Effect of modified Montmorillonite on the morphology and mechanical properties of Poly(Ethylene-Terephtalate) /Poly(Ethylene) blends - Role of the polarity and thermal stability of...

Conference Paper · April 2011

1 author:

Mohamed Yousfi
Institut National des Sciences Appliquées de Lyon

Effect of Modified Montmorillonite on the Morphology and Mechanical Properties of Poly(ethyleneterephtalate)/Polyethylene Blends Role of the Polarity and Thermal Stability of the Surfactant

M. Yousfi[b], J. Soulestin[a,b], M.F. Lacrampe[a,b], B. Vergnes[c]*

[a] Université Lille Nord de France, F-59000 Lille, France
[b] Ecole des Mines de Douai, Department of Polymers and Composites Technology & Mechanical Engineering, F-59508 Douai, France
[c] MINES ParisTech, CEMEF, UMR CNRS 7635, F-06904 Sophia-Antipolis, France,
** Ecole des Mines de Douai, Department of Polymers and Composites Technology & Mechanical Engineering, 941 rue Charles Bourseul, BP 10838, F-59508, Douai, France*

**Corresponding author: jeremie.soulestin@mines-douai.fr*

Abstract. PET/PE blends were prepared using three different types of commercially available organically modified montmorillonite (OMMT) (Cloisite 15A, 30B and 10A) using conventional polymer melt extrusion process. Characterization of the structure and morphology of nanocomposites obtained is performed using scanning electron microscopy and X-ray diffraction. Mechanical tests of PET/PE/OMMT nanocomposites were analyzed according to the type of organo-modified in nanoclay. It seems that the size of PE nodule phase depends strongly on the chemical structure of the quaternary ammonium surfactant organo-modified of nanoclay. However, the ductility of PET/PE blends depends mainly on the thermal stability of the organoclay. Indeed, a brittle behavior is observed in the presence of C10A probably due to strong surfactant degradation during extrusion process. Then, PET/PE blends were studied prepared using only surfactant those which correspond to (Cloisite 15A, 30B and 10A) to evaluate the effect of the organo modifier without the presence of the monmorillonite lamellae. A decrease in the size of PE droplets was observed wich varies with a trend similar to what found in the presence of clay. It shows unambiguously that the key factor for organoclay compatibilization efficiency of PET/PE blends is the surfactant modifier itself and not the monmorillonite lamellae.

Key words: Poly(ethylene terephthalate), polyethylene, compatibilization, nanoclay, organic modifier, morphology, mechanical properties, thermal stability.

Introduction

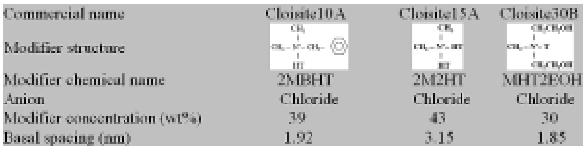
During the past twenty years, many studies have highlighted the interest of the use of nanoparticles (carbon nanotubes[1, 2], silica[3], clays[4-6]) to improve the properties of polymer blends playing both the role of structural reinforcement and compatibilizer. According to different authors, in particular, when the clay used are organo-modified, the nature of the surfactant influences the location of clay layers in the blend and affects the coalescence behaviour and effectively reduces the size of the dispersed phases, reduces the interfacial tension. However, Bailly et al[7], recently raise the issue in the case of organoclays on the fact that it is not clear if the interfacial energy reduction is due to the nanoparticles themselves or to contamination by surfactant. Indeed, the presence of clay affects the viscosity of immiscible polymer system, and makes interpretation of morphological results very complicated. Thus, for different authors, it was difficult to clearly decouple the effect of the surfactant from the effect of the clay. Therefore, it is of prime importance to study the effect of the organic modifier without the presence of the montmorillonite lamellae and its implications on the morphological properties of PET/PE blends. The aim of this work was to prepare PET/PE blends using different organoclays in order to evaluate the effect of clay organic modifier in compatibilizing immiscible polymer blends on the morphology and mechanical properties of the final nanocomposites. Three modified clays (Cloisite 30B (C30B), Cloisite 15A (C15A) and Cloisite 10A (C10A)) were used wich consist of montmorillonite modified with a quaternary ammonium ion (surfactant). The C30B, C15A and C10A have a special affinity with PET, polyolefins, and both PET and polyolefins, respectively. In the second part of this paper, the effect of each surfactant without the presence of montmorillonite was studied separately to assess the contribution of the surfactant alone on the blends morphology. Blends with and without OMMT were prepared by extrusion. Microscopy, X-ray diffraction and mechanical tests were used to highlight the improvement of the blend morphology and the effectiveness of clay and/or surfactant as an agent in compatibilizing PET/polyolefin blends.

Experimental

Materials

Polyethylene terephtalate and low density polyethylene (Riblene FL20) used in this work were supplied by ACORDIS and Polymeri Europa, respectively. The clays used for the preparation of PET/PE clay hybrids are sodium montmorillonite modified by 2MBHT: dimethyl, benzyl, hydrogenated tallow (Cloisite® 10A (C10A)), 2M2HT: dimethyl, dehydrogenated tallow (Cloisite® 15A (C15A)) or MHT2EOH: methyl, tallow, bis-2-hydroxyethyl (Cloisite® 30B (C30B),) with quaternary ammonium chloride supplied by Southern Clay Products (USA). HT, Hydrogenated tallow (~65% C18; ~30% C16; ~5% C14) (table I). The organic modifiers used in the preparation of PET/PE/surfactants blends are Benzyldimethylhexadecyl ammonium chloride from Acros Organics, dioctadecyl dimethyl ammonium chloride from Sigma Aldrich and Benzylbis (2-hydroxyethyl) dodecyl ammonium chloride from Sachem Europe.

Table 1. Modifier Specifications for Used Montmorillonites



Commercial name	Cloisite10A	Cloisite15A	Cloisite30B
Modifier structure			
Modifier chemical name	2MBHT	2M2HT	MHT2EOH
Anion	Chloride	Chloride	Chloride
Modifier concentration (wt%)	39	43	30
Basal spacing (nm)	1.92	3.15	1.85

Sample preparation

PET/PE (80/20 wt%) and PET/PE/Cloisite (80/18/2 wt%) blend-based composites were carried out using a conical twin screw micro compounder [type Rheomex CTW5]. Before extrusion, PET pellets were dried in a vacuum oven overnight at 80°C before being loaded into extruder because its sensitivity to moisture. Blends of each composition were prepared under the same mixing conditions. The rotational speed was 50 rpm, this corresponds to an average shear rate of 50 s-1 and a residence time of 62 s. The temperature was fixed to 270°C. For mechanical testing (traction), the extrudate were molded directly from the micro compounder on an Thermo MiniJet Injection Molding System. For XRD characterization, disks 40 mm in diameter and 1 mm thick have also been made from solid granules by hot pressing, in a press mark Dolouets at a temperature of 270 ° C by applying a pressure of 11 MPa for 5 min.

Characterization

Blends morphologies were examined by scanning electron microscopy (SEM) using a Hitachi S4300 SE/N at accelerating voltage of 15 kV and a probe current of 130 pA. The samples were fractured in liquid nitrogen and then coated with gold to avoid charging on the fractured surface. SEM photographs of the PET/PE and PET/PE/Cloisite© blends were made from injection moulded pieces fractured in liquid nitrogen. To quantitatively analyze the morphology of the fractured surface of the samples, the average PE domain diameters were obtained with an image analysis software (ImageJ©). XRD curves were recorded on a D8 Bruker horizontal diffractometer operating at 40 kV and 40 mA with a beam consisting of CuKα radiation (λ = 1.78897 Å). Data were collected in the 2θ region 2-10°, with a step size of 0.004° and a counting time of 30 s/step. The basal spacing of the OMMT before and after intercalation was estimated from the position of d001 peak in the XRD diffractogram, according to the Bragg equation. The tensile tests were carried out in an Instron 5585H equipment at a cross-head speed of 10 mm/min and at 23°C ± 2°C and 50 ± 5% relative humidity. The mechanical properties (stress max, stress at break, ductility, measured as the percent elongation at break) were determined from the load-displacement curves. A minimum of five tensile specimens were tested for each reported value.

Results and discussion

Thermal stability of organoclays

The thermal stability of commercially organo-modified Montmorillonites was examined by TGA measurements in air before they are dispersed in PET/PE blends. The weight loss curves of organosilicates between room temperature and 700 ° C are shown in figure 1(a). As expected, for all organoclays, the extent of mass loss increases as the test temperature becomes higher. However, the rate of surfactant loss increases dramatically from 240 to 400 °C. The onset temperature of decomposition of C10A, C15A and C30B is 180°C, 238°C and 230°C respectively. These temperatures are lower than the temperature of transformation of the blends and possible degradation of the surfactant modifier of the clay is possible in these conditions especially in the case of C10A. To determine the mass loss of the surfactant at 270 ° C, isothermal TGA measurements were performed in air (figure 1(b). A ramp temperature of 100 ° C/min was chosen to go from ambient to 270 ° C. Thus, in less than 3 minutes of measurement, the mass loss of C15A and C30B are low (~ 3%) because of the presence of moisture. However, there is a loss of about 10% for C10A. Once the temperature 270 ° C is reached, there is a similar weight loss between C15A and C30B during the first minute scan at this temperature which is around 5% while the mass loss reached 15% with C10A. After 3 minutes of scanning at 270 ° C, the slope of mass loss decreases and tends to stabilize. Indeed, after 8 minutes of measurement at 270 ° C the mass loss is 9%, 13% and 21% for C30B, C15A and C10A respectively.

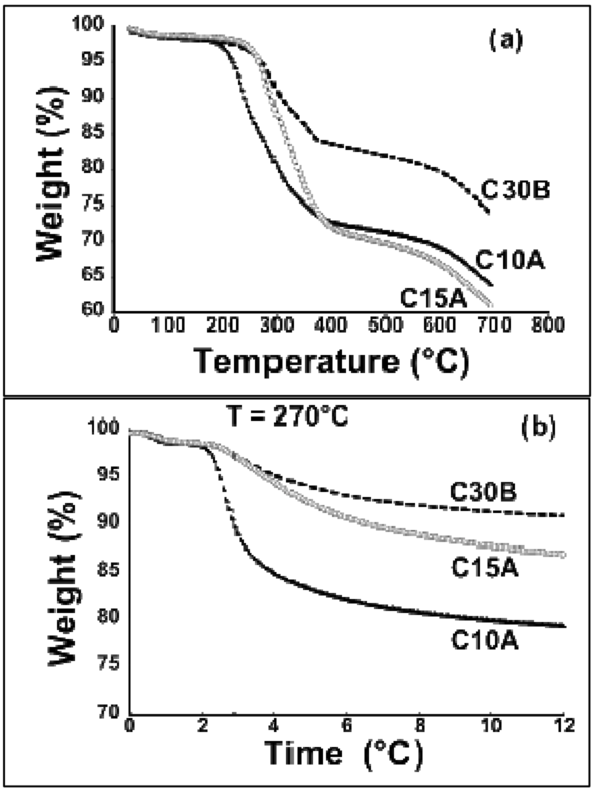


Fig. 1. TGA curves under air environment with a scanning rate of 20°C/min (a) and weight loss kinetics at 270°C under air of organoclays C10A, C15A and C30B (b). Between room temperature and 270 ° C, the heating rate was 100 ° C / min.

X-ray diffraction analysis of

PET/PE/nanoclay blends

Figure 2 shows the XRD patterns of pure C10A, C15A, C30B and PET/PE blend with clay. The primary (001) diffraction of neat C30B is located around 2θ = 5.62°, which means an interlayer spacing (d-spacing) of 1.82 nm. When C30B clays were added to PET/PE blend, XRD peak is shifted to lower angles indicating the increase in interlayer spacing by the intercalation of polymer. The average maximum distance between the platelets was of about 3.23 nm instead of 1.82 nm before polymer intercalation. When C10A clays were used, a behavior similar to C30B was obtained. The average maximum distance between the platelets was of about 3.12 nm instead of 1.89 nm before polymer intercalation. For the PET/PE with C15A, it was observed no displacement but just the narrowing of the characteristic clay peak (

d = 3.27 nm). However, this does not prove that intercalation did not occur because PET could intercalate and substitute the surfactant in the interlayer region. Therefore, one can conclude that despite the increments in the organoclay interlayer distances [Δd(001)] are different, although the three systems have similar final interlayer distances (Table II). Further noted in all the figures is the existence of a shallow diffraction peak located right around 2θ = 6.4°, (d-spacing: 1.60 nm).

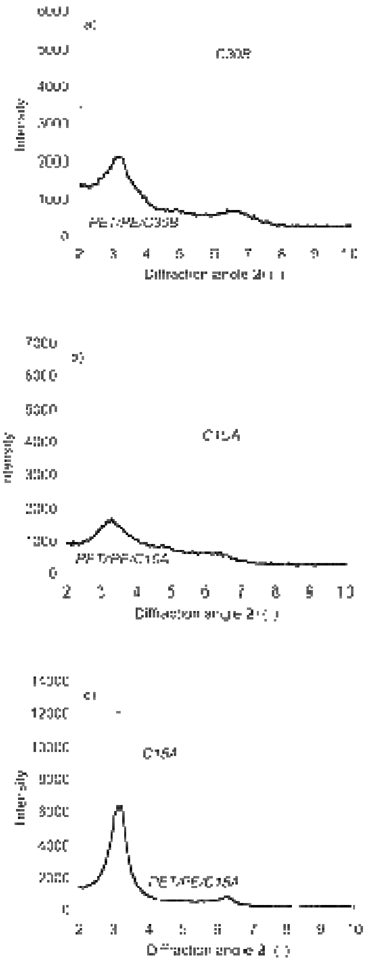


Fig. 2. XRD patterns for the organoclays and the PET/PE/ Cloisite© blends.

a) C30B, b) C10A, c) C15A.

Table 2. Initial and after blending basal spacing d(001) of the clays as well as its increment upon mixing with PET/PE blends

Clay	Initial d(001) nm	After blending d(001) nm	Δd(001) nm
10A	1.89	3.12	1.23
15A	3.27	3.27	0
30B	1.82	3.23	1.41

Morphology of PE domains

Figure 3 shows the cryofractured surfaces of PET/PE blends without and with 2wt% organo-modified nanoclay. During the fracture process, many domains are pulled away from their previous positions and deep holes are observed. For PET/PE blends, higher diameters of the PE domains and the existence of a clear interface are observed, which is typical morphology of poor interfacial bonding. With the exception of C10A, the addition of nanoclay induces a significant change in the PE nodules particularly in the presence of C15A. The change of morphology indicates that the compatibility of PET and PE is improved greatly in the presence of organo-modified C15A nanoclay. C15A leads to the highest decrease of the PE droplet size whereas, C30B is less efficient. For example, the average domain size of the PE in PET/PE/C15A nanocomposites decreases from 7.6 μm to about 1.6 μm with the addition of 2wt% of C15A organoclay and 3.6 μm in the case of 2wt% C30B. Noted that with C10A, a very slight change in nodule size is observed compared to the other two types of clays probably due to its high degradation during extrusion. To explain why it is very difficult to predict the effect of the addition of organoclay on the morphology of a PET/PE blend based solely on its initial affinity with the matrix or the dispersed phase, by using the expression (1) proposed by Serpe et al[8]:

$$D \approx \frac{\frac{4\Gamma_{PE\ PET}}{\dot{\gamma}\,\eta_{blend}}\left(\frac{\eta_{PE}}{\eta_{blend}}\right)^{0.84}}{1-\left(4\cdot\phi_{PE}\cdot\varphi_{PET}\right)^{0.8}} \qquad (1)$$

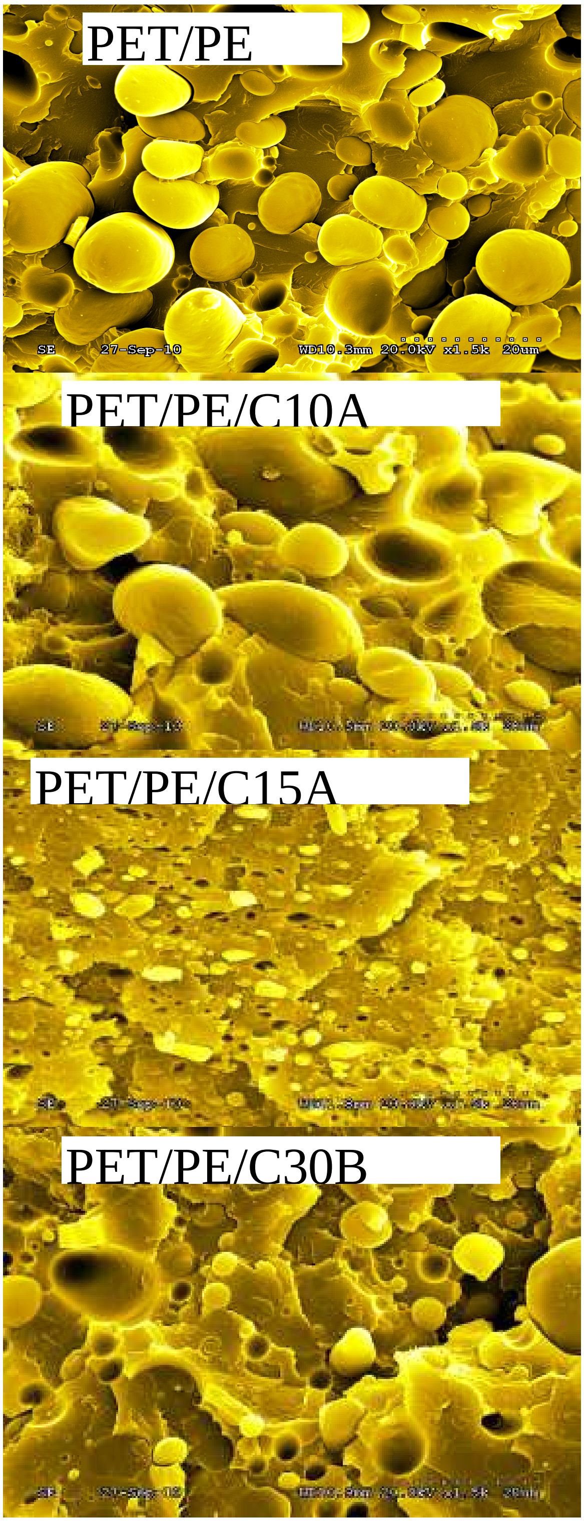


Fig. 3. SEM micrographs of fracture surfaces of the PET/PE/ Cloisite© blends (PET/PE = 80/18, organoclay concentration = 2 wt%).

where D is the droplet size, Γ the interfacial tension, η the viscosity, $\dot{\gamma}$ the shear rate and φ the volume fraction. This relationship shows that, eventhough the interfacial tension has a great influence on the droplet size, the viscosity ratio is also important in the case of a viscoelastic system like PET/PE/clay blends. Indeed, the addition of organoclay can affect the viscosity of the blend and counteract the effect of interfacial tension.

Mechanical properties of PET/PE/Organoclays

When tensile properties of PET/PE/O-MMT nanocomposites are compared with those of neat PET/PE blends, it can be seen that the addition of C10A organoclays has a negative effect on stress and elongation at break of PET/PE blend (figure 4). PET/PE blend is ductile whereas PET/PE/C10A blends are brittle. However, the ductility was partially preserved with the addition of C15A and C30B organoclay. This ductility decrease is unlikely to be the consequence of the inorganic clay presence, because the stress max did not increase significantly with the addition of the clay. This trade-off of mechanical properties has been very often reported in many studies concerning PET/nanoclay nanocomposites [9]. Indeed, the low thermal stability of these organoclays resulted in chemical decomposition of PET matrix by α,β elimination [9]. Considering that C10A is the most thermally unstable, which explains the brittle mechanical behavior of PET/PE/C10A compared to other blends in the presence of C15A or C30B, (Tdegradation ~ 180 ° C for C10A and ~ 240 ° C for C15A & C30B) (figure 2).

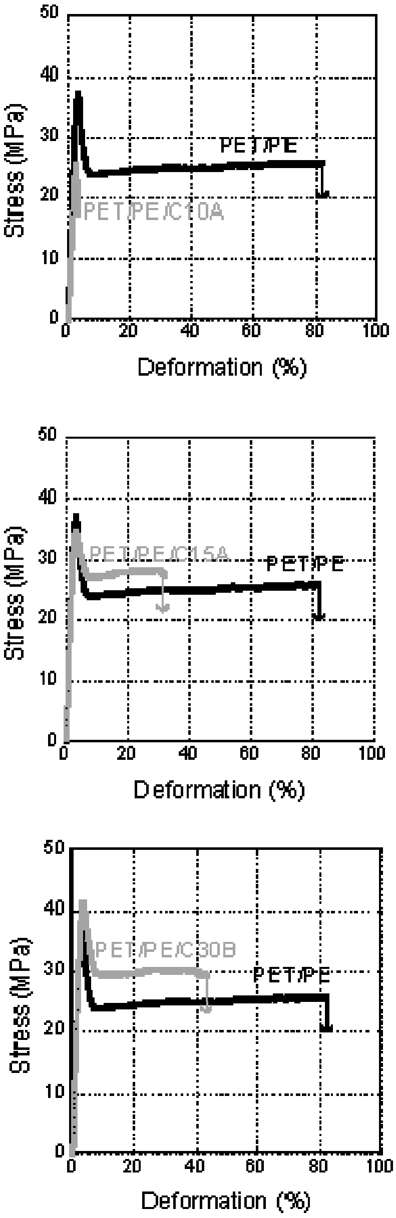


Fig. 4. Mechanical behaviour Instron tets of PET/PE and PET/PE/O-MMT nanocomposites. Mass concentration of clay is 2wt%.

Surfactant effect on PET/PE properties without the presence of montmorillonite lamellae

Morphology of PET/PE/surfactants

In Figure 5 below, presents the SEM images of PET/PE blends 80/20 with and without the presence of 0.6wt% of quaternary ammonium surfactants. The choice of the surfactant content is based on the fact that there is an average quantity of surfactant mass in most commercial organoclays around 30wt% (table I). In this study, clay was added at 2wt%, which corresponds to a surfactant concentration of 0.6wt%. As already discussed previously, in the case of PET/PE blends, large polydisperse nodules with an average size of 8 µm are observed, which characterizes the morphology of an immiscible system polymer. When adding the surfactant, a decrease in the size of the nodules is noticed, similar to the decrease observed in the presence of clay. Indeed, the mean PE droplet size is 3.7, 2.2 and 1.9 µm for S10A, S30B and S15A respectively. This result shows unambiguously that the surfactant controls the morphological structure of the PET/PE blends and not the monmorillonite lamellae.

Mechanical properties of PET/PE/surfactants

The results show (Figure 6) that regardless of the type of surfactant, a loss of ductility as reported in the presence of organoclay is observed. Elongation at break is about 50% instead of 80% for PET / PE without surfactant. As already mentioned before and according to the reaction of Hoffmann, thermal degradation of surfactants in the polymer transformation induces the presence of water and according to several authors [9] leads to hydrolysis of PET and therefore its ductility decreases. The presence of aldehyde as other products of decomposition of the surfactant can cause crosslinking of the PET matrix at high temperature with the formation of a branched structure and hence a stiffening of the matrix and loss of ductility. Moreover, the ductility of PET/PE/S10A is better than the corresponding PET/PE/C10A. According to Cervantes et al[10], the formation of water that can come from the clay itself at high temperature and which accentuate the effect of the phenomenon of hydrolysis of PET matrix. This probably explains the improvement in ductility of PET/PE/S10A compared to that of PET/PE/C10A.

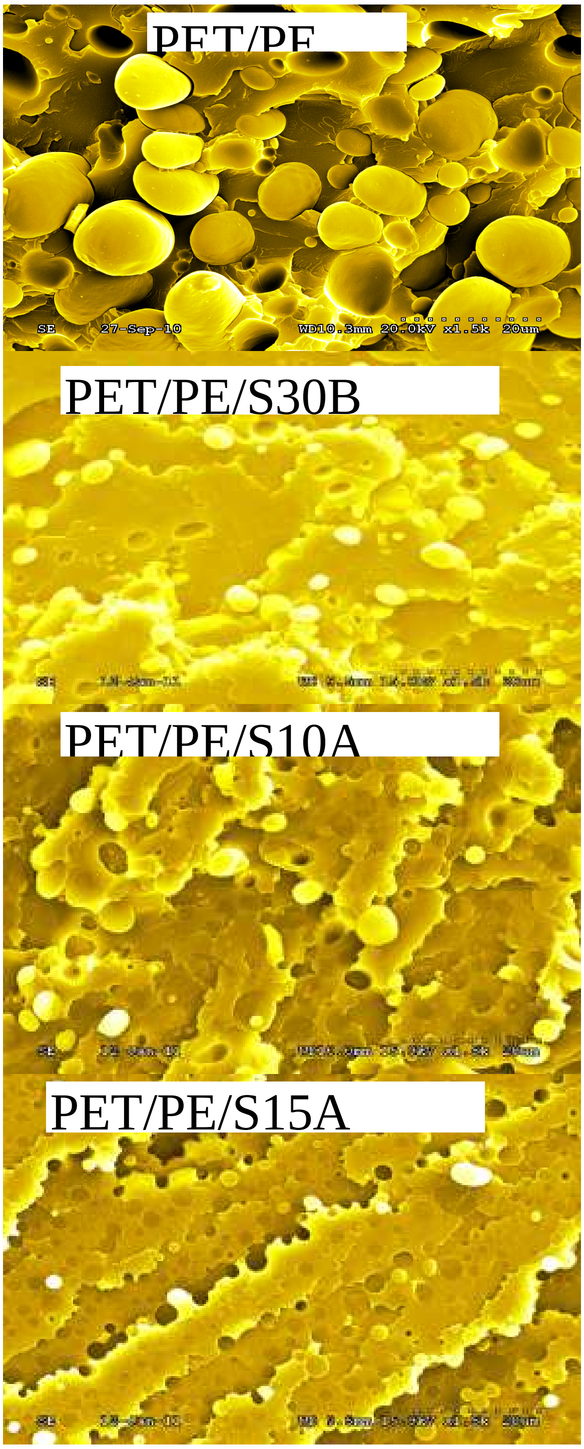


Fig. 5. SEM micrographs of fracture surfaces of the PET/PE/surfactant blends (PET/PE = 80/19.4, surfactant concentration = 0.6 wt%).

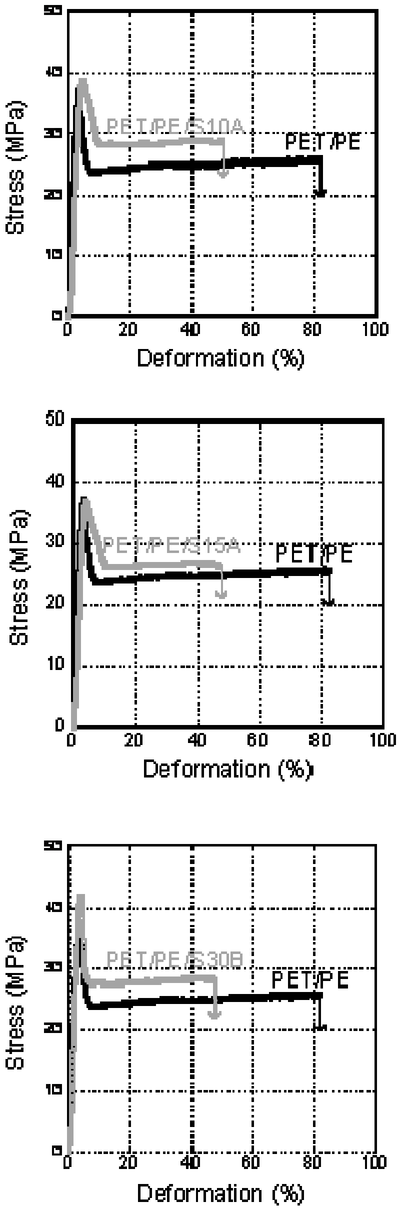


Fig. 6. Mechanical behaviour Instron tets of PET/PE and PET/PE/Surfactants blends. Mass concentration of surfactants is 0.6wt%.

Conclusions

The efficiency of organoclays for compatibilizing an immiscible PET/PE blend was studied as function of the chemical structure of the surfactants used for the modification of the clay. The morphology was examined by SEM observations and XRD measurements. The addition of organoclay generally led to a decrease in the average size of PE dispersed phase, as compared to the unfilled blends. The highest compatibilizing efficiency was observed for C15A organoclay. The morphological structures of organoclays filled PET/PE blends were found to be similar to the structures of unfilled blends. Moreover, the efficiency of the types of surfactants was equivalent to the one of the corresponding organoclay. Consequently, it is clearly shown that the key factor for organoclay compatibilization efficiency of PET/PE blends is the surfactant modifier itself and not the presence of montmorillonite platelets. However, this study clearly shows that both the mechanical and morphological structure of the PET/PE blends can not rely solely on the initial affinity of surfactants with the blend components but must also take into account the thermal degradation of these surfactants as compared to the temperature of the extrusion.

Acknowledgements

This work was supported by financial funding from NanoMines, a group of the Institut Carnot M.I.N.E.S. (Paris) in the frame of the project “Nanostructures”. The authors acknowledge Damien Betrancourt and Laurent Charlet from Ecole des Mines de Douai for their help in microscopy and extrusion experiments, respectively.

References

1. A-C. Baudouin, C. Bailly , J. Devaux. *Polymer Degradation and Stability*, **95**, 389 (2010).

2. A-C. Baudouin, J. Devaux, C. Bailly. *Polymer*, **51**, 1341 (2010).

3. W. Tong, YJ. Huang, CL. Liu, XL. Chen, Q. Yang, GX. Li. *Colloid and Polymer Science*, **288**, 753 (2010).

4. SS. Ray, S. Pouliot, M. Bousmina, LA. Utracki. *Polymer*, **45**, 8403 (2004).

5. SS. Ray, M. Bousmina. *Macromolecular Rapid Communications*, **26**, 450 (2005).

6. SS. Ray, M. Bousmina. *Macromolecular Rapid Communications*, **26**, 1639 (2005).

7. AC. Baudouin, T. Fang, J. Devaux, C. Bailly. *Polymer*, **52**, 149 (2011).

8. K-H. Kim, J. Huh, H. Won. Macromolecular research, 15, 178 (2007).

9. JM. Cervantes, JV. Cauich-Rodriguez, H. Vazquez-Torres, LF. Garfias-Mesias, DR. Paul. *Thermochimica Acta*, **457**, 92 (2007).