Synthesis and characterization of polyurethane/bentonite nanoclay based nanocomposites using different diisocyanates: relation between mechanical and thermal properties

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Abstract. Polyurethanes (PUs) and polyurethane nanocomposites (PUNC) with bentonite nanoclay were prepared by the reaction of toluene-2,4-diisocyanate (TDI), dimeryl diisocyanate (DDI) and isophorone diisocyanate (IPDI) with two different polymers: hydroxyl terminated polybutadiene (HTPB) and polytetramethylene ether glycol (PTMEG), and the chains were further extended with 1,4-butanediol (1,4-BDO) to get final PUs and PUNCs. PUNCs were prepared by dispersing within the polymers a commercial and a synthesized bentonite nanoclay by mechanical dispersion. Mechanical properties showed that the addition of a small amount of nanoclay resulted in a significant increase in tensile strength and reduction in elongation at break (maximum increase of 2.3 and 5-times reduction, respectively, for a HTPB-TDI-BDO PUNCs). Thermal analysis revealed that the addition of nanoclays improved the thermal stability and increased decomposition temperature of PUNCs. We concluded that there is a positive correlation between mechanical and thermal properties as a result of nanoclay addition.

1. Introduction
PUs have found an extensive use in numerous commercial applications such as coatings, foams, adhesives, sealants, synthetic leathers, membranes, elastomers, as well as in many biomedical applications [1] [2]. Considerable attention has been paid in the literature to develop an understanding of the structure–property relationships of polyurethanes (PUs), which has acquired significance because of the broad range of applications of these materials.

Due to the diversity of combinations of flexible and rigid segments, materials can be formulated with different properties, from soft and flexible elastomers to hard thermoplastics with a high modulus [3]. Rigid or hard segments in polyurethanes consist of diisocyanate residues, chain extenders and urethane groups. The more symmetric the molecules of diisocyanate and the chain extenders, the easier will the hard segments crystallise, and the higher will be the tensile strength.
If the hard segments contain bulky aromatic or cycloaliphatic groups, the rigidity will increase, resulting in interchain steric hindrance. In the case of polybutadiene, the soft segments consist of flexible non crystalline polymer chains.

HTPB, mixed with BDO and cured with the diisocyanates HDI, DDI, CHDI, MDI and TDI has been studied [4]. Isophorone diisocyanate (IPDI) was used to cure HTPB [5].

Polymer-layered silicate nanocomposites have gained a great deal of attention due to their superior properties like high dimensional stability, high heat deflection temperature, reduced gas permeability, improved flame retardancy, and enhanced mechanical properties compared to pure polymers [6]. The nanoscale clay particles can be dispersed to a scale of few nanometers in the polymer matrix, and such dispersions are produced by shear or chemical reactions or a combination of both [7]. In a previous contribution [8] we have shown that an increase in decomposition temperature was observed when nanoclay was loaded at 3.5% onto an elastomeric PU made from TDI, PTMEG and BDO, while not when nanoclay content was lower (1.5%). Increasing of the decomposition temperature was attributed to the reduced diffusion of decomposition products within the polymer matrices [17]. In this contribution, we prepared PUNCs based in two different polyols and cured with TDI, DDI and IPDI and chain extended with 1,4-BDO, and their mechanical and thermal properties were studied to find correlations.

2. Materials and Methods

Reactives: a polyether polyol poly(tetramethylene)glycol (Voranol®, mean molecular weight 2435 g/mol, hydroxyl index 56), was obtained from Mentvil Argentina S.A, Buenos Aires. HTPB was from chinese origin, with a M_w of 4300 Da and a polydispersity index of 1.4. An isomeric mixture of tolydene diisocyanate (TDI) was utilized as received from Petroquímica Río Tercero S.A, Córdoba, Argentina. Isophorone diisocyanate (IPDI) at 98% was purchased from Aldrich Co and DDI was purchased from Henkel Corporation. The reactive nanoclay Cloisite C30B containing 90 mequiv./100 g clay of quaternary ammonium ions was donated by Southern Clay Products, US. The quaternary ammonium ion has the structure N+(CH₂CH₂OH)₂(CH₃)T, with T representing an alkyl group of approximately 65% C₁₈H₃₇, 30% C₁₆H₃₃, and 5% C₁₄H₂₉. A N-dodecil quinolinium-interchanged bentonite (Nanoclay*) was prepared by intercalation of natural bentonite (Lake Pellegrini bentonite, Patagonia, Argentina, provided by National Mining Service Laboratory, Segemar) for 2 hours at 80°C and then separating the supernatant by filtering. Differential scanning calorimetry (DSC) studies were performed in a Q20 apparatus (TA Instruments), using 5 mg samples in opened heating pans, at a heating rate of 10°C/min.

3. Synthesis of polyurethanes

The polyols, PTMEG and HTPB, were dried under vacuum for one hour. PTMEG or HTPB were allowed to react with a calculated quantity of the diisocyanate viz. TDI, DDI or IPDI at room temperature in a three-necked reaction kettle with a mechanical stirrer under vaccum (4 mm Hg). The diisocyanate was added dropwise from the dropping funnel over a period of 15 min. The catalyst dibutyl tin laureate (DBTL) was added to the polyol in the beginning itself. The mixture was stirred continuously for about 30-45 min to obtain NCO terminated prepolymer. This was allowed to react further with the required amount of the crosslinker for about 15 min or until the reaction mixture became viscous. This was followed by degassing after which the mixture was poured into preheated teflonated moulds. The curing was allowed to proceed at room temperature for 7 days. After cooling the crosslinked polyurethanes were used for testing. For preparing PUNCs, nanoclay was dispersed in the correspondent polymer by mixing with a Cowles blades at 3000 rpm for 1 minute. The composition of the polyurethanes synthesised and their number codes are given in Table 1.
Table 1. Polyurethanes and polyurethane nanocomposites (PUNCs) prepared from hydroxy-terminated polybutadiene (HTPB) and poly-tetramethylene glycol (PTMEG) cured with 2 different isocyanates and chain extender with 1,4-butanediol (BDO).

| Sample | PTMEG | HTPB | TDI | DDI | IPDI | BDO | Nanoclay, % w/w |
|--------|-------|------|-----|-----|------|-----|----------------|
| 1      | 60    | -    | 28,2| -   | -    | 7,2 | N-dodecyl quinolinium-interchanged bentonite, 1 |
| 2      | 60    | -    | 28,2| -   | -    | 7,2 | Cloisite 20 A, 1 |
| 3      | 60    | -    | 28,2| -   | -    | 6,9 | Cloisite 20 A, 1 |
| 4      | 15    | -    | -   | -   | 5    | 1,5 | - |
| 5      | 15    | -    | -   | -   | 5    | 1,5 | Cloisite 20 A, 1 |
| 6      | -     | 69,4 | 6,24| -   | -    | 3,72| - |
| 7      | -     | 38,2 | -   | 3,6 | 0,7  | -   | - |
| 8      | -     | 69,4 | 6,24| -   | -    | 3,72| Cloisite 20 A, 1 |
| 9      | -     | 38,2 | -   | 3,6 | 0,7  | -   | Cloisite 20 A, 1 |
| 10     | -     | 179,38| 68,70| - | 10,39| -   | Cloisite 20 A, 1 |
| 11     | -     | 179,50| 66,24| - | 10,44| -   | Cloisite 20 A, 1 |

4. DSC Studies
In general, the process of PU decomposition normally begins at a temperature between 200 and 370°C. The emerging isocyanates from decomposition react among themselves to form dimers and trimers, which in turn, in a second stage, decompose to produce substituted ureas and isocyanurates. This second stage occurs in a range of temperatures between 350 and 500°C. At higher temperatures than 500°C, products formed completely decompose to give volatile material and a carbonaceous residue (third stage) [9].

The thermal degradation temperature of isocyanurate rings is ca. 300–340°C, while in the case of traditional polyurethanes, it does not exceed 250°C [2]. This may suggest that our PU have a certain degree of isocyanurate chemicals bonds in its structure.

4.1 Polyurethanes with PTMEG

There have been proposed three mechanisms for the decomposition of urethane bonds: dissociation to isocyanate and alcohol, formation of primary amine and olefin, and formation of secondary amine and carbon dioxide. These reactions may proceed simultaneously or separately [10].

Generally, polyurethanes decompose in three steps and the temperature which the weight loss is maximum in the range of 380-500 °C. In glycerine containing PUs, ramified structures are generated, increasing the amount of flexible chains and lead to relative stability, because the possibility of ordering the main molecular chain is increased. The first stage was associated with the hard segment degradation and the second one, with the soft segment [11].

In Table 2 we summarize the main findings about the thermal behaviour of the PU and PUNCs synthesized:
Table 2. Thermal behaviour of the PU and PUNCs synthesized with PTMEG.

\( T_1 \): Temperature of the first exothermic peak

\( T_2 \): Temperature of the second exothermic peak

| Sample | \( T_1 \)   | \( T_2 \)   |
|--------|-------------|-------------|
| 1-PTMEG-TDI-BDO | 387.07      | 408.34      |
| 2-PTMEG1% Nanoclay*-TDI-BDO | 382.20      | 415.11      |
| 3-PTMEG1% C20A –TDI-BDO | 390.96      | 431.36      |
| 4-PTMEG-IPDI-BDO | 365.19      | 419.94      |
| 5-PTMEG 1% C20A-IPDI-BDO | 365.70      | 409.76      |

In the samples with PTMEG-TDI-BDO we can observed that the incorporation of two types of nanoclays considerably increased the decomposition temperatures of the second stage (7 °C and 23 °C) and this results are coherent with the work of Yun, Tien and Kung Hwa Wei [12], who studied the influence of the type of nanoclays (with 1OH, 2OH and 3OH) and observed that PU with nanoclay with higher content of OH groups improved thermal stability. Results are shown in Figure 1.

![Figure 1](Universal V4.3A TA Instruments)

**Figure 1.** Differential scanning calorimetry (DSC) thermograms for 1: PTMEG-TDI-BDO, 2:PTMEG1%+Nanoclay*-TDI-BDO and 3: PTMEG+1% C20A –TDI-BDO.

In the samples with PTMEG-IPDI-BDO we observed that the incorporation of nanoclay did not affect the first exotermic peak, and also did not improve thermal stability in the second peak. On the other side, Saha et al. [13] observed that the addition of a similar nanoclay in a PU based on PTMEG-IPDI-BDO improved the thermal stability, although in that case with higher percentages than 1%.  

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4.2 Polyurethanes with HTPB
The decomposition of PU with HTPB occurs in two stages, one exothermic and the other endothermic. The initial exotherm results from the positive energy balance of the endothermic depolymerization process and the exothermic cyclization and cross-linking process of the HTPB that has not undergone depolymerization. The second process is mostly the result of depolymerization of the cross-linked residue formed in the cyclization and cross-linking reactions of the first decomposition step [14].

In Table 3 we summarize the main findings about the thermal behaviour of the PU and PUNCs synthesized:

**Table 3.** Thermal behaviour of the PU and PUNCs synthesized with PTMEG.

| Sample                  | $T_1$  | $T_2$  |
|-------------------------|--------|--------|
| 6-HTPB-TDI-BDO          | 370.85 | 454.83 |
| 7-HTPB-IPDI-BDO         | 368.84 | 456.52 |
| 8-HTPB 1% C20A-TDI-BDO  | 372.85 | 465.46 |
| 9- HTPB 1% C20A-IPDI-BDO| 373.40 | 468.04 |
| 10- HTPB-DDI-BDO        | 383.42 | -      |
| 11- HTPB 1% C20A-DDI-BDO| 374.73 | -      |
In Figure 3, the endotherm for PUNC was at a temperature more than 10°C higher than PU without nanoclay:

![DSC thermograms for 6:HTPB-TDI-BDO and 8: HTPB 1%+C20A-TDI-BDO.](image)

**Figure 3.** Differential scanning calorimetry (DSC) thermograms for 6:HTPB-TDI-BDO and 8: HTPB 1%+C20A-TDI-BDO.

In Figure 4, same behaviour was observed for the endotherm of PUNC cured with IPDI. This suggested that the effect was not dependent on the curative utilized but could be explained because of the addition of nanoclay. In the samples with TDI and IPDI we could also observe (apart for the temperature increase of the endothermic peak (10.5°C for TDI and 11.5°C for IPDI) that the PUNC with 1% nanoclay increased the temperature of the second exothermic peak (2°C for TDI and 4.5°C for IPDI).
Figure 4. Differential scanning calorimetry (DSC) thermograms for 7: HTPB-IPDI-BDO and 9: HTPB+1% C20A-IPDI-BDO.

In Figure 5, PUs cured with DDI did not show the same effect as with TDI and IPDI, as a three broad exotherms were seen at around 370-380°C, 430-440°C and 490-500°C. The addition of nanoclay decreased the temperature for the first exothermic peak (8.5°C) and no endotherm could be observed. This effect could be explained by the fact that DDI is an aliphatic isocyanate with a high MW: other studies showed that a larger portion of layered silicates is distributed in the hard-segment phase when aliphatic isocyanate is used as curative [12]. Then interaction between different aliphatic chains are weakened by the presence of nanoclay, because their bonds are weaker compared to aromatic isocyanates or even aliphatic ones with lateral chains of low molecular weight (such as those of IPDI).
5. Mechanical properties
The results from stress-strain and Shore hardness essays performed on the prepared samples are shown in table 4.

Table 4. Mechanical properties of the synthesized polyurethanes and polyurethane nanocomposites (PUNCs).

| Sample                     | Tensile strength (MPa) | Strain at maximum load (%) | Shore A Hardness |
|---------------------------|------------------------|----------------------------|------------------|
| 1-PTMEG-TDI-BDO           | 0.45                   | 270                        | 90               |
| 2-PTMEG1% Nanoclay*-TDI-BDO | 4                     | 105                        | 95               |
| 3-PTMEG1% C20A-TDI-BDO    | 4                      | 105                        | 89               |
| 4-PTMEG-IPDI-BDO          | 0.08                   | 900                        | 70               |
| 5-PTMEG 1% C20A-IPDI-BDO  | 0.12                   | 240                        | 75               |
| 6-HTPB-TDI-BDO            | 0.09                   | 800                        | 55               |
| 7-HTPB-IPDI-BDO           | 0.1                    | 900                        | 60               |
| 8-HTPB 1% C20A-TDI-BDO    | 0.21                   | 160                        | 40               |
|         | 9- HTPB 1% C20A-IPDI-BDO | 10- HTPB-DDI-BDO | 11- HTPB 1% C20A-DDI-BDO |
|---------|--------------------------|-----------------|-------------------------|
| tensile | 0.14                     | 0.4             | 0.12                    |
| strength| 170                      | 390             | 950                     |
| strain  |                          |                 |                         |
| at max  |                          |                 |                         |

Table 4: Mechanical properties of the synthesized polyurethanes and polyurethane nanocomposites (PUNCs).

It was shown that the addition of 1% nanoclay resulted in an increase of nearly 10 times on the tensile strength and a three-fold reduction in strain at maximum load for PTMEG-TDI polyurethanes extended with 1,4-BDO. There were no differences between a laboratory-prepared nanoclay (sample No 2) and a commercial Cloisite nanoclay PUNC (sample No 2). Therefore, Cloisite was used for preparing other PUNCs. When IPDI was used as curing agent for PTMEG, nanoclay had a significant effect mostly in elongation at break (4-fold increase) while tensile at break diminished only around 30%.

When HTPB was used as polyol the addition of nanoclay doubled tensile at break and reduced elongation 5 times for PUNC cured with TDI. On the other hand, the utilization of the aliphatic isocyanate IPDI rendered an increase of more than 4 times in elongation at break, while tensile strength was not significantly affected (0.1 and 0.14%, respectively). In the case of PTMEG polyol cured with DDI we observed that the effect of nanoclay on tensile strength was low, possibly because the interactions among the long aliphatic chain of DDI are obstructed by nanoclay. However, elongation was more than doubled, indicating that chains are not fully restricted in their motion by nanoclay interaction. It was pointed out that mechanical bonding on the surface of nanoparticles and the stress field around is a result of shear mixing, which results in nanoclay load bearing properties [15]. Respect to mechanical resistance, polymer matrices also influence mechanical resistance through craze initiation above a critical matrix ligament thickness [16]. This highlights the importance of good dispersion of nanoclay within polymers, in order to obtain an exfoliated nanoclay and avoid the formation of crazes, fostering a high crack initiation energy.

6. Conclusions

Our results suggested that mechanical properties are correlated with thermal properties for the elastomeric materials studied. PUNC cured with TDI and IPDI displayed an increase in tensile strength with the expectable reduction in strain at maximum load. At the same time, decomposition temperature (second exotherm peak) augmented, possibly due to the reduced diffusion of decomposition products within the polymer matrices, as nanoclays are known to reduce gas permeability. The DSC results showed a slight increase of the melting temperature with Cloisite loading. The study of the thermal stability confirmed that the nanocomposites are thermally more stable than the unmodified systems. A significant increase in mechanical properties was obtained even at low percentages of nanoclay (1%) compared to the usual amounts incorporated in PUNCs (3 to 5%).
7. References

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