*Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 1, 61–67*

# LAPONITE CLAY IN HOMOPOLYMER AND TRI-BLOCK COPOLYMER MATRICES
## Thermal and structural investigations

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Macromolecule/laponite nanomaterials were studied by DSC and X-ray diffraction techniques. The matrices are poly(ethylene)glycols at various molecular masses and poly(ethylene oxides)-poly(propylene oxides)-poly(ethylene oxides) tri-block copolymers. The latter were tuned by modulating the molecular masses, at constant hydrophilic/hydrophobic ratio, and the hydrophilicity. For all the investigated systems, the enthalpy of melting ($\Delta H_m$) is nearly constant up to a given composition thereafter it increases monotonically reaching the value of the pure macromolecule. We proposed a model to interpret the DSC data.

Briefly, it was invoked a mechanism of interaction following which some segments of the adsorbed macromolecule are anchored to the laponite (RD) particles and the remaining segments are radiating away from the surface. The portion of the macromolecule in contact with RD does not contribute to $\Delta H_m$ whereas that radiating away from the clay does. Once that the RD surface is saturated, the excess of the macromolecule behaves like the pure one. The proposed model allowed to compute successfully the $\Delta H_m$ values. The X-ray diffraction experiments ruled out the polymer intercalation between the silicate sheets.

***Keywords:*** *dispersion in polymer matrices, DSC, laponite, poly(ethylene)glycols, poly(ethylene oxide)poly(propylene oxide)poly(ethylene oxide), X-ray diffraction*

## Introduction

Filling polymers with inorganic particles is a procedure used to improve the stiffness of the materials, to reinforce thermal and mechanical properties as well as the chemical stability, to enhance the resistance to the fire, decrease the gas permeability, etc. The clays uniform dispersion in the polymer matrix produces a new class of materials called polymer/clay nanocomposites. Obviously, at least, one dimension of such particles has to be in a nanometer range. The combination of the properties of the parent components may allow to materials whose features may be superior to those of the single species. Several are the actual applications and even more are the potential uses of polymer/clay nanocomposites [1]. Meneghetti and Qutubuddin [2] discussed on the possible application of such materials in batteries and packaging films. For instance, a non-refrigerated packaging system has to maintain food freshness for few years; the features of such nanocomposites are promising within this issue. Nafion/clay nanocomposite membranes for proton exchange membrane [3] and direct methanol [4] fuel cells were studied. Also, polymer/clay nanocomposites are successfully used in glues for the manufacturing of pressure moulds in the ceramic industry [5].

Layered clays are available in nature and, consequently, their cost is very low. However, due to their high purity the synthetic clays are preferred comprising laponite (RD), which presents a large surface area. It has the molecular formula [6] $Si_8(Mg_{5.45}Li_{0.4})O_{20}(OH)_4Na_{0.7}$ that is the unitary cell of the disk-like shape platelet with a diameter of ca. 25 nm and a thickness of 1 nm [7].

Depending on the nature of the components and the procedure of preparation [8], different types of composites may be formed and their structure is important for the applications purpose. For instance, it is reported [1] that the mechanical performance is improved if the nanocomposites are exfoliated because the inorganic particles are thinner and the surface area available to the polymer for the association is very high.

Among the several physico-chemical techniques (rheology [9], X-ray diffraction [10, 11], TEM [12, 13], etc.) used to characterize the nanocomposites, the calorimetric method (DSC [14–17], TG [13, 16], etc.) has to be mentioned. Within this topic, the calorimetry is used as a complementary technique whereas appropriate experiments and suitable approaches to interpret the obtained data may provide information at molecular level on the association between clay and polymer. With this in mind, we decided to perform a systematic DSC study on dispersions of laponite clay

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*1388–6150/$20.00*

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in homopolymer and copolymer matrices. Also, some X-ray diffraction experiments were carried out. The poly(ethylene oxides)-poly(propylene oxides)-poly-(ethylene oxides) were chosen as copolymers. They are denoted as $EO_aPO_bEO_a$ where a and b are the number of the repetitive units of the ethylene oxide (EO) and propylene oxide (PO), respectively. These macromolecules not only exhibit interesting features but also they are not toxic [18]. They form in solvent media aggregates [18, 19] with solubilizing capacity towards hydrophobic additives [20, 21]; furthermore, they stabilize aqueous RD suspensions [22] by building up a steric barrier around to the inorganic particle displacing the adsorbed organic contaminants [23]. The effects of the copolymer molecular mass by fixing the EO/PO ratio ($EO_{76}PO_{29}EO_{76}$ and $EO_{132}PO_{50}EO_{132}$) and the hydrophilicity of the copolymer ($EO_{76}PO_{29}EO_{76}$ and $EO_{13}PO_{30}EO_{13}$) were investigated. To discriminate the role of the EO and PO segments, some poly(ethylene) glycols and polypropylene glycols (PPGs) homopolymers were also considered. The melting of PPGs having low molecular mass (to 1200 g mol$^{-1}$) was not detected.

## Experimental

### *Materials and samples preparation*

Laponite (RD) grade is a Rockwood Additives Ltd. product. Polyethylene glycols (PEGs) 400, 2000, 20000 and 35000 g mol$^{-1}$ are from Fluka. The selected copolymers (BASF products) are $EO_{76}PO_{29}EO_{76}$ (F68, nominal *Mw*=8350 g mol$^{-1}$), $EO_{13}PO_{30}EO_{13}$ (L64, nominal *Mw*=2900 g mol$^{-1}$) and $EO_{132}PO_{50}EO_{132}$ (F108, nominal *Mw*=14600 g mol$^{-1}$).

The macromolecule/RD nanomaterial was prepared by physically mixing RD with the polymer matrix in the molten state. The composition was changed in a wide range and expressed as macromolecule mass percent (mass%).

### *Methods*

The calorimetric measurements were carried out by using a TA Instruments DSC (2920 CE). The heating run was set up at 10°C min$^{-1}$. The melting temperature ($T_m$) was defined as the onset of the melting endotherm peak. The experiments were performed under nitrogen flow atmosphere (flow rate= 60 cm$^3$ min$^{-1}$) from –30 to 160°C temperature range. The sample pan was in aluminum and the reference one was empty. The samples mass was ca. 5 mg. The temperature and the calorimetric calibration procedure was performed by using indium standard (the melting temperature is 156.51°C and the enthalpy of melting is 28.71 J g$^{-1}$).

The X-ray powder diffraction spectra were registered in the range $2° < 2\theta < 60°$ by using a Philips diffractometer (PW1050/39 X Change) equipped with a copper anode (Cu-K$_\alpha$, 1.5418 Å).

## Results and discussion

### *Melting of pure macromolecules*

From the DSC curves for pure PEGs, the enthalpy of melting ($\Delta H^*_m$) was determined and used to calculate the fraction of crystallinity ($x_c$) as $\Delta H^*_m/\Delta H^*_c$ being $\Delta H^*_c$ the enthalpy of melting of 100% crystalline PEG whose value is 204.8 J g$^{-1}$ [24]. The $x_c$ values are high for large molecular masses (Table 1). Note that $x_c$ for PEG 2000 is in a good agreement with the literature one obtained from NMR studies [25]. Based on PPGs measurements $\Delta H^*_m$ of copolymers may reflect only the melting of the EO units in agreement with the behaviour of poly(oxyethylene)-*b*-poly(oxybutylene)/poly(oxybutylene) blends [26] whose crystallinity was calculated by ascribing the melting enthalpy to the EO units. On this basis, enthalpies of melting per gram of poly(ethylene oxide) block (PEO) in the copolymers ($\Delta H^*_{m,\,PEO}$) were calculated and plotted *vs.* the PEO block molecular mass in Fig. 1 where, for a comparison purpose, $\Delta H^*_m$ as a function of the macromolecule molecular mass was also reported. $\Delta H^*_m$ of the copolymers agree with those reported in the literature [27] and are dissimilar from those of PEGs. Such a difference disappears when $\Delta H^*_{m,\,PEO}$ values are compared. Accordingly, a single line can be drawn through the experimental points proving that the PEO block in the copolymer is responsible for the melting and its thermal behaviour is not influenced by the binding with the PPO blocks. These results are consistent with the melting temperature ($T_m$) data reported in Fig. 1. The $x_c$ of the PEO block is high for the large number of EO units.

**Table 1** Enthalpy of melting and crystallinity for pure macromolecule[a]

| Macromolecule | $\Delta H^*_m$ | $x_c$ |
|---|---:|:---:|
| PEG 400 | 73.7 | 0.36 |
| PEG 2000 | 170.2 | 0.83; 0.82[b] |
| PEG 20000 | 197.4 | 0.96 |
| PEG 35000 | 178.6 | 0.87 |
| L64 | 27.3 | 0.34 |
| F68 | 132.5 | 0.81 |
| F108 | 137.0 | 0.84 |

[a]Unit: $\Delta H^*_m$, J g$^{-1}$, [b]From NMR data [25]

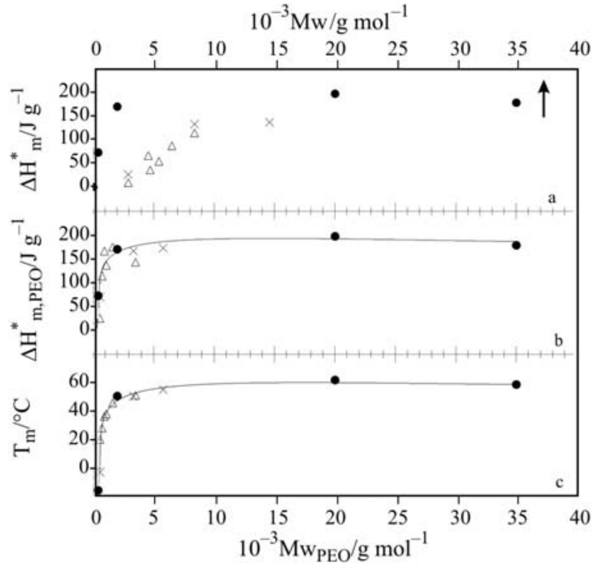

**Fig. 1** **a** – Enthalpy of melting/g of macromolecule as a function of molecular mass of the macrolecule. b – dependence on the poly(ethylene oxide) molecular mass of the melting enthalpy/g of poly(ethylene oxide), c – melting temperature. ● – PEGs, (Δ, x) – copolymers, Δ – data from [27]. x – present work. Lines are guides for eye

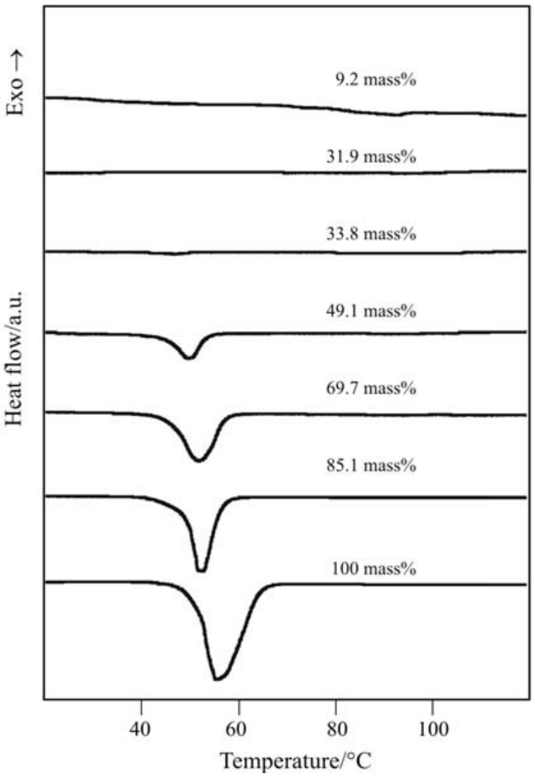

**Fig. 2** DSC curves of PEG 2000/laponite system at 10°C min$^{-1}$ heating rate

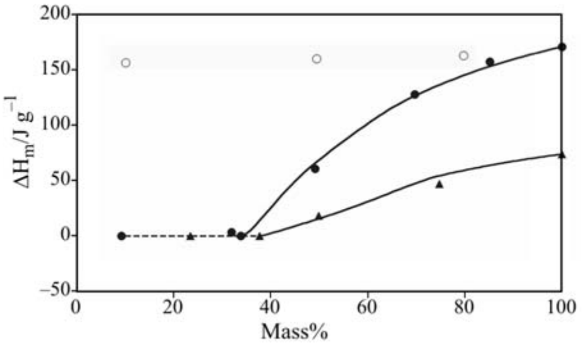

**Fig. 3** Dependence on the polymer mass% of the enthalpy of melting for the systems: ▲ – PEG 400/laponite; ● – PEG 2000/laponite;○ – PEG 2000/NaCl. Lines are calculated according to Eqs 3a – --- and 3b – ––

### *Melting of macromolecules filled with laponite clay*

The addition of RD to the macromolecule matrix generates a shift of the $T_m$ onset towards lower values whereas the profile of the melting endotherms remains unchanged. A similar effect is observed for the copolymers. Examples dealing with the PEG 2000/RD system are illustrated in Fig. 2. The enthalpy of melting ($\Delta H_m$) and $T_m$ as functions of the macromolecule mass% are represented in Figs 3–6. As a general feature, the profile of $\Delta H_m$ is the same regardless of the nature of the system. Namely, $\Delta H_m$ is nearly constant up to a given composition thereafter it increases monotonically reaching the value of the pure macromolecule. As concerns the homopolymers, the $\Delta H_m$ constant values are null for PEGs 400 and 2000 and different from zero for the higher homologues (Figs 3 and 4). The onset of the enthalpy increase takes place at lower compositions the larger is the polymer molecular mass. As concerns the tri-block copolymers (Fig. 5), comparing F68 and F108 turns out that increasing molecular mass, at fixed hydrophilic/hydrophobic ratio, generates an increase of $\Delta H_m$ in the dilute region and a change in the $\Delta H_m$ *vs.* mass% slope in the concentrated domain. The comparison between F68 and L64 shows that the copolymer hydrophobicity strongly influences the $\Delta H_m$ magnitude a consequence of the small crystallinity of L64; moreover, it generates higher $\Delta H_m$ values in the dilute region (Fig. 5). Our results are consistent with the Strawhecker and Manias reports [14] that the presence of montmorillonite fillers causes a decrease of PEG 136000 $\Delta H_m$. Similar results were obtained for the nanocomposites constituted by carbon black and polyethylene of low density [15]. However, contrary to these findings, Chen and Chang [28] reported that the polymer crystallinity increases in the low clay concentration domain.

To verify whether the shape of $\Delta H_m$ *vs.* mass% curve reveals specific interactions, the PEG 2000/NaCl system was investigated. By replacing RD with NaCl generates a linear function of $\Delta H_m$ with the NaCl composition (Fig. 3). A similar result was exhibited by the PEGs/LiClO$_4$ systems [25];

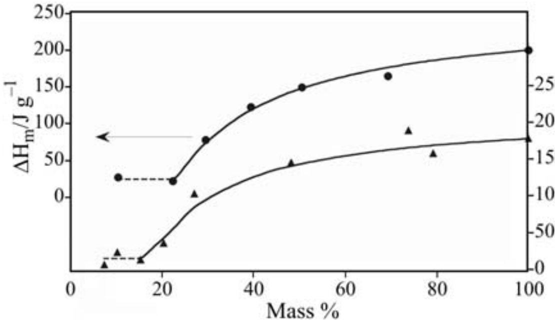

**Fig. 4** Dependence on the polymer mass% of the enthalpy of melting for the systems: ▲ – PEG 35000/laponite; ● – PEG 20000/laponite. Lines are calculated according to Eqs 3a – --- and 3b – —

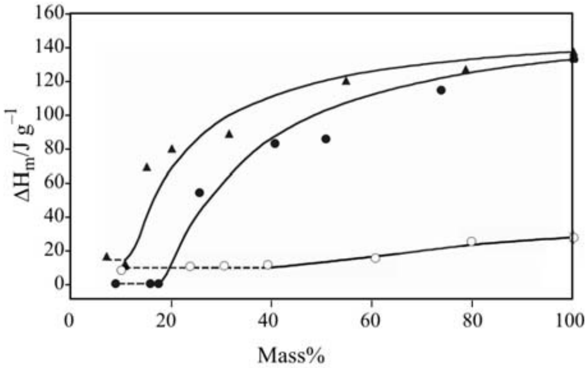

**Fig. 5** Dependence on the copolymer mass% of the enthalpy of melting for the systems: ○ – L64/laponite; ● – F68/laponite; ▲ – F108/laponite. Lines are calculated according to Eqs 3a – --- and 3b – —

the decreased $\Delta H_m$ upon the $LiClO_4$ addition was ascribed to the reduction of the polymer crystallinity that inhibits the crystallization because the polymer reorganizes itself around the small cation [9]. Such an effect likely takes place in the PEG 2000/NaCl system for which $\Delta H_m$ as well as $T_m$ decrease upon the electrolyte addition. More complex seems to be the RD-macromolecule interaction phenomenon somewhat characterized by a critical association composition (cac) in agreement with the break displayed by the enthalpy curve. The value of cac decreases with the macromolecule size for PEGs and for copolymers highlighted by the same EO/PO ratio; moreover, it is larger the more hydrophobic the copolymer is. The quantitative aspect will be treated later.

Finally, the addition of RD to the macromolecule generates a $T_m$ decrease with a slope system specific (Fig. 6). The $T_m$ shifts to lower values for the nanocomposites, based on organomodified montmorillonite and poly(ε-caprolactone), produced by the silicates addition was ascribed to the exfoliated structures of the formed nanomaterials [29].

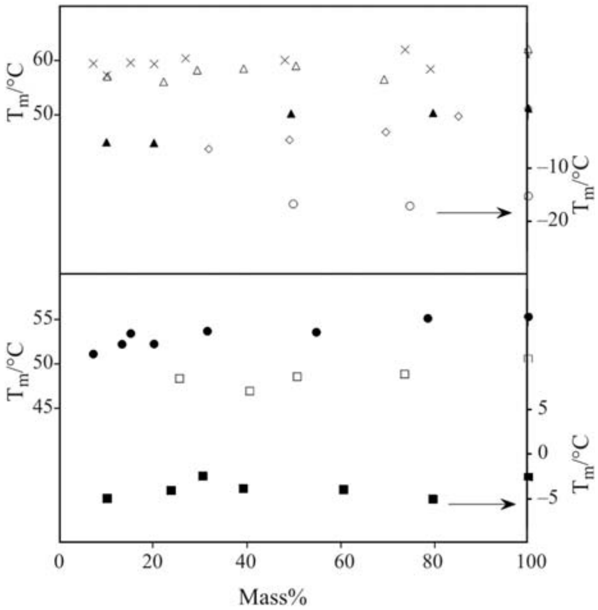

**Fig. 6** Dependence on the polymer mass% of the temperature melting for the systems composed of laponite and x – PEG 35000; △ – PEG 20000; ◇ – PEG 2000; ○ – PEG 400; ● – F108; □ – F68; ■ – L64. The filled triangles refer to the PEG 2000/NaCl system

### *A model for DSC data analysis*

Depending on the nature of the components [8], the association between the layered silicates and the macromolecule may allow to the formation of three main types of composites, i.e., the phase separated microcomposites, the exfoliated nanocomposites and the intercalated nanocomposites. The former are generated when the polymer cannot be intercalated between the silicate sheets. The exfoliated nanocomposites are featured by the silicate layers uniformly dispersed in a continuous polymer matrix whereas the intercalated nanocomposites are characterized by the presence of a single extended polymer chain between layers.

It was reported [30] that PEG intercalated in the phyllosilicates (montmorillonite and hectorite) assumes the helical conformation typical of the crystalline state which is the result of the combination of conformational arrangements [31]. We remind that a pure PEG changes its conformation from helical to disordered when it is melted [31].

It is well recognized that calorimetry is very sensitive to the nature of the interactions and could provide indirect insights on the formed structures. To this aim, the experimental enthalpies (Figs 3–5) have to be modelled. We propose a mechanism of interaction following which some segments of the adsorbed macromolecule are anchored to the RD particles and the remaining segments are radiating away from the surface. The portion of the macromolecule in contact with RD does not contribute to $\Delta H_m$ likely due to either a conformation typical of an amorphous polymer or a crystalline polymer, which cannot melt because of constraints due to the RD anchoring. The portion of macromolecule radiating away from the clay likely possesses the same features of the semicrystalline polymer. Once that the RD surface is saturated, the excess of the macromolecule amount behaves like the pure one. Therefore, one may write

$$\Delta H_m = x_f \Delta H_m^* + (1 - x_f) x_t \Delta H_m^* \qquad (1)$$

where $x_f$ is the fraction of the free macromolecule and $x_t$ is the fraction of the segments away from the RD surface with respect to the total number of segments of the adsorbed molecule and it is a function only of the system nature. The first term at the right hand side of Eq. (1) is the contribution for the melting of the free macromolecule and the second one for the melting of the macromolecule segments radiating away from the RD surface (a sketch representation of this approach is illustrated in Fig. 7). $x_f$ is a function of both the macromolecule mass percent (mass%) and the macromolecule mass percent at the saturation point (cac). In particular

$$x_f = \begin{cases} 0 & \text{up to saturation} \qquad (2a) \\ 1 - \dfrac{\text{cac}}{\text{mass\%}} & \text{above the saturation} \qquad (2b) \end{cases}$$

and $\Delta H_m$ is given by

$$\Delta H_m = \begin{cases} x_t \Delta H_m^* \quad \text{up to saturation} & (3a) \\ \Delta H_m^* - \dfrac{\text{cac}}{\text{mass\%}} (1 - x_t) \Delta H_m^* & \\ \qquad\qquad \text{above the saturation} & (3b) \end{cases}$$

For a given system, Eq. (3a) predicts a constant value and allowed to calculate $x_t$. Equation (3b) predicts a linear decrease of $\Delta H_m$ with 1/mass%. The crossing point between these two straight-lines provides the cac value. Figure 8 shows some examples, which clearly evidence the break points. From the cac value the largest amount of macromolecule which can be associated to 1 g of RD (ω) was calculated as cac/(100–cac). The ω and $x_t$ values are reported in Table 2. Introducing $x_t$, cac and the experimental $\Delta H_m^*$ (Table 1) in Eq. (3b), $\Delta H_m$ was calculated. It is noteworthy that the computed values match very well the experimental points for all the systems (Figs 3–5).

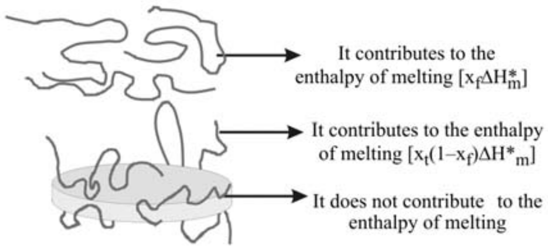

**Fig. 7** Sketch representation of the proposed model

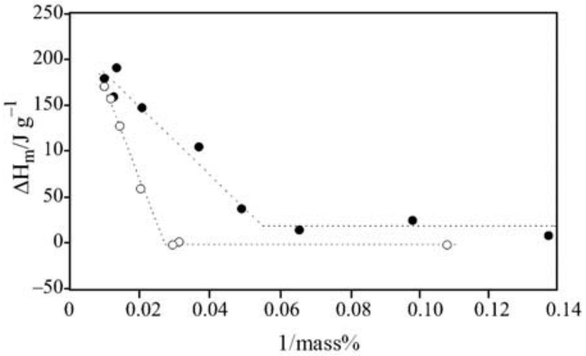

**Fig. 8** Enthalpy of melting as a function of the inverse of the polymer mass% for the ● – PEG 35000/laponite and ○ – PEG 20000/laponite systems

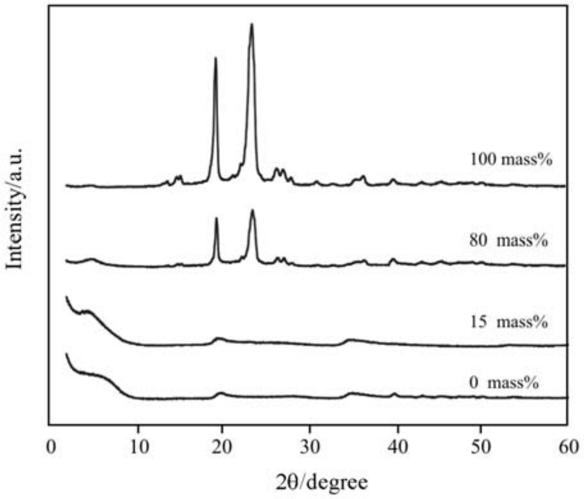

**Fig. 9** X-ray diffraction patterns of laponite/PEG 35000 systems at some polymer mass%

The forces at the macromolecule/RD interface play a relevant role on the stability of the dispersion [5] and their nature can be tuned by varying the macromolecule features. To this purpose, we analyzed PEGs of different size and $EO_aPO_bEO_a$ whose structure was

**Table 2** Parameters for the macromolecule-laponite association

| Macromolecule | ω | $x_t$ |
|---|---|---|
| PEG 400 | 0.787 | 0 |
| PEG 2000 | 0.595 | 0 |
| PEG 20000 | 0.301 | 0.12 |
| PEG 35000 | 0.211 | 0.10 |
| L64 | 0.961 | 0.34 |
| F68 | 0.235 | 0 |
| F108 | 0.142 | 0.10 |

changed systematically. This choice was based on recent [22] thermodynamic and kinetic studies for the adsorption of $EO_aPO_bEO_a$ and their homopolymers at the RD/aqueous solution interface. Even if the previous investigations [22] dealt with aqueous systems, we thought it would be interesting to explore the interactions between RD and some macromolecules in the absence of solvent media.

As concerns the homopolymers, the $x_t$ value is null for PEGs at low molecular mass whereas it is ca. 0.10 for the larger sized homologues. The $x_t$ dependence on the molecular mass reveals that RD establishes the number of ethylene oxide segments that may be in contact with the clay. The lack of melting allowing to null $x_t$ values indicates that short macromolecules are fully in contact with RD. Certainly, the $x_t$ parameter cannot give insight on the issue whether the formed structures are intercalated or not. Therefore, some X-ray experiments were carried out to gain direct information on this aspect. The X-ray diffractogram shows that bare RD does not present ordering (Fig. 9) and it is nearly equal to that registered for powdered RD [32]. The addition of PEG 35000 (15 mass%) makes the clay more ordered, as the diffractogram in the low 2θ regime shows. The lack of diffraction peaks in such a domain allows to rule out the polymer intercalation between the silicate layers. The addition of RD to PEG 35000 (80 mass%) induces a lowering of the intensity of the diffraction peaks (at 19.3 and 23.5°) that is much higher than that expected on the basis of the polymer composition. This suggests that RD plays a relevant effect on the crystalline state of the polymer that is in agreement with the DSC results.

As concerns the copolymers, it turns out that F68 behaves like a PEG at small size ($x_t$=0) and F108 like a PEG at large size ($x_t$=0.1). In other words, for a constant EO/PO ratio, increasing the molecular mass exercises the same effect as that for PEGs. From the comparison between the $x_t$ values for L64/RD and F68/RD (Table 2), one argues that if one fixes the number of PO units, the decrease of PEO block dimension leads to a reduction of the association to RD. Based on the PEO block size, one should expect a nearly null $x_t$ value for L64/RD so that one may deduce that the PO segments exercise a relevant role on the association process with RD opposing to the interactions between the EO units and RD.

Finally, interesting are the ω values. In fact, they discriminate between PEGs and tri-block copolymers (Table 2). In particular, ω decreases in a no-linear manner with PEG molecular mass showing that the saturation of 1 g of RD requires less and less amount of the polymer upon increasing its size. The copolymers behave similarly even if the ω dependence on the molecular mass is different.

## Conclusions

DSC and X-ray diffraction experiments were carried out on dispersions of laponite clay in the PEGs and $EO_aPO_bEO_a$ tri-block copolymers matrices. The PEGs differed for the molecular mass. The copolymers were tuned by modulating the molecular mass, at constant EO/PO ratio, and the hydrophilicity. For all the studied systems, the enthalpy of melting ($\Delta H_m$) is nearly constant up to a given composition thereafter upon further macromolecule addition it increases monotonically reaching the value of the pure macromolecule. When laponite is replaced by NaCl a linear variation of $\Delta H_m$ is observed revealing that a complex laponite-macromolecule interaction phenomenon takes place. We proposed a model to interpret the $\Delta H_m$ data as functions of the copolymer composition. It was proposed an approach following which some segments of the adsorbed macromolecule are anchored to the RD particles and the remaining segments are radiating away from the surface. The portion of the macromolecule in contact with RD does not contribute to $\Delta H_m$ whereas the other part radiating away from the clay does. Once that the RD surface is saturated, the excess amount of the macromolecule behaves like the pure one. The proposed model allowed to compute successfully the $\Delta H_m$ values. The X-ray diffraction experiments revealed the exfoliated structure for the polymer/laponite nanocomposite.

## Acknowledgements

We are grateful to the Ministry of Instruction, University and Research for the financial support. We thank Prof. V. Turco Liveri for giving us the opportunity to perform X-ray diffraction measurements.

## References

1 H. Mark, Plastics, Additives and Compounding, 2 (2000) 34.
2 P. Meneghetti and S. Qutubuddin, Thermochim. Acta, 442 (2006) 74.
3 P. Bébin, M. Caravanier and H. Galiano, J. Membrane Sci., 278 (2006) 35.
4 D. H. Jung, S. Y. Cho, D. H. Peck, D. R. Shin and J. S. Kim, J. Power Sources, 118 (2003) 205.
5 H. Fischer, Mater. Sci. Eng. C, 23 (2003) 763.
6 D. W. Thompson and J. T. Butterworth, J. Colloid Interface Sci., 151 (1992) 236.
7 G. Avery and J. D. F. Ramsay, J. Colloid Interface Sci., 109 (1986) 48.
8 M. Alexandre and P. Dubois, Mater. Sci. Eng., R. Rep., 28 (2000) 1.
9 W. Loyens, P. Jannasch and F. H. J. Maurer, Polymer, 46 (2005) 915.

10 P. B. Messersmith and E. P. Giannelis, Chem. Mater., 6 (1994) 1719.
11 E. P. Giannelis, R. Krishnamoorti and E. Manias, Adv. Polym. Sci., 118 (1999) 108.
12 M. W. Weimer, H. Chen, E. P. Giannelis and D. Y. Sogah, J. Am. Chem. Soc., 121 (1999) 1615.
13 F. Chavarria and D. R. Paul, Polymer, 45 (2004) 8501.
14 K. E. Strawhecker and E. Manias, Chem. Mater., 15 (2003) 844.
15 A. Danch and W. Osoba, J. Therm. Anal. Cal., 84 (2006) 331.
16 D. Y. Yang, Q. X. Liu, X. L. Xie and F. D. Zeng, J. Therm. Anal. Cal., 84 (2006) 355.
17 H. Fukushima, L. T. Drzal, B. P. Rook and M. J. Rich, J. Therm. Anal. Cal., 85 (2006) 235.
18 W. Loh, Encyclopedia of Surface and Colloid Science; A. T. Hubbard, Ed.; Marcel Dekker: New York, 2002; p. 802.
19 R. De Lisi, G. Lazzara, R. Lombardo, S. Milioto, N. Muratore and M. L. Turco Liveri, J. Solution Chem., 35 (2006) 659.
20 R. De Lisi, G. Lazzara, S. Milioto and N. Muratore, J. Colloid Interface Sci., 300 (2006) 368.
21 G. Lazzara, M. Gradzielski and S. Milioto, Phys. Chem. Chem. Phys., 8 (2006) 2299.
22 R. De Lisi, G. Lazzara, R. Lombardo, S. Milioto, N. Muratore and M. L. Turco Liveri, Phys. Chem. Chem. Phys., 7 (2005) 3994.
23 R. De Lisi, G. Lazzara, S. Milioto and N. Muratore, Langmuir, 22 (2006) 8056.
24 E. L. Chaikof and E. W. Merrill, Net. Polym. Mater., 2 (1990) 125.
25 T. H. Joykumar Singh and S. V. Bhat, Bull. Mater. Sci., 26 (2003) 707.
26 J. Xu, J. P. A. Fairclough, S. Mai, A. J. Ryan and C. Chaibundit, Macromolecules, 35 (2002) 6937.
27 F. Zhang and B. Stühn, Colloid Polym. Sci., 284 (2006) 823.
28 H. W. Chen and F. C. Chang, Polymer, 42 (2001) 9763.
29 P. B. Messersmith and E. P. Giannelis, J. Polym. Sci.: Part A Polym. Chem., 33 (1995) 1047.
30 P. Aranda and E. Ruiz-Hitzky, Chem. Mater., 4 (1992) 1395.
31 Y. Dong, J. B. Dixon and G. N. White, Colloid Polym. Sci., 284 (2006) 347.
32 T. N. Blanton, D. Majumdar and S. M. Melpolder, Advances X-ray Analysis, 42 (2000) 562.

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DOI: 10.1007/s10973-006-7814-9