Synthesis of a Polyurethane/Clay Nanocomposite Used as Coating: Interactions Between the Counterions of Clay and the Isocyanate and Incidence on the Nanocomposite Structure

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ABSTRACT: The use of nanocomposites in textile applications, and in particular of polyurethane (PU) coatings reinforced by various additives [clay and polyhedral oligomeric silsesquioxane (POSS)], has grown in recent years. Some interesting results have been obtained, especially with Cloisite 30B (a montmorillonite organo-modified by an alkyl ammonium cation bearing two primary hydroxyl functions): the thermal behavior and the reaction to fire were improved, but the structure (microcomposite, exfoliated, intercalated) was not really determined. This study focuses on polyurethane coatings reinforced with Cloisite 30B. The interactions between the diisocyanate and the counterions of Cloisite 30B and the structure obtained were demonstrated and discussed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 238–244, 2005

Key words: polyurethanes; nanocomposites; coatings; organoclay; thermal properties

INTRODUCTION

Nanotechnology is recognized as one of the most promising fields for the technological development of this century, as Richard Feynman foresaw it in 1959.[1] Nanocomposite polymers are a class of polymers reinforced with a small amount (typically 1 to 10% in weight) of particles with nanometric size. When filled by silicate nanoparticles with only one dimension (over the three dimensions) in the nanometer range, this kind of polymer is called polymer-layered silicate nanocomposites (PLSNs), the layered silicate of which is often cation-exchanged montmorillonite (MMT). The properties of PLSNs such as thermal stability, reaction to fire, or mechanical properties are generally improved.[2,3] These improvements are related to the dispersion of the layered silicate in the polymeric matrix. The best results are obtained with exfoliated structures, except for the flammability properties (exfoliated and intercalated structures seem to have the same effects).[4]

Some work has been carried out to use PLSNs in textile applications. Two ways have been considered: the first was the melt spinning of PLSNs yarns, which can subsequently be woven or knitted, and has been demonstrated as a promising approach for textile fire-retardant applications.[5,6] The second way was to synthesize polyurethane (PU) coatings with layered silicate to provide flame retardancy to the coated textile structure: it has been demonstrated as a way to reduce the harmful effects of a fire.[7] Different kinds of cation-exchanged MMT (Cloisite) have been studied so far. Some promising results have been obtained with Cloisite 30B (which is MMT organo-modified by an alkyl ammonium cation bearing two primary hydroxyl functions, presented later in the experimental section): the thermal stability and the reaction to fire were notably improved. The cone calorimetry by oxygen consumption tests showed that the fabrics with PU/Cloisite 30B had a lower peak of heat release rate (the peak intensity was reduced by 55% compared with the coating without Cloisite 30B). The overall smoke opacity decreased and the time to ignition increased; the improvement of these parameters highlights the potential use of Cloisite 30B in flame-retardant applications for textile coatings.

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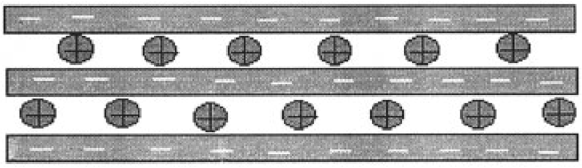

Figure 1 Structure of montmorillonite.

In this article, we focus on the polyurethane coatings reinforced with Cloisite 30B. Some encouraging results have been obtained, although the structure of the composite was not fully determined. However, the relationship between the improved polymer properties and the structure of composite is well established: the best results are generally obtained with nanocomposite structures (intercalated or exfoliated). The synthesis method of a polyurethane nanocomposite is reported herein to obtain the most appropriate structure to improve the properties of the related PU. The interactions between the counterions of the Cloisite 30B and the diisocyanate used to synthesize the polyurethane are also investigated.

EXPERIMENTAL

Materials

The additive used for the preparation of the polyurethane nanocomposite is Cloisite 30B (C30B) supplied by Southern Clay Products (Gonzales, TX). This type of clay belongs to the MMT family and is naturally hydrophilic, which hinders the dispersion of the clay particles in most polymer matrices. MMT belongs to the smectite family, characterized by negatively charged aluminosilicate layers bounded by electrostatic forces by alkaline cations, such as sodium cations or ammonium cations in organo-MMT located in the interlayer space (see Fig. 1). The counterion of the Cloisite 30B is a methyl tallow alkyl bis-2-hydroxyethyl quaternary ammonium cation (see Fig. 2). Cloisite 30B was delivered in the form of a fine powder.

The components for the synthesis of the PU/MMT coating are polyoxytetramethylene glycol (POTM; $\overline{M_n} = 2000$ g mol^{-1}), butanediol (BD) supplied by Aldrich Chemicals (Milwaukee, WI), and isophorone diisocyanate (IPDI) supplied by Bayer AG (Leverkusen, Germany). The process used to synthesize the polyurethane was carried out in two stages. For the first stage, two reactors were necessary. The first reactor was used to synthesize a prepolymer resulting from the reaction between POTM and IPDI in respective molar proportions of 1 : 2. The mixture was maintained at 100°C for 24 h under constant stirring. The chemical reactor was swept by a nitrogen flow in open circuit to avoid possible reaction between IPDI and water. The second reactor was used to obtain the mixture between IPDI and Cloisite 30B. The amount of IPDI was the same as that in the first reactor, and the quantity of Cloisite 30B was 5% in weight of polyurethane. The mixture was maintained at room temperature for 22 h under a nitrogen flow and constant stirring. The mixture of the second reactor was then added to the first one, and was maintained at 100°C for 2 h under constant stirring, in which the reactor was always kept under a nitrogen flow. This step allowed the two mixtures to homogenize and to finish the formation of the prepolymer. In the second stage, the excess of IPDI was made to react with 2.7 mol of chain extender (BD). This reaction was carried out in the presence of a catalyst, 0.2% dibutyl tin dilaurate, for 48 h at a temperature of 80°C. Normally, the exact quantity of BD is 3 mol (molar proportions of POTM/IPDI/BD were 1/4/3). Actually, however, IPDI reacts with the OH functions of the counterions of the Cloisite 30B, so that the quantity of BD had to be adjusted.

Characterization

Assessment of the IPDI consumed by counterions of Cloisite 30B

Two methods were used to estimate the quantity of IPDI consumed by the counterions of Cloisite 30B (the quantity of IPDI and Cloisite 30B are related to the proportions used for the synthesis of the PU with 5 wt % of Cloisite 30B). The first method is a back titration method. The quantity of free isocyanate functions was estimated according to the following principle: in the presence of an appropriate solvent, an excess of secondary amine (dibutylamine or DBA) reacts with the isocyanate functions by forming urea groups. The remaining quantity of secondary amine is then proportioned by a hydrochloric acid solution (0.5 mol/L). This method was inspired by the NF T 52-132 and NF T 52-133 standards on the titration of isocyanate functions.[8] The titration equations are as follows.

$$\underset{\text{isocyanate}}{\text{R-NCO}} + \underset{\text{DBA in excess}}{(C_4H_9)_2NH} \rightarrow \underset{\text{urea group}}{\text{R-NH-CO-N}(C_4H_9)_2} \tag{1}$$

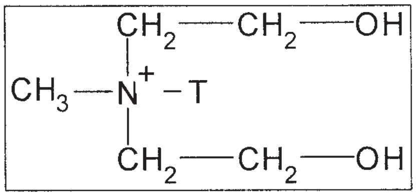

Figure 2 Counterion of Cloisite 30B (where T stands for tallowalkyl).

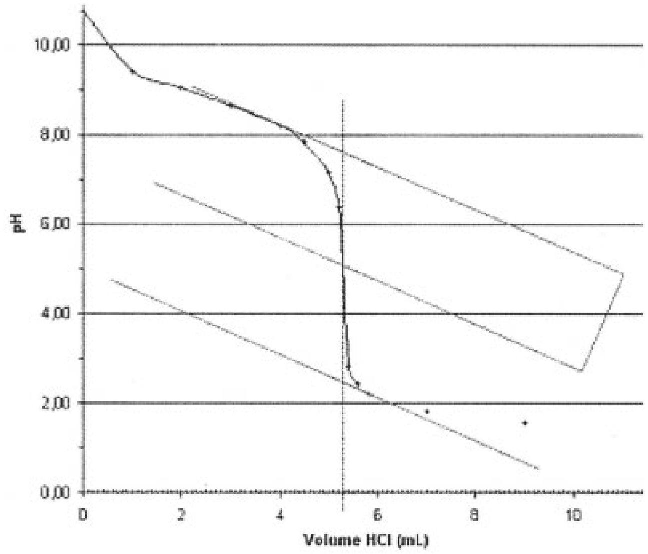

Figure 3 Curve of titration of the quantity NCO functions in the IPDI solution.

$$\underset{\text{remaining DBA}}{(C_4H_9)_2NH} + \underset{\text{hydrochloric acid}}{H^+} \rightarrow (C_4H_9)_2NH_2^+ \qquad (2)$$

The titration of the remaining DBA was carried out by a pH metric method (pHM210 MeterLab, Radiometer Analytical, London, UK). The equivalent volume was graphically determined according to the classical method of tangents. The pure IPDI and the mixture IPDI/Cloisite 30B were measured.

The second method used was infrared spectroscopy. The measurements were performed with a Nexus 870 spectrometer (Nicolet Analytical Instruments, Madison, WI). The samples (mixture IPDI/C30B) were placed between two KBr pellets obtained from finely crushed KBr powder. The sample was then placed in the spectrophotometer chamber swept by a flow of dry air. The areas of the different peaks at the initial time and at the final time were then determined. The one concerning the NCO peak (2257 cm^{-1}) varied, and this variation was compared with the area of the CH_2 peak considered as constant (2600–3030 cm^{-1}) to obtain the concentration of IPDI.

Transmission electron microscopy (TEM)

TEM images were obtained using a CM 200 microscope (Philips, Eindhoven, The Netherlands) at an accelerated voltage of 120 kV. Ultrathin sections (80 nm) were prepared at −130°C using a UCT ultramicrotome equipped with an FCS cryochamber (both from Leica Mikrosysteme GmbH, Wetzlar, Germany).

Wide-angle X-ray diffraction (WAXD) at low-angle region

A PU/MMT sample was molded (just after the second stage of synthesis of PU/MMT) into a plate to give a solid sample (20 × 20 × 2 mm thick). These samples were used to collect XRD data on a Siemens D500 diffractometer (University of Reading, UK), Cu–K_α radiation ($\lambda = 1.5406$ nm) with a 0.02° 2θ step size and a 2-s step time, within the scan range of 1–10°.

Thermogravimetric analysis (TGA)

TG analyses were performed using a Netzsch STA 449C thermobalance (Netzsch-Gerätebau GmbH, Bavaria, Germany) at 10°C/min, from 20 to 1000°C, under flowing air (60 mL/min). Samples (~ 10 mg) were placed in open platinum pans. The precision on temperature measurements was ±0.5°C.

RESULTS AND DISCUSSION

Assessment of the IPDI consumed by counterions of Cloisite 30B

By back titration of NCO

The method by back titration gave an equivalent volume of 5.3 mL for the pure IPDI (see Fig. 3). The specific rate of isocyanate functions was determined using the following equation:

$$\%\ \text{NCO} = \frac{100 \times n_{\text{NCO}} \times M_{\text{NCO}}}{m_{\text{IPDI}}} \qquad (3)$$

with

$$n_{\text{NCO}} = \frac{p_{\text{DBA}} \times m_{\text{DBA}}}{M_{\text{DBA}}} - \frac{C_a \times V_e}{1000} \qquad (4)$$

where % NCO is the specific rate of isocyanate functions, that is, the mass percentage of available isocyanate functions relative to the mass of analyzed IPDI;

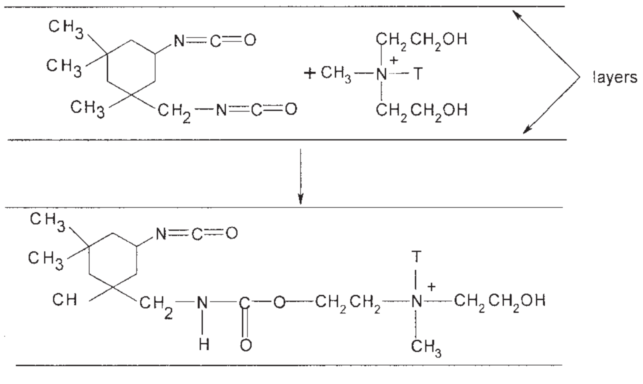

Figure 4 Reaction between IPDI and a counterion.

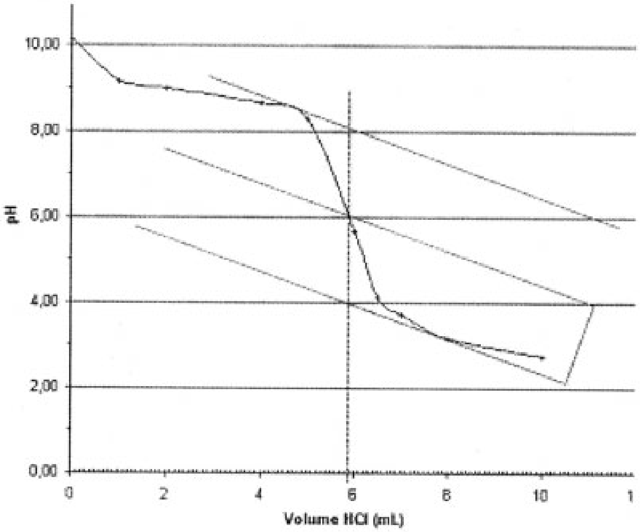

Figure 5 Curve of titration of the quantity NCO functions in the IPDI/Cloisite 30B mixture.

n_{NCO} is the mole of titrated isocyanate functions; M_{NCO} (=42.02 g/mol) is the molar mass of the isocyanate function; m_{IPDI} is the mass of IPDI used for the titration; m_{DBA} is the mass of *N*-dibutylamine; M_{DBA} (=129.25 g/mol) is the molar mass of *N*-dibutylamine; p_{DBA} (=0.995) is the purity of *N*-dibutylamine; V_e is the equivalent volume (mL); and C_a is the concentration of the hydrochloric acid solution.

The % NCO found was 37.8%, which is in good agreement with the supplier's data (37.7–37.8%).

The counterions of Cloisite 30B present two hydroxyl groups. It is thus possible to promote a reaction between IPDI and the counterions (see Fig. 4). This method would lead to a polyurethane nanocomposite with mixed morphology (intercalated and exfoliated),[9] but the reaction was between the prepolymer and the counterions. In our study, an IPDI monomer (IPDI) was directly introduced to react with the counterions, and the quantity of IPDI reacting with counterions was evaluated; it is thus possible to adapt the quantity of chain extender (BD) to be added in the second stage of PU/MMT synthesis.

The equivalent volume found for the IPDI/Cloisite 30B mixture was 5.9 mL (see Fig. 5), so the % NCO decreased to 33.5%.

By infrared spectroscopy

To confirm the previous results, some measurements were carried out by infrared spectroscopy. The specific rate of isocyanate functions (r[NCO]) was determined using the following equation:

$$r[\mathrm{NCO}] = \frac{[\mathrm{NCO}]_0 - [\mathrm{NCO}]}{[\mathrm{NCO}]_0} = 1 - \frac{A(\mathrm{NCO})[t_f] \times A(\mathrm{CH_2})[t_0]}{A(\mathrm{CH_2})[t_f] \times A(\mathrm{NCO})[t_0]} \tag{5}$$

where $[\mathrm{NCO}]_0$ is the concentration of NCO at the initial time; $A(\mathrm{NCO})[t_0]$ and $A(\mathrm{NCO})[t_f]$ are the integrated absorbances of NCO at the initial time (t_0) and the final time (t_f) of the reaction with $\upsilon(\mathrm{NCO}) \approx 2257$ cm^{-1}; and $A(\mathrm{CH_2})[t_0]$ and $A(\mathrm{CH_2})[t_f]$ are the integrated absorbances of $\mathrm{CH_2}$ and $\mathrm{CH_3}$ at the initial time (t_0) and the final time (t_f) of the reaction with $\upsilon(\mathrm{CH_2}) \in [2600\text{–}3030]$ cm^{-1}.

The initial time corresponded to the spectrum of the mixture after a few minutes of stirring of IPDI and Cloisite 30B. Three spectra corresponding to the initial time were carried out. The final time was determined after the stabilization of $A(\mathrm{NCO})[t_f]/A(\mathrm{CH_2})[t_f]$. In Fig-

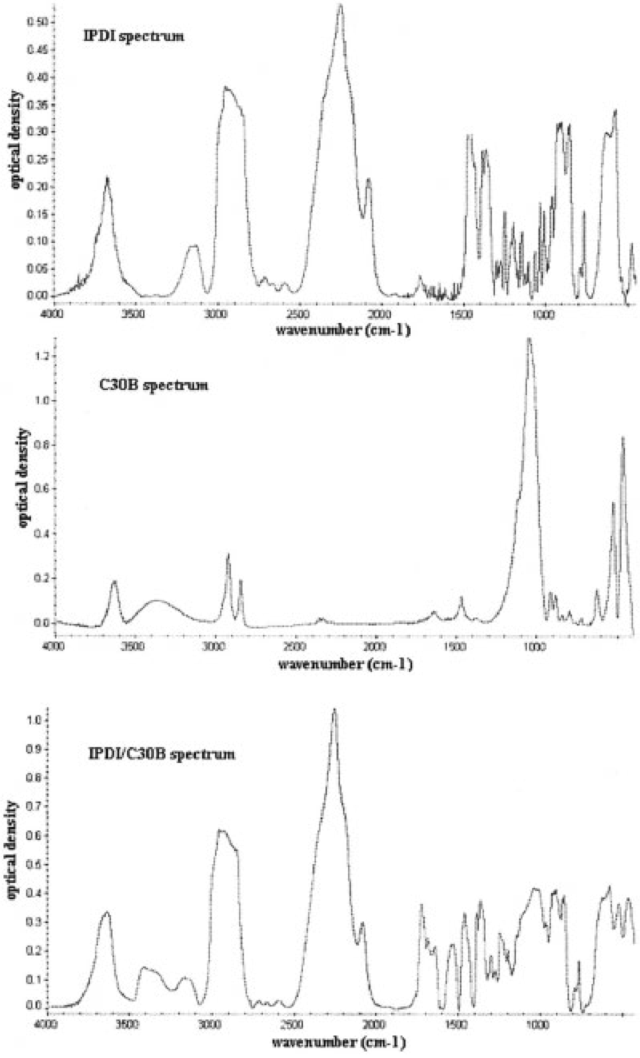

Figure 6 Infrared spectra of IPDI, Cloisite 30B, and IPDI/Cloisite 30B at final time.

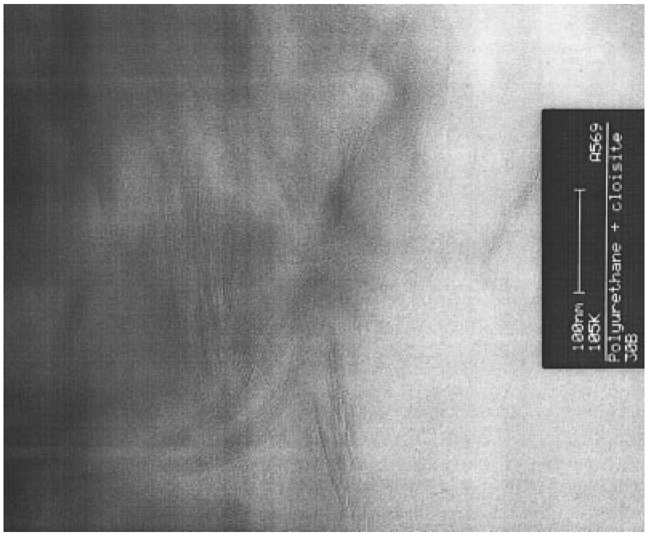

Figure 7 TEM image of an intercalated nanocomposite PU/Cloisite 30B.

ure 6, the characteristic peaks of the IPDI (υ(NCO) $\approx$ 2257 cm^{-1} and $\upsilon(CH_2)$ and $\upsilon(CH_3) \in$ [2600–3030] cm^{-1}) and the characteristic peak of hydroxyl group of the counterions of Cloisite 30B [υ(OH) $\approx$ 3300 cm^{-1}] can be observed. For the IPDI/Cloisite 30B mixture at the final time, we see that a new peak appeared at 1720 cm^{-1}, corresponding to the C=O function, which proves that the reaction between the NCO functions of IPDI and the OH functions of the counterions of Cloisite 30B occurs to form urethane links: r[NCO] = 11.9% and the % NCO decreases to 33.3%.

The two methods allowed us to conclude that the reaction effectively occurs between IPDI and the counterions of Cloisite 30B. The counterions can then be used to start some PU chains, which are grafted onto the silicate layers, and this reaction should facilitate the intercalation or the exfoliation of the layers of Cloisite 30B in the PU matrix. It is thus necessary to adapt the quantity of BD: only 2.7 mol of BD need be used as chain extender and not 3 mol.

TEM

The actual nature of a nanocomposite can be observed using TEM images. Figure 7 shows a typical micrograph of the PU containing 5 wt % of Cloisite 30B. The dark lines represent the sheets of Cloisite 30B, the thickness of which is about 1 nm. The spaces between the dark lines represent the interlayer spaces. As shown in this photograph, the structure of the nanocomposite seems to be rather an intercalated structure. No exfiolated sheet is observed in the PU matrix. A reason that explains why we did not obtain an exfoliated structure is probably the high functionalization of the alcohol functions of the counterions of the Cloisite 30B by the diisocyanate. During the chain growth, some crosslinking reactions can occur and this reaction should prevent the exfoliation of the layers from taking place. The distance measured on the image gives us an approximate interlayer distance of 3.8 nm.

XRD

To better estimate the distance between two layers, XRD can be used. The WAXD curves of Cloisite 30B and PU/Cloisite 30B are shown in Figure 8. The curve concerning Cloisite 30B presents a broad peak at $2\theta = 4.9°$, which indicated that the *d*-spacing between two silicate layers is about 1.9 nm {calculated with

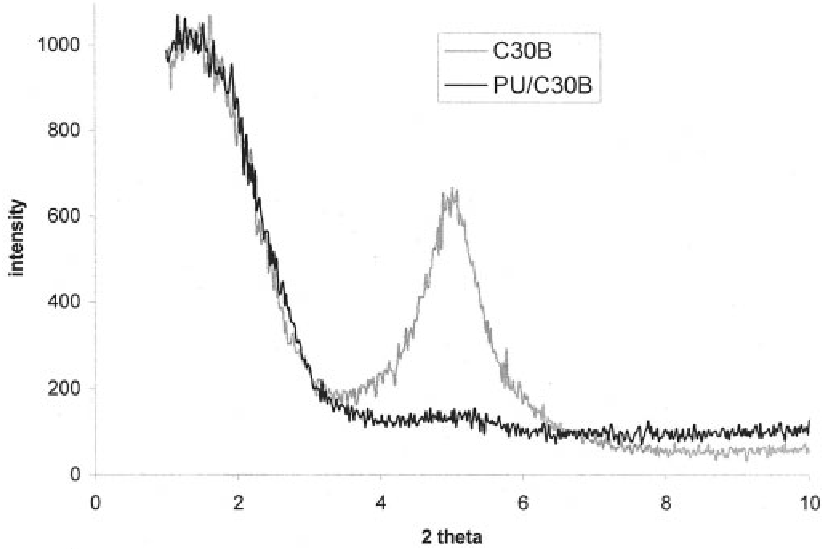

Figure 8 Wide-angle X-ray diffraction curves of Cloisite 30B and PU/Cloisite 30B.

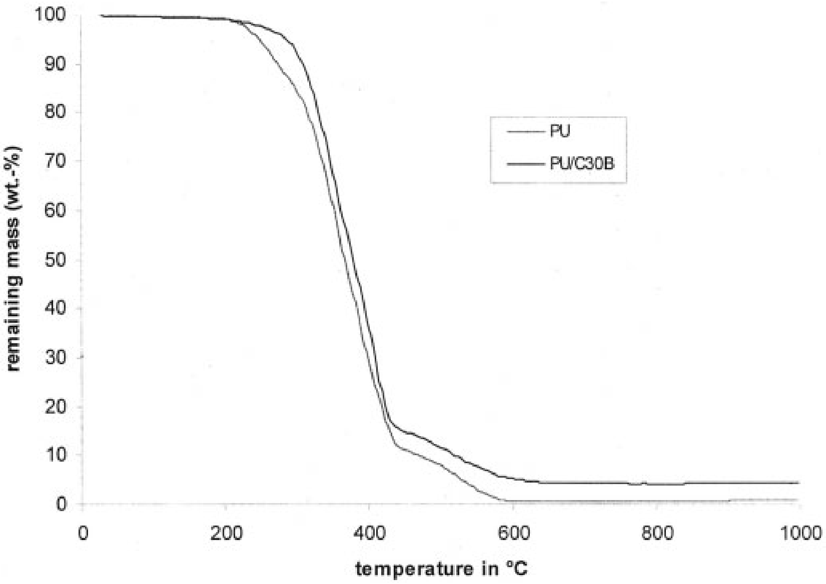

Figure 9 TG behavior of PU and PU/Cloisite 30B.

Bragg's law $d = \lambda/[2 \sin(\theta)]\}$. This typical peak of Cloisite 30B disappeared on the IPDI/Cloisite 30B curve. This disappearance could be explained either by the exfoliation of the silicate or by a high disorder of the clay.[3] If the silicate layers were exfoliated, the *d*-spacing would become too high and could not be detected by the XRD methods, and if the clays were not well ordered, it would fail to produce a Bragg diffraction peak. However, TEM experiments showed the intercalated structure of PU/Cloisite 30B. It can then be supposed that a peak should be observed at lower 2θ values (at about 2.3°, this value was calculated from the interlayer distance measured on the TEM image).

Thermogravimetric analysis

A number of studies on the thermal degradation of PU have previously been published.[10–20] The first stage of degradation of PU is mainly a reaction of depolymerization.[10–13,15] This depolymerization starts generally between 200 and 250°C, and corresponds to the failure of urethane links, which leads to the release of the polyol and of the isocyanate used to synthesize the PU chains. The monomers then slowly volatilize, and there is a profusion of secondary reactions (urea formation) and rearrangements. At 500°C, all the urethane groups are decomposed and the final degradation of PU corresponds to the decomposition of urea groups.[21]

TG curves of PU and PU/Cloisite 30B are shown in Figures 9 and 10. The general trend of the curves allows to conclude that PU/Cloisite 30B has a better thermal stability than PU (Fig. 9). PU started to degrade from 200°C in two main stages (from 200 to 430°C and from 430 to 580°C, these stages corresponding to the results seen in the literature) and forms only a residue of 0.1% of the initial weight. The PU/Cloisite 30B presents a similar behavior (in two stages), but is more thermally stable, particularly between 200 and 320°C, that is, during the start of the decomposition (Fig. 10). Actually, we obtain 95% of the initial weight of PU at 250°C compared with 285°C for PU/Cloisite 30B. It degrades totally at around 650°C by forming a more important residue (~ 4.5%), which corresponds to the rest of Cloisite 30B. The clay can thus be considered as responsible for the improvement of the thermal stability.

CONCLUSIONS

The original aspect of the synthesis of this polyurethane nanocomposite was to use the counterions of the Cloisite 30B to initiate the growth of the PU chains. The reaction between the counterions of Cloisite 30B and IPDI was evidenced by two different techniques (titration and infrared spectroscopy). The TEM observations revealed an intercalated structure, even if it was difficult to precisely measure the exact *d*-spacing of the Cloisite 30B in the PU matrix because of a parasite peak on the WAXD curves. The TG results showed an improvement in the thermal stability, particularly at the start of the degradation (an increase of 35°C was observed), in spite of the small amount of Cloisite 30B used (5 wt %). This improvement is better than that observed in the first study.[6] Thus, the process (which is different in this study) is substantially important in obtaining a good dispersion of the Cloisite 30B in the PU matrix.

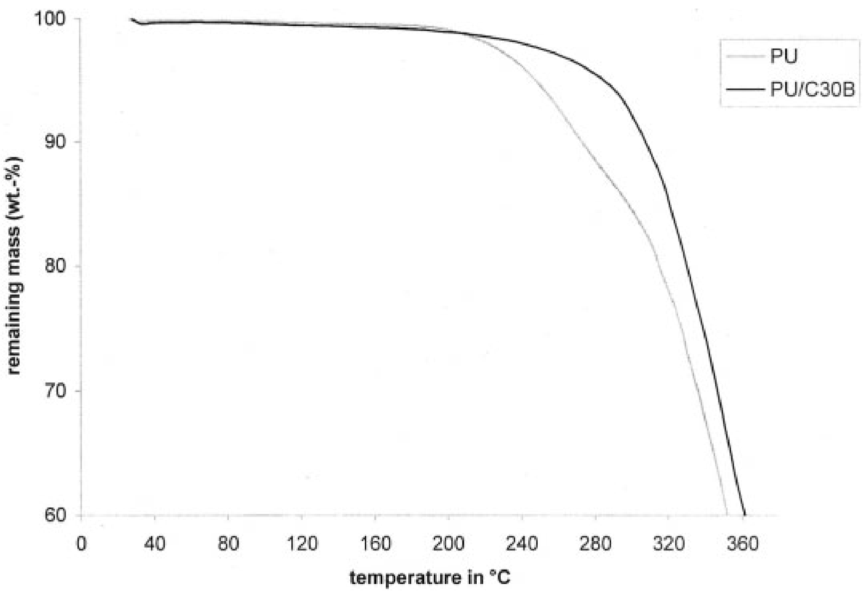

Figure 10 TG behavior of PU and PU/Cloisite 30B during the start of decomposition.

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