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**NANOCOMPOSITES OF SEGMENTED POLYURETHANES
INCLUDING POLY (2-ALKYL-2-OXAZOLINE) SEQUENCES WITH
MONTMORILLONITE**

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Abstract: A series of polyurethane/montmorillonite nanocomposites have been synthesized using poly(tetramethyleneglycol), α , ω -dihydroxylated poly(2-alkyl-2-oxazoline), 4,4-diphenylmethane diisocyanate or 4,4-dicyclohexylmethane diisocyanate and montmorillonite. The inorganic component was added after the polyurethane synthesis or during its preparation (in situ polymerization). The influence of the composition, of the montmorillonite amount and of the preparation approach on the dispersion degree of the clay in the polymer matrix and implicitly on the mechanical strength of the new materials was studied by means of spectral and thermal analysis, X-ray diffraction and dynamic-mechanical analysis. The development of H-bonds and of specific montmorillonite- poly(2-alkyl-2-oxazoline) sequence interactions were found to be the cause for improved mechanical properties of the corresponding polyurethanes and their nanocomposites with the inorganic compound.

Keywords: keyword 1, keyword 2, keyword 3, keyword 4, keyword 5 (max. 5 TNR 9 pt)

1. INTRODUCTION

Polymer composites are widely used in applications such as transportation, construction, electronics and consumer products. The main problem related to the processing and use of such hybrid materials is the interfacial incompatibility between inorganic and organic polymers, which causes often failure in common composites. One of the recent approaches considered to alleviate the interfacial and the tenacity problems is considered to be the uniform dispersion of the inorganic filler, in a small amount, in the polymer matrix at a nanometer scale to form inorganic-polymer nanocomposites [1, 2]. Strong interfacial interactions developed in these conditions between the dispersed inorganic filler and the polymer matrix yield improved performances when compared to micro- and macro-composites, leading to enhanced mechanical, thermal, barrier properties and increased biodegradability as compared to the virgin polymer. They have emerged in the last two decades as an efficient strategy to upgrade the structural and functional properties of synthetic polymers, gaining great importance, both in industry and in academic areas. Recently, there has been a growing interest in the development of polymer-clay nanocomposites [2]. Layered aluminosilicates or clays are between the most suited inorganic materials for the design of hybrid nanocomposites, by economic reasons, as well as considering their physico-chemical characteristics (high in-plane strength, stiffness, heat durability, very rich intercalation chemistry) [2]. Two major findings have stimulated the revival of interest in these materials: first, the report from the Toyota research group of a Nylon-6 (N6)/montmorillonite (MMT) nanocomposite [2], for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, the observation by Vaia et al. [3] that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Thereafter, different approaches, including solution, melt intercalation and in-situ polymerization, were developed to maximize dispersion in these systems [2, 4]. In our days, efforts are being conducted globally, using almost all types of polymer matrices. Due to the poor compatibility of hydrophilic silicate inorganic fillers with hydrophobic organic monomers and polymer matrices, their modification is usually an imperative requirement as a first step in the preparation of high performance polymer/clay nanocomposites [2, 4]. There is a deeper particular interest in studies providing clues for exploiting silicate-polymer interactions to tune nanocomposite material properties without chemical modification [4]. Different authors evidenced [5 - 7] the possibility to manipulate materials mechanical behavior by exploiting the specific segment - platelet attraction in microphase segregated block or segmented copolymers including blocks

with significant polarity. Thus, the preparation procedure and the composition are currently selected based on the design requirements of the final hybrid materials, the selection of appropriate polymer matrix – inorganic reinforcing agent combinations being an important stage in obtaining prerequisite properties.

In this context, taking in consideration the compatibility of poly(2-alkyl-2-oxazoline) (PROZO) with most of the common polymers, as well as their ability to interact with inorganic polar compounds [8], some new polyurethanes (PU) based on such polymers derivatives were synthesized, envisaging their application as a matrix component in inorganic-polymer nanocomposites [9, 10]. Polyurethane is a popular choice of material for a large range of applications, due to its known high functionality, blood compatibility and good mechanical properties. Furthermore, its properties can be tailored to meet the diversified demands by simply adjusting the composition. Thus, the wide applicability of polyurethane (PU) is mainly due to the broad selection of monomers from a large list of macrodiols, diisocyanates, chain extenders and crosslinkers [11].

The new segmented polyurethanes were prepared using poly(tetramethylene oxide) (PTMG), α,ω -dihydroxylated poly(2-alkyl-2-oxazoline) (PROZO) [12], [4,4'-methylenebis(phenyl isocyanate)] (MDI) or [4,4'-methylenebis(cyclohexyl isocyanate)] (H12MDI). The two macrodiols with significant polarity were chosen considering the high biological environment stability induced by PTMG, not susceptible to oxidative and hydrolytic degradation, and the ability of PROZO to develop specific interactions with inorganic polar supports [8]. The two different diisocyanates (MDI and H12MDI) were used in order to modulate the mechanical properties. Stokes et al. [13] have shown that using an aromatic diisocyanate one may obtain lower stress cracking in the final polyurethane as compared to that of polyurethanes based on aliphatic ones. Montmorillonite (MMT) was used as an inorganic filler, mainly due to its ability to develop specific intermolecular interactions, especially with compounds containing carbonyl groups [2]. To avoid PU degradation, associated with melt processing, solvent casting and *in situ* polymerization approach were found to be the preferred processing routes.

The comparative study has as a goal both, the development of new materials and a better understanding of the effect of polymer composition, of inorganic material content and of preparative approach on the degree of dispersion of clay in the polymer matrix, implicitly on the final properties of such hybrid materials.

2. METHODS AND RESULTS

2.1. Experimental procedures

Materials. 4,4'-Methylenebis(cyclohexyl isocyanate) (H12MDI, Fluka), 4,4'-methylenebis(phenyl isocyanate) (MDI, Merck), poly(tetramethylene oxide) (PTMG, Fluka, 2000 g mol⁻¹), poly(ethylene oxide) (PEO, Fluka, 2000 g mol⁻¹) and the dibutyltin dilaurate catalyst (Fluka) were used as received. The solvents: dry *N,N*-dimethylformamide (DMF, Merck), absolute methanol (Merck), anhydrous diethylether (Merck), *N,N*-dimethylacetamide (Merck), and methylene chloride (Merck), were used without further purification. Montmorillonite (MMT, Fluka, average particle size of 75 μ m) was dried before use. Hydroxylated poly(2-alkyl-2-oxazoline) telomers (PROZO, where R is methyl-PMOZO, or ethyl-PEOZO) were synthesized according to the literature [12].

Nanocomposites preparation. Segmented polyurethane (PU) were synthesized using a two-step solution polymerization method from 4,4'-methylenebis(cyclohexyl isocyanate) or 4,4'-methylenebis(phenyl isocyanate), PTMG or PEO as glycols for the soft segment, and PROZO dihydroxylated telomer as a chain extender, feed in a 3:1:2 molar ratio. Typically, the reaction was performed in dry DMF, at 60 °C, under inert atmosphere (nitrogen), with stirring, for 16 h. The chain extender was added in a second step, after 4–6 h, depending on reaction system composition. The crude product was poured in absolute methanol, diethylether or into the mixture of the two solvents, depending on its composition. The precipitate was separated by filtration, dried in vacuum at 35 °C and then maintained in a desiccator to constant weight. The yields ranged from 75 to 90%. Polyurethanes without PROZO chain extender were also synthesized for comparison.

The nanocomposites were prepared by combining a mixture of MMT in methylene chloride with the polymer solution in methylene chloride (I), or by a solvent exchange approach (II) consisting in the combination of a *N,N*-dimethylacetamide/water/MMT mixture with *N,N*-dimethylacetamide and polyurethane, followed by heating, to ensure dissolution and final sonication of the mixture (30 min) [14]. Thin films were cast at room temperature (Ia, IIa) or in an oven at 40 °C (IIb), under air flow, dried in vacuum to constant weight, stored in desiccator and then subjected to analysis.

For the *in-situ* polymerization approach the synthesis of the hybrid materials was carried out by swelling first the appropriate clay amount successively in the carefully dried involved macrodiols or in their mixture, followed by addition of DMF and diisocyanate. Then the reaction was performed according the before mentioned procedure.

Measurements. ¹H-NMR and Fourier transform infrared (FT-IR) spectra were registered with an Avance DRX400 (Bruker) spectrometer working at 400 MHz (DMSO-*d*₆ or CDCl₃ were used as solvents and TMS as internal standard) and a Vertex 70 (Bruker) spectrophotometer, respectively.

Wide-angle X-ray diffraction (WAXD) investigations were performed using a D8 Advance (Bruker) diffractometer with an integrated detector with scintillation and a CuK source with a wavelength of $\lambda = 1.54 \text{ \AA}$, at a scanning rate of $0.01^\circ \text{ s}^{-1}$, in the 2θ range of $1.5\text{--}30^\circ$.

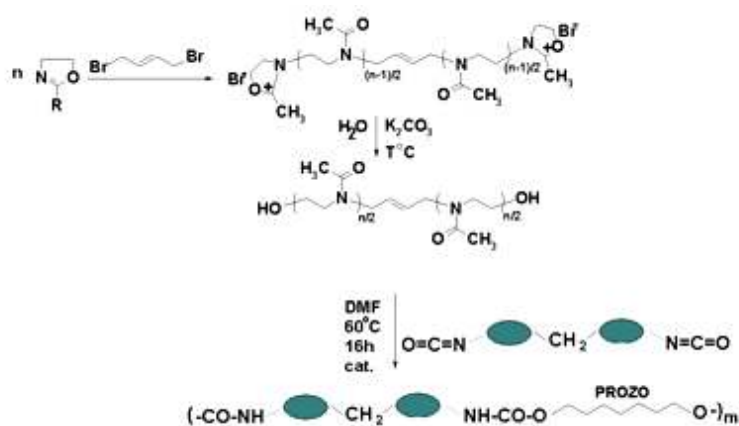
Thermal behavior investigations were performed via differential scanning calorimetry (DSC) (heating / cooling rate of $10^\circ \text{ C min}^{-1}$) and thermogravimetric analysis (ramp rate of $10^\circ \text{ C min}^{-1}$) with a Mettler 851 system.

Stained (gold) or unstained clay/polyurethane nanocomposite films were observed by scanning electron microscopy (SEM) with a Quanta 200 apparatus, working in low vacuum mode. Some samples were irradiated at pulse mode (20 pulses) at a laser energy density per pulse of 571 mJ/cm^2 .

The glass transition temperature (T_g), flexural storage modulus (E') and the dissipation factor ($\tan \delta$) of the PU and PU nanocomposites were determined *via* dynamo-mechanical analysis (DMA) using a Pyris Diamond type instrument (Perkin Elmer) at a frequency of 1 Hz and a ramp of $3^\circ \text{ Cmin}^{-1}$. Tensile tests were performed on thin film samples, approximately $10 \text{ mm} \times 9.5 \text{ mm} \times 0.3 \text{ mm}$ at a constant displacement rate of 50 mN min^{-1} .

2.2. Results and discussions

The PROZO based polyurethanes were synthesized according Scheme 1.



Scheme 1. Synthesis of PROZO-based polyurethanes.

The main prepared polyurethanes and their composites are presented in Table 1. Only PROZO based PUs gave continuous, resistant films before or after MMT insertion.

The PUs formation was confirmed by spectral data. In the $^1\text{H-NMR}$ spectra new signals, assigned to the protons in the isocyanate moiety (hard segment), appear in the $0.8\text{--}2.0 \text{ ppm}$ or $6.9\text{--}7.8 \text{ ppm}$ range, near the signals of the polyether soft segment, situated at 1.5 ppm ($-\text{CH}_2-$) and 3.4 ppm ($-\text{CH}_2\text{O}-$) in PTMG and at 3.55 ppm in PEO. The signals attributed to the PROZO sequence appear at 1.0 ppm ($-\text{CH}_3$ protons in ethyl group from PEOZO), 1.8 ppm ($-\text{CH}_3$ protons in methyl group from PMOZO), 2.3 ppm ($-\text{CH}_2-$ protons in ethyl group from PEOZO) and 3.4 ppm ($-\text{CH}_2\text{-N-}$ protons in the main chain), respectively. The peak for the proton from the NH urethane group appears at 8.0 ppm .

The FT-IR spectra (figure 1) include new signals in the $3304\text{--}3330 \text{ cm}^{-1}$ range, assigned to the NH-amide stretching vibrations. The other characteristic peaks are situated at $1716\text{--}1731 \text{ cm}^{-1}$ (free or hydrogen-bonded urethane carbonyl), 1630 cm^{-1} (stretching band of tertiary amide carbonyl group), 1528 cm^{-1} (CHN vibration of associated secondary urethane groups), 1240 cm^{-1} (C–O–C asymmetric stretching), 1210 cm^{-1} (coupled C–N and C–O–C symmetric vibration), 1105 cm^{-1} (C–O–C symmetric stretching vibration). In PU/MMT the hydrogen bonding is very complex giving rise to specific inter-urethane, urethane-ether, urethane-amide, polyurethane-silicate layers interactions reflected in the FT-IR spectra features. Usually the carbonyl region in the FT-IR spectra is the most appropriate to analyze the hydrogen bonding properties [15–17]. For the obtained PU/MMT systems the comparison of the ratios of the A_{1709}/A_{1731} absorbance, considered a hydrogen bonding index involving urethane groups [18], and of $A_{1639.6}/A_{1731}$ ratio, considered an interaction index for the C=O groups from polyurethane structure involving inorganic clay [16, 18], clearly points on the existence of specific clay-PROZO sequence interactions competing with inter-urethane hydrogen bonds and urethane group-silicate interactions. The band situated in the 1635 cm^{-1} proximity is increasing, enlarging or splitting, the effect being more evident for in-situ prepared formulations. The relationship between them is clearly related to the inorganic filler content and its degree of dispersion in the polymer matrix.

The thermal stability and the onset of Tg value, for both - PTMG and PROZO - sequences are increasing by the addition of the nanoclay. DMA measurements evidenced a broadening of the peak for PROZO in $\tan \delta$ at higher temperature, assigned to a reduced PROZO segment mobility, due to the interaction of PROZO - clay particles (Fig. 2). The durification effect is more evident and selective for the materials prepared by *in situ* polymerization, depending on the glycol addition order. If PTMG is the first added or the two glycols are simultaneously introduced in the reaction vessel the Tg value for PTMG is mostly affected, due to the interactions facilitation (lower Tg).

Table 1: Prepared polyurethanes and the corresponding PU/MMT hybrid materials.

No.	Polyurethane	Macrodiol	PROZO content ^a wt. %	MMT amount wt. %
1	PEOZO:H12MDI 1:1	HO-PEOZO-OH Mn ~ 3300 g mol ⁻¹	-	0, 5, 10
2	PTMG:H12MDI 1:1	PTMG	-	0, 5, 10
3	PTMG:H12MDI:PEOZO 1:3:2	PTMG HO-PEOZO-OH Mn ~ 2040 g mol ⁻¹	60	0, 3, 5, 10
4	PTMG:H12MDI:PEOZO 1:3:2	PTMG HO-PEOZO-OH Mn ~ 1400 g mol ⁻¹	43	0, 5
5	PTMG:H12MDI:PMOZO 1:3:2	PTMG HO-PMOZO-OH Mn ~ 1800 g mol ⁻¹	42	0, 3, 5, 10
6	PTMG:MDI 1:1	PTMG	-	0, 5, 10
7	PTMG:MDI:PEOZO 1:3:2	PTMG HO-PEOZO-OH Mn ~ 2040 g mol ⁻¹	50	0, 3, 5, 10
8	PEO: H12MDI 1:1	PEO Mn ~ 2000 g mol ⁻¹	-	0, 3, 5, 10
9	PEO: H12MDI:PEOZO 1:3:2	PEO HO-PEOZO-OH Mn ~ 3300 g mol ⁻¹	55	0, 3, 5, 10
10	PTMG:MDI:PEOZO	PTMG HO-PEOZO-OH Mn ~ 2000	35	5
11	PTMG:MDI:PMOZO	PTMG HO-PMOZO-OH Mn ~ 1800 g mol ⁻¹	43	5

a – from ¹H-NMR and elemental analysis data

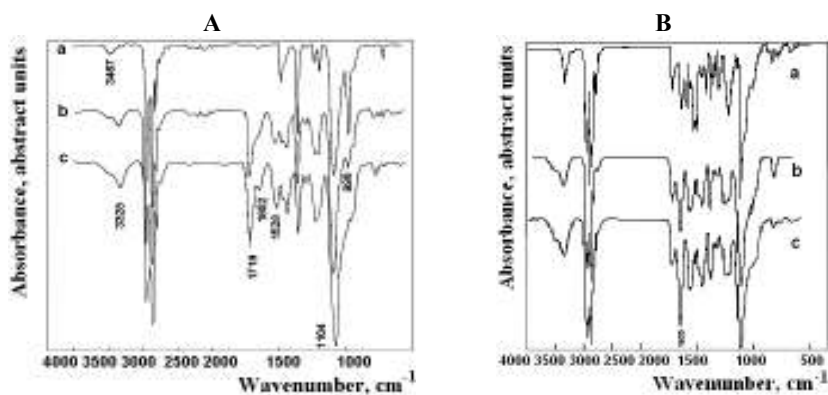


Figure 1. Typical FT-IR spectra for: (A) a) PTMG, b) PTMG:H12MDI, c) PTMG:H12MDI+10 wt% MMT and (B) a) PTMG:MDI:PMOZO+5%MMT, *in situ*, b) PTMG:H12MDI:PMOZO, c) PTMG:H12MDI:PMOZO +10 wt% MMT

XRD and SEM investigations (figs. 3, 4) revealed that multiscale levels of organization exist within the nanocomposite structure, depending on the matrix nature, percentage of included clay and preparation method.

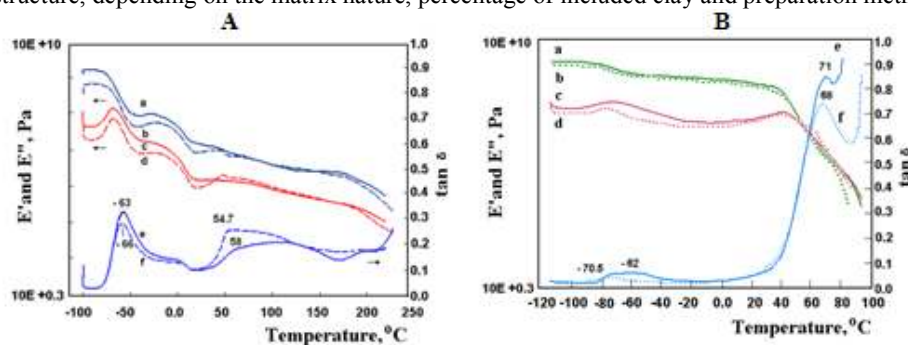


Figure 2. Flexural storage modulus (E'), loss modulus (E'') and loss tangent ($\tan \delta$) determined *via* DMA for the PTMG:DCI:PEOZO polyurethane (b, d, f) and its nanocomposite (a, c, e) with a 10 wt % MMT (A) and with 5wt% MMT, obtained by solvent casting (A) and in-situ polymerization approach (B), respectively.

When PROZO based PUs were used as a matrix, mostly intercalated – exfoliated or flocculated morphologies could be evidenced for the compositions with the MMT amount ranging from 1 to 10 wt%. By contrary, the others (including only PTMG or PE) were characterized by particles agglomeration and cracks development.

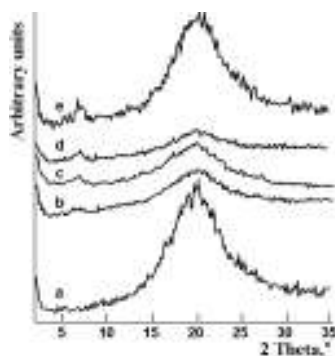


Figure 3. X-ray diffraction patterns of the PTMG:MDI:PEOZO/MMT nanocomposites with different clay contents: (a) 0, (b) 3, (c) 5, (d) 5 and (e) 10 wt %. The examined films were prepared by alternative Ia (patterns a and e) or IIb (patterns b, d) and by *in situ* polymerization (c), respectively.

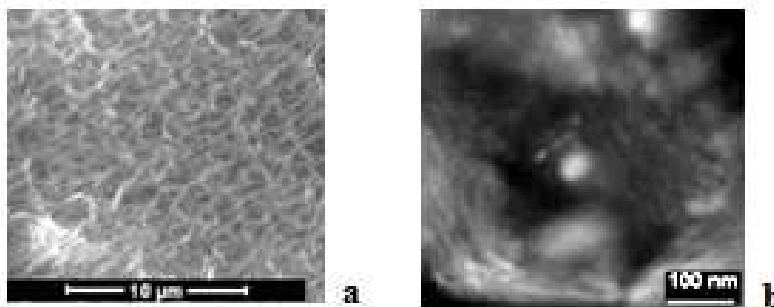


Figure 4. Typical SEM microphotographs for the prepared nanocomposites: (a) 10 wt% MMT in PTMG:MDI:PEOZO/MMT and (b) 10 wt% MMT in PTMG:H12MDI:PMOZO.

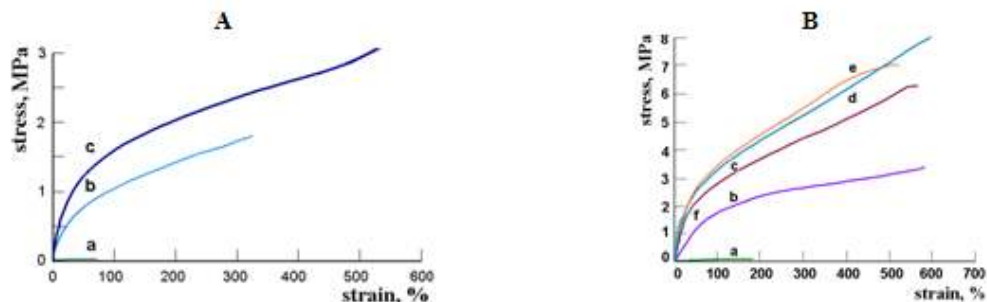


Figure 5. Stress - strain curves for: (A) unloaded PUs: a) PTMG:H12MDI; b) PTMG:H12MDI:PMOZO; c) PTMG:MDI:PEOZO; (B) a) PTMG:MDI; (b) PTMG:MDI:PEOZO and its corresponding hybrid materials loaded with different MMT amounts: c) 3, d) 5, e) 10 wt %, f) 5 wt %. Preparative alternatives: c, d, e- solvent exchange method (IIb) and f- in situ polymerization.

3. CONCLUSION

In conclusion, the inclusion of PROZO polar sequences in the polyurethane structure gives rise to improved mechanical behavior of PUs as well as of the hybrid products such as polymer/clay nanocomposites. These results were explained by a reinforcement provided by hydrogen bonding in PUs and the facilitate dispersion of silicate layers, as a result of specific polymer/clay interactions in the corresponding nanocomposites, emerging in a compatibilization effect.

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