

Improvement of Nanoclays Dispersion Through Microwave Processing in Polyurethane Rigid Nanocomposite Foams

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ABSTRACT: Polyurethane rigid nanocomposite foams were synthesized by *in situ*-polymerization using both pristine and organically modified layered silicates. The effect of synthesis conditions, in particular the effect of different dispersing techniques, on morphology and mechanical properties of polyurethane nanocomposite foams was studied. To promote dispersion, clays were dispersed either in polyols or isocyanate and were subjected to a well known dispersion method, like ultrasonication, but also to a new dispersion method, based on microwaving. The morphological characterization of the foams, carried on using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy, proved that the technology based on

microwave processing is able to provide very good silicates dispersion and requires very short application time to be effective. Further confirmations of the importance of the clay organo-modifier are still present. Mechanical characterization of foams show that clay interferes with H-bond formation and then the overall compressive performance of PU nanocomposite foams depends on the competition between the positive reinforcing effect of clay and the negative effect on H-bond formation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3667–3674, 2010

Key words: polyurethanes; nanocomposites; foams; thermosets; microwave; mechanical properties

INTRODUCTION

Nanocomposites based on thermoset polymers are mainly obtained by *in situ* intercalative polymerization method: the layered silicate is swollen within the liquid monomer or prepolymer so the polymer formation can occur between the intercalated sheets. During swelling, the monomer diffuses from the bulk into the galleries between the silicate layers. Depending on the degree of penetration of the monomer into the layered silicate structure, different types of nanocomposites can be obtained ranging from intercalated to exfoliated or delaminated. To obtain the beneficial properties of the large surface area of the dispersed phase in nanocomposites, nanoparticles must be fully dispersed at nanolevel. The dispersion of silicate in the liquid monomer may be aided using several techniques such as high speed stirrer, high shear mixer and, more commonly, ultrasonication.^{1–4}

The different effectiveness of various dispersion techniques such as high shear mixer, high speed stirrer, and sonication were reported for elastomeric

polyurethane by Rhoney et al.,¹ who showed that both high shear and sonication are able to provide a reinforcing effect, albeit a slight one, to the polymer matrix. Evidence for the reinforcement effect is demonstrated as an increase in magnitude of the bending modulus below the glass transition temperature for both sets of results. High shear mixing, however, does not offer as much clay surface area to the polymer matrix as does the sonication method. Similar conclusions were reached also by Gintert et al.,² comparing magnetic stirring, high intensity mixing blade, and ultrasonication bath for dispersion of clay in polyimide resin solution. Sometimes, to increase monomer viscosity for transferring more effectively shear stress to a secondary phase, particular methodology, like a cryo-compounding, has been used as reported by Koerner et al.³ The key idea of cryo-compounding lies on maximizing thermoset viscosity by halting cure before gelation and by compounding at subambient temperatures near the resin's glass transition temperature. High shear forces, due to the very high viscosity of the system, facilitate homogenization of the layered silicate nanocomposite in the thermoset, as confirmed by TEM results.

Dealing with a particular class of thermoset polymers, i.e., polyurethane foams, reported papers^{5–15} proposed long time mechanical stirring or ultrasound treatment for developing polyurethane foam

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nanocomposite. Mondal et al.⁹ dispersed the clay first in polyol by stirring it for 48 h at 80°C; Harikrishnan et al.¹⁰ mixed polyol and clay for 24 h at 60°C with mechanical stirrer. Xu et al.¹¹ mixed the appropriate content of dried organoclay powder with 100 g polyether polyols for 2 min at ambient temperature, and subsequently applied an oil bath sonication to the suspension of organoclay in polyether polyols at 50°C for 2 h. Patro et al.¹³ dispersed clay in either polyol or isocyanate in a 1-L closed stainless steel container for 24 h at 60°C by gentle stirring, using a mechanical stirrer. Kabir et al.,¹⁴ dealing with carbon nanofibers/polyurethane foam composite, used high-intensity ultrasonic horn (Ti-horn, 20 kHz, and 100 W/cm²) for dispersing clay in polyurethane raw materials and found out that there is an optimum sonication time depending on sonication power, base amount material and wt % of filler used: for example, to obtain polyurethane foams with the highest yield strength, the best sonication time for 100 g of material comprising 0.5 g of carbon nanofibers is 22 min.

In this work we propose a new dispersion method, which has never been proposed in literature to our best knowledge, to obtain very good clay dispersion based on microwave processing: it will be shown that this technique is able to provide very good silicate dispersion and requires very short application time to be effective, in spite of very long treatments required when sonication is used. Microwave irradiation is a very efficient heating method, which provides similar heating inside and outside of a substance. For this reason, it has recently been used in nanocomposites synthesis for the initiation of in situ polymerization or curing process as it provides a fast heating, allowing similar intragallery and extragallery polymerization (or curing) rate.^{16–19} This is a very important feature as exfoliated structures are successfully obtained when sufficient intragallery polymerization takes place.²⁰ In this article we show that this technique may be usefully employed not only for initiation of polymerization or curing, as already reported, but also for promoting intercalation and exfoliation of the clays in PU raw materials (both polyols and isocyanate). Comparison with well-known sonication technique will be drawn. Moreover, the effect of different synthetic route will also be considered.

EXPERIMENTAL

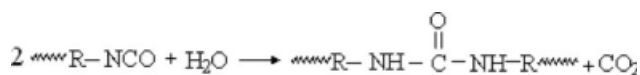
Materials

The raw materials employed in foam synthesis were:

- polymeric MDI (methane diphenyl diisocyanate) Voranate M600 supplied by Dow Chemicals

characterized by NCO% = 30.5, average functionality = 2.8, viscosity to 25°C = 600 mPa s;

- a mixture of polyester polyols (Isoexter 4530, supplied by Coim, Italy, with hydroxyl value = 510 mgKOH/g, viscosity to 25°C = 11000 mPa s and Isoexter 4537 supplied by Coim, Italy, with hydroxyl value = 350 mgKOH/g, viscosity to 25°C = 4900 mPa s) and a polyether polyol, Voranol RN 490 supplied by Dow Chemicals with hydroxyl value = 490 mgKOH/g, viscosity to 25°C = 6000 mPa s;
- catalysts: Polycat 8, i.e., *N,N*-dimethyl cyclohexylamine (DMCHA), and Polycat 5, i.e., pentamethyl-diethylene triamine (PMDETA), both supplied by Air Products;
- surface-active agent: polysiloxane-polyether copolymer (Tegostab B8471) supplied by Goldschmidt, Italy;
- blowing agent: blend of 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane (Solkan 365/227, Solvay Fluor) and water reacting with isocyanate lead to the formation of CO₂:



The amount of blowing agent used was calculated to obtain foams with a density of $32 \pm 1 \text{ kg/m}^3$.

The layered silicates employed are: Dellite LVF (LVF): intensively purified natural montmorillonite (MMT), supplied by Laviosa Chimica Mineraria (Livorno, Italy); mean dimension 7–9 μm; Cloisite 30B (C30B): bis(2-hydroxyethyl)methyl tallow ammonium modified montmorillonite, supplied by Southern Clay Products, mean dimension 6 μm.

Synthesis methodology

Foams were prepared according to different routes, using a two step procedure. First, a constant amount of clay (5 wt % on total foam mass), which was previously dehydrated overnight in a oven at 110°C, was dispersed in polyols mixture or crude isocyanate; ultrasonication or microwave treatments were used to help dispersion. Ultrasonication was performed using a sonication apparatus that provides a maximum sonication power of 300 W with a frequency of 40 kHz, while microwave treatment was done by a microwave oven (700W power, 2.45 GHz). According to some early trials, ultrasonication was applied for 100 min, whereas microwave treatment for 2 min. In particular, microwave processing was applied through 15 s step, followed by intermediate cooling to 50°C using a water/ice/acetone bath, because, on the contrary, a quick temperature increase was observed (without intermediate cooling the polyol or isocyanate temperature reached 220°C).

The total time required for microwave processing, including intermediate cooling steps, was 5 min. In case of ultrasonication processing, the mixture temperature has never exceeded 55°C and therefore no intermediate cooling was carried out.

Foams for which clay was dispersed in polyols were prepared as follows. Initially the clay was dispersed in the polyols by either sonication or microwave treatment using conditions reported earlier. After that, the required amounts of blowing agent, water, catalysts, and surfactant were added to the dispersion and stirred for 1 min; then the polyols mixture was mixed thoroughly with predetermined amount of isocyanate for 15 s using a high-speed stirrer and then poured into an open mold for free rise polymerization. For foams made by dispersing the clay in isocyanate, clay, previously dried, was added to isocyanate in a sealed container and then subjected to either sonication or microwave treatment. The clay-dispersed isocyanate was stirred with the polyol mixture (containing polyols, surfactant, water, catalysts and blowing agent) for 15 s using a high-speed stirrer and then poured into an open mold for free rise polymerization. After preparation, each foam was kept in an oven at 70°C for 24 h, to complete the polymerization reaction. After conditioning, several samples have been cut to carry on characterization.

In the nomenclature adopted here to describe the foams, the clay type (C30B or LVF), the dispersion treatment (ultrasonication US, or microwave MW) and the dispersing medium (polyols, POL, or isocyanate, ISO) are indicated. For example the nomenclature C30B_US_POL indicates foam comprising C30B clay (constant amount 5 wt %), subjected to ultrasonication treatment after dispersion in polyols, while LVF_MW_ISO indicates foam comprising Dellite LVF (constant amount 5 wt %), subjected to microwave treatment after dispersion in isocyanate.

Characterizations

To assess potential reaction between hydroxyl groups contained in the organo-modifier of C30B and -NCO group of isocyanate, mixtures based on this clay and isocyanate were analyzed by Fourier transform infrared spectroscopy (FTIR). FTIR spectra were collected on a Nicolet Nexus 670 (Thermo Scientific), using 32 scans between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} . Also FTIR spectra of foams prepared have been collected by using KBr disks.

Morphological characterization of the foams was carried on through X-ray Diffraction analyses which were performed on a XPERT equipped with a $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation source; XRD experiment were carried on both clay powders and polyurethane nanocomposite foams. The degree of intercalation

and delamination were monitored also by Transmission Electron Microscope (TEM, Philips mod. EM 208). Samples for TEM analyzes were cut from ultrathin specimens using a Leica Ultracut UCT microtom. The morphology of the foams has been studied also by means of E.S.E.M. (environmental scanning electron microscope, Philips XL 30). The material has been cut with a razor blade and then analyzed; the accelerating voltage is set at 20kV to avoid degradation of the sample.

The compressive strength of the foams were measured according to ASTM D1621 using a Galdabini Sun 2500 dynamometer on $50 \times 50 \times 50 \text{ mm}$ specimens, using a crosshead speed of 5 mm/min.

RESULTS AND DISCUSSION

The reaction between layered silicates like as C30B and isocyanate has already been proved by several authors for different synthetic conditions^{6,21,22}; in this study, we will find out if the synthesis condition used here are such that this reaction takes place. For doing that, the evaluation of new groups' formation was carried on through Lambert-Beer's law. Using this one, for samples of unknown optical path, semi-quantitative analyses may be carried on employing the following relation²³:

$$\frac{A}{A_{\text{ref}}} = \frac{\varepsilon \times b \times C}{\varepsilon_{\text{ref}} \times b \times C_{\text{ref}}}$$

where A = absorbance [dimensionless], ε = extinction coefficient [L/mol mm], b = optical path [mm] and C = concentration [mol/L]; the subscript "ref" refers to an internal standard, that is a chemical group which does not take place to reaction and then has a constant concentration in different samples. This relation shows that the ratio between absorbance height or area is proportional to the ratio between concentrations. In our study, the reference group (i.e., the internal standard) is the aromatic ring which shows an absorbance peak at 1607 cm^{-1} ; we analyzed also the concentration of $-\text{N}=\text{C}=\text{O}$ group (2275 cm^{-1}), which may decrease due to isocyanate reaction, and concentration of carbonyl group (1721 cm^{-1}) which may increase due to the reaction of isocyanate with hydroxyl group of organomodifier of C30B or bonded water.²²⁻²⁴

FTIR spectra for neat methane diphenyl diisocyanate (MDI) and its mixtures with constant amount of C30B, treated under different conditions (i.e., ultrasonication, MDI_C30B_US, or microwave process, MDI_C30B_MW) are reported in Figure 1; the ratios between absorbance area of specific peak and internal standard (ref, 1607 cm^{-1}) are reported in Table I. Considering semiquantitative measurements

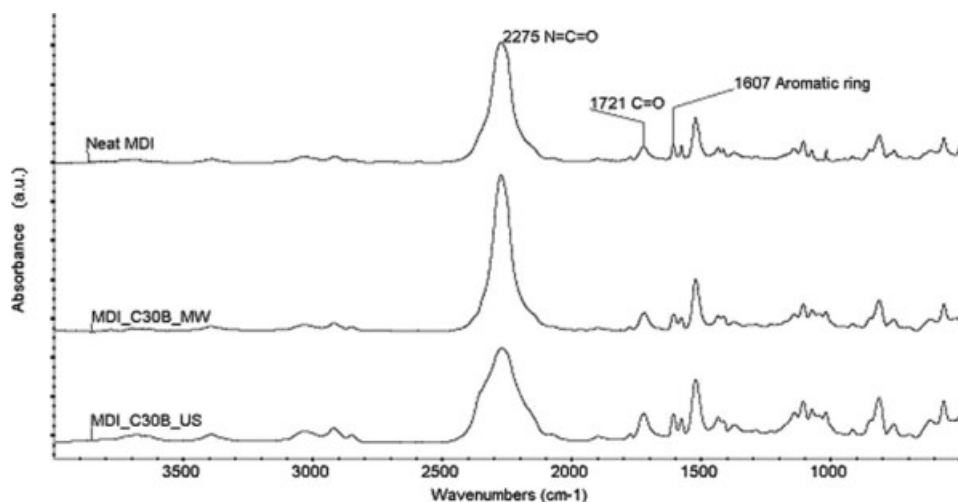


Figure 1 FTIR spectra of neat isocyanate (neat MDI) and isocyanate containing C30B after microwave (MDI_C30B_MW) or ultrasonication (MDI_C30B_US) treatment.

in Table I, we observed, as already reported by other authors, that —NCO groups partly disappear, while C=O groups form for both samples analyzed, as the ratio between 2275 and 1607 cm^{-1} areas decreases, whereas between 1721 and 1607 cm^{-1} increases. Indeed, NCO groups are involved in reaction with hydroxyl groups of organomodifier or bonded water on montmorillonite giving urethane and urea. The results also showed that the extent of reaction is higher for sonicated than microwaved sample, owing probably to the longer treatment time.

Structural and morphological characterization results

The XRD analyses of nanocomposite foams prepared are reported in Figures 2 and 3 for foams filled with C30B and LVF, respectively. Also XRD spectra of pristine clay and neat polyurethane foam are shown. As may be seen for C30B filled foams, there are significant increases of the d -spacing of the clay for every dispersion method used, as diffraction peaks of filled foams take place at lower value of 2θ angle than pristine clay. Using Bragg's relation:

$$n\lambda = 2d \sin \theta$$

where n is the reflection order, λ is the wavelength (1.541874 Å for our measurements), θ is the diffraction angle and d the interplanar distance, the inter-

TABLE I
FTIR Ratio Between Peak Area (A) at 2275 and 1607 cm^{-1} and at 1721 and 1607 cm^{-1}

	Neat MDI	MDI_C30B_MW	MDI_C30B_US
$\frac{A_{2275}}{A_{1607}}$	50.01	44.24	28.06
$\frac{A_{1721}}{A_{1607}}$	2.35	2.47	2.61

lamellar distance may be evaluated; the results of d_{001} , i.e., first reflection order distance ($n = 1$), are reported on Tables II and III. The d -spacing for C30B clay, which is higher than that of unmodified clay LVF because of the intercalation of organic compatibilizer, is further increased when the clay is dispersed in both polyol and isocyanate raw materials: the interplanar distance becomes twice or more with respect to that of pristine clay. The results obtained also show that the extent of clay intercalation is very similar for both ultrasonic and microwave processed mixtures. This means that the much shorter microwave treatment (2 min) has fairly the same effectiveness than the longer ultrasonic process (100 min). This trend may be due to the different driving forces of the two different dispersion methods: while ultrasonication is based on transmission of mechanical stress to the mixture to make both clay or raw material molecules to move, microwave process acts through variation of electric and magnetic field, because microwaves are, in fact, electromagnetic

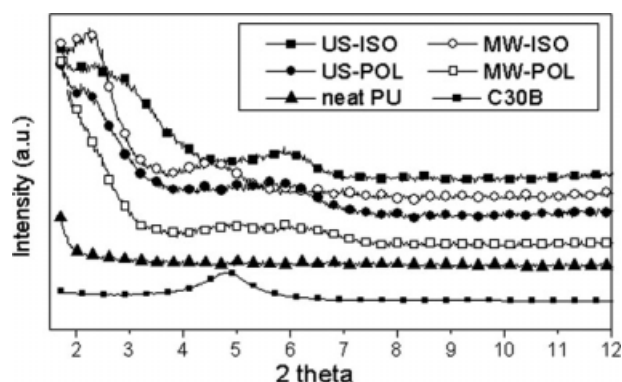


Figure 2 XRD spectra of neat PU, pristine C30B and C30B filled foams obtained by different processing method.

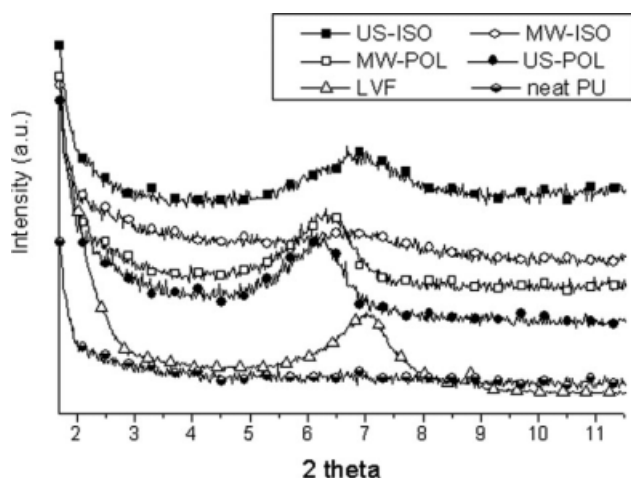


Figure 3 XRD spectra of neat PU, pristine LVF and LVF filled foams obtained by different processing method.

waves with very high frequencies (2.45 GHz for domestic use). When polar molecules or ions are involved in a variable electric field (which produces a variable magnetic field), they tend to move according to their polarity and field direction, colliding toward themselves and/or the neighboring molecules. This causes an exciting effect on material molecules, which increases their kinetic energy. This phenomenon, which is well known on industrial scale for polymer dielectric heating, may be responsible also for the increase of interlayer distance of clay here considered. The increase in kinetic energy may probably force apart the clay platelets, thus increasing interlamellar distance. Considering that clay containing great amount of ions and polar groups, (such as Mg^{2+} , Al^{3+} , NH_4^+ for tallow ammonium modified clay, OH, etc), this effect is very enhanced, thus leading to the observed increases in the interplanar distance. As the increase in kinetic energy due to microwave processing is more quick than that due to shear transmission, it is clear that the dispersing time needed when microwave is used is much shorter than when ultrasonication one is employed.

XRD data also show that the increase in interlayer spacing is somewhat higher when clay is dispersed in polyol than in isocyanate, both for ultrasonic and microwave process. This may be due to the higher viscosity of polyols, which favors the transmission

TABLE II
Interlayer Distance d_{001} for Pristine C30B and C30B Filled Foams

	C30B	C30B MW-POL	C30B US-POL	C30B MW-ISO	C30B US-ISO
2 theta	4.83	<2	2.07	2.25	2.45
d (Å)	18.29	>44.20	42.68	39.27	37.61

US or MW = ultrasonic or microwave process.
POL or ISO = clay dispersed in polyol or isocyanate.

TABLE III
Interlayer Distance d_{001} for Pristine LVF and LVF Filled Foams

	LVF	LVF MW-POL	LVF US-POL	LVF MW-ISO	LVF US-ISO
2 theta	7.09	6.35	6.25	6.65	6.85
d (Å)	12.61	13.93	14.15	13.30	12.91

US or MW = ultrasonic or microwave process.
POL or ISO = clay dispersed in polyol or isocyanate.

of mechanical stress in sonication process, and higher polyol polarity which increases the extent of molecules movements along the electric field in case of microwave process. Beside intercalated structures, filled foams show also some tactoids (in agreement with SEM and TEM analyses), as inferred from the diffraction peak at about the same diffraction angles of the neat clay.

Analyzing XRD data for foams filled with unmodified LVF clay, it may be seen that no significant intercalation takes place, whatever the dispersing method and raw materials used. This is a further confirmation of what is still well known for nanocomposite polymers and what we already reported for polyurethane foams¹⁵: the compatibility between clay and polymer matrix is an essential requirement to obtain successful dispersion. LVF, in fact, is a highly purified montmorillonite without any compatibilizer, thus it has very low chemical compatibility, while the hydroxyl group on organo-modifier of C30B seems to be essential to promote good clay dispersion. Although the variations in interlayer spacing are very low, also for foams filled with unmodified clay (LVF) the better results are obtained dispersing the clay in polyol, for the same reasons aforementioned.

TEM images (Fig. 4) are in agreement with XRD data: for C30B filled foams agglomerated as well as intercalated and delaminated structures are present, whereas for LVF mainly agglomerates of about 150–200nm dimension are visible. While intercalated and delaminated structures are generally not visible by use of SEM, tactoids may be seen. SEM analyses show some undispersed fillers for both C30B and LVF filled foams, although agglomerates are less and have lower mean size for C30B filled foam (Fig. 5).

Mechanical properties of polyurethane nanocomposite foams

To study the effect of different layered silicates on physical-mechanical properties of polyurethane foams, compressive strength has been measured. The results obtained are reported in Figure 6; due to well known polyurethane foam anisotropy, properties in both parallel and perpendicular rise direction have been evaluated.

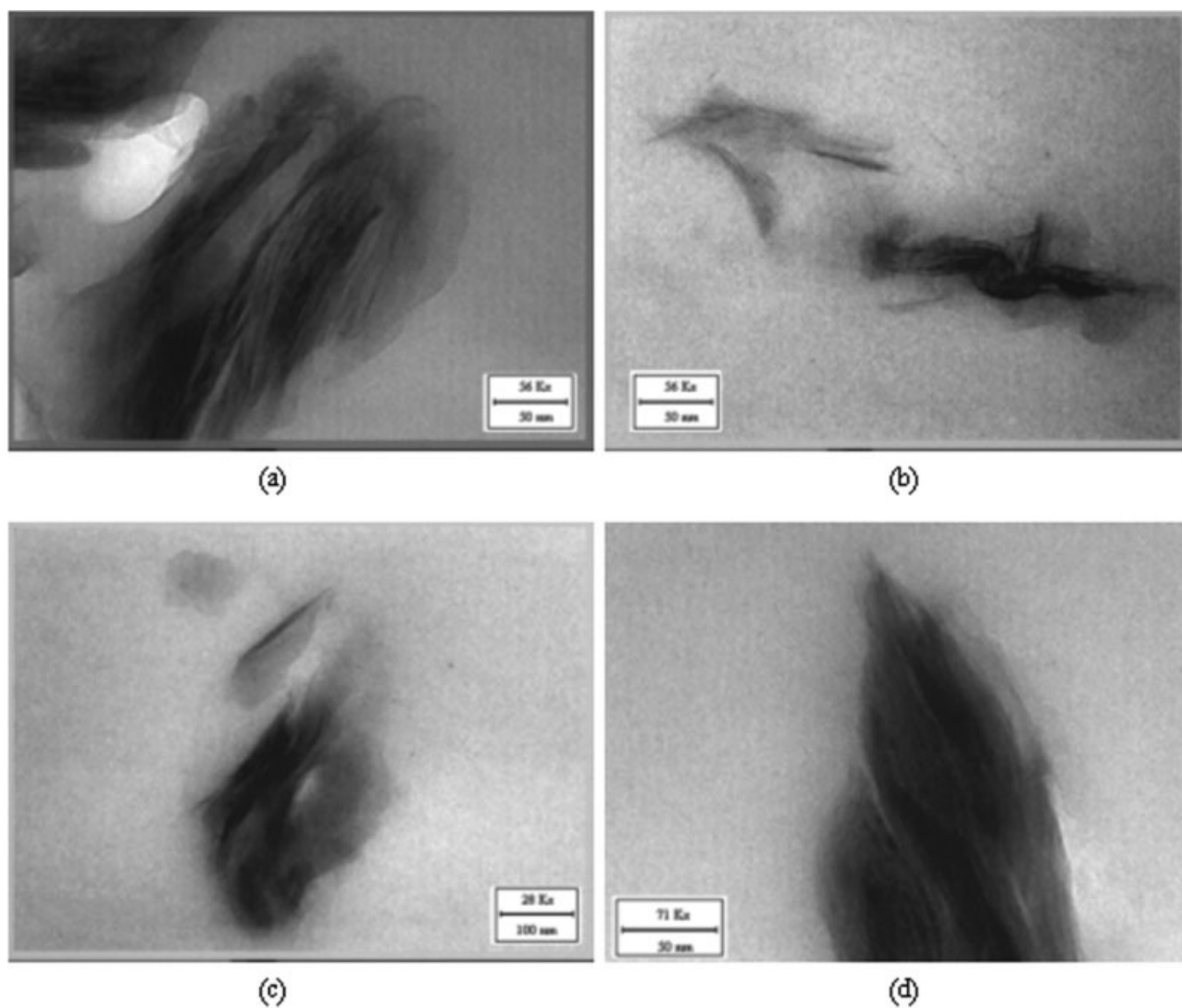


Figure 4 TEM images of POL_C30B_MW (a, b) and POL_LVF_MW (c, d) foams

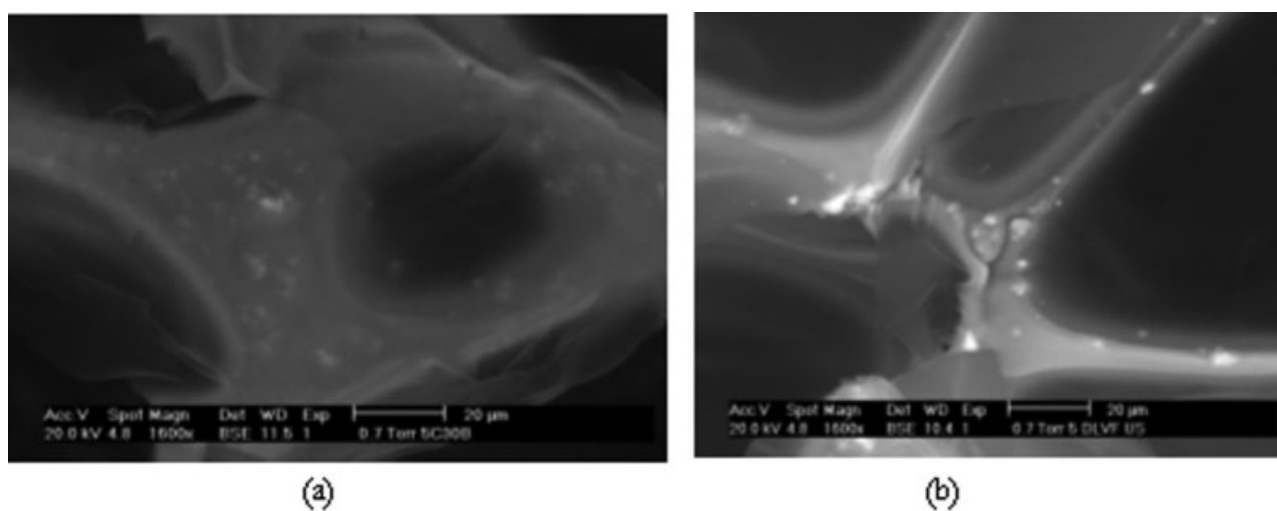


Figure 5 SEM images of POL_C30B_US (a) and POL_LVF_US (b) foams

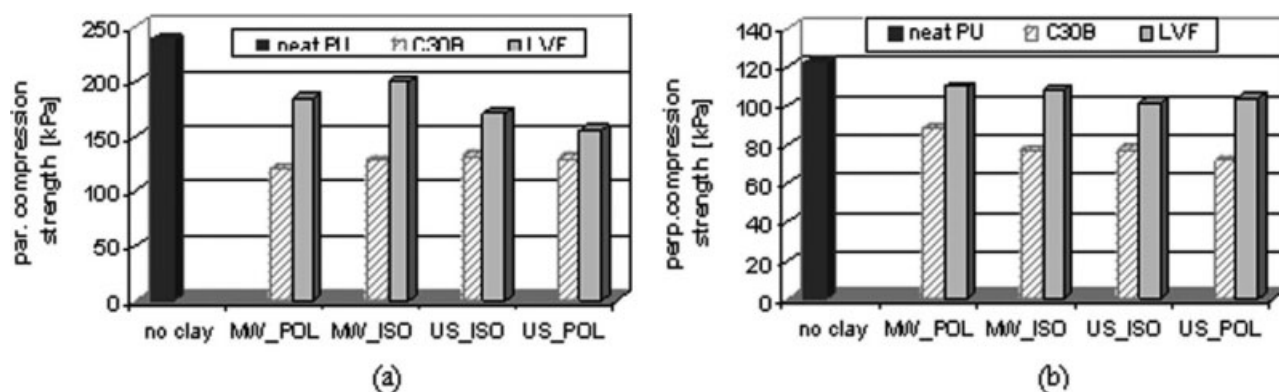


Figure 6 Compression strength in parallel (a) and perpendicular (b) rise direction for polyurethane nanocomposite foams.

It can be clearly seen that the presence of clay, both modified (C30B) and unmodified (LVF) one, leads to a worsening of compression strength properties in both parallel and perpendicular rise direction, in particular, the decrease in properties is greater for foams filled with modified C30B clay. In polyurethane rigid foams, the compression strength is expected to increase when reinforcing fillers (like layered silicates) are used,⁴ but also H-bond formation greatly contributes to the strength of the foams.⁶ The presence of layered silicates may interfere with H-bond formation, particularly when a “reactive” clay, like C30B, is used. Indeed, PU molecules can be grafted onto the clay surface or organic compatibiliser through reaction between $-NCO$ groups of isocyanate and OH groups of the clay, as previously showed by FTIR analyses; thus the clay may interfere with the H-bond formation in PU causing a negative effect on the properties of PU nanocomposite foams.

To study H-bond formation, FTIR analysis is a convenient technique for its semiquantitative determina-

tion. H-bonding has been studied considering carbonyl region ($1600\text{--}1800\text{ cm}^{-1}$), where the 1735 cm^{-1} band is caused by free carbonyl while the band at 1705 cm^{-1} is due to hydrogen-bonded carbonyls, as hydrogen bonding causes a peak shift toward lower wavenumbers.^{25,26} The degree of the carbonyl groups participating in hydrogen bonding can be described by the carbonyl hydrogen bonding index R ²⁷:

$$R = \frac{C_{\text{bonded}} \times \varepsilon_{\text{bonded}}}{C_{\text{free}} \times \varepsilon_{\text{free}}} = \frac{A_{1705}}{A_{1735}}$$

where C is the concentration, ε is the extinction coefficient, A is the intensity of the peak, the subscripts “bonded” and “free” refers to H-bonded and free carbonyls, respectively. Greater values of R indicate increased participation of the carbonyl group in hydrogen bonding.

FTIR spectra of some of polyurethane nanocomposite foams prepared are reported in Figure 7.

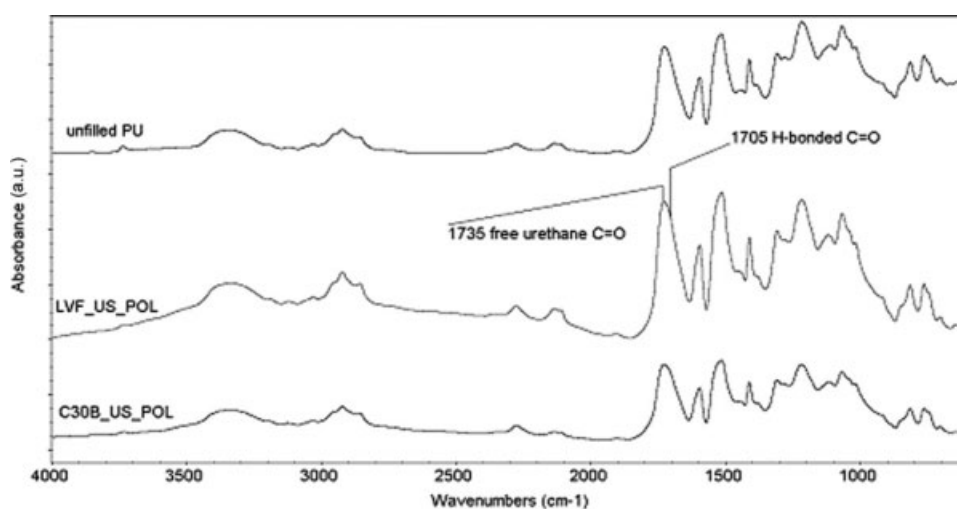


Figure 7 FTIR spectra of unfilled polyurethane foam (PU), polyurethane foam filled with LVF predisposed in polyol, subjected to ultrasonication (LVF_US_POL) and polyurethane foam filled with C30B predisposed in polyol, subjected to ultrasonication (C30B_US_POL).

TABLE IV
Hydrogen Bonding index (R) of Unfilled PU Foam (PU), Polyurethane Foam Filled with LVF Predispersed in Polyol, Subjected to Ultrasonication (LVF_US_POL) and Polyurethane Foam Filled with C30B Predispersed in Polyol, Subjected to Ultrasonication (C30B_US_POL)

	PU	LVF_US_POL	C30B_US_POL
R index	0.45	0.30	0.12

Considering the region between 1800 and 1600 cm^{-1} , as the overlapping of absorbance peaks relative to free and H-bonded carbonyl groups, the deconvolution of peak is needed. A flat baseline, from 1635 and 1800 cm^{-1} , was chosen and second derivatives of the spectra were used to find out the number of Gaussian peaks²⁴; the correlation coefficient of different fitting processes was found to be more than 0.998. The values of hydrogen bonding index R obtained from spectra in Figure 7 are reported in Table IV. It can be seen that hydrogen bonding degree decreases when layered silicates are added to polyurethane foams; moreover the decrease of R is greater when the C30B is used, owing probably to its better dispersion degree, which is more effective in preventing hydrogen bonding.

Thus, these results show that clay interferes with the H-bond formation in polyurethane foams, causing a negative effect on the properties of PU nanocomposite foams and that the overall performance of PU nanocomposite foams depends on the competition between the positive reinforcing effect of clay and the negative effect on H-bond formation. Similar conclusions were reported also by Cao et al.⁶ although they provided no evidence for them. Considering the foams here reported, we can conclude that for LVF filled foams, which show worse clay dispersion and higher H-bonding index, the decrease of compression strength with respect neat foam is lower than that of C30B filled foams, which show lower hydrogen index, owing to the better clay dispersion.

To enhance mechanical properties, it might be useful to reduce clay content for diminishing negative effect on H-bond formation, maintaining reinforcing effect which generally takes place also at very low (some wt %) filler content⁴; further studies are needed.

CONCLUSIONS

Several nanocomposite polyurethane foams, comprising pristine and organomodified clays, have been prepared using in situ polymerization method. Layered silicates have been dispersed in raw materials (either polyols or isocyanate) using ultrasonication or microwave irradiation. The results obtained showed that microwave irradiation is an efficient method for clay dispersion; moreover, microwave

treatment gives the same dispersion degree, but in much shorter time (about 95% shorter) and with lower energy consumption, than ultrasonication. For both dispersion methods, the importance of chemical compatibility between polymer and clays for achieving good dispersion has been further proved: only using proper organo-modified clay a very high dispersion degree is achieved. Although the good silicates dispersion, compressive properties of polyurethane rigid nanocomposite foam are worse than those of unfilled because it was showed that clay interfere with H-bond formation: the overall compressive performance of PU nanocomposite foams depends on the competition between the positive reinforcing effect of clay and the negative effect on H-bond formation.

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