

The role of surfactant type on morphology and thermal behavior of PET nanocomposites

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Abstract: - A bentonite (Argel 35) in its pristine and purified form and a sodium montmorillonite (Cloisite Na⁺) were organically modified with alkyl ammonium and phosphonium surfactants as well as a mixture of both salts to prepare *poly(ethylene terephthalate)* (PET) nanocomposites by melt blending. Intercalated nanocomposites were obtained when ammonium and ammonium-phosphonium salts mixture modified clays were used. Organoclays obtained with the salts mixture, especially the purified clays, seem to be best suited to obtain PET nanocomposites with higher thermal stability. The Argel 35 clay characteristics were similar to those of Cloisite-Na⁺ when modified with the same surfactants.

Keywords: - Nanocomposites; Organoclays; Ammonium; Phosphonium

I. INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic polyester with excellent physical properties. However, the disadvantages such as low rate of crystallization and low thermal distortion temperature and low modulus have limited its application as an engineering plastic [1]. One way to enhance its properties and minimize these drawbacks is by using PET nanocomposites instead of neat PET [2-6]. Several methods have been reported to prepare polymer/clay nanocomposites. Among them, melt blending is the most used due to its simplicity and economically favorable processing [7].

Preparation of PET nanocomposites by melt processing requires high melt processing temperatures. Therefore, the thermal stability of the organic component chosen to modify the clay becomes an important factor. High processing temperatures can lead to changes in surfactant structure (thermal degradation), which in turn affect the polymer melt intercalation thermodynamics during processing leading to changes in the nanocomposite physical and mechanical properties. Furthermore, decomposition of the surfactant may produce undesired side reactions with the polymer matrix [8].

Alkyl ammonium cationic surfactants are most commonly used for the organic modification of montmorillonite to promote the compatibilization of the clay with a given polymer [9]. The thermal stability of these salts, however, is not very high and therefore, organoclays prepared with quaternary alkyl ammonium salts are not particularly suitable for the manufacture of high processing temperature polymer nanocomposites. Processing temperatures above 250 °C result in alkyl ammonium surfactant decomposition which affects the polymer/clay interface [10]. Shah and Paul [11] have shown that organoclay degradation during compounding can limit the extent of intercalation or exfoliation in polymer/clay nanocomposites. In order to overcome this limitation, thermally stable surfactants such as alkyl pyridinium [12], alkyl quinolinium [13], alkyl phosphonium [14-17], alkyl stibonium [18] or alkyl imidazolium [7,19] salts have been suggested as alternative routes to alkyl ammonium modifiers. Organoclays based on these surfactants generally present a higher thermal stability than conventional ammonium modified clays and may be potentially useful for preparing nanocomposites with polymeric matrices requiring high processing temperatures such as poly(ethylene terephthalate).

The literature [14-17,20,21] reports that organoclays prepared with alkyl phosphonium salts may be a viable alternative to produce melt processed PET/organoclay nanocomposites. However, up to now, only a few studies have been reported on PET/phosphonium organoclay nanocomposites and indicated that a conventional microcomposite structure was obtained. Thus, challenges still remain in order to produce PET/organoclay nanocomposites. In this study, organic modifiers based on alkyl ammonium (cetyl trimethyl ammonium bromide), alkyl phosphonium (hexadecyl tributyl phosphonium bromide) salts as well as a mixture of both salts were used to produce organoclays for PET nanocomposites preparation. The goal was to evaluate the influence of these organically modified clays on the thermal and morphological properties of the PET nanocomposites.

II. EXPERIMENTAL

2.1. Materials

Poly(ethylene terephthalate) (PET), BG1180-W, supplied by Braskem (Bahia/Brazil), with an intrinsic viscosity 0.80 ± 0.02 dL/g; acetaldehyde content 1.0 ppm; melting point $245 \pm 5^\circ\text{C}$ and density $1.39 - 1.41$ g/cm³ was used as polymer matrix.

Sodium bentonite clay, *Argel 35* (ARG), supplied by Bentonit União Nordeste (BUN-Campina Grande/Brazil), in powdered form, with particle size ≤ 45 μm , was used as filler in the PET nanocomposites preparation. The cation exchange capacity (CEC) of this bentonite ARG was determined by method described by Phelps and Harris [22] and found to be 92 meq/100 g and the montmorillonite content estimated by XRD measurements is 63%. For comparative purposes a sodium montmorillonite, Cloisite Na⁺ (CL), provided by Southern Clay Products (Texas/USA) was also used as filler in the PET nanocomposites preparation. According to the supplier, the Cloisite Na⁺ has a CEC of 92.6 meq/100 g.

Alkyl Ammonium and alkyl phosphonium surfactants (Table 1) were used as received to modify the bentonites clays. These surfactants were supplied by Vetec and Sigma-Aldrich, respectively.

Table 1. Cationic surfactants.

Surfactant	Average molecular formula	Supplier
Cetyl trimethyl ammonium bromide (A)	C ₁₆ H ₃₃ (CH ₃) ₃ NBr	Vetec
Hexadecyl tributyl phosphonium bromide (P)	C ₁₆ H ₃₃ (C ₄ H ₉) ₃ PBr	Sigma-Aldrich

2.2. Clay Purification

Contaminants present in bentonites can affect polymer/clay interactions and the intercalation or exfoliation extent in the final nanocomposite. Therefore, the use of a purification procedure prior to bentonite organophilization and incorporation into polymers may be important. Previous data [23] indicated that the ARG bentonite used in this study contains a minor fraction of non-layered minerals such as quartz and carbonates and small amounts of organic matter as contaminants. Thus it was purified according to the procedure reported by Leite *et al.* [24]. After purification the sample was washed with distilled water and centrifuged at 2400 rpm for 15min. The solids obtained were dried at 60°C for 24h, ground and sieved (325 mesh sieve) to particles with less than 45 μm before being characterized and organically modified. The purified clay was coded as ARGP.

2.3. Clay Organic Modification

Both pristine (ARG) and purified (ARGP) bentonites as well as the sodium montmorillonite (CL) were organically modified by cation exchange reaction with the alkyl ammonium (A), alkyl phosphonium (P), and an equivalent mixture of both alkyl ammonium and alkyl phosphonium (A-P) organic salts. The individual organic salts or their mixture were slowly added to a vigorously stirred aqueous clay dispersion kept at $70 \pm 5^\circ\text{C}$ [23]. In all cases the amount of surfactant added was equivalent to the clay CEC. After 30min under stirring the clays were allowed to stand at room temperature for 24h, filtered and washed free of bromide anions, dried at 60°C for 48h and ground in an agate mortar to pass through 325 mesh sieve. ARG, ARGP and CL organically modified clays with alkyl ammonium (A), alkyl phosphonium (P) and the mixture of the both salts (A-P) were coded ARG_Ox, ARGPO_x and CLO_x, where x is A, P and A-P.

2.4. PET Nanocomposites Preparation

PET/organoclay nanocomposites with a nominal content of 1 wt% organoclay were melt compounded in a Haake torque rheometer operating at 260°C and 60 rpm for 10min and denoted as PET/ARG_Ox, PET/ARGPO_x, PET/CLO_x. Prior to processing, the PET polymer and the organoclays were dried for 6h at 160°C and 60°C, respectively. Immediately after processing hybrids for XRD characterization were compression molded (2min under compression) as disc shaped specimens with 25 mm diameter and 1 mm of thickness in a hot press operating at 260°C.

2.5. Characterization

Infrared spectroscopy (FTIR). FTIR characterization was carried out using a Nicolet Avatar TM 360 Fourier transform infrared spectrometer operating in the range of 400–4000 cm⁻¹. KBr/clay pressed disks were used for clay and organoclay characterization.

X-ray diffraction (XRD). XRD analysis was performed at room temperature on a Shimadzu XRD-6000 X-ray generator operating at 40 kV and 30 mA, and the X-ray beam was monochromatized to $\lambda(\text{CuK}\alpha) = 0.154056$ nm wavelength. The samples were scanned for an interval of 2θ between 1.5 and 10.0° at a rate of 2°/min. XRD plots were used to determine the mean interlayer spacing of the basal plane (d_{001}) of natural and organophilic clays and in the PET hybrids.

Thermogravimetry (TG). TG characterization of bentonite and organobentonites were performed on a Shimadzu TG apparatus, S1HA model with samples of about 15 mg of material. The samples were heated at 10°C/min under 50 ml/min air flow. Mass loss curves were recorded from 30 to 900°C.

Differential scanning calorimeter (DSC). DSC was carried out on 5 mg samples placed in aluminum pans on a Perkin Elmer DSC7 operating under nitrogen atmosphere. Samples were heated from 30 to 280°C at a heating rate of 10°C/min, kept for 2 min at 280°C and cooled to 30°C at the same rate.

III. RESULTS AND DISCUSSION

3.1. Infrared spectroscopy

Figure 1 shows the typical spectrum of unmodified clays (ARG, ARGP and CL). The major bands observed could be assigned to stretching vibrations of Al–OH (absorption near 3630 cm^{-1}) corresponding to inner hydroxyl groups, lying between the tetrahedral and octahedral sheets and is typical for smectite with high amount of Al in the octahedral layer. The broad band near 3420 cm^{-1} is attributed to hydroxyl stretching vibrations (free and interlayer water molecules) and the band near 1639 cm^{-1} is related to the (H–O–H) bending vibrations of water molecules adsorbed on montmorillonite [25]. The two peaks at 915 cm^{-1} and 840 cm^{-1} were attributed to the bending vibrations of Al–Al–OH and Al–Mg–OH hydroxyl groups on the edges of the clay platelets. The peak at 525 cm^{-1} is associated with Si–O–Al bending vibrations [25,26]. The band at 3420 cm^{-1} and the peaks at 3630 cm^{-1} , 915 cm^{-1} , 840 cm^{-1} and 525 cm^{-1} did not change after purification which is taken as an indication that the Al^{3+} and Mg^{2+} ions from the octahedral sheet were not removed and the surface acidity of both bentonites (ARG and ARGP) is nearly equivalent suggesting that the purification procedure adopted did not modify the bentonite structure.

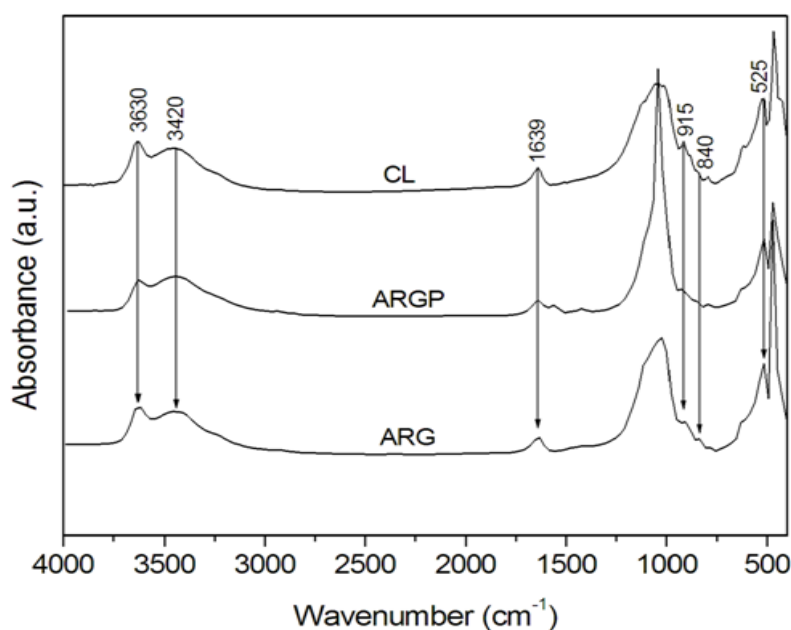


Figure 1. FTIR spectra of pristine (ARG), purified (ARGP) and commercial (CL) clays.

FTIR data of alkyl ammonium (A), alkyl phosphonium (P), mixture of both surfactants (A-P) as well as of organically modified clays with these same surfactants are shown in Figure 2 (a-c). The modified clays presented absorption bands at ca. 2921-2929 cm^{-1} , 2850-2854 cm^{-1} and 1401-1480 cm^{-1} (Table 2) which correspond, respectively, to the asymmetric stretching (ν_{as}), symmetric stretching (ν_s) and asymmetric bending (δ_{as}) vibrations modes C–H in methylene groups of surfactants alkyl chains indicating the incorporation of alkyl ammonium and alkyl phosphonium ions within the clays galleries [25,27].

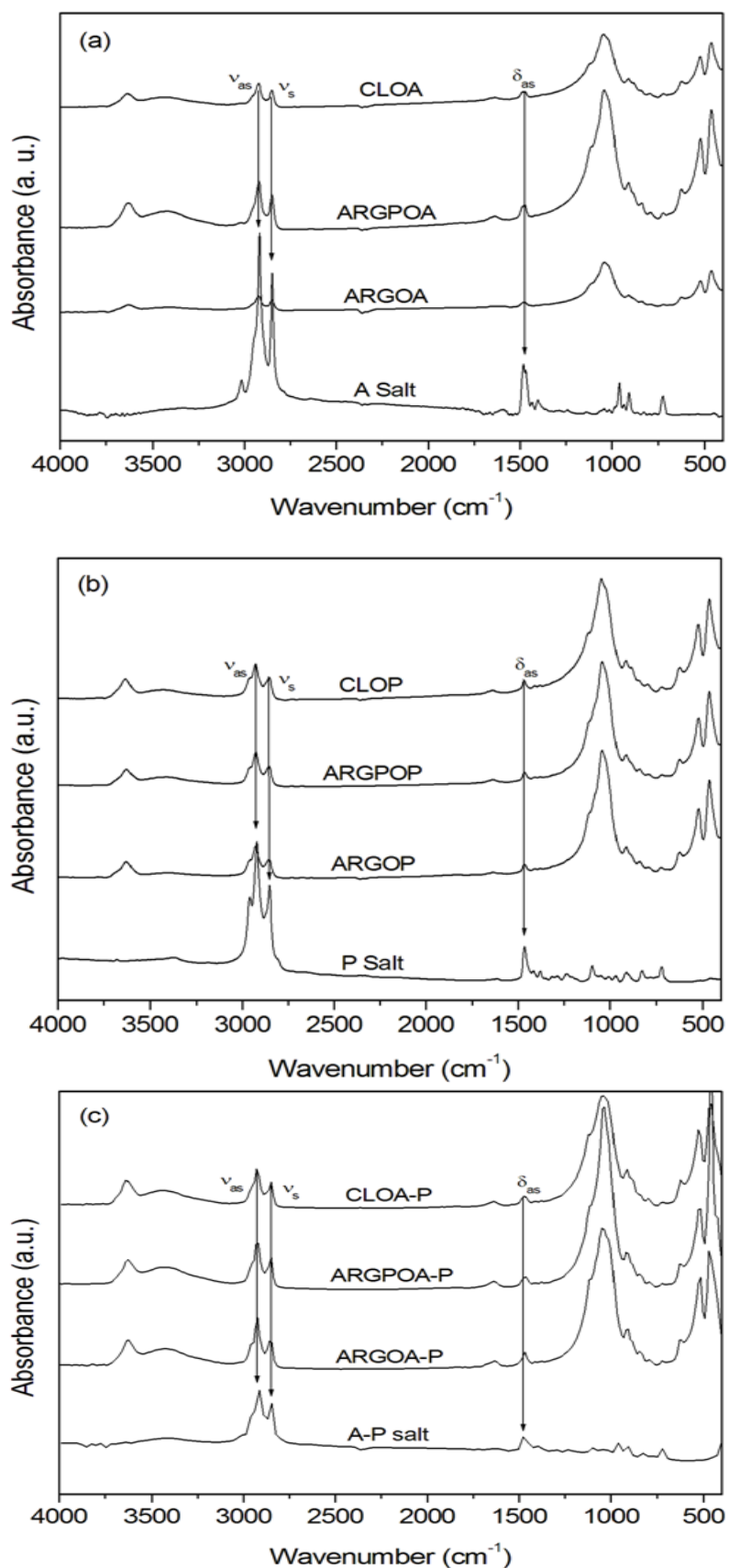


Figure 2. FTIR spectra of: (a) alkyl ammonium salt (A salt), ARGOA, ARGPOA and CLOA; (b) alkyl phosphonium salt (P salt), ARGOP, ARGPOP and CLOP and (c) alkyl ammonium-alkyl phosphonium salt mixture (A-P salt), ARGOA-P, ARGPOA-P and CLOA-P.

Table 2. FTIR data for neat surfactants and organoclays.

Sample	Wavenumber (cm ⁻¹)		
	$\nu_{as}(\text{C-H})^a$	$\nu_s(\text{C-H})^b$	$\delta_{as}(\text{C-H})^c$
A Salt	2917	2849	1478
ARGOA	2921	2850	1480
ARGPOA	2921	2850	1472
CLOA	2921	2850	1480
P Salt	2920	2852	1461
ARGOP	2927	2854	1401
ARGPOP	2926	2854	1461
CLOP	2928	2853	1465
A-P Salt	2915	2846	1481
ARGOA-P	2924	2852	1472
ARGPOA-P	2926	2850	1468
CLOA-P	2929	2850	1477

^aasymmetric stretching vibrations modes C-H in methylene groups of surfactants alkyl chains;

^bsymmetric stretching vibrations modes C-H in methylene groups of surfactants alkyl chains;

^casymmetric bending vibrations modes C-H in methylene groups of surfactants alkyl chains.

The position of ν_{as} and ν_s shift depends on the kind of surfactant used in organoclay preparation. For the modified clays with 100% of alkyl ammonium (ARGOA, ARGPOA and CLOA) both ν_{as} and ν_s absorptions bands are similar to those of the neat surfactants (Figure 3a and Table 2). According to Majdan et al. [28] and Xi et al. [29] this is an indication that the alkyl ammonium cations confined within the clay galleries preserve an essentially all-*trans* conformation that represents a solid-like environment of surfactant within the montmorillonite layers. In this case the *gauche* conformers are considered to be a minority.

For the clays modified with 100% of alkyl phosphonium (ARGOP, ARGPOP and CLOP), both ν_{as} and ν_s absorptions bands associated with the aliphatic chain of the surfactant shifted to higher frequencies compared with those of the neat surfactant, (Figure 3b and Table 2), which was associated with the introduction of *gauche* conformers in the hydrocarbon tail. According to Li and Ishida [10], if the conformational disorder of the chains increases an upward frequency shift is observed on the FTIR spectra. As reported by Majdan et al. [28], the ν_s vibration is less sensitive to surfactant conformation than the ν_{as} one. A similar behavior, i.e., an upward frequency shift was observed for the modified clays with the mixture of alkyl ammonium and alkyl phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) (Figure 3c and Table 2). In this case, both ν_{as} and ν_s absorptions bands shifted to higher frequencies indicating a higher content of *gauche* conformers in the organoclays prepared with the mixture of alkyl ammonium and alkyl phosphonium salts if compared to the ammonium and phosphonium modified organoclays [29-31].

Tasi and Mizukami [32] and Okamura et al. [33] stated, based on theoretical calculations and experimental data, that the most important factors ruling the conformational behavior of free *n*-alkanes are the van der Waals interactions. They also described that weak interactions would result in an increased number of *gauche* conformer and that repulsive interactions between silicate surface and hydrocarbon chain are due to the different nature of the hydrocarbon chains of alkyl molecules (hydrophobic) and surface silicate (hydrophilic). These repulsive forces between the silicate wall and the confined amine molecules are limited by the clay basal distance.

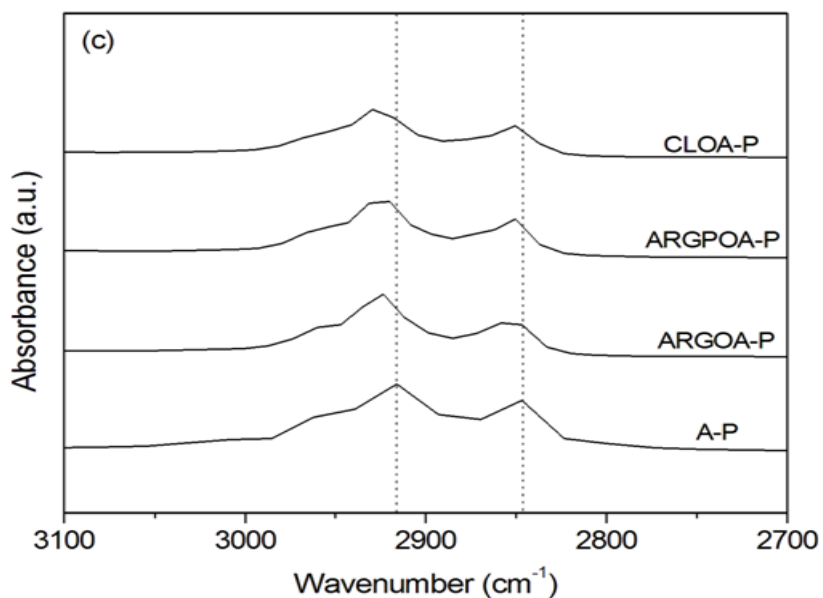
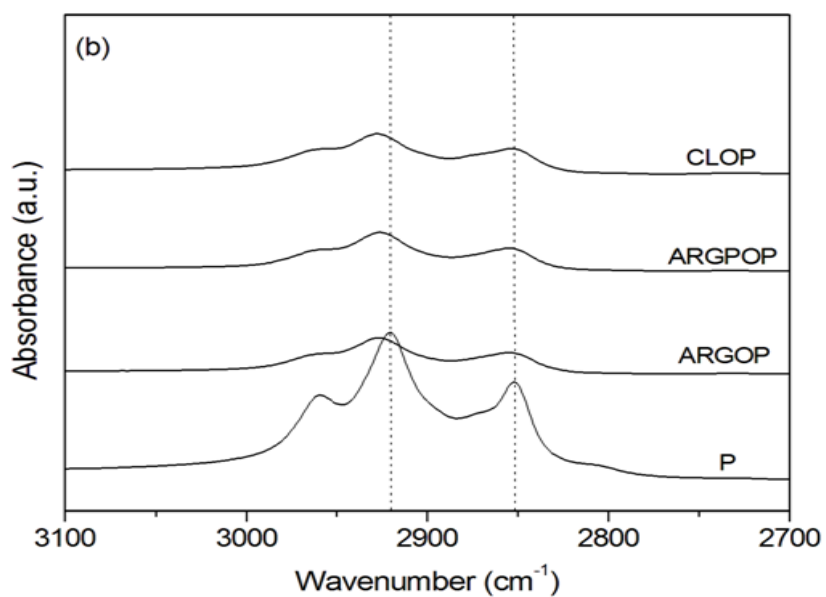
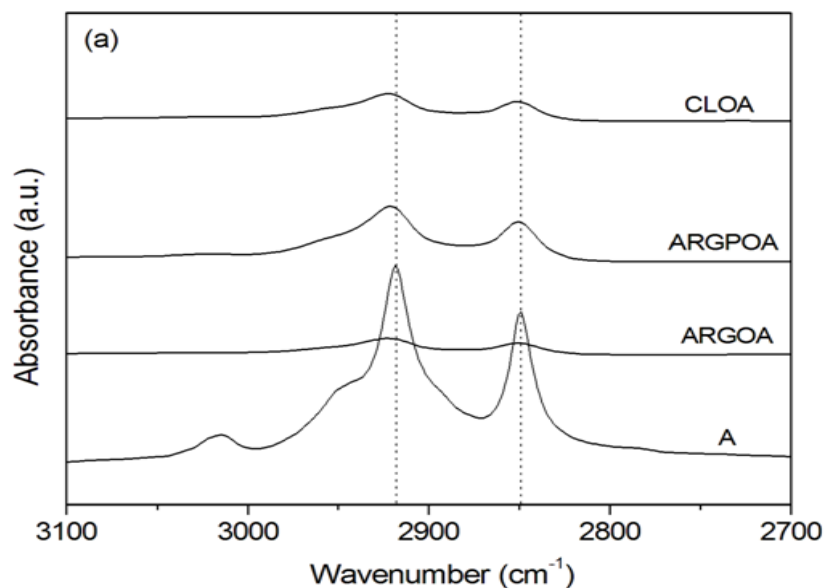


Figure 3. FTIR spectra in the 3100-2700 cm^{-1} region for the organic salts and modified clays: (a) alkyl ammonium salt (A), ARGOA, ARGPOA and CLOA; (b) alkyl phosphonium (P), ARGOP, ARGPOP and CLOP and (c) alkyl ammonium-alkyl phosphonium salt mixture (A-P), ARGOA-P, ARGPOA-P and CLOA-P.

3.2. X-ray diffraction

XRD patterns of unmodified clays (ARG, ARGP and CL) (Figure 4) confirm the major presence of montmorillonite (M) with reflections relative to the planes (001), (002) and (005) and also the presence of minerals such as kaolinite (K) and quartz (Q), designated as impurities [34]. The clay purification led to a considerable decrease on the amount of kaolinite present in the ARG without, however, promoting the structure collapse. These data corroborate the FTIR results.

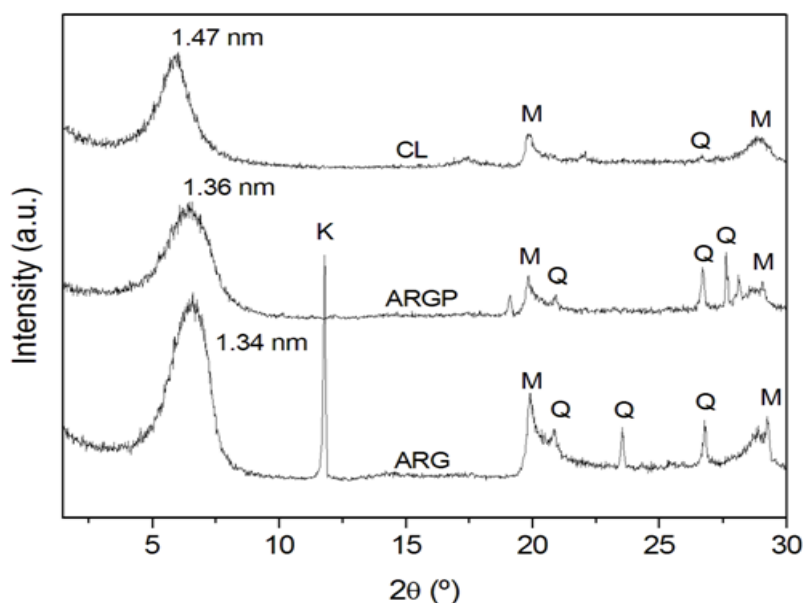
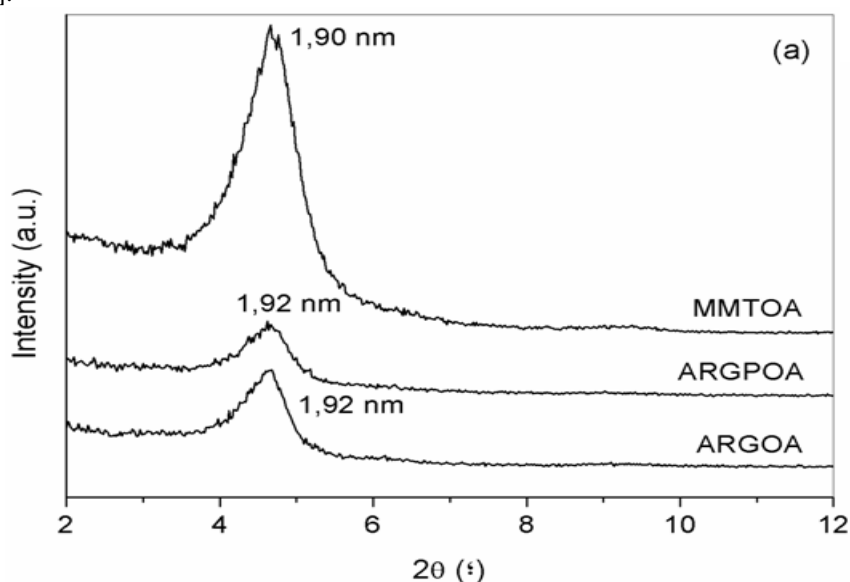


Figure 4. X-ray diffraction patterns of pristine (ARG), purified (ARGP) and commercial (CL) clays.

Figure 5 shows the XRD patterns of organically modified clays. The d_{001} values of the clays modified with the alkyl phosphonium salt (ARGOP, ARGPOP and CLOP) (Figure 5b) and with the mixture of alkyl ammonium and alkyl phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) (Figure 5c) were higher than those of the modified clays with alkyl ammonium salt (ARGOA, ARGPOA and CLOA) (Figure 5a). This can be related either to the lower packing density of the alkyl phosphonium or to their molecular conformation into the clay layers [35].



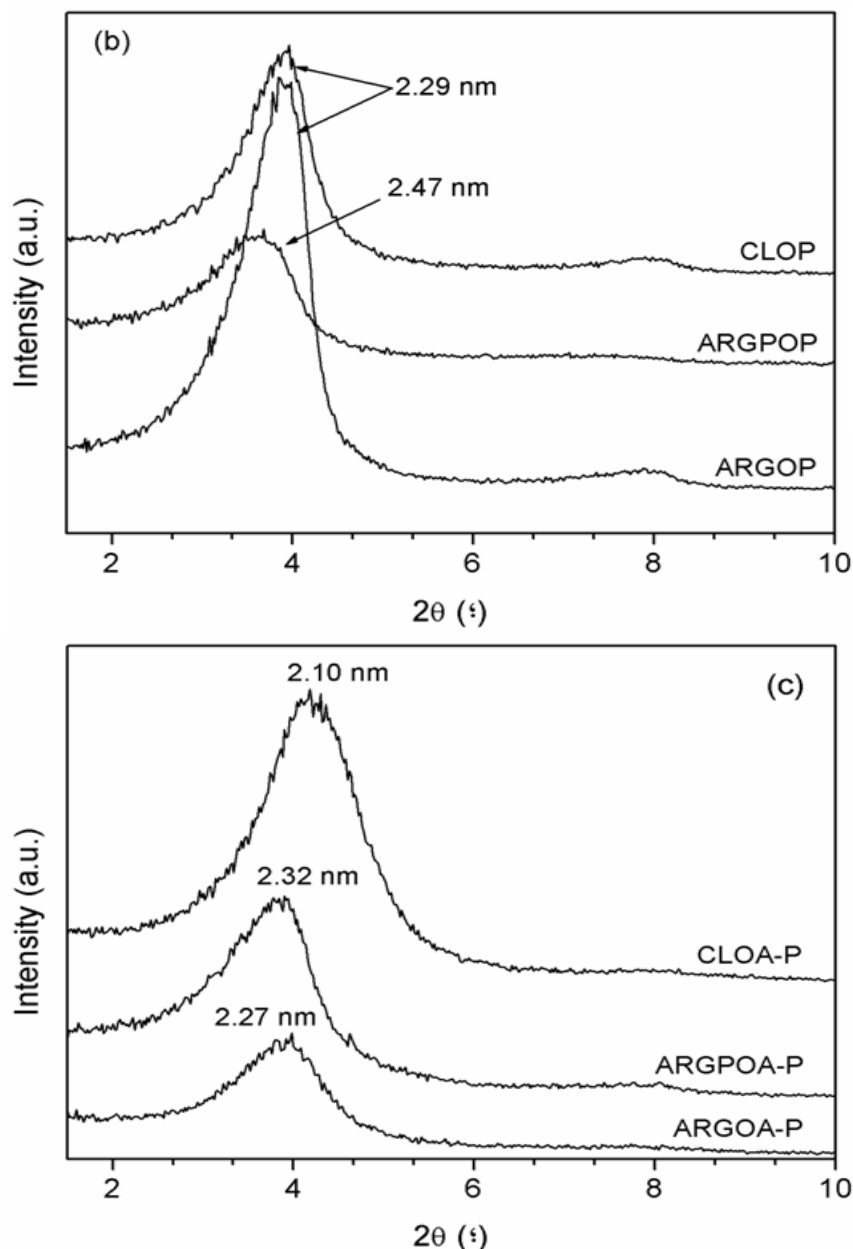


Figure 5. X-ray diffraction patterns of: (a) modified clays with alkyl ammonium (A); (b) alkyl phosphonium (P) and (c) alkyl ammonium-alkyl phosphonium salt mixture (A-P).

3.3. Thermogravimetric analysis

Figure 6 shows typical TG plots of mass loss as a function of temperature in the range 30-1000°C for unmodified clays. Decomposition steps for these samples are shown in Table 3.

Unmodified clays display two thermal degradation transitions. The first one (T_{H_2O}) occurred at 71-88°C temperature range and is attributed to the volatilization of both free water (i.e., the water sorbed on the external surfaces of crystals) and water inside the interlayer space which form hydration spheres around the exchangeable cations. The second transition (T_{OH}) took place at higher temperatures (708-720°C) and is attributed to the loss of structural water resulting from clay dehydroxylation [9]. The purified clay (ARGP) displays an additional mass loss step at 420°C (Figure 6). This step can be due to the residues from the purification process as evinced by FTIR (Figure 1) where absorption bands at 1423 and 1558 cm^{-1} attributed to asymmetric vibrations modes CH_3 and carbonates residues, respectively, were observed [36,37].

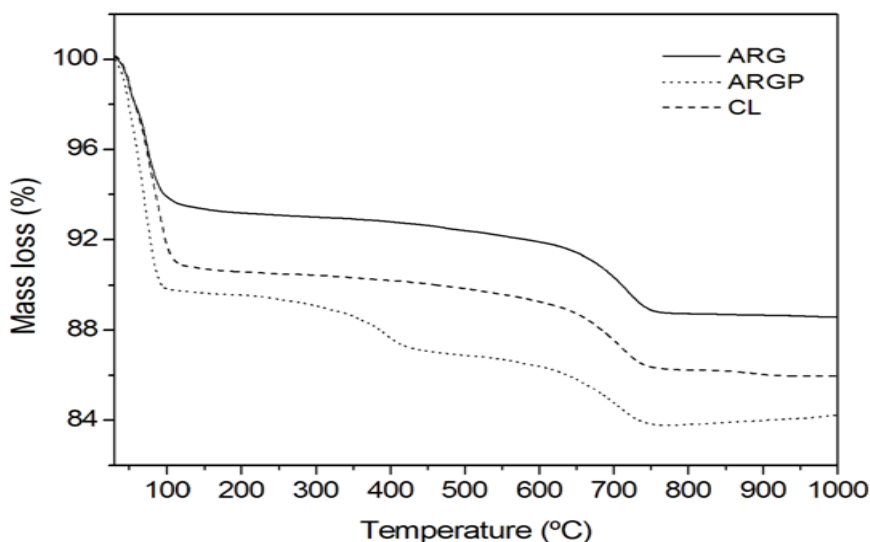
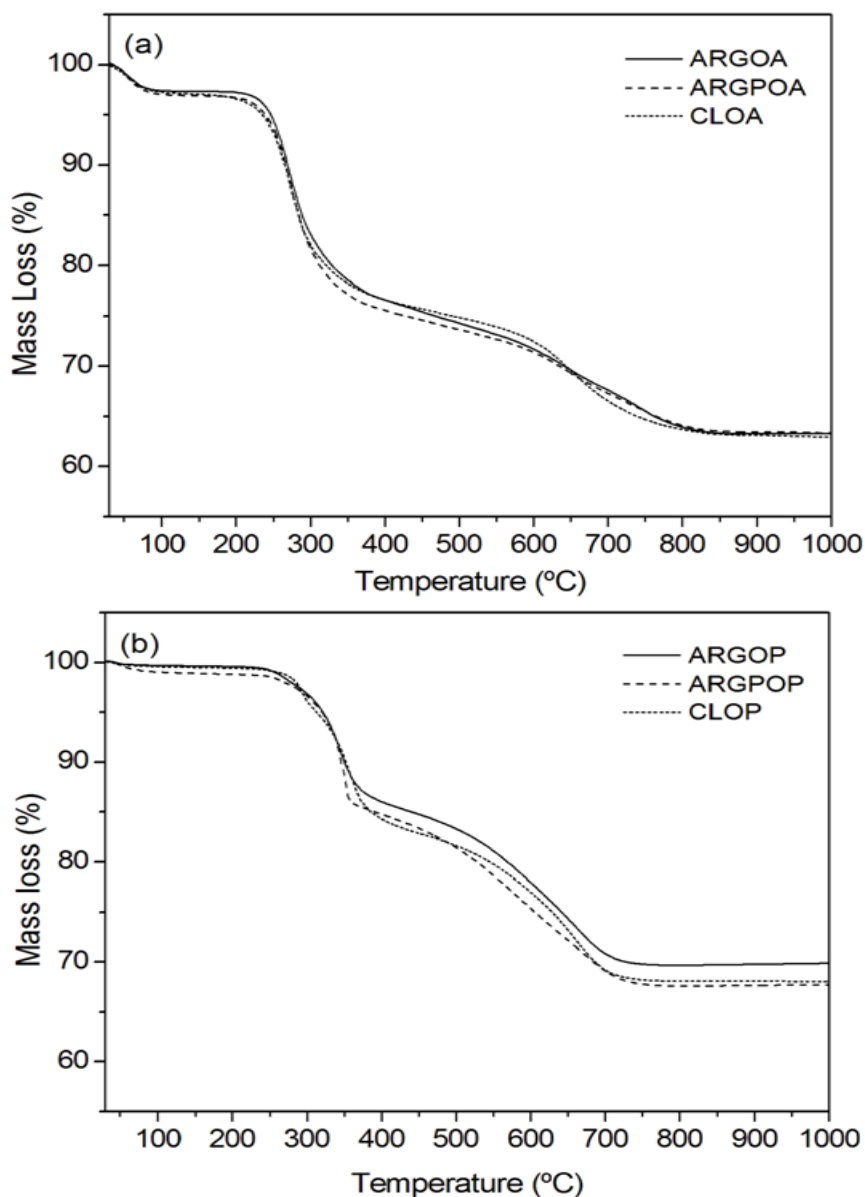


Figure 6. TG curves of pristine (ARG), purified (ARGP) and commercial (CL) clays.

Table 3. Decomposition steps for the neat surfactants, unmodified and organically modified clays.

Sample	Dehydration		Surfactant decomposition			I. Dehydroxylation
	T _{H2O} (°C)	Water (wt%)	T ₀ (°C)	T _{max} (°C)	Loss organic salt (wt%)	T _{OH} (°C)
ARG	74	6.67	----	----	----	720
ARGP	71	10.25	----	----	----	708
CL	88	9.31	----	----	----	708
A Salt	----	----	200	283	93.65	----
ARGOA	54	2.66	200	272	20.86	689
ARGPOA	50	3.24	192	275	21.57	652
CLOA	53	2.66	176	273	20.68	651
P Salt	----	----	250	393	98.47	----
ARGOP	46	0.69	224	343	13.98	665
ARGPOP	47	1.18	243	346	14.37	588
CLOP	39	0.72	239	325	13.90	659
A-P Salt	----	----	200; 344	263; 389	49.12	----
ARGOA-P	46	2.04	204	326	15.13	658
ARGPOA-P	49	1.31	212	275	18.50	646
CLOA-P	49	1.01	203	301	15.64	661

Organoclays TG curves are displayed in Figure 7. The amount of water in the galleries is reduced in the organoclays compared with unmodified reflecting the weaker hydration of the organic cations. The type of organic cation used in clay organophilization affected both the volatilization temperature values (TH₂O) and the amount of water adsorbed (Table 3). Alkyl phosphonium modified clays (ARGOP, ARGPOP and CLOP) and those modified by the mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) showed smaller TH₂O values and water content than alkyl ammonium modified clays (ARGOA, ARGPOA and CLOA) which is consistent with the more hydrophobic nature of alkyl phosphonium ions [16].



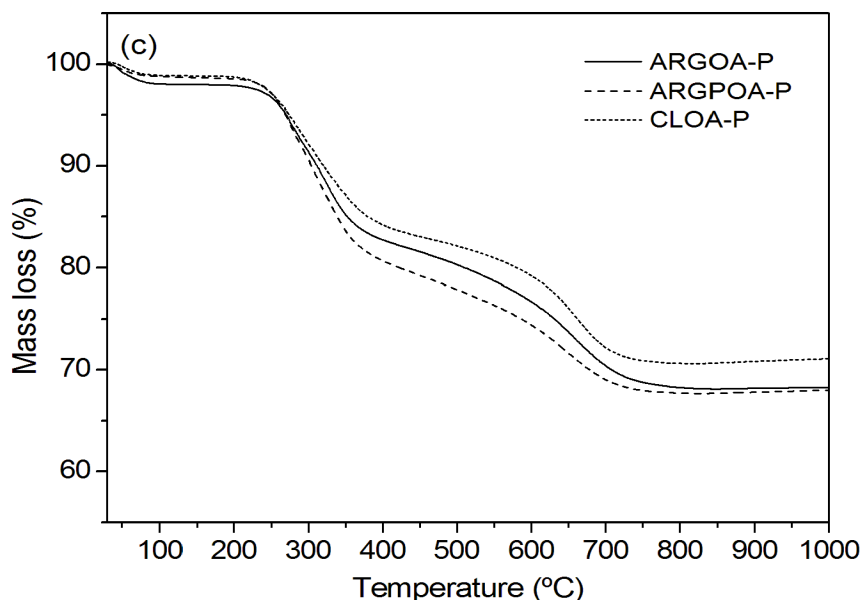


Figure 7. TG curves of clays modified with: (a) alkyl ammonium (A); (b) alkyl phosphonium (P) and (c) alkyl ammonium-alkyl phosphonium salt mixture (A-P).

The decomposition of alkyl ammonium and alkyl phosphonium salts occurred in one step. This indicates that the surfactant is mainly adsorbed inside the interlayer spaces through cation exchange process only [38]. In the case of both salts mixture the decomposition occurred in two steps and this was attributed to the presence of ammonium and phosphonium surfactants in the clays galleries (Figure 8).

The clays modified with alkyl phosphonium salt (ARGOP, ARGPOP and CLOP) and with the mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) display greater onset temperature (T_0) and higher maximum surfactant decomposition temperature (T_{max}) than their alkyl ammonium counterparts (ARGOA, ARGPOA and CLOA) (Table 3). The thermal decomposition of the alkyl ammonium modified clays (ARGOA, ARGPOA and CLOA) occurs around 273°C and the organic fraction in the organoclays determined by the total mass loss from 200 to 500°C was 20-21%, equivalent to c.a. 100% of the clay CEC. On the other hand the decompositions of the organoclays prepared with alkyl phosphonium (ARGOP, ARGPOP and CLOP) and mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) occur around 340 and 300°C and the total organic contents were estimated to be 13-14% and 15-18%, (equivalent to 42 and 30% clay CEC), respectively.

As expected, by comparison with the unmodified clays, organoclays display a lower dehydroxylation temperature (T_{OH}), which is attributed to the lower relative amount of inorganic material in the organoclays. However, the type of surfactant employed practically did not affect this transition [38,39].

In summary the data shows that all organoclays obtained in this study can be used in the PET nanocomposites preparation, using the melt intercalation method since their decomposition temperatures are higher than those of PET processing (~260°C). However, clays modified with the alkyl phosphonium salt (ARGOP, ARGPOP and CLOP) or with the mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) are the most appropriate for the PET processing due to their higher thermal-oxidative stabilities.

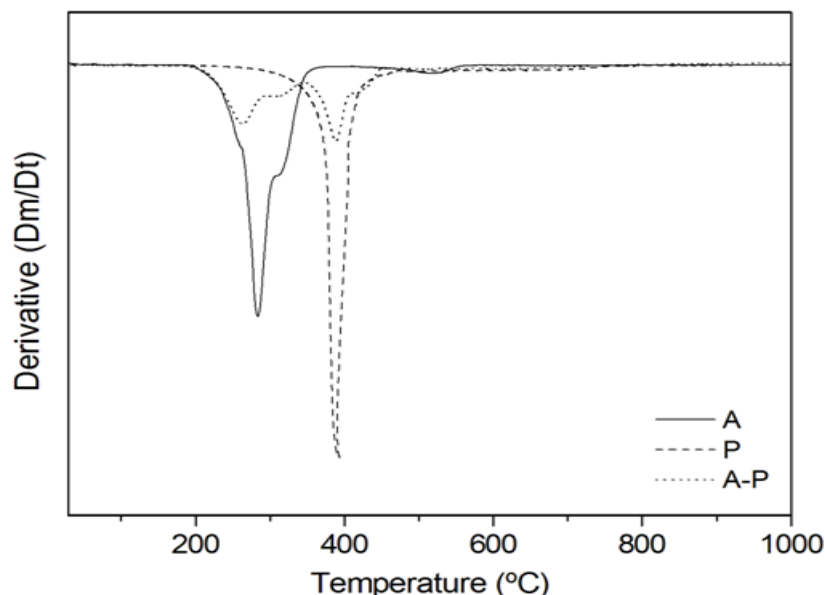


Figure 8. DTG plot of alkyl ammonium (A), alkyl phosphonium (P) and alkyl ammonium-alkyl phosphonium salt mixture (A-P).

3.4. Structure of PET hybrids

Since the thermal stability of phosphonium modified clays is higher than that of ammonium modified clays the literature [14-17,40] reports that they may be potentially useful for melt compounding and processing of nanocomposites at high temperatures. To check this premise, the organoclays prepared in this study were melting compounded with PET (1 wt%) and the influence of organoclay identity in nanocomposite structure was evaluated. The basal spacing (d_{001}) of all modified clays with the alkyl ammonium salt (ARGOA, ARGPOA and CLOA) and the mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) increased when incorporated into the PET resulting in a well-ordered multilayer morphology with alternating polymeric and inorganic layers (Figure 9a and c). This indicates that nanocomposites with intercalated structure were obtained. On the other hand, the d_{001} spacing of organophilized clays with alkyl phosphonium salt (ARGOP, ARGPOP and CLOP) remained practically unaffected when incorporated into the PET polymer (Figure 9b). Although, the organophilized clays with the phosphonium salt (ARGOP, ARGPOP and CLOP) presented larger values of d_{001} and higher termo-oxidative stability (Table 3), in this study the incorporation of these ones into the PET did not result in nanocomposites formation. The smaller affinity of phosphorus cations presents in the alkyl phosphonium salt with the terminal groups of PET chain can be the reason for such behavior. The success in intercalation/exfoliation of layered silicates is not only associated with the increase in clay basal spacing which allows the insertion of polymer chains within clay galleries, but also with strong interactions between the clay and the polymer chains [3,41,42]

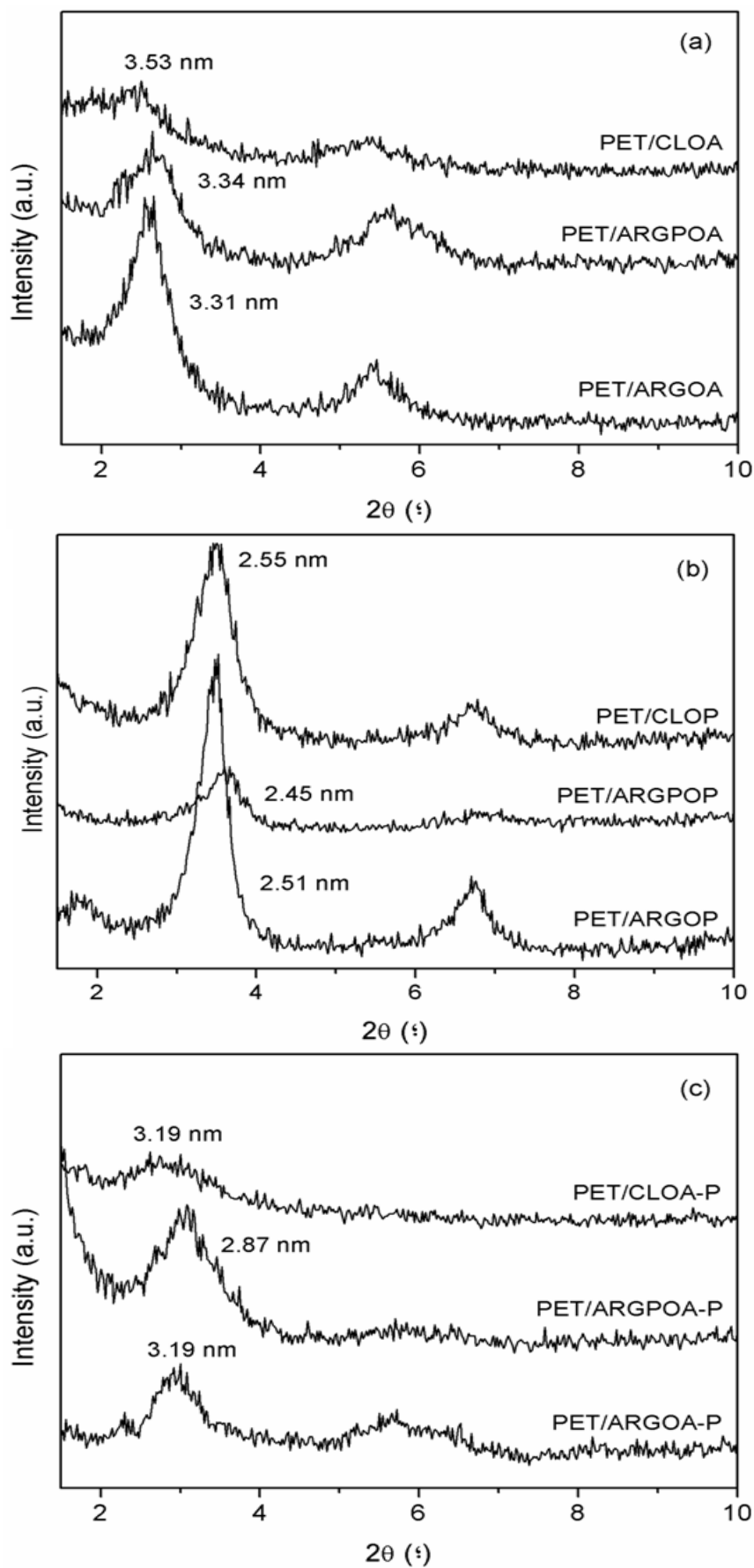


Figure 9. X-ray diffraction patterns of PET/organoclay hybrids whose clays were modified with: (a) alkyl ammonium (A), (b) alkyl phosphonium (P) and (c) alkyl ammonium-alkyl phosphonium salt mixture (A-P).

3.5. Thermal stability of PET hybrids

The thermal stability of pure PET and PET/organoclays hybrids was evaluated under air atmosphere. The thermo-oxidative decomposition temperature data at 10 wt% mass loss (T_{D10}) are reported in Table 6. The data indicates that PET thermo-oxidative stability did not change with the incorporation of alkyl ammonium organophilized clays (ARGOA, ARGPOA and CLOA). On the other hand, PET T_{D10} containing organoclays prepared with alkyl phosphonium (ARGOP, ARGPOP and CLOP) and with the mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) are 6-14°C higher than that of neat PET (Table 4). It is believed that the higher thermal stability of the clays modified with quaternary phosphonium salt possibly acts as a mass-transport barrier of the volatile products generated during decomposition increasing the thermal stability of the system [15,16,43].

The incorporation of modified clays with the mixture of both ammonium and phosphonium salts (ARGOA-P, ARGPOA-P and CLOA-P) tended to inhibit PET crystallization behavior as evinced by a decrease in the crystallization temperature of these hybrids (Table 4). On the other hand, organoclays prepared with alkyl ammonium (ARGOA, ARGPOA and CLOA) and with alkyl phosphonium (ARGOP, ARGPOP and CLOP) act as nucleating agents to PET. It is believed that the developing crystallization nuclei resulting from interaction of segments of the PET molecules with the surface of clay is associated with the kind of conformation of organic salts in clays galleries. This is in agreement with the results reported Calcagno et al. [44].

Table 4. Thermal-oxidative decomposition temperatures at 10 wt% mass loss (T_{D10}) and crystallization temperature (T_c) of neat PET and of PET/organoclay hybrids.

Samples	T_{D10} (°C)	T_c (°C)
Neat PET	427.0	163.6
PET/ARGOA	436.1	203.8
PET/ARGPOA	427.0	198.0
PET/CLOA	424.0	202.2
PET/ARGOP	433.5	195.9
PET/ARGPOP	433.5	180.5
PET/CLOP	437.1	199.8
PET/ARGOA-P	434.0	162.7
PET/ARGPOA-P	441.1	162.7
PET/CLOA-P	431.0	158.7

IV. CONCLUSION

The surfactants used in organoclays preparation influenced the thermal and morphological characteristics of the hybrids obtained. In this study nanocomposites were not obtained when phosphonium organoclays were added to PET. However, intercalated PET/organoclay nanocomposites were obtained when alkyl ammonium organoclays and the mixture alkyl ammonium-alkyl phosphonium organoclays were used. Organoclays obtained with the mixture salts, especially the purified clays, seem to be best suited to obtain PET nanocomposites with higher thermal stability. In addition the incorporation of these organoclays tended to inhibit the PET crystallization behavior what is profitable in the production of transparent bottles. The characteristics of Argel clay were similar to those of Cloisite- Na^+ when modified with the same surfactants. So, just as organically modified Cloisite- Na^+ , pristine and purified Argel organoclays can also be used in PET nanocomposites preparation.

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