Effect of nanoclay loading on the thermal decomposition of nanoclay polyurethane elastomers obtained by bulk polymerization

Javier Quagliano¹ and Javier Bocchio²

¹Organic Synthesis Division and ²Analytical Division, Applied Chemistry Department (DQA), Argentine R&D Institute for the Defense (CITEDEF), Buenos Aires, Argentina.
E-mail: jquagliano@citedef.gob.ar

Abstract. Thermoplastic urethane (TPU) nanocomposite was prepared successfully by dispersion at high shear stress of the nanoclay in polyol and further bulk polymerization. Our results from DSC studies showed an increase in decomposition temperature when nanoclay was loaded at 3,5% on elastomeric PU made from TDI, PTMEG and BDO, while not when nanoclay content was lower (1,5%). The exotherms at 370-375ºC could be ascribed to the decomposition of the hard segments according to previous work.

1. Introduction

Nanocomposites of polyurethane exhibit improvement in various properties compared to the conventional microcomposites such as outdoor resistance of coatings [1], heat resistance, gas permeability, and flammability [2,3,4,5]. Mineral fillers as high-modulus additives are used as reinforcing agents in polymeric materials. In particular, polyurethane/clay nanocomposites have attracted great interest in recent years. They have gradually become more widely accepted in applications such as automobile parts [4,6].

On a broad basis, the preparation of polyurethanes (PU) is typically classified by the sequence of addition of the reactants (one-step, two-step or prepolymer process) or by the number of components, which the user has to mix together (a one-component or a two-component system).

Thermoplastic polyurethanes (TPU) have a two phase structure because of the thermodynamic incompatibility of the hard and soft segments of PU chain. Phase separation of hard segment from polyol soft segment determines elastomeric properties. Phase separation, leading to domain microstructure, has been postulated to explain the unusual viscoelastic properties of segmented PU [7].

In general, PU are formulated with an excess isocyanate to improve elastomeric properties during post-curing reactions. Mechanical properties of PU elastomers could be controlled by changing the molar ratio of two different monomer components [8]. The NCO/OH ratio determines the physical properties of PU, being generally a ratio of 1 the better for improving physical properties. The type of polyol, isocyanate, chain extender and synthesis conditions determines the physical and mechanical properties of PU, rendering a wide variety of materials with properties ranging from a soft foam to extremely hard and impact/tear-resistant materials.

Additionally, the way of incorporation of nanoclay into the PU matrix greatly affects its physical properties. The simplest approach of mixing nanoclay and PU is to physically mix them both, resulting
in physical trap forces such as polar, hydrogen bonding and shear between the clay and the polymer [9]. Other mixing methods were reported in the state of the art. As an example, in one method for rigid PU foams, organoclay was dispersed first in the isocyanate component ultrasonically. It was found that using toluene as common solvent enhanced dispersion significantly [10]. Bulk and melt processing polymerization were compared as two methods of incorporation of nanoclay into thermoplastic polyurethane matrix [11].

The glass transition and decomposition temperatures of nanoclay PU increase with increasing clay content, due to the restricted motion of chains and barrier property of the clay platelets. In PU/clay nanocomposites, hard segments are highly attracted to the silicate surface but soft segments are not attracted in order to push the platelets apart to regain entropy [12,13]. Functionalized nanoclays were reported to increase the $T_g$ gradually to the range of 60 to 62°C for 5 wt% loading in PU based thermoset adhesive [14]. On the other side, Thirumal and coworkers [16] observed that the glass transition temperature ($T_g$) decreases on loading of organically-modified nanoclay. These findings highlights that thermal behaviour depends on several factors such as type of TPU, clay incorporation method and how platelets are dispersed within the PU matrix.

Introduction of nanoclay limits the motion of TPU molecule and leads the nanocomposites to exhibit higher thermal stability [20]. Decomposition temperatures for 10% weight loss was at least 10°C higher than control sample for nanoclay-reinforced PU foams up to 2% pphp (parts percent polyol basis) and were between 350 and 380°C [17]. For thermoplastic PU (TPU) based on HMDI, PTMEG and BDO and loaded with nanoclay from 1 to 9% (pphp), decomposition temperatures were increased from 400 °C for control TPU to almost 450 °C for 5% nanoclay filled. The authors found that all the specimens of PU nanocomposites showed two stages of thermal degradation. The first stage is dominated by the degradation of the hard segment and the second stage correlated well with the thermal dissociation of the soft segment [18]. It is common knowledge that strong dipole-dipole, hydrogen bond interactions and crystallinity that nanoclay addition imparts improve heat resistance. Also for organoclay-modified PU foams enhancement degree of thermal stability and flame retardancy of composites was reported to coincide well with the sequences of gallery spacing of organoclay in the PU matrix [15].

In this contribution we report our preliminary results on the effect of nanoclay incorporation over the decomposition temperature of an elastomeric PU based on poly(tetramethylene)glycol (PTMEG), toluene diisocyanate (TDI) as curing agents and 1,4-butanediol (BDO) as chain extender.

2. Materials and Methods

Reactives: a polyether polyol poly(tetramethylene)glycol (Voranol®, mean molecular weight 2000 g/mol, hydroxyl index 56), was obtained from Mentvil Argentina S.A, Buenos Aires. An isomeric mixture of tolylene diisocyanate (TDI) was utilized as received from Petroquímica Río Tercero S.A, Córdoba, Argentina. 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’(CH$_2$CH$_2$OH)$_2$(CH$_3$)T, with T representing an alkyl group of approximately 65% C$_{18}$H$_{37}$, 30% C$_{16}$H$_{33}$, and 5% C$_{14}$H$_{29}$.

The soft segment of elastomeric PU was synthesized from poly(tetramethylene)glycol (PTMEG), while the hard segment was synthetized from TDI and 1,4-butanediol (BDO, Sigma Aldrich, US) as chain extender.
OCT (organoclay)-polyurethane nanocomposite: OCT-polyol nanocomposites were prepared by two-step or prepolymer bulk polymerization. Increasing quantities of OCT (nanoclay) were added to the polyol, while stirring at 2000 rpm for 10 minutes. The resulting OCT-polyol nanocomposites were reacted with TDI for 120 minutes at 60ºC to form the prepolymer under vacuum (4 mm Hg). Then BDO was added as chain extender for 30-60 minutes the same temperature until elastomeric material developed, evidenced by the increased thickness and final formation of a gummy and soft material. Post-cure was made at ambient temperature for at least 7 days.

Differential scanning calorimetry (DSC) studies were performed in a TA model Q20 apparatus belonging to the Department. Samples were heated at 5ºC/min under a nitrogen atmosphere.

3. Results

We obtained PU elastomers adding TDI to the polyol at 60ºC and adding BDO as chain extender in a second stage. The NCO/OH initial ratio was set to 1. When BDO was added, the reaction crude increased its viscosity until a hard elastic material was formed. For obtaining the nanocomposites, nanoclay was incorporated in the polyol fraction at high shear (2000 rpm) for 10 minutes.

In the following Table, we summarized the temperatures at with thermal peaks were obtained for different elastomeric PU.

Table 1: Decomposition temperatures of nanoclay PU elastomers based on PTMEG polyol, TDI and BDO as chain extender

| OC (pphp, %) | Hard domain | Soft domain | Main temperature of peaks in DSC (ºC) | Decomposition temperature (ºC) |
|--------------|-------------|-------------|--------------------------------------|---------------------------------|
| 0            | TDI         | PTMEG       | 330/390                              | 390                             |
| 0            | TDI-BDO     | PTMEG       | 287/375/422                          | 422                             |
| 1,5          | TDI-BDO     | PTMEG       | 350/370/412                          | 412                             |
| 3,5          | TDI-BDO     | PTMEG       | 320/370/427                          | 427                             |

OC: organoclay. pphp (parts of OC on a percent polyol basis).

Linear PU made from TDI and PTMEG only showed less heat resistance than those branched with BDO, evidenced by a 20-30 ºC reduction in decomposition temperature. Decomposition temperatures were 10ºC lower for 1,5% loaded nanoclay PU than for control sample. However, 3,5% loaded sample decomposed 5 ºC after the control, coincidently with the majority of the reports [1,2,3,4]. The exotherms at 370-375ºC could be adscribed to the decomposition of the hard segments, according to previous reports [18, 20]. Saiani and coworkers [21] assigned the observed high-temperature endothermic transitions to the disruption of an ordered structure appearing in the hard phase under certain annealing conditions and to the microphase mixing of the soft and hard segments. Overall, decomposition temperatures were in the same range as for other elastomeric PU systems. For example, it was around 440ºC when poly(caprolactone) was the soft segment, and 4,4-methylene bis (cyclohexyl isocyanate) and BDO conformed the hard segment [19] and around 420ºC for a similar PU system cured with the aliphatic isophorone diisocyanate (IPDI) instead of aromatic TDI [22]. The thermal stabilization effect of nanoclay can be explained because nanoclay hinders the diffusion of the volatile degradation products (carbon dioxide, carbon monoxide, water molecules, etc.) from the bulk of the polymer matrix to the gaseous phase [20].
4. Conclusions

TPU nanocomposite was prepared successfully by dispersion at high shear stress of the nanoclay in the polyol and further bulk polymerization. Our results from DSC studies showed an increase in decomposition temperature when nanoclay was loaded at 3.5% on elastomeric PU made from TDI, PTMEG and BDO, while not when nanoclay content was lower (1.5%). The exotherms at 370-375ºC could be ascribed to the decomposition of the hard segments according to previous work. Our results justify further research with this PU system to determine specifically which nanoclay content improves thermal resistance without affecting general properties of this system.

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