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COMPATIBILIZING AGENTS INFLUENCE ON MECHANICAL PROPERTIES OF PP/CLAY NANOCOMPOSITES

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S-a investigat din punct de vedere mecanic influența concentrației de argilă şi a utilizării unui sistem cu doi agenți de compatibilizare. Argila Cloisite –Na a fost modificată organic cu o polietermonoamină, iar, ca agent de compatibilizare secund, s-a adăugat polipropilena maleinizată (MA-PP) sau stiren-etilen-butilen-stirenul maleinizat (MA-SEBS). Nanocompozitele de polipropilenă astfel obținute au prezentat cristalinitate şi grosime lamelară crescută. Nanocompozitele cu MA-PP au prezentat, în general, proprietăți mecanice îmbunătățite, în special rezistența la tracțiune, rezistența la fluaj şi la testare ciclică, în timp ce nanocompozitele cu MA-SEBS au prezentat o îmbunătățire a curgerii superioare şi o creştere a ductilității.

The influence of Clay concentration and of two compatibilizers system use was investigated from mechanical point of view. Cloisite-Na Clay was organically modified with a polyethermonoamine and, as second compatibilizer, the maleated polypropylene (MA-PP) or maleated styrene-ethylene-buthylene-styrene (MA-SEBS) were added. Polypropylene nanocomposites with increased crystalline phase and lamellar thickness were obtained. The nanocomposites with MA-PP showed an overall improvement in mechanical properties, especially in tensile strength, creep strain and cyclic test, while those with MA-SEBS presented an improvement in neck propagation, as well as an increase in ductility.

Keywords: polypropylene nanocomposites, layered silicate, creep, mechanical properties

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1. Introduction

Hybrid organic-inorganic materials had become a topic of interest in material science since exhibit properties superior to those of their individual components. To optimize the performance properties of these materials, a good interaction between inorganic phase and organic matrix is desirable [1].

In order to improve the compatibility between nonpolar polymers such as polypropylene (PP) and nanosized filler, the surface of layered silicates must be modified in order to obtain intercalated or exfoliated structures [2-4]. The most common compatibilizer used for obtaining PP/clay nanocomposites is maleated polypropylene (MA-PP). Several studies [5-8], reported the use of MA-PP as compatibilizer due to formation of hydrogen bonds between OH or COOH groups and the oxygen groups of the silicate, which enhance the interaction between filler and polymer [9].

The incorporation of layered silicates into polymers, leads to increased stiffness while the ductility and toughness are reduced. In order to overcome this decrease, others replaced MA-PP with maleated styrene-ethylene-buthylene-styrene (MA-SEBS), considering that elastomer particle addition is needed to restore the tensile ductility and impact toughness [2, 10-14].

Efforts were made to improve the compatibility between PP and layered silicates, to improve an exfoliated structure [9]. Layered silicates are generally modified by cationic exchange reactions with quaternary ammonium surfactants [15, 16], however, the modification is not limited to exchange reactions and can also be done using functional oligomers with polar groups [9, 17, 18].

In the overall process, there are several key factors that influence the dispersion of layered silicates into PP matrix, when using melt technique, including the type of organic modifier, the functional groups of the compatibilizer, the viscosity of the system and appropriate processing conditions [19].

This study reports the influence of compatibilizing agents on mechanical properties of PP/Clay nanocomposites. The modification of clay was done with a polyethermonoamine by swelling, due to the dipole-dipole interaction that can occur between components, compatibility between PP and modifier [20], and reaction with maleic group. Two sets of nanocomposites were obtained: one with MA-PP and another with MA-SEBS.

2. Materials

The PP matrix used for this study was a homopolymer produced by LyondellBasell. The grade name is HP400R and has the density = 0.905 g/cm^3, a melt flow rate = 25 g/10 min at 230°C, 2.16 kg load.

The Na-Cloisite (ClNa) was purchased from Southern Clay Products, Inc. The water content was about 7 wt-% at original state and the particle size of agglomerates was less than 13 μm.

Polyethermonoamine used has the trade name Elastamine RE1-2007 amine. This compatibilizer was given by Huntsman and is a hydrophilic polyethermonoamine of approximately 2000 g/mol molecular weight, with a PO/EO mole ratio of about 10/31.

Maleated polypropylene G-3015 was purchased from Eastman Chemical Company. It contains 1 wt-% maleic anhydride, presents an acidic number of 15 mg KOH/g and has a molecular weight of 47.000 g/mol.

Maleated styrene-ethylene-buthylene-styrene Kraton FG 1901 G with a content of 30 % polystyrene was supplied by Kraton.

3. Experimental part

Elastamine can be used to modify the layered silicates either by cationic exchange reactions if it is protonated or by dipole-dipole reactions [18]. The modification of Cloisite-Na with Elastamine was done at a 1:1 wt ratio by mixing the silicate with the amine into a mortar for 10 minutes [21]. After mixing the components were allowed swelling for 24 hours. This modification was made by keeping the Na+ between the silicate platelets and considering the dipole-dipole interactions which can occur between components [18, 22].

Nanocomposites were prepared by dispersing the modified Cloisite into a mixture of polypropylene with 5 wt-% MA-PP (MG) or with 5 wt-% MA-SEBS (MS). A Prism Eurolab 16 co-rotating twin-screw extruder was used for preparation of the nanocomposites. The temperature of the extruder was 200 °C from hopper to die. The screw speed was maintained at 300 rpm. The screws used were set in a strong configuration with 3 mixing zones having 90 degrees spaced mixing disks as part of the zone. The final nanocomposites contain 1, 2 and 4 wt-% unmodified silicate. Dried pellets of the nanocomposites were injection-molded into test bars for following mechanical test using a Haake minijet from Thermo Scientific. The temperature of the cylinder was 200 °C, the temperature of the mould was 70 °C and the injection pressure was 800 bars.

Two sets of nanocomposites were obtained with MA-PP or with MA-SEBS. The nanocomposites were denoted EXY while the mixtures of PP with maleated compatibilizers were denoted MY, E coming from elastamine; X being the concentration of clay - 1, 2 or 4 wt-% and Y being G for nanocomposites with MA-PP and S for nanocomposites with MA-SEBS.

4. Characterization techniques

DSC-TG analyses were carried out using a Netzsch DSC-TG type STA 449 C Jupiter differential scanning calorimeter – thermal analyzer. About 5 mg of each nanocomposite was weight in the Al2O3 DSC pan and placed in the DSC cell. The samples were heated in the temperature range from 25 °C to 550 °C, at a heating rate of 10 °C/min and under a current of air of 50 cm^3/min. The % degree of crystalline phase (X) was estimated using the standard equation:

$$X = \frac{\Delta H}{\Delta H_{100}} 100 \tag{1}$$

where ΔH is the enthalpy of melting of the analyzed sample and ΔH100 is the reference value for the enthalpy of melting of 100 % crystalline polymer. For isotactic polypropylene, ΔH100 is 209 J/g [15, 16, 23].

Dynamic mechanical thermal analysis measurements in shear mode were performed using a Paar-Physica MCR500 modular compact rheometer fitted with SRF20 fixtures for rectangular solid torsion bars and a CTD600 convection oven. The tests were run in a temperature range from 25 to 160 °C with a frequency of 1 Hz, a strain of 0.01% and a constant heating rate of 1 °C/min. During heating the sample is subjected to a tensile load of 0.5N to allow for thermal expansion of the material.

Tensile, creep and cyclic tests were conducted on an Instron-5569 universal testing machine equipped with an electro-mechanical sensor for the control of longitudinal strains. The tensile force was measured by a 5 kN load cell.

Unnotched Charpy impact tests were performed on an Instron-CEAST 9050 testing machine equipped with a Data Acquisition System (DAS) and with an instrumented hammer of 50J. Ductile-brittle behaviour was observed by using this equipment.

5. Results and discussions

DSC results are summarized in Table 1. Table 1 shows the crystallization behavior of neat PP and PP–clay nanocomposites and the melting temperatures. It can be observed that the melting temperature of PP increases with the addition of maleated compabilizers as well as with the increasing of clay concentration up to 4 wt%.

Table 1

Degree of crystalline phase and melting behavior

Sample	Melting peak, T_m (°C)	Degree of crystalline phase, X_m (%)	Lamellar thickness*, *l* (nm)
PP	166.8	34.1	6.26
MA-PP	167.3	33.4	-
PP/MA-PP	164.3	33.6	5.51
MA-SEBS	-	-	-
PP/MA-SEBS	168.2	33.2	6.79
E1G	167.8	36.9	6.63
E2G	168.4	35.6	6.87
E4G	169.4	35.8	7.31
E1S	167.5	34.3	6.52
E2S	169	33.3	7.13
E4S	169.3	35.3	7.27

*Computed using Thomson–Gibbs equation

By adding maleated compatibilizers the degree of crystalline phase decreases, the materials presenting somewhat similar values. On the other hand, when modified silicate was added, it was observed that the degree of crystalline phase increased. This can be attributed to the nucleating effect of nanofiller. Moreover, by using the DSC result, the lamellar thickness (*l*) was estimate by using the Thomson–Gibbs equation [24, 25]:

$$l = \frac{2\gamma T_m^0}{\Delta H_0 \rho (T_m^0 - T_m)} \tag{2}$$

where T^0_m is the equilibrium melting temperature, T_m is the detected melting temperature by DSC, γ the surface free energy, ΔH_0 the heat of fusion for 100% crystalline PP, and ρ the density. The lamellar thickness values are presented in Table 1. It can be noticed the melting temperature (T_m) increases, so does the lamellar thickness. So, as a result, it can be said that the nanocomposites are characterized by higher melting temperatures due to greater lamellar thickness caused by increase in silicate content [26].

Fig. 1 a, b present the variation of the relative storage modulus with temperature for nanocomposites with MA-PP or MA-SEBS in comparison with neat PP. In the temperature range studied it can be observed that the nanocomposites with MA-PP have higher G’ values.

Relative storage modulus evolution of the nanocomposites compared with that of neat PP showed an increase with increasing the temperature and filler content.This can be described as a relative stiffness improvement with the temperature. The nanocomposites with MA-PP showed a better thermal stability provided by the increase of the filler content above temperatures at which, the polymer matrix becomes softer. This can be related to a stronger reinforcement effect of the clay particles for higher temperatures.

Fig. 1 c, d show the relative loss modulus values as function of temperature, different trends being observed (higher value for MA-PP,and lower ones for PP/MA-SEBS nanocomposites) when compared to the neat PP. Moreover, nanocomposites with MA-PP exhibited an increase of relative loss modulus with the increase of silicate content, while in PP/MA-SEBS nanocomposite the relative loss modulus decreases. This behaviour could be microstructure-dependent related to the matrix-filler interactions.

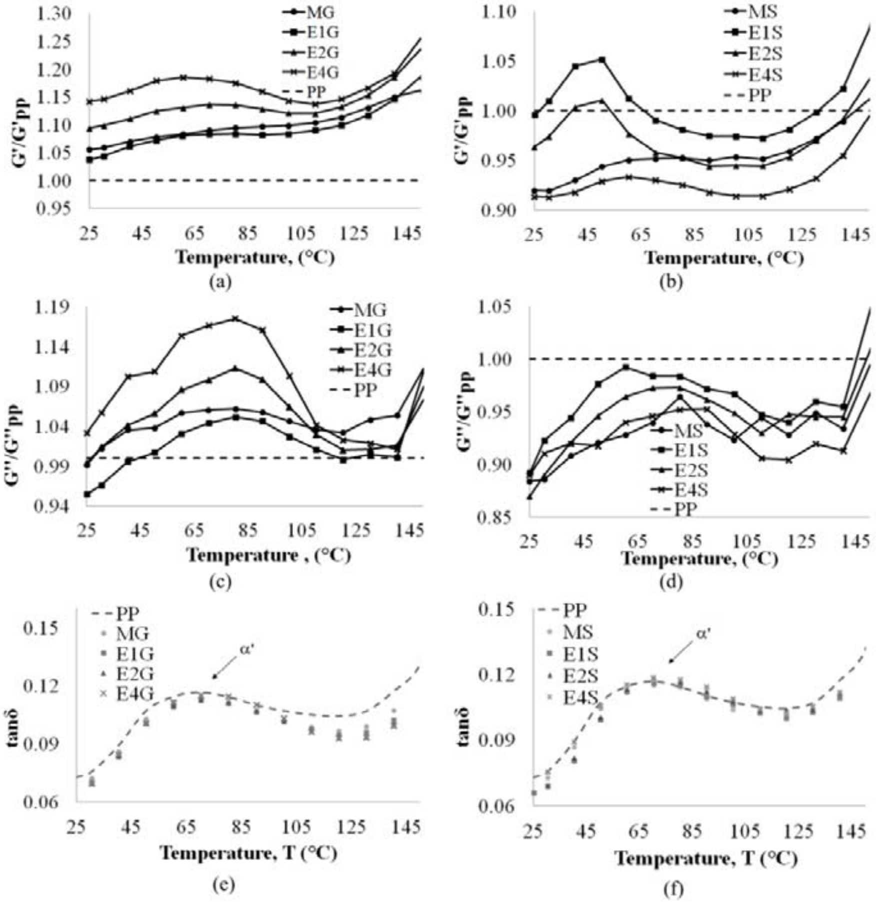

Fig. 1. Silicate influence on dynamic mechanical thermal analysis: (a) relative storage modulus for nanocomposites with MA-PP; (b) relative storage modulus for nanocomposites with MA-SEBS; (c) relative loss modulus for nanocomposites with MA-PP; (d) relative loss modulus for nanocomposites with MA-SEBS; (e) tanδ for nanocomposites with MA-PP and (f) tanδ for nanocomposites with MA-SEBS

Furthermore, the nanocomposites with MA-PP presented lower tanδ values than MA-SEBS nanocomposites (Fig. 1 e, f). This could be related to a better adhesion between polymer and filler which resulted in a macromolecular phase with a more restricted mobility. When analyzing the tanδ curves it can be observed the secondary relaxation α' (which relates to the crystal morphology) [27] between 45 and 85 °C. As can be seen, the position of this relaxation shifts towards higher temperatures in nanocomposites. Corroborating this with the lower values of the tanδ, observed for the nanocomposites in the α' relaxation temperature range, one can assume that this effect is related to different crystalline morphologies with lower molecular mobility, i.e., an improved crystalline phase, as pointed out by DSC [14].

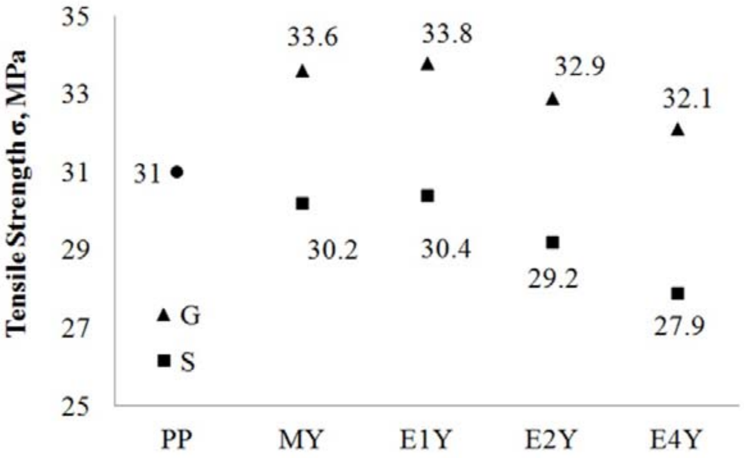

Fig. 2. Variation of tensile strength at yield for nanocomposites with MA-PP or MA-SEBS

Tensile strength at yield (TS) was determined from the stress-strain curves using a cross head speed of 50 mm/min. Fig. 2 shows the comparison between results of TS obtained on nanocomposites with MA-PP and those with MA-SEBS, respectively. It can be observed that the nanocomposites with MA-PP present a higher value of tensile strength. The presence of maleated polypropylene increases the tensile stress, while the increase in silicate content decreases the tensile stress at yield. In samples with MA-SEBS, the properties presented lower values. Moreover, a similar behavior can be observed as the silicate amount increases.

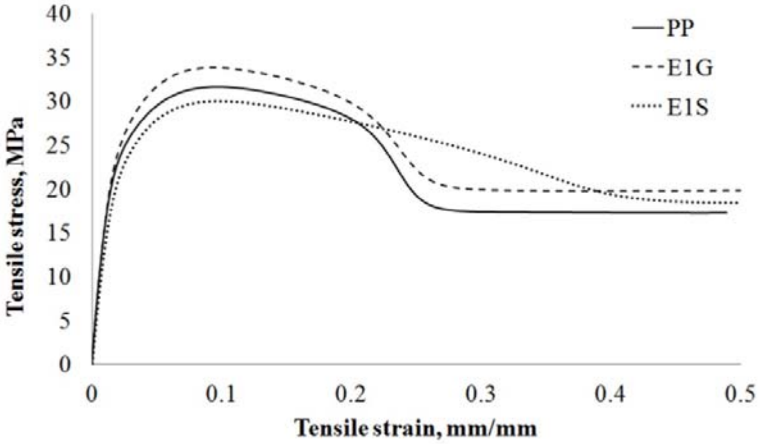

Fig. 3. Necking propagation for nanocomposites with 1% layered silicate

Moreover, as shown in Fig. 3, the nanocomposite with MA-SEBS presented higher neck propagation strengths than neat PP and nanocomposites with MA-PP. The strong interactions between the modified filler and compatibilizer slowed down the plastic deformation of the polymer interface, increasing matrix-filler stress transfer [14].

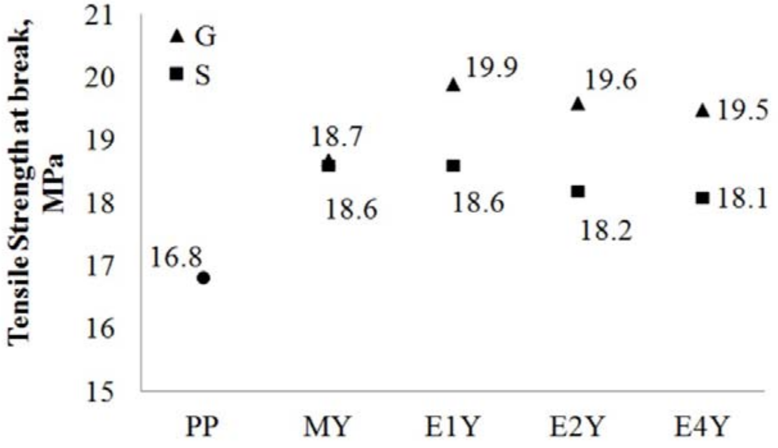

Fig. 4. Variation of tensile strength at break for nanocomposites with MA-PP or MA-SEBS

Even though, a great influence was not observed in tensile strength at yield for the nanocomposites, moreover, the properties presented a small reduction, where as the tensile strength at break was improved. In Fig. 4 it can be noticed that both type of compatibilizers, MA-PP and MA-SEBS, present the same influence on tensile strength at break. Furthermore, the addition of elastamine modified silicate increases the tensile strength at break with 18.5 % in nanocomposites with MA-PP, while in nanocomposites with MA-SEBS, the modified silicate present no influence. Also, it was observed that an increase in content of modified silicate showed a small influence on strength at break on nanocomposites with MA-PP or MA-SEBS.

The Young modulus was determined from stress-strain curves obtained with a cross head speed of 1 mm/min. Its variation for ES composites versus EG composites is presented in Fig. 5. The comparison of the corresponding samples with the same composition, gives higher performance for the latter in all cases. The difference in mechanical performance shows how important is compatibilizer nature and the clay treatment process. Since both compatibilizers can undergo imide bond formation with the primary amine intercalated between silicate platelets, it cannot be said that the imide formation influence the properties in this case [28]. The difference in properties can be attributed to the compatibilizer backbone, MA-PP being stiffer as compared with MA-SEBS which is tougher [29].

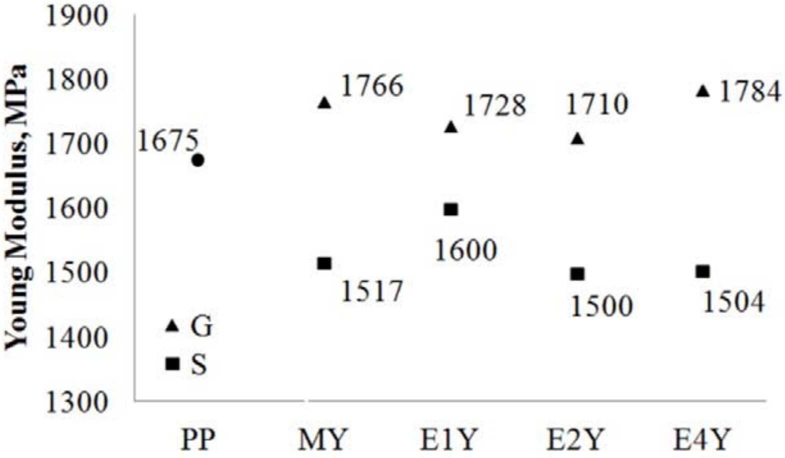

Fig. 5. Young’s modulus variation in nanocomposites with MA-PP or MA-SEBS

Young modulus is slightly higher for the MA-PP nanocomposites, as a consequence of the higher stiffness of the silicate particles when compared to the polymer matrix. The highest modulus was achieved for the E4G nanocomposite, this behavior being attributed to the higher interactions between the silicate platelets and maleic groups which restrict the movement of PP chains near the silicate particles. The formation of a more flexible interface, related to the presence of an elastomeric phase (SEBS) influences the materials stiffness, as well.

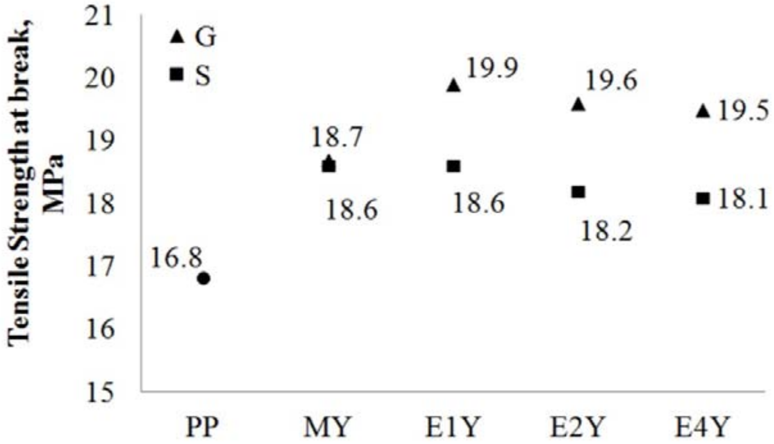

Fig. 6. Strain at creep after 1 h for nanocomposites with MA-PP or MA-SEBS

Nanocomposites’ total creep strains are presented in Fig. 6. Short term creep tests were carried out at room temperature [30], in which the creep stress was selected at a level around 68% of ultimate tensile strength of the polymeric matrix. So, for the creep measurements, the loading was 21 MPa and the creep time was one hour for all specimens. The setup was made in order to follow: (i) the initial elastic elongation; (ii) primary creep; (iii) secondary creep. The results are in accordance with tensile and Young modulus tests.

For neat PP a high initial creep rate occurred in the primary creep stage. Compatibilizing the modified layered silicate with MA-PP remarkably reduced the initial creep rate in the primary stage which ended up in a lower steady state creep rate within the secondary creep stage. In comparison, the nanocomposites with MA-SEBS as compatibilizer showed an increase in initial creep rate. In both cases, the amount of filler incorporated into nanocomposites showed a small effect on total creep strain [31].

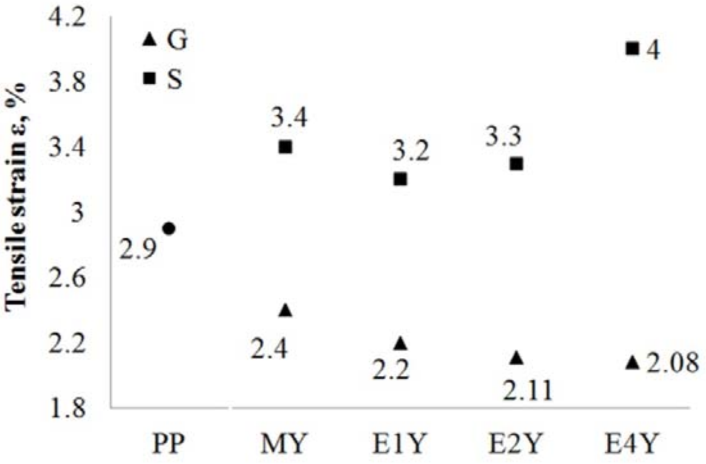

Fig. 7. Tensile strain after 10 cycles for nanocomposites with MA-PP or MA-SEBS

Cyclic tests were performed using a stress-controlled program between minimum stress σ_{min} = 15 MPa and maximum stress σ_{max} = 25 MPa [32] with strain rate $\acute{\varepsilon}$= 8.3 × $10^{-2}s^{-1}$. The specimens were loaded to the maximum stress σ_{max}, unloaded to the minimum stress σ_{min}, reloaded up to σ_{max}, unloaded down to σ_{min}, etc. The tests on neat PP and nanocomposites consisted of 10 cycles, a cross-head speed of 100 mm/min being chosen. Short time fatigue test were performed in order to observe the homogenous deformation (before necking) of the materials obtained.

In Fig. 7 are represented the tensile strain values ε after 10 cycles for nanocomposites with MA-PP or MA-SEBS in comparison with neat PP and the influence with silicate concentration. Nanocomposites with MA-PP present hardening with increasing of silicate content, while the nanocomposites with MA-SEBS show softening probably, due to rubbery phase. The softening increases with increasing of silicate content (in nanocomposites with MA-SEBS) probably as result of high friction that occurs at the interface between rubbery phase and filler.

Unnotched Izod impact strength tests showed in general decreased values for nanocomposites (table 2). When the content of modified silicate increases, the nanocomposites show a decrease in their properties. However in ES nanocomposites, the MA-SEBS produces an increase in ductility which reflects into a small decrease in impact strength as compared with EG nanocomposites [29].

Table 2

Unnotched Izod impact strength and ductility index

Sample	IzodUnnotched Impact strength, (kJ/m^2)	Ductility Index, (%)
MM	60,7	50,5
MG	50,6	38,8
MS	55,7	55,3
E1G	42,9	34,1
E2G	35,9	22,8
E4G	36,4	34,7
E1S	56,7	58,3
E2S	53,4	58,6
E4S	54,5	62

The results presented showed differences in the mechanical properties obtained from the static tensile tests and the dynamic mechanical analysis between nanocomposites with MA-PP and MA-SEBS. These differences could be related to the amount and nature of the polymer-particle interface. It can be supposed that in the nanocomposites with MA-SEBS, the maleic polar groups interact with the silicate platelets by forming a more flexible interface due to the elastomeric nature of SEBS. On the other hand, in the nanocomposite with MA-PP, the interaction is quite similar to the previous one, except that the compatibilizer possesses a similar backbone as the matrix, thus a stiffer interface can be obtained between the polymer and the modified filler [14].

6. Conclusions

Nanocomposites with increased degree of crystalline phase and lamellar thickness were obtained by increasing the modified silicate concentration due to nucleating effect of the nanofiller. The increase in lamellar thickness reflected into an increased melting temperature in nanocomposites.

DMTA results showed that nanocomposites with MA-PP presented improved stiffness as well as thermal stability with increasing modified silicate concentration.

Nanocomposites with improved mechanical properties were obtained. An overall improvement in mechanical properties was observed for the nanocomposites with MA-PP as compared with those with MA-SEBS. Thus, in tensile test the nanocomposites with MA-PP presented improved stiffness, while the ones with MA-SEBS presented an improvement of neck propagation. The total creep strain was at a significantly lower level under high creep load situation when MA-PP was used.

Cyclic test shows that by increasing the modified silicate content in nanocomposites with MA-PP the materials presented hardening, while in nanocomposites with MA-SEBS showed softening. Increasing the silicate content in nanocomposites with MA-SEBS caused an increase in softening due to high friction that occurs at the interface between rubbery phase and filler.

The addition of MA-SEBS produces an increase in ductility which reflects into a small decrease in impact strength as compared with EG nanocomposites.

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REFERENCES

[1]. *Zulfiqar S., Ahmad Z., Ishaq M., Saeed S., Sarwar M.I.*, "Thermal and mechanical properties of SEBS-g-MA based inorganic composite materials", Journal of Material Science **42**, 93–100, 2007.

[2]. *Tjong S.C., Bao S.P.*, "Fracture toughness of high density polyethylene/SEBS-g-MA/montmorillonite nanocomposites", Composites Science and Technology **67**, 314–323, 2007.

[3]. *Tjong S.C., Meng Y.Z., Hay A.S.*, "Novel preparation and properties of polypropylene–vermiculite nanocomposites", Chem. Mater. **14**, 44–51, 2002.

[4]. *Hasegawa N., Okamoto H., Kato M., Usuki A.*, "Preparation and mechanical properties of polypropylene–clay hybrids based on modified polypropylene and organophilic clay", J. Appl. Polym. Sci. **78**, 1918–1922, 2000.

[5]. *Kawasami M., Hasegawa W., Kato M., Usuki A., Okada A.*, "Preparation and mechanical properties of polypropylene-clay hybrids", Macromolecules **30**, 6333-6338, 1997.

[6]. Nam P.H., Maiti P., Okamoto M., Kotaka T., Hasegawa N., Usuki A., "A hierarchical structure and properties of intercalated polypropylene/clay nanocomposites" Polymer **42**, 9633-9640, 2001.

[7]. *Kato M., Usuki A., Okada A.*, "Synthesis of polypropylene oligomer-clay intercalation compounds", J Appl Polym Sci **66**, 1781-1785, 1997.

[8]. *Liu X., Wu Q.*, "PP/clay nanocomposites prepared by grafting-melt intercalation", Polymer **42**, 10013-10019, 2001.

[9]. *Modesti M., Lorenzetti A., Bon D., Besco S.*, "Thermal behaviour of compatibilised polypropylene nanocomposite: Effect of processing conditions", Polymer Degradation and Stability **91**, 672-680, 2006.

[10]. *Tjong S.C., Meng Y.Z.*, "Impact-modified polypropylene–vermiculite nanocomposites", J. Polym. Sci. Part B: Polym. Phys. **41**, 2332–2341, 2003.

[11]. *Tjong S.C., Bao S.P.*, "Impact fracture toughness of polyamide-6/ montmorillonite nanocomposites toughened with a maleated styrene/ ethylene butylene/styrene elastomer", J. Polym. Sci. Part B: Polym. Phys. **43**, 585–595, 2005.

[12]. *Chen W.C., Lai S.M., Chen C.M.*, "Preparation and properties of styrene–ethylene–butylene–styrene block copolymer/clay nanocomposites: I. Effect of clay content and compatibilizer types", Polymer International **57**, 515–522, 2008.

[13]. *Tjong S.C., Bao S.P., Liang G.D.*, "Polypropylene/Montmorillonite Nanocomposites Toughened with SEBS-g-MA: Structure–Property Relationship", J. Polym. Sci. Part B: Polym. Phys. **43**, 3112–3126, 2005.

[14]. *Ardanuy M., Velasco J.I., Antunes M., Rodriguez-Perez M.A., de Saja J.A.*, "Structure and Properties of Polypropylene/Hydrotalcite Nanocomposites", Polymer Composites **31**, 870–878, 2010.

[15]. *Usuki A., Kato M., Okada A., Kurauchi T.*, "Synthesis of Polypropylene-Clay Hybrid", J. Appl. Polym. Sci. **63**, 137-139, 1997.

[16]. *D.W .Van Krevelen*, Properties of polymers, Elsevier, Amsterdam, 1990.

[17]. *J.R. Fried*, Polymer science and technology, Prentice Hall, Upper Saddle River (N.J.), 2003.

[18]. *Lin J.J., Chang Y.C., Cheng I.J.*, "Novel Mechanism for Layered Silicate Clay Intercalation by Poly(propylene oxide)-Segmented Carboxylic Acid", Macromolecular Rapid Communications **25**, 508–512, 2004.

[19]. *Bao S.P., Tjong S.C.*, "Impact essential work of fracture of polypropylene/montmorillonite nanocomposites toughened with SEBS-g-MA elastomer", Composites: Part A **38**, 378–387, 2007.

[20]. *Evans R.K., Dominguez R.J.G., Clark R.J.*, "Polyether amine modification of polypropylene", U.S. Patent **2001/0039312 A1**, 2001.

[21]. *Yoshimoto S., Ohashi F., Ohnishi Y., Nonami T.*, "Synthesis of polyaniline–montmorillonite nanocomposites by the mechanochemical intercalation method", Synthetic Metals **145**, 265–270, 2004.

[22]. *Potarniche C.G., Vuluga Z, Christiansen J.deC., Radovici C., Kristensen P.K.*, "Influence of Two Compatibilizers on Clay/PPNanocomposites Properties", Polymer Engineering And Science, **53**, 403-409, 2013.

[23]. *Wunderlich B.*, Macromolecular physics. Crystal melting, Academic press, New York, 1980.

[24]. *Bassett D.C.*, Principles of polymer morphology, University Press, UK: Cambridge, 1981.

[25]. *Hoffman J.D., Millerr R.L., Marand H., Roitman D.B.*, " Relationship between the lateral surface free energy σ and the chain structure of melt-crystallized polymers", Macromolecules **25**, 2221-2229, 1992.

[26]. *Yuan Q., Misra R.D.K.*, "Impact fracture behavior of clay–reinforced polypropylene nanocomposites", Polymer **47**, 4421–4433, 2006.

[27]. *McCrum E., Read B.E., Williams G.*, Anelastic and dielectric effects in polymeric solids, Wiley, London, 1967.

[28]. *Walter P., Mader D., Reichert P., Mulhaupt R.*, "Novel polypropylene materials", J. Macromol. Sci. **A36**, 1613– 1639, 1999.

[29]. *Garcia-Lopez D., Picazo O., Merino J.C., Pastor J.M.*, "Polypropylene–clay nanocomposites: effect of compatibilizing agents on clay dispersion", European Polymer Journal **39**, 945–950, 2003.

[30]. *Drozdov A.D., Christiansen J.deC., Klitkou R., Potarniche C.G.*, "Viscoelasticity and viscoplasticity of polypropylene/polyethylene blends", International Journal of Solids and Structures **47**, 2498–2507, 2010.

[31]. *Zhang Z., Yang J.L., Friedrich K.*, "Creep resistant polymeric nanocomposites", Polymer **45**, 3481–3485, 2004.

[32]. *Drozdov A.D., Christiansen J.deC., Potarniche C.G.*, "Cyclic viscoelastoplasticity of polypropylene:effects of crystalline structure", Acta Mech **221**, 201–222, 2011.