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Influence of Bentonite Type in Waterborne Polyurethane Nanocomposite Mechanical Properties

Eliane Ayres, Rodrigo L. Oréfice, Denise Sousa*

Abstract: Aqueous dispersion of polyurethane ionomer (PUD), based on poly (propylene glycol) (PPG) as soft segment, isophorone diisocyanate (IPDI) as diisocyanate, dimethylol propionic acid (DMPA) as ionic center, hydrazine (HZ) as crosslinker and triethyl amine (TEA) as neutralizer, was reinforced with 1 to 5 wt % of clay to obtain nanocomposites. Substitution of Na^+-montmorillonite for bentonite was made by using three types of bentonite. The tensile strength and elongation at break decreased for all nanocomposites having 5% clay in comparison to pristine polyurethane. The enhancement of mechanical properties over pristine polyurethane was achieved only by using 1% of clay. The structure of layered silicates in polyurethane was found to be maintained in some extent as evidenced from wide-angle X-ray diffraction analysis. Nevertheless, the rather weak and broad diffraction peaks appearing in the curves of bentonite clays nanocomposites indicated that a nanostructure of silicate in waterborne PU system has been formed using a low cost raw material and an environmental friendly aqueous polymer precursor.

Keywords: aqueous system; bentonite; nanocomposite; polyurethane

1. Introduction

Polyurethane (PU) is a segmented polymer that is well known for its favorable properties derived from the existence of heterogeneous, microphase separated domains. The extent of hard segments primarily determines the modulus of polyurethane while the flexible soft segment predominately influences the elastic nature of polyurethane.[1] Polyurethane properties can be adjusted by two approaches: the first is to change the molecular structure of polyurethane by modification of its three basic building blocks: polyether or polyester, diisocyanate, and chain extender. The second is to introduce inorganic fillers into the polyurethane matrix. Among the inorganic fillers, montmorilonita (MMT), a smectite 2:1, is widely used in the formulation of nanocomposites. The smectite 2:1 structure is based on three units in which one tetrahedral sheet of one unit layer is adjacent to another tetrahedral sheet of another layer. In this case, the oxygen atoms are opposite one another and bonding between the layers is weak. Also there is a high repulsive potential on the surface of the layers due to isomorphous substitution. These two factors contribute to the increase of the *c*-spacing between the layers due to the penetration of water. Montmorillonite containing small, monovalent cations, such as Na^+ or Li^+ can take up water and the interlayer spacing may increase abruptly up to 30-40 Å and continues to increase to several hundred Angstroms with water content.[2] Recently PU/clay nanocomposites have attracted increasing interest.[3–6] The efficiency of the clay to modify the properties of the polymer is primarily determined by the degree of its dispersion in the polymer matrix. In the preparation of PU/clay nanocomposites, several workers

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Department of Metallurgical and Materials Engineering, Federal University of Minas Gerais, Rua Espírito Santo 35/206, Belo Horizonte, MG-30160-030, Brazil
Fax: (+55) 31 3238 1815
E-mail: rorefice@demet.ufmg.br

have modified the MMT by using organic modifiers such as alkylammonium in order to improve the compatibility between MMT and polyurethane.[7] Otherwise, the use of waterborne polyurethanes (PUD) to produce nanocomposites (CPUD) is relatively easy to achieve. As both the clay and the polymer can be well dispersed in water, the clay can be incorporated into the polymer without the need for pre-treatment. In this type of nanocomposite processing, water is used as swelling agent to make the basal space of silicate layers widen. PU-clay nanocomposites have successfully been prepared by using this method.[8] Moreover for waterborne polyurethane systems, only water is lost during drying process, thus rendering these systems safe with regard to the environment. They are non-toxic, non-flammable and do not generate polluted air. The aim of this study was to investigate the effect of substitution of MMT for bentonite, a low cost clay mineral precursor that contains about 60-95% of montmorillonite. CPUD nanocomposites were studied and their mechanical properties were correlated to the characteristics of the organophilic clays and the nanocomposite morphology.

2. Experimental

2.1. Materials

Poly (propylene glycol) (PPG, $M_n =$ 1000 g/mol) and poly (propylene glycol) (PPG, $M_n = 2000$ g/mol) were provided by Bayer (Brazil). Isophorone diisocyanate (IPDI) was also obtained from Bayer (Brazil). Dibutyl tin dilaurate (DBDLT) and hydrazine (HZ, solution 64%) were obtained from Miracema Nuodex (Brazil) and Arch Química (Brazil) respectively. All these chemicals have been employed throughout the work without any treatment. Triethylamine (TEA, 98%, Vetec) and 2, 2- bis (hydroxymethyl) propionic acid (DMPA, 98.3%, Fluka) were purchased and used as received. Four different clays were used: a commercial montmorillonite (MMT) (Cloisite® Na^+) was purchased from Southern Clay Products and used as reference. Other three sodium bentonites: Bragel FF (Brazil), Argel (Argentina) and Volclay (USA) were provided by Bentonit União Nordeste from Brazil and were used without any kind of treatment or purification.

2.2. Synthesis of the Waterborne Polyurethane Dispersion (PUD)

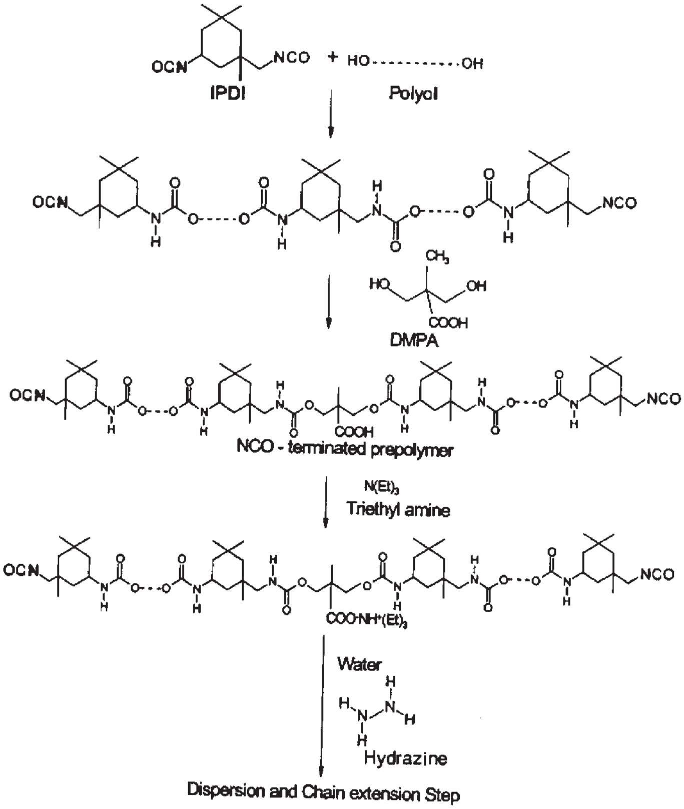
PUD was prepared by the prepolymer mixing process that employs a 250 ml three-neck glass flask equipped with a heating mantel, a mechanical stirrer, a thermometer, and nitrogen atmosphere. PPG 1000, PPG 2000, DMPA and IPDI ($NCO/OH =$ 2.3) were added to the reactor in the presence of DBDLT and the reaction was carried out at 70-75 °C under nitrogen atmosphere. When the amount of residual NCO groups reached the theoretical value (checked by n-dibutylamine titration), TEA was added to the pre-polymer to neutralize carboxylic acid species. The pre-polymer was then dispersed in water and the chain extender (HZ) was immediately added. The obtained PUD contained 25wt% solids and have pH of about 7.5. The process and the formulation used are shown in Scheme 1 and Table 1 respectively.

2.3. Nanocomposites preparation

Nanocomposites (CPUD's) containing 1 to 5% wt of clay were obtained by simply mixing the previously prepared aqueous dispersion of clay with PUD. The clay aqueous dispersions were prepared by stirring vigorously the mixture for 24 h at room temperature. Films were produced by casting the dispersions in a Teflon mould and allowing then to dry at room temperature for 1 week. Afterwards the films were placed in an oven at 60 °C for 24 h for post-curing.

2.4. Characterization

A Fourier transform infrared spectrophotometer (FTIR; Perkin Elmer, model Spectrum 1000) was used to identify the chemical structure of waterborne polyurethane/ clay nanocomposites. Measurements were carried out using the attenuated total reflectance (ATR) technique from 32 scans with a resolution of 4 cm^{-1}.



Scheme 1.
Schematic Representation of the PUD/Clay Nanocomposite Preparation Process.

An X-ray diffractometer (XRD, Philips model PW 3710) was used to examine ordering in clay and CPUD's nanocomposites. The X-ray beam was Ni-filtered Cu Kα radiation ($\lambda = 1.54$ Å). Data were obtained in the 2θ range of 3.5050°– 9.9950° at a scan rate of 0.01° min^{-1}.

Tensile tests were conducted on an EMIC-DL3000 Universal Testing System with a crosshead speed of 0.1 $\text{m} \cdot \text{min}^{-1}$ for specimens according to ASTM D638 standard. Each value was the average of three measurement and the standard desviation of the obtained results was always less than 5%.

3. Results and Discussion

3.1. Structure and Morphology of the CPUD Nanocomposites

Figure 1 shows the ATR-IR spectra of the pristine polyurethane ionomer (PUD) and the nanocomposite CPUD-MMT. The presence of characteristic peaks due to C=O from urethane (1733, 1703 cm^{-1}) and N–H (1550 cm^{-1}) confirmed the formation of urethane group [–NHCOO–]. With the absence of N=C=O (2270 cm^{-1}) stretching peacks in Figure 1, it was concluded that all the residual –NCO groups were consumed during the chain extension step. ATR-IR spectra also show the characteristic C–O

Table 1.
Formulation of the waterborne polyurethane/clay dispersion[d].

IPDI[a]	PPG 1000	PPG 2000	DMPA	TEA[b]	H_2O[c]	HZ
8.37	4.96	9.27	0.92	0.70	74.72	1.06

[a] NCO/OH molar ratio = 2.3.
[b] Equivalents of TEA equal those of DMPA.
[c] Appropriate amount of water is added to form a dispersion of solid content 25 wt %.
[d] 0.01% of DBDLT based on IPDI, PPG and DMPA.

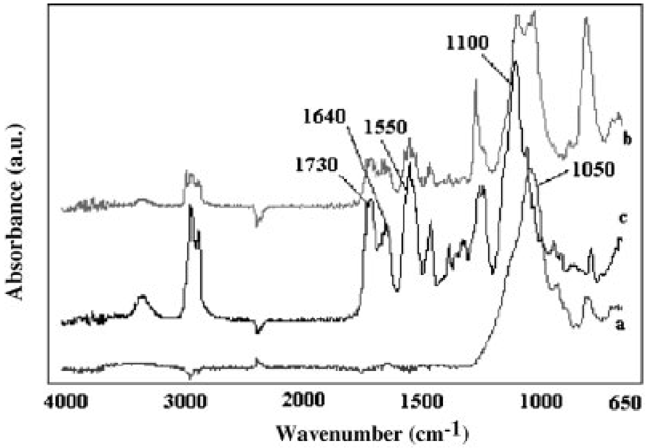


Figure 1.
IR spectra of the Bragel FF (a), PUD (b) and CPUD-Bragel FF (c).

stretching band of the macroglycol at 1100 cm^{-1} and Si–O at 1050 cm^{-1}.

The state of dispersion of clay particles can be inferred from Figure 2 The hydrophilic pristine MMT exhibits a XRD diffraction peak at $2\theta=7.2\,^{\circ}$. The interlayer spacing, calculated from this peak using the Bragg equation $2d\ sin\ \theta=n\lambda$ is 1.21 nm. In the case of the nanocomposites, the intergallery distance has been intercalated to a distance slightly greater than that of pure MMT (1.4 nm). On the other hand, the rather weak and broad diffraction peaks appearing in the curves of nanocomposites (a), (b) and (c), could indicate either that a partially intercalated/exfoliated nanostructure of silicate in waterborne PU system has been achieved or that there is sufficient disorder generated by the preparation process of the nanocomposites. A different situation is observed in the curve of nanocomposite (d). In this case, the presence of a

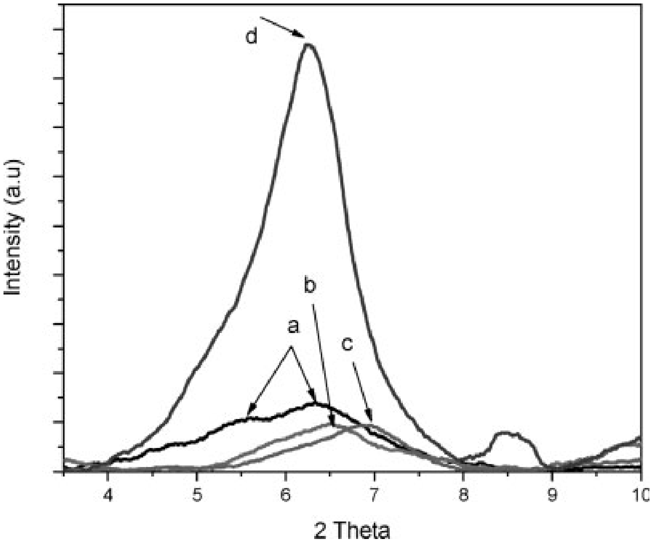


Figure 2.
WAXD patterns of nanocomposites containing 5 wt% of: (a) MMT (d = 1.4 nm and 1.57 nm), (b) Bragel FF (d = 1.36 nm), (c) Argel (d = 1.28 nm) and (d) Volclay (d = 1.41 nm).

Table 2.
Characteristc parameters of CPUD's obtained from WAXD measurements.

Characteristic parameters	MMT	BragelFF	Argel	Volclay
$d_{(001)}$	1.40	1.36	1.28	1.41
D (nm)	3.68	6.20	6.20	7.17
D/d_{001}	2.60	4.50	4.80	5.0

sharp peak shows that the clay retained an ordered structure although the interlayer spacing has been increased slightly compared to that of MMT powder.

According to S. Ray et al.,[9] from WAXD patterns, the crystallite size of intercalated stacked silicate layers of each CPUD could be calculated by using Scherrer equation, i.e. D is given by

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where k is a constant (the value generally $= 0.9$), λ is the X-ray wavelength ($=0.154$ nm), β is the width of the WAXD peak (in radian unit) and is measured by the full width at half maximum, and θ is the WAXD peak position. The calculated values of D for each CPUD are presented in Table 2. Also dividing the value of D by $d_{(001)}$ value of each CPUD, we can estimate the number of the stacked individual silicate layers dispersed in the matrix.

According to Table 2, nanocomposites of montmorillonite and bentonite showed a slight different behaviour. It is clear that the type of clay affected the structure of the resulting nanocomposites. The data suggested that a more efficient dispersability of the pure montmorilonitte (reference material) was achieved and the stacking of the silicate layers became more disordered. This may be related to the presence of impurities in the bentonite clays that do not exhibit intercalation properties. Otherwise, the particles derived from pure MMT were broken into small tactoids and uniformly dispersed in the PU matrix.

3.2. Tensile Properties

Typical stress-strain curves of PUD and CPUD's of the four types of clay are shown in Figure 3 and the corresponding tensile properties are summarized in Table 3. The enhancement of Young's modulus is due to the reinforcement provided by the presence of inorganic silicate. The higher modulus of nanocomposite derived from montmorillonite in comparison to the bentonite based nanocomposites can attributed to the larger

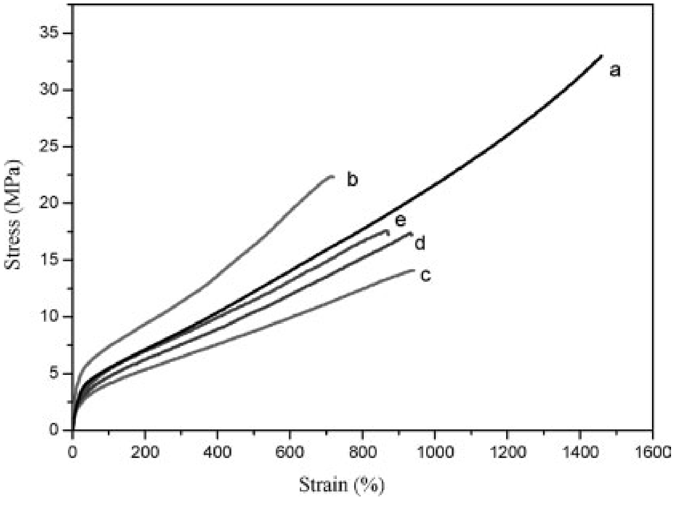


Figure 3.
Stress-strain curves of: (a) pure PUD, (b) CPUD-MMT, (c) CPUD-Bragel, (d) CPUD-Argel and (e) CPUD-Volclay.

Table 3.
Tensile properties of waterborne polyurethane nanocomposites.

Material	Modulus (MPa)	Maximum stress* (MPa)	Elongation at break (%)
PUD	24	33	1457
CPUD-MMT	133	22	725
CPUD-Bragel	51	14	942
CPUD-Argel	49	17	932
CPUD-Volclay	83	18	866
CPUD-MMT (1%)	56	39	1194

* The standard deviation was always less than 5%.

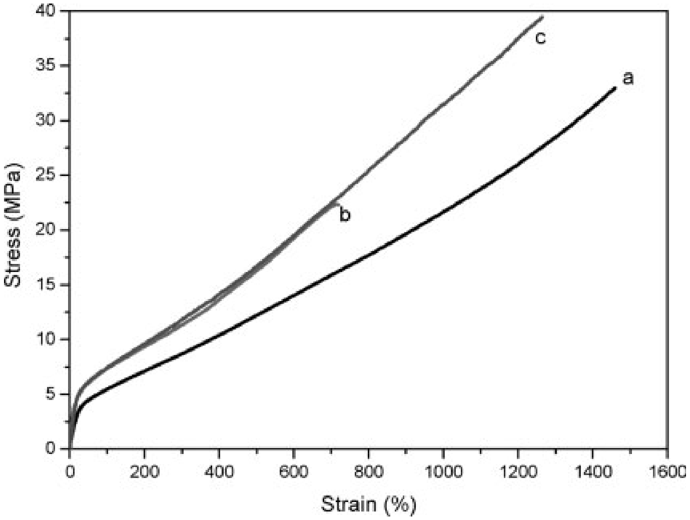


Figure 4.
Stress-strain curves: (a) pure PUD, (b) CPUD-MMT and (c) CPUD-MMT (1%).

interfacial area between montmorillonite and polyurethane matrix due to smaller size of the aggregates as indicated in Table 2.

More important, tensile strength decreased for all four clay nanocomposites in comparison to pristine PUD. Such decrease can be attributed to the presence of aggregates of clay in the polyurethane. With 1% of clay, however, the tensile strength of CPUD-MMT increased over pristine PUD as showed in Figure 4 and Table 3.

We could conclude that the enhancement of properties achieved by the addition of clay is directly related with its degree of dispersion in the polymer matrix. By controlling the amount of clay we can increase the dispersion efficiency. In this case, the presence of impurities in the bentonite clay is less relevant and its utilization is viable.

4. Conclusions

Waterborne PU was prepared through prepolymer mixing process and reinforced with different types of bentonite to obtain nanocomposites. MMT Cloisite® Na$^+$ was used as reference material. According to WAXD diffraction curves, the polyurethane/clay nanocomposites formed intercalated structures with some disorder. Mechanical properties of polyurethane were enhanced by introducing 1% of

MMT. With 5% of clay, however, the tensile strength and elongation of break drastically decreased due the presence of aggregates. Probably by controlling the amount of clay, bentonite based nanocomposites can be an attractive low cost material. In addition aqueous dispersion of PU are non-toxic, non flammable and do not pollute the air.

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