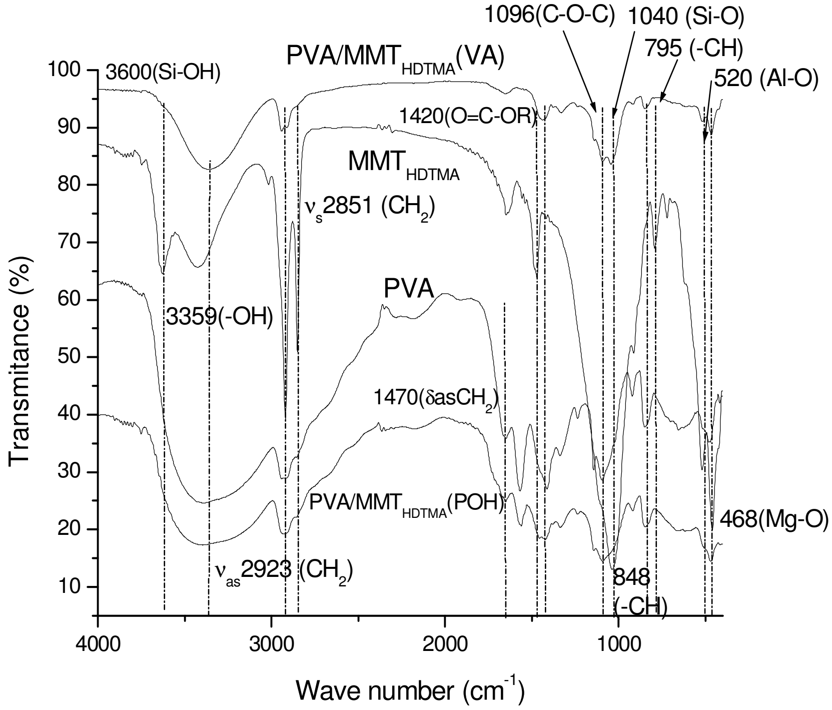


Figure 2. FTIR Spectra of: PVA; MMTHDTMA; PVA/MMTHDTMA (5 wt %) (VA); PVA/MMTHDTMA (5 wt %) (P).

immediately afterward was added HDTMA salt in excess of 50 wt% at a temperature of 80 °C. It was continuously stirred with a magnetic stirrer, during hours several. The organoclay (MMT_{HDTMA}) was washed until total elimination of halide (Cl^-) and finally the samples were dried under reduced pressure.

Preparation of organoclays modified with polyvinyl alcohol

In the *first* system, Scheme 1 (a), the organoclay (MMT_{HDTMA}) was treated with the monomer (VA) for 24 hours with stirring at room temperature to get the swelling

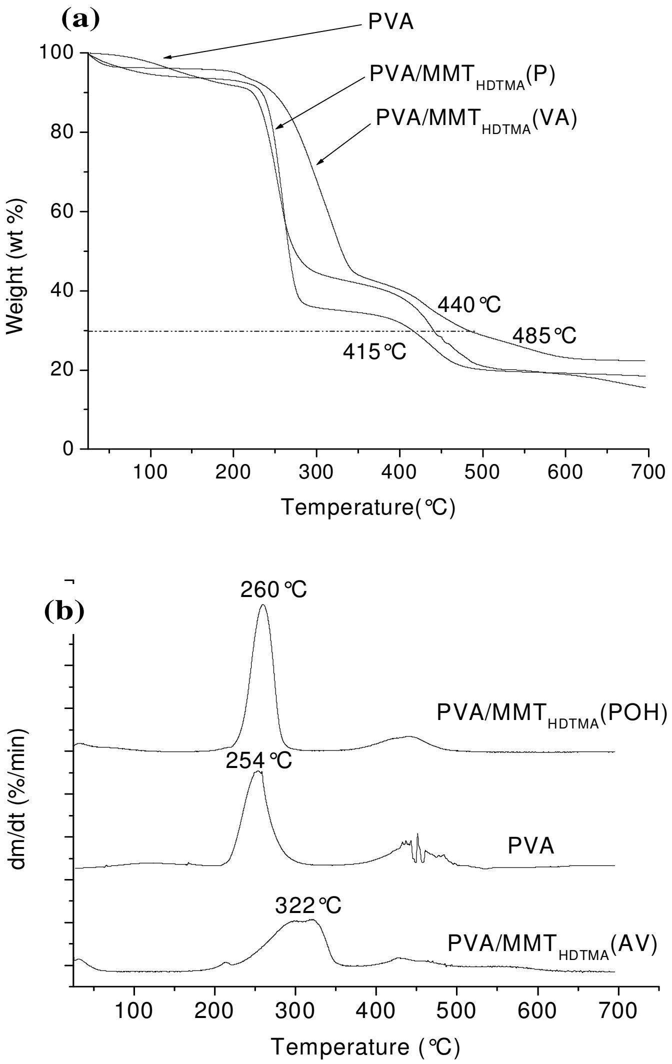


Figure 3. (a) TG and (b) DTG curves of: PVA, PVA/MMTHDTMA (P) and PVA/MMTHDTMA (VA).

of clay with the load of MMT$_{HDTMA}$ 5% compared to vinyl acetate. Reached the treatment time, the suspension was placed in the polymerization reactor and mixed with propyl alcohol ($CH_3CH_2CH_2OH$: anhydrous Q chemical groups. M = 60.10 g / mol. Boiling point: 97.4 ° C. ID 30 = 1.385. d = 0.8040. 99% purity) in a ratio of 1.5 with respect to the monomer and then adding the initiator (benzoyl peroxide: $C_{14}H_{10}O_4$.Veteco. M = 242.23 g/mol) at a concentration 1 wt% with respect to vinyl acetate. The reactor was closed and the process conditions were: 70°C with mechanical stirring for 5 hours in an inert atmosphere of N_2 to avoid possible inhibition of polymerization reaction due to the presence of oxygen.

Once the MMT$_{HDTMA}$/polyvinyl acetate (PVAc) alcoholysis was performed with methanol (CH_3OH: Merck KGaA. M = 32.04 g / mol. Purity 99.9%. G/cm^3 d = 0.791 to 0.793) and a 5 wt% solution of potassium hydroxide (KOH Veteco. Purity 85 wt%. M = 56.11 g/mol) / methanol (MeOH) at a temperature of 60°C, with mechanical mixing for 1 hour.

In the *second* system, Scheme 1 (b), the MMT$_{HDTMA}$ was treated with P during 24 hours with stirring at room temperature and the same concentration of MMT$_{HDTMA}$ (5 wt% on monomer).

Reached the treatment time, the suspension was placed in the polymerization reactor and mixed with the monomer (VA) in the same proportion as the first system; the subsequent steps were the same.

Pure polyvinyl alcohol was also prepared by in situ polymerization in order to compare the final properties of both materials.

Preparation of HDPE/ organoclays modified with PVA

HDPE pellets (95 wt.%) and modified organoclays (5

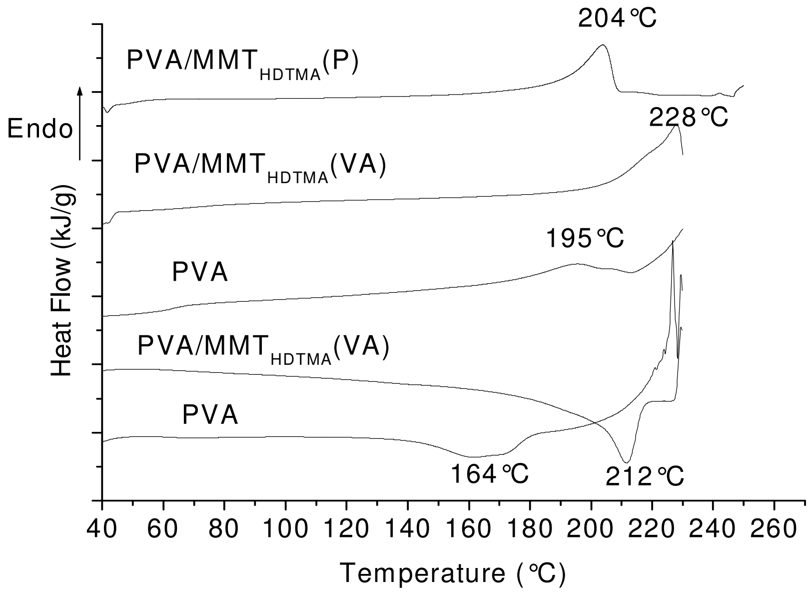


Figure 4. DSC of: PVA, PVA/MMTHDTMA (5 wt%) (VA) and PVA/MMTHDTMA (5 wt%) (P).

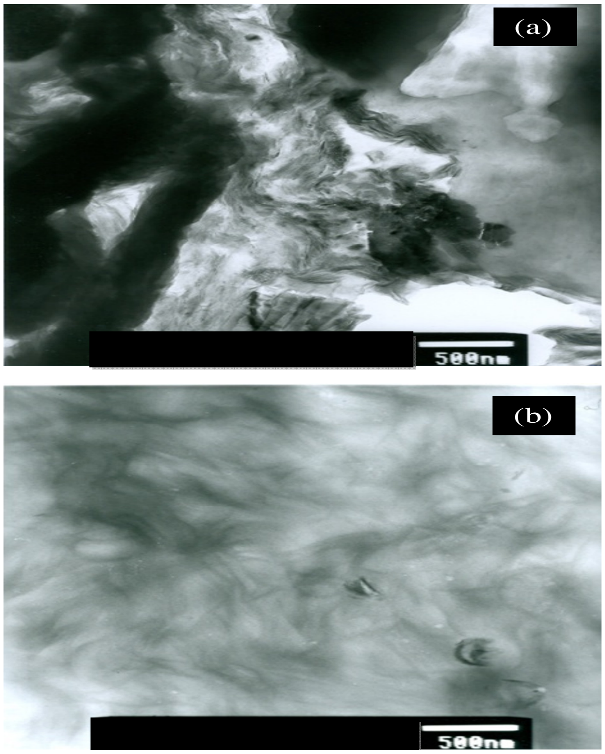


Figure 5. TEM micrographs of HDPE modified by (a) PVA/MMTHDTMA (P) and (b)

wt.%) were mixed using melt compounding processing in a Haake torque rheometer Rheocord 9000 equipped with a mixing chamber and roller rotors at 90 r.p.m. and 190 ºC.

Characterization

The materials obtained were characterized by X-ray diffraction (XRD) in a Rigaku diffractometer Miniflex,

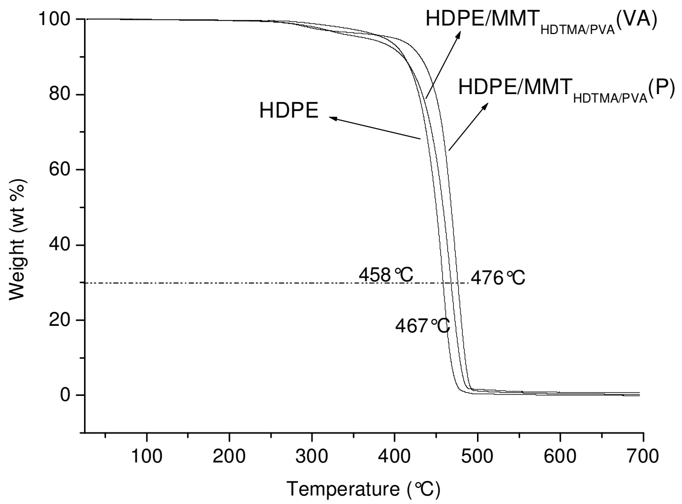


Figure 6. TG curves of: HDPE, HDPE/MMTHDTMA/PVA (P) and HDPE/MMTHDTMA/PVA (VA).

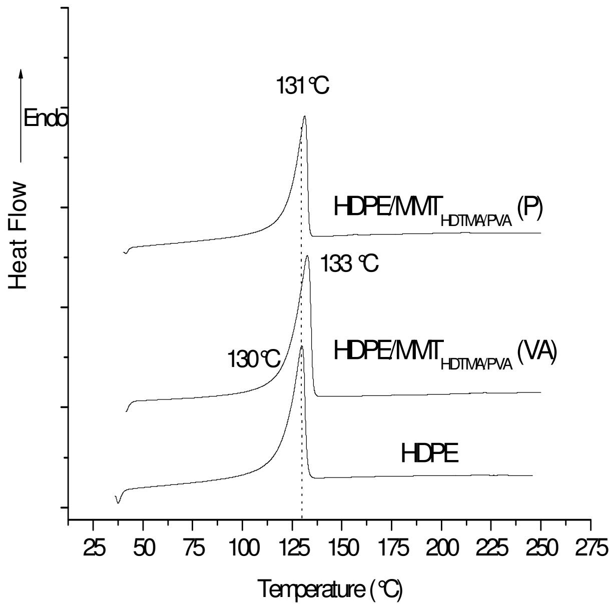


Figure 7. DSC of: HDPE, HDPE/MMTHDTMA/PVA (P) and HDPE/MMTHDTMA/PVA (AV).

ranging from 2□□□□2°-10°, also by infrared spectroscopy (FTIR) using a FTIR Perkin Elmer, 1720x, with a frequency resolution of 2 cm^{-1}.

Transmission electron microscopy (TEM) was carried out in a Jeol JEM 2000FX microscope operating at 200 kV. The ultra thin sections of specimens were cut by cryoultramicrotome, RMC Poweer Tome XL, using a diamond knife at a temperature of -40 °C. Thin sections of 60 nm were transferred into a copper grid.

To study the thermal properties thermogravimetry (TGA) were performed on a TGA Q500 v6.7 with a heating rate of 10°C/min and differential scanning calorimetry on a DSC 2920 in an N_2 inert atmosphere.

RESULTS AND DISCUSSION

XRD analyses

The X-ray diffractogram (XRD) (Figure 1) shows that in the sample of PVA/MMT$_{HDTMA}$ (VA) the angle 2□ = 4.4° was reduced very low to the angle characteristic of the

Table 1. Interplanar distance of organoclay, PVA/MMTHDTMA (VA) and PVA/MMTHDTMA.

Material	d (Å)
MMT_{HDTMA}	18.6
PVA/MMT_{HDTMA} (VA)	20.08
PVA/MMT_{HDTMA} (P)	-

clay (MMT_{HDTMA}: 2θ = 4.7°) in the plane (001) and is reflected in the small increase in the interplanar distance (Table 1). This could be a small polymer intercalation between the layers of clay or a rearrangement of the alkyl chains in the clay.

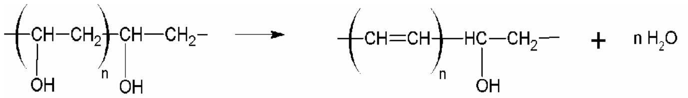
As for the diffractogram of the sample of PVA/MMT_{HDTMA} (P), it shows a disappearance of the peaks between 2 θ = 2 ° - 10 °, which would indicate a possible exfoliation, since the PVA chains could have destroyed completely the ordered structure of the clay.

FTIR analyses

The incorporation of the clay in the polyvinyl alcohol was verified by FTIR tests from the characteristic bands of these clays. The Figure 2 shows the characteristic vibration bands of PVA of 3000-3700 cm^{-1} (-OH stretching), 2923 cm^{-1} (-CH stretching), 1420 cm^{-1} (O=C-OR), 1096 cm^{-1} (COC stretch) and 848 cm^{-1} (angular deformation-CH), also those for the clay bands: 1040 cm^{-1} that is associated with the deformation outside of the plane MMT_{HDTMA} the Si-O group and for the Al-O bond (520 cm^{-1}) and Mg-O (468 cm^{-1}).

Thermogravimetric analyses

The curves obtained by thermogravimetry for the PVA matrix (Figure 3 a) have 3 stages of decomposition. The first step in the range of 50℃ to 200℃ is the result of ambient moisture loss. The second stage, observed in the range of 200℃ to 400℃ is associated with the process of dehydration of PVA. The following equation represents the mechanism of dehydration of PVA (Finch, 1973) produced in the second stage of thermal decomposition:



$$\left(\underset{OH}{CH}-CH_2\right)_n\underset{OH}{CH}-CH_2- \longrightarrow \left(CH=CH\right)_n-\underset{OH}{HC}-CH_2- \;+\; n\,H_2O$$

The third stage, above 400 ℃ is characterized by volatile products degradation, generated by thermal breakdown to occur in the chains of PVA.

The Figure 3a-b shows that the PVA/MMT_{HDTMA} (VA) material present enhanced thermal resistance and the other material such as PVA/MMT_{HDTMA} (P) has the properties in the same order as the pure PVA.

This improvement in thermal properties can be expected because the monomer enters between the clay layers and subsequently formed polyvinylalcohol and an intercalated structure is achieved between the clay layers. In the other case with the propyl alcohol was formed hydrogen bond between the clay. This caused the saturation of the clay; consequently the ingress of the monomer was very low.

DSC ANALYSES

To determine the degree of crystallinity in DSC equipment, the samples were heated at a rate of 10℃/min in a temperature range between 40℃ and 240℃.

The DSC curves of pure PVA (Figure 4) show an endothermic event between 180℃ and 200℃, indicating a melting temperature (T_m) of 195℃ and an exothermic event between 180℃ and 150℃ , indicating a crystallization temperature (T_c) of 165℃.

Concerning the DSC curves of PVA/MMT_{HDTMA} (VA), they show an increase in melting temperature (T_m) and crystallization temperature (T_c) with respect to pure PVA to be T_m = 228℃ and T_c = 212℃. This can be attributed to the clay acting as nucleating agent approaching the T_c to T_m.

With regard to the material of PVA/MMT_{HDTMA} (P) it has a T_m = 204 ° C, higher than the pure polymer but 14℃ lower than the PVA/MMT_{HDTMA} (VA). That is, the PVA/MMT_{HDTMA} (VA) has better thermal properties compared to pure PVA. The polymer-modified sodium MMT and MMT_{HDTMA} (P) have much lower melting temperature than the first.

Morphological analyses and thermal properties of HDPE modified with PVA-treated organoclays

In the technique of melt processing, only exfoliated/intercalated structures are obtained when organoclay is used with compatibilizers which may commonly be copolymers with the backbone of the same nature of polymer matrix (Chiu et al., 2010).

For the systems evaluated on this paper, it has been observed that using polyvinyl alcohol-treated organoclays leads to improved organoclay dispersion into polyolefin on a nanometric scale, without using a copolymer as compatibilizer (Carrera et al., 2013). This can be seen in Figure 5b where there was a greater dispersion of the modified clay in the HDPE polymeric matrix showing a structure exfoliated. Figure 5a shows a mixed intercalated/agglomerated. These results are consistent with the x-ray diffractograms of both materials in which is not observed at low angles no peak.

Thermogravimetric and DSC analysis (TGA) (Figure 6-7) also showed that structures strongly influenced the nature of the HDPE. Figure 6 reveals that both the HDPE/MMT$_{HDTMA/PVA}$ (P) and HDPE/MMT$_{HDTMA/PVA}$ (VA) have a 9℃ to 18℃ higher decomposition temperature.

CONCLUSIONS

The organoclay was modified with polyvinyl alcohol using two methods of preparation. The results show that the organoclay that was processed for the solvatation prior to the in situ polymerization with vinyl acetate presents significant improvements in the thermal resistance compared to organoclay that was treated with propyl alcohol. This is due that clay initially contacting with the vinyl acetate is intercalated between layers of the same and in the next step does not allow the entry of propyl alcohol, which favors the subsequent intercalation/exfoliation of that clay in the polymer matrix of polyvinyl alcohol, the opposite happens when the propyl alcohol is initially in contact with the clay layers because it is saturated with this solvent when contacted with the monomer to carry out the in situ polymerization, the strong interaction between propyl alcohol and clay trough hydrogen bonding formation, makes it difficult the intercalation and / or exfoliation subsequent of the clay in the polymer matrix.

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