DOI: 10.1002/masy.200951222

Effect of a Nanodispersed Clay Fillers on Glass Transition of Thermosetting Polyurethane

C. Esposito Corcione, A. Maffezzoli, D. Cannoletta*

In this work polyurethane (PU) matrix nanocomposite, obtained using an organically modified montmorillonite (OMM), was synthesized and characterized. An amount of organoclay ranging from 2% up to 6% by volume was added to the polyol component of the resin before mixing with isocyanate. The microstructure of the composites was investigated by X-ray diffraction. The glass transition temperature (T_g) of PU nanocomposites, measured using differential scanning calorimeter, increases with increasing the volume fraction of OMM. On the other hand, the heat capacity increment, ΔC_p, decreases from that the unfilled PU to that of the sample with 5.7% vol of OMM. Therefore a corresponding increase of the rigid amorphous fraction of PU nanocomposites with nanoclay was observed. Finally, the definition of molecular cooperativity was discussed for this system and the characteristic length of the cooperative region was determined, using the approach proposed by Donth.

Keywords: nanocomposites; polyurethanes; rigid amorphous fraction

Introduction

Polyurethanes (PUs) are unique polymeric materials with a wide range of physical and chemical properties with applications as coatings, adhesives, fiber, foams and elastomers.[1] Since polyurethane/clay nanocomposite was introduced by Pinnavia,[2] many polyurethane/clay nanocomposite have been proposed.[3–8] In contrast to micro composites, impressive improvements in performance were achieved with a small amount of filler. This was ascribed to the high aspect ratio of the exfoliated clay layers. The most studied nanocomposites are composed of thermoplastic or thermosetting matrix and an organically modified montmorillonite (OMM).[9–13] Natural montmorillonite consisted of layers made up of two silicate tetrahedron fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The physical dimensions of these platelet-like shaped silicate layers were typically of about 100 nm in diameter and 1 nm in thickness. Isomorphic substitution within the layers generates negative charges that are normally counter-balanced by cations (Na^+, $Ca^{2+,}$ K^+) residing in the interlayer galleries space.[14] Since momtmorillonite is hydrophilic and it is characterized by a poor affinity with hydrophobic organic polymers, organic cations such as alkylammonium cations are used to change the originally hydrophilic silicate interlayer spacing into a hydrophobic surface. The organic cations lower the surface energy of silicate layers and enhance the miscibility between the silicate layers and the polymer matrix.[15–19]

In this work nanocomposite obtained using an organically modified montmorillonite (OMM) in a polyurethane matrix was synthesized and characterized. The microstructure of the composites was investigated by X-ray diffraction. The glass transition temperature T_g of PU nanocomposites, was measured together with the heat capacity increment, ΔC_p, using differential scanning calorimeter (DSC). The rigid amorphous fraction of the PU nanocomposites was

---

Dipartimento di Ingegneria dell'Innovazione, Università del Salento Via Monteroni 73100, Lecce, Italia
E-mail: carola.corcione@unile.it

calculated and it increases with increasing volume fraction of OMM. Finally, the definition of molecular cooperativity was discussed for this systems and the characteristic length of the cooperative region was determined, using Donth equation.

Experimental Part

Materials

The organoclay, supplied by Laviosa (Livorno, Italy), are commercially available as Dellite HPS and Dellite 43B. Dellite HPS is a purified unmodified natural montmorillonite, while Dellite 43 B is an OMM derived from natural montmorillonite especially purified and modified with a high content of dimethyl benzylhydrogenated tallow ammonium salt.

A two-component aromatic polyester based polyurethane consisting of a prepolymer and 60% solution of an aromatic polyester polyol in ethyl acetate was used. The cross-linker, Polurene FP 75 consisted of an aromatic isocyanate TDI/TMP (toluene diisocyanate - trimetylpropane). The polyol Polurene FP28A is a copolymer of isophthalic acid and di-ethylene glycol. Polurene FP 28A and FP 75 are the components of a solvent based adhesive currently used for flexible food packaging and technical laminates.

Nanocomposites were obtained through in situ intercalative polymerization method.[20]

Characterization Techniques

- Wide Angle X-ray diffraction (WAXD) were collected on a PW 1729 Philips, using Cu Kα radiation in reflection mode ($\lambda = 0.154$ nm).The samples were step-scanned at room temperature from $2\theta = 1.3^\circ$–10° in order to determine the d-spacing of organoclay, Polyol-OMM systems and nanocomposites. The samples were held in the diffractometer using a socket glass sample holder.
- Glass transition temperature (T_g) of PU nanocomposites was measured using differential scanning calorimeter (DSC METTLER 622 Toledo). Dynamic scans have been run between $-100\,^\circ$C and $50\,^\circ$C at $10\,^\circ$C/min under nitrogen atmosphere. The samples were analyzed by DSC after curing (performed at room temperature and hence above T_g) cooling the samples down to $-100\,^\circ$C at $10\,^\circ$C/min. Measurements were performed using samples of about 20 mg. The instrument was calibrated with indium and zinc for temperature and enthalpy measurements, and with sapphire for specific heat measurement, using a heating rate of $10\,^\circ$C/min. The DSC experiments were repeated at least three times to check the repeatability of results.

Results and Discussion

Organofiller Characterization

The results of X-ray diffraction patterns and thermogravimetric analysis of unmodified and modified montmorillonite samples, Dellite HPS and Dellite 43B respectively are reported in Table 1.

Polyol-OMM Mixtures

A comparison between the X-ray diffraction patterns of Dellite 43B and the nanofilled polyol obtained by mixing intercalation with Dellite 43B is reported in Figure 1.

XRD patterns of samples filled with 2.1% vol., 4.2% vol. and 5.7% vol., clearly show that the original peak of silicate Dellite 43B is shifted to angle smaller than $2\theta = 1.3^\circ$ (corresponding to a d-spacing > 6.7 nm). This suggests that the organoclay, during mixing with the polyol, was at least intercalated with a lamellar spacing higher than 6.7 nm or it was exfoliated.

Table 1.
Physical properties of Dellite 43B and Dellite HPS

Sample	Volume fraction of organic content x_{org} (%)	2Θ	d-spacing (nm)
HPS	0	6.8°	1.3
43B	28.9%	4.7°	1.9

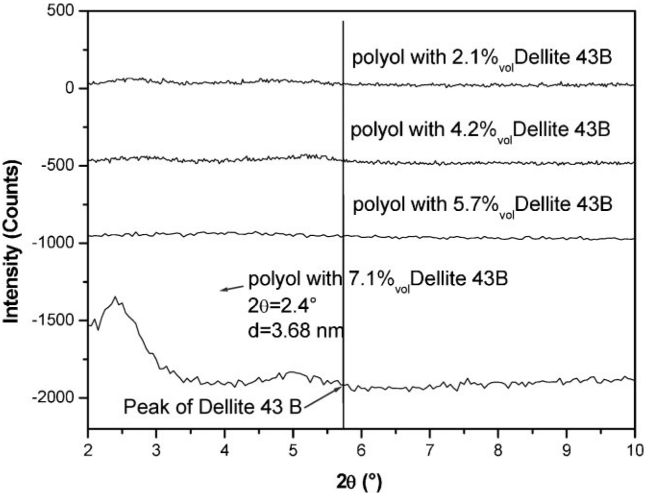

Figure 1.
X-ray diffraction patterns of Dellite 43B and polyol filled with different concentration of the same nanofiller.

The sample filled with 7.1% vol. of OMM shows a peak centered at about $2\theta = 2.4°$, corresponding to a d-spacing of 3.68 nm. This indicates that the OMM was intercalated during mixing, but intercalation is less efficient than in the case of samples filled with a higher content of OMM. Nevertheless, the presence of exfoliated OMM even in this sample cannot be excluded.

Polyol Nanocomposite Crosslinking and Characterization

The viscosity of the polyol nanocomposite was reduced adding ethyl acetate and then the isocyanate curing agent. Curing was performed at room temperature for 1 week. The basal distances of crosslinked PU nanocomposites, obtained by X-ray diffraction are reported in Figure 2.

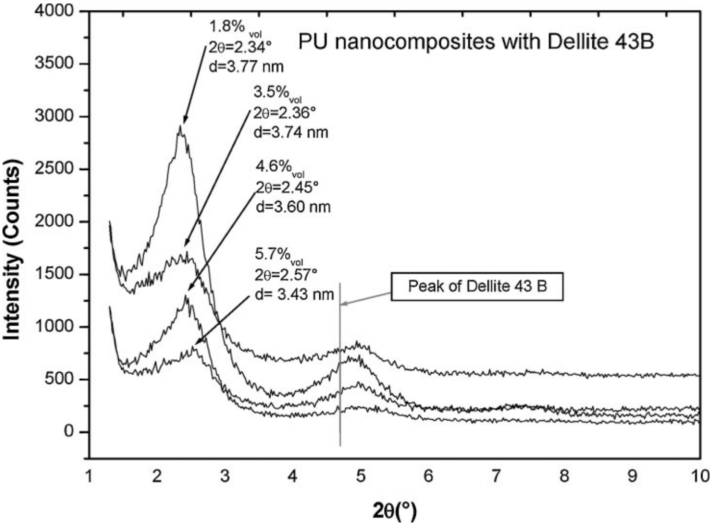

Figure 2.
XRD patterns of PU nanocomposites with 43 B.

The comparison between XRD spectra of Figure 1 and Figure 2 obtained on the polyol and on the crosslinked polyurethane respectively shows a reduction of basal distance, even if it is still higher than that of neat OMM. Diffraction peaks at higher angles indicate that the addition of the solvent is probably responsible of decreases of the lamellar spacing. The higher affinity of polyol toward ethyl acetate with respect to ammonium salts, is likely to determine its extraction from the OMM interlamellar galleries, resulting in a d-spacing decrease.[20]

Nanocomposites Thermal Properties

The glass transition temperature T_g of PU nanocomposites were measured using differential scanning calorimeter as half step temperature. T_g increases from 238 K for the unfilled polyol to 241 K for the crosslinked polyurethane. Increasing the OMM content, T_g reaches 254.2 K for the sample with 5.7%vol of Dellite 43B. The corresponding specific heat (C_p) change, calculated as the step height, has shown in Figure 3. On the other hand, the change at T_g of heat capacity, ΔC_p, normalized to the weight of the overall organic fraction, given by PU and organic modifier of the clay, decreases from 1.02 J/gK for the unfilled polyol to 0.74 J/gK for the sample with 5.7%vol of Dellite 43B, as reported in Table 2. As shown in Figure 4, the decrease of ΔC_p with T_g follows the behavior suggested by Boyer for crosslinked polymers [21]:

$$\Delta c_p = a + \frac{b}{T_g} \tag{1}$$

This result indicates that an analogy between nanofilled and crosslinked polymers can be drawn. In this case, many polymer chain segments interacts with the surface of OMM that acts as additional crosslinking points in the PU matrix, leading to a decrease of the ΔC_p.

A rigid amorphous fraction x_{ra} [22,23] can be calculated as the ratio between the change of heat capacities of filled PU $\Delta C_p(f)$ to that of unfilled one, $\Delta C_p(u)$:

$$x_{ra} = 1 - \frac{\Delta C_p(f)}{\Delta C_p(u)} \tag{2}$$

The values of x_{ra} calculated with Equation 2 are also reported in Table 2. The rigid amorphous fraction of the PU nanocomposites increases with increasing volume fraction of Dellite 43B. The segmental mobility is significantly reduced as OMM increases indicating that chains immobilization occur when they are intercalated between OMM lamellae. This behavior can

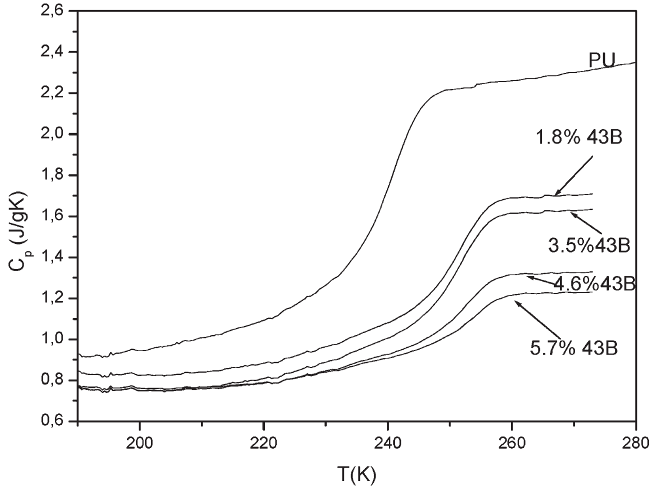

Figure 3.
Comparison between C_p curves of unfilled PU with PU filled with Dellite 43B.

Table 2.
Thermal parameters of all samples of nanocomposites and cooperativity length ε_α calculated from Donth equation

PU with %vol Dellite 43B	T_g(°K)	Δc_p (J/gK) Normalized to PU and organic modifier weight	X_{ra}	ΔT (K)	ξ_α(nm)
0	241 ± 4.8	1.02 ± 0.09	0	15.89 ± 0.032	1.1 ± 0.02
1.8	248.6 ± 4.5	0.88 ± 0.081	0.14 ± 0.01	15.01 ± 0.022	1.3 ± 0.01
3.5	251.9 ± 5.2	0.80 ± 0.09	0.22 ± 0.02	15.13 ± 0.04	1.3 ± 0.03
4.6	252.9 ± 2.8	0.79 ± 0.053	0.23 ± 0.009	15.21 ± 0.07	1.3 ± 0.011
5.7	254.2 ± 5.2	0.74 ± 0.09	0.28 ± 0.06	17.37 ± 0.05	1.2 ± 0.05

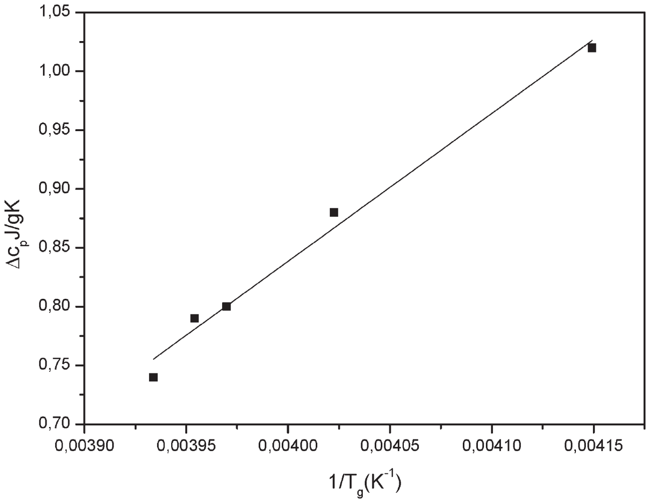

Figure 4.
Comparison between experimental data of ΔC_p of unfilled PU and PU filled with Dellite 43B as function of $1/T_g$ with that of Boyer model.

be compared to those of semi crystalline polymer where a rigid amorphous fraction is typically observed.[24–29] Similarly OMM lamellae can act similarly to lamellar chain folded crystals presenting polymer molecules partially immobilized and even bridging two OMM stacks. x_{ra} increases mainly when 1.8% of OMM was added. Any further increase of x_{ra} with OMM amount is less dramatic, indicating a lower efficiency of the dispersion. In other words a lower number of PU chain is intercalated for each additional fraction of OMM added to the PU. Two competing models exist to describe the organization of the lamellae of a semi crystalline polymer within the spherulites, i.e. the Heterogeneous Stack Model, HET,[30] and the Homogeneous Stack Model, HSM.[31]The characteristic length, ξ_α of a cooperativity rearranging region (CRR), defined by as a subsystem of the sample which, upon a sufficient fluctuation in energy, can rearrange into another configuration independently of its environment, was also calculated, using Donth equation:

$$\xi_\alpha = \sqrt[3]{3 * \frac{k_B T_g^2 \Delta C_p}{\pi * ((C_p^l + C_p^g)^2 * (\delta T)^2 * \rho))}} \tag{3}$$

Where C_p^l and C_p^g are respectively the heat capacities of liquid and glass, k_B is the Boltzmann constant, δT is the mean temperature fluctuation, estimated the from the width of the glass-transition step ΔT as $\delta T \cong 0.4\Delta T$ and ρ is the mass density of the bulk.

The values of ξ_α, calculated with Equation 3 and reported in Table 2 are of the same order of those calculated for semi crystalline polymers [26] and for other clay nanocomposites.[32] ξ_α has a very limited change when OMM is added to the PU. This could be associated with the presence in the nanocomposite of free chain segments and of freezed molecules. The former are affected by the OMM only in terms of activation energy of segmental mobility, showing ξ_α values equal to those of neat PU. The last are intercalated chain segments completely immobilized and responsible of the rigid amorphous fraction. These results indicate that HET model is probably more suitable to explain the behavior of these nanocomposites at T_g. Therefore the higher T_g can be explained assuming that the nano dispersed filler is responsible of higher energy barrier to chain mobility but it does not limit the size of CRR.

Conclusion

Nanocomposite obtained using a montmorillonite, modified with organic cations, in a polyurethane matrix were synthesized and characterized. A mix of exfoliated and intercalated layers was observed in all composites according to the structural and macroscopic properties of the nanocomposites. A significant increase of T_g of nanocomposites with OMM content was also observed, confirming the good dispersion of the nanofiller. The intercalation of polyester polyol between OMM lamellae was easily achieved by mixing. The decrease of the heat capacities with the glass transition temperature follows the behavior predicted by the Boyer equation. The presence of a significant fraction of rigid amorphous was revealed by calorimetric analysis. In analogy with the interpretation of rigid amorphous fraction used for semi crystalline polymers the Heterogeneous Stack Model was considered closer to the behavior of these nanocomposites. Furthermore a substantially constant value of the characteristic size of the cooperativity rearranging region at T_g was calculated.

Acknowledgements: This work has been funded by Italian government under the project Prin 04 ‘‘Polyurethane based adhesives and coatings for flexible packaging modified with nanofillers’’.

[1] K. Byung Kyu, J. W. Seo, H. M. Jeong, *European Polymer Journal* **2003**, *39*, 85.
[2] Z. Wang, T. J. Pinnavia, *Chem Mater* **1998**, *10*(12), 3769.
[3] C. Zilg, R. Thomann, R. Mulhaupt, *J. Adv Mater* **1999**, *11*(1), 49.
[4] K. J. Yao, M. Song, D. J. Hourston, D. Z. Luo, *Polymer* **2002**, *43*(3), 1017.
[5] T. K. Chen, Y. I. Tien, K. H. Wei, *J. Polym Sci: Polym Chem* **1999**, *37*(13), 2225.
[6] T. K. Chen, Y. I. Tien, K. H. Wie, *Polymer* **2000**, *41*(4), 1345.
[7] Y. I. Tien, K. H. Wie, *Polymer* **2001**, *42*(7), 3213.
[8] Y. I. Tien, K. H. Wie, *Macromolecules* **2001**, *34*(26), 9045.
[9] S. Komarneni, *J. Mater Chem.* **1992**, *2*, 1219.
[10] H. Gleiter, *Adv Mater* **1992**, *4*, 474.
[11] B. M. Novak, *Adv Mater* **1993**, *5*, 422.
[12] R. F. Ziolo, E. P. Giannelis, B. A. Weinstein, M. P. O'Horo, B. N. Granguly, V. Mehrota, M. W. Russel, D. R. Huffman, *Science* **1992**, *257*, 219.
[13] F. Bauera, H.-J. Glasela, E. Hartmanna, H. Langgutha, R. Hinterwaldner, *International Journal of Adhesion & Adhesives* **2004**, *24*, 519.
[14] L. Torre, E. Frulloni, J. M. Kenny, C. Manferti, G. Camino, *J Appl Polym Sci* **2003**, *90*, 2532.
[15] K. Yano, A. Usuki, A. Okada, T. Kurauchi, O. Kamigaito, *J. Polym Sci, Part A: Polym Chem* **1993**, *31*, 2493.
[16] As Moet, A. Akelah, *Mater Lett* **1993**, *18*, 97.
[17] L. P. Meier, R. A. Shelden, W. R. Caseri, U. W. Suter, *Macromolecules* **1994**, *27*, 1673.
[18] M. W. Noh, D. C. Lee, *Polm Bull* **1999**, *42*, 619.
[19] F. Dietsche, R. Mullaupt, *Polym Bull* **1999**, *43*, 395.
[20] C. Esposito Corcione, P. Prinari, D. Cannoletta, G. Mensitieri, A. Maffezzoli, *International Journal of Adhesion & Adhesives* **2008**, *28*, 91.
[21] R. F. Boyer, *Macrolol. Sci. Phys.* **1973**, *B-7*, 487.
[22] C. Schick, E. Donth, *Phys. Scr.* **1991**, *43*, 423.
[23] B. Hahn, J. Wendorff, *Macromolecules* **1985**, *18*, 718.
[24] X. Lu, P. Cebe, *Polymer* **1996**, *37*, 4857.
[25] S. Iannace, A. Maffezzoli, G. Leo, L. Nicolais, *Polymer* **2001**, *42*, 3799.
[26] H. Xu, P. Cebe, *Macromolecules* **2004**, *37*, 2797.

[27] A. Minakov, D. Mordvintsev, R. Tol, C. Schick, *Thermochim Acta* **2006**, *442*, 25.
[28] A. Saiter, N. Delpouve, E. Dargent, J. M. Saiter, *European Polymer Journal* **2007**, *43*, 4675.
[29] N. Delpouve, A. Saiter, J. F. Mano, E. Dargent, *Polymer* **2008**, *49*, 3130.
[30] B. B. Sauer, B. S. Hsiao, *Polymer* **1995**, *36*(13), 2553–2558.
[31] C. Alvarez, I. Sics, A. Nogales, Z. Denchev, S. S. Funari, T. A. Ezqurra, *Polymer* **2004**, *45*, 3953.
[32] H. Xia, M. Song, *Thermochimica Acta* **2005**, *429*, 1.