Invited Paper

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Micro and nanocomposites of polybutadienebased polyurethane liners with mineral fillers and nanoclay: thermal and mechanical properties

Abstract: Micro and nanocomposites of hydroxyl terminated polybutadiene (HTPB)-based polyurethanes (NPU) were obtained using five mineral fillers and Cloisite 20A nanoclay, respectively. Samples were prepared by the reaction of HTPB polyol and toluene diisocyanate (TDI), and the chain was further extended with glyceryl monoricinoleate to produce the final elastomeric polyurethanes. Mechanical and thermal properties were studied, showing that mineral fillers (20% w/w) significantly increased tensile strength, in particular nanoclay (at 5% w/w). When nanoclay-polymer dispersion was modified with a silane and hydantoin-bond promoter, elongation at break was significantly increased with respect to NPU with C20A. Thermal properties measured by differential scanning calorimetry (DSC) were not significantly affected in any case. The molecular structure of prepared micro and nanocomposites was confirmed by Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy. Interaction of fillers with polymer chains is discussed, considering the role of silanes in compatibilization of hydrophilic mineral fillers and hydrophobic polymer. The functionalization of nanoclay with HMDS silane was confirmed using FTIR. Microstructure of NPU with C20A nanoclay was confirmed by Atomic Force Microscopy (AFM).

1 Introduction

Polyurethane compositions are utilized as liners to bond to composite propellants, and are mainly based on hydroxyl-terminated polybutadiene (HTPB). Liner properties can be tailored to a certain extent with the selection of appropriate fillers, and several compositions are utilized for these purposes. HTPB-based rubbers, filled with carbon black and antimonium oxide were used as liners for composite propellants. Carbon black acted as the reinforcing filler while Sb_2O_3 gave fire retardancy as well as reinforcement [1]. Wingborg and Sandén [2] used carbon black and aerosol as fillers in HTPB-polyurethane liners, while studying adhesion. Benli and coworkers [3] investigated the effect of different mineral fillers in HTPB-based liners cured with IPDI and chain extended with triethylamine. They utilized two different types of carbon black; and also silica, aluminum oxide, and zirconium(III) oxide as fillers. They concluded that these fillers do not considerably change the thermal degradation temperatures up to a load of 16% (w/w). Kakade and coworkers [4] have studied the effect of a variety of fillers for HTPB rubber liners. They found that using carbon black as the principal filler with a combination of silica and antimony trioxide as a fire retardant, gave adequate properties.

Besides conventional mineral fillers, nanofillers are additives that are conveniently incorporated into the polymer matrix to obtain polymeric nanocomposites. These nanofillers have at least one of its dimensions in the nanometer range. The mixing of clay with polymer matrices to form nanocomposites appears to have begun in late 1940s, with a resurge in early 1990s [5]. Recent literature has reported improvements on several properties of organically modified layered silicates (OMLS) polymer nanocomposites [6-12]. The presence of

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organoclay produces a deeper interaction filler/matrix at the interface compared with conventional fillers [13]. The type of nanofillers, state and degree of dispersion can be manipulated in order to obtain an array of properties so far not achievable from polyurethanes filled with micrometer size inorganic filler particles [14]. For example, it was reported that only 10 phr (parts per hundred of rubber) of organoclay are enough to obtain a similar mechanical behaviour as the compound with 40 phr of carbon black [13]. Polymer nanostructured materials with nanoclays were demonstrated to play a key role in reducing the flammability on coating systems in solid rocket exhaust plumes [15, 16]. A small amount of nanofiller up to 5% is generally sufficient to improve mechanical properties of polyurethanes [6, 17-21] and also thermal resistance properties [22].

In spite of the improved affinity of nanoclays for polymers compared to unmodified clay, compatibilization of nanoclay with silanes is made to further improve this affinity. Hexamethyl disilazane (HMDS) is a silane capable to introduce trimethylsilyl group in molecules having an active H atom, such as nanoclay. To increase affinity of mineral fillers to hydrophobic elastomers, bonding agents are added. Among bonding agents for rubbers there is a variety of additives, including Carbon Black and hydantoins [24].

In order to verify the incorporation of silane into nanoclay, we have chosen infrared spectroscopy as an analytical tool. Infrared spectroscopy was reported as a good method to mark the absorption bands of silanes, to verify if a reaction between the filler and silane occurred [25]. In this contribution we report the effect of five mineral fillers on the properties of HTPB-based microcomposites and three nanocomposites with nanoclay on their thermal and mechanical properties. FTIR and Raman spectroscopy is utilized to confirm incorporation of fillers to the polyurethane backbone, while AFM technique is applied to verify that a nanocomposite with nanoclay is obtained. The effect of silanization of hydrophilic nanoclay filler with HMDS is presented, together with the effect of a hydantoin-bonding agent on NPU properties.

2 Experimental Procedure

Materials: Hydroxyl-terminated polybutadiene, HTPB (hydroxyl index 0,051 eq./100 g, M_w 3000 g/mol) was from was purchased from Zibo Qilon Chemical Industry Ltd., China. A 70:30 mixture of 2,4 and 2,6 isomers of toluene diisocyanate (TDI) was utilized as received from Petroquímica Río Tercero S.A. (PRIII), Córdoba, Argentina.

Dibutyl tin laureate (DBTL) was purchased from Sigma Aldrich Argentina. Chain extender glycerol monoricinoleate (MRG) was a commercial product (99% purity) from local suppliers (Quimex Sudamericana). Titanium dioxide was of 99% commercial grade material, grinded up to a particle size in the range of 10-15 µm and used at 20% (w/w). The other fillers were also utilized at 20% (w/w) and were standard analytical laboratory reagents, except from Lithopone and Carbon Black ("Negro de Humo") that were commercial samples (Quimex Sudamericana S.A.). Carbon Black mean particle size was 1,5 µm. Lithopone (a mixture of barium sulfate and zinc sulfide) had an uneven particle size as seen by Scanning Electron Microscopy, from 2 to 4 µm. Calcium carbonate (aragonite-tupe crystals) and zinc oxide were 99.5% purity from Merck Co., U.S. Mean particle sizes were 1.5 and 0.4 µm, respectively. Cloisite 20A (dimethyl-dihydrogenated tallow quaternary ammonium montmorillonite) was a commercial nanoclay purchased from Southern Clay Products, U.S. used at a concentration of 5%. Bonding promoter Dantocol DHE (N,N-di(2-hydroxyethyl)-5, 5-dimethyl hydantoin) was 99% purity and obtained from Glyco Inc., Greenwich, U.S. Hexamethyl disilazane (HMDS) was 99% purity and obtained from Sigma Aldrich U.S.

2.1 Synthesis of polyurethane micro and nanocomposites

HTPB (69.4 g) was deaerted under vacuum at 60-70 °C, for two hours. The chain extender glycerol monoricinoleate (MRG, 4.25 g), was added in one step together with the corresponding mineral filler (20% w/w) and stirred at 250 rpm in a 500 ml glass reaction kettle under vacuum (5 mm Hg) for about 1 hour at room temperature (20 ºC). When nanoclay composites (NPU) were prepared, dispersion was carried out by mixing at 2000 rpm for 15 minutes with a high speed laboratory mixer (IKA brand) using a 5 cm diameter round-bottom blade. After this period, this mixture was allowed to react with the corresponding modifier (HMDS silane or Dantocol DHE hydantoin) mixing for a further hour at 250 rpm. Afterwards a calculated quantity of the toluene diisocyanate (TDI), 6.2 g (which corresponded to a NCO/OH ratio of 1) together with DBTL catalyst (0.05%) were added. Mixing continued for a further 10 minutes at 250 rpm under vacuum at room temperature, after which the mixture was poured into preheated metal moulds. The curing was allowed to proceed at 70 °C for 24 hours. Samples were used for testing only after at least one week of further curing at room temperature. PU with the following components: HTPB/TDI/MRG/TiO$_2$ was

used as reference sample for purposes of comparison and analysis, this is the composition used for a standard liner. Differential scanning calorimetry (DSC) studies were performed in a TA model Q20 apparatus. Samples were heated at 5 °C/min under a nitrogen atmosphere.

Fourier transform infrared (FT-IR) spectroscopy studies were performed using a Nicolet 520 spectrometer with a KBr window, with a resolution of 4 cm-1, number of scans 64, between a wavelength interval from 600 and 4000 cm-1. A Spectra Tech ATR (attenuated total reflectance) attachment with a horizontal ZnSe crystal was used. The collected spectra were analyzed by means of Omnic 3.0 software.

Tensile strength at break and elongation at maximum load were obtained utilizing a MTS DS/2 universal testing machine utilizing dumbbell-shaped probes, at a velocity of 50 mm/sec according to ASTM D-638.

Raman spectroscopic studies were performed with a Renishaw apparatus model Invia, with a 785 nm laser of 300 mW, 50X augmentation within 100 to 3200 cm^{-1}.

Atomic force microscopy (AFM) was performed with a Bruker UltraObjective apparatus using a silicon point of 10 nm radius and with a force from 21 to 100 N/m under the tapping mode (National Institute for Industrial Technology, INTI, Buenos Aires).

Mineral filler mean particle size was obtained from scanning electron microscopy (SEM) utilizing a Focused Ion Beam (FEI) NanoLab 650 Dual Beam microscope (Micro and Nanotechnology Center, INTI, Buenos Aires).

Figure 1: FT-IR spectra for five HTPB-based polyurethane microcomposites with different mineral fillers at 20% (w/w).

Figure 2: FT-IR spectra for three HTPB-based nanocomposites (NPU). Top to bottom: nanoclay C20A (a), NPU with C20A nanoclay (b), NPU with C20A plus hexamethylene disilazane (HMDS) (c) and NPU with C20A plus Dantocol DHE (d).

3 Results

In Figure 1 we observed that the spectra of PU with mineral fillers were quite similar, reflecting the absorption bands of polyurethanes (Figure 1). The absence of -NCO absorption band around 2266 cm^{-1} indicates complete consumption of diisocyanate in formation of the urethane network. Bands were assigned as follows: absorption at around 3300 cm^{-1} corresponded to N-H, while C-H bands were found in the region between 2800 and 2900 cm^{-1}. Other main bands were at 1735 cm^{-1} (C=O stretching of urethane group), 1600 cm^{-1} (NH deformations) and 1450 cm^{-1} (CH$_2$ and CH bending) [26, 27].

Spectra for Cloisite 20A nanoclay and NPU are presented in Figure 2. All NPU had a peak at 1260-1265 cm^{-1}. As this peak was not seen in C20A additive alone, it was concluded that the band corresponded to the interaction of C20A with forming polyurethane. As it was of very low intensity in HMD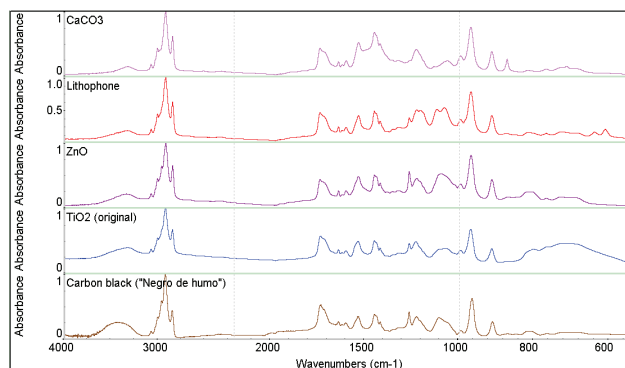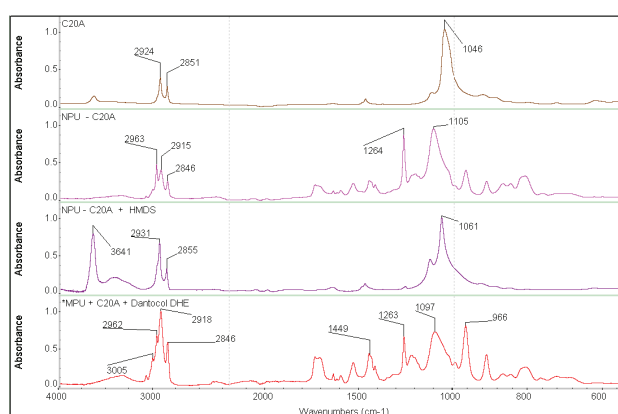S-treated C20A NPU (sample c) it is possible that silane reaction with OH groups in nanoclay impeded reaction of these groups with isocyanate when forming polyurethane.

NPU with C20A (sample b) showed sharp and intense bands at 1105, 1264, 1449 and 2929 cm^{-1}. Main bands for C20A were found at 916, 1046, 1468, 2851 and 2924 cm^{-1}, accordingly with previous reports [28]. C20A band at 1050 cm^{-1} corresponded to the stretching vibration of Si-O-Si [29]. In sample (c) the peak located at 1060 cm^{-1} was particularly broad. This very strong band was assigned to the Si-O-Si stretch in silane modified clays, indicating surface modification of nanoclay by incorporation of HMDS silane. Band at 3641 cm^{-1} was assigned to Si-OH hydroxyl stretching in clays modified using silanes [30]. In silanized clays an increase in the Si-O peak at a frequency around 1050 cm^{-1} is observed [31, 32]; which we observed at 1060 cm^{-1}. This suggested that HMDS was chemically

incorporated to nanoclay structure. Nanocomposite with C20A plus bond promoter Dantocol DHE (sample d) showed a distinctive peak at 1097 cm^{-1} also seen in C20A nanoclay but with low intensity. In all three NPU samples the peaks close to 2850 and 2920 cm^{-1} were due to the -CH asymmetric and symmetric stretching of -CH$_2$ groups from chemical structure of surfactant in C20 nanoclay [30].

Raman spectra of microcomposites with mineral fillers under consideration are shown in Figure 3.

Characteristic bands for TiO$_2$ (anathase phase) were found at 396, 515 and 638 cm^{-1}. Sample with CaCO$_3$ displayed typical filler absorption bands at 1086 and 1430 cm^{-1}. Lithopone sample showed sulphate band at 988 cm^{-1} and sulphur band at 350 cm^{-1}. Typical absorption bands for cis-1,4; trans-1,4 and 1-2-vinyl in HTPB were confirmed between 1620 and 1680 cm^{-1}. Carbonyl peaks of all PU microcomposites were found around 1700 cm^{-1}, while free carbonyl is found at 1735 cm^{-1}. This indicated that mineral fillers were bonded to C=O, as wave number was shifted to lower values [26, 33].

The following Figure 4 shows Raman spectra of nanocomposites prepared. In general it was found that the positions of peaks from distinctive functional groups were nearly identical in both pristine polyurethane and the PU/organoclay nanocomposite, which means that the segmented structure of polyurethane was not affected by the presence of organoclay [34].

In general spectra of nanocomposites were similar to that of neat PU without any treatment. NPU with C20A has similar bands to those characteristic of montmorillonite-based C20A: at 550 cm^{-1} and 450 cm^{-1}, corresponding to the stretching vibration of Al-O, and the bending vibration of Si-O, respectively [35]. Bands at 1610 cm^{-1} corresponded to aromatic isocyanate, 1440 cm^{-1} to N=C=O scattering (symmetric stretch), while also urethane (amide functional group at ca. 1303 cm^{-1}) were identified [36]. In silanized nanoclay the main sample bands seen with FTIR were confirmed but somewhat displaced. This could be due to the fact that molecules with different elements of symmetry, certain bands may be active in IR, Raman, both or neither. Dantocol DHE absorption bands are clearly seen as narrow peaks. NPU with bonding agent Dantocol DHE showed additional peaks corresponding to this bonding agent.

Strain-stress properties of PU and NPU samples are shown in Table 1. It was observed that microcomposites increased tensile strength from 55 (Lithopone) to 260% (Carbon Black) respect to sample with TiO$_2$, which was used as reference for properties comparison and analysis.

A three-fold increase in tensile strength was found with nanocomposites with Cloisite 20A nanoclay (5%
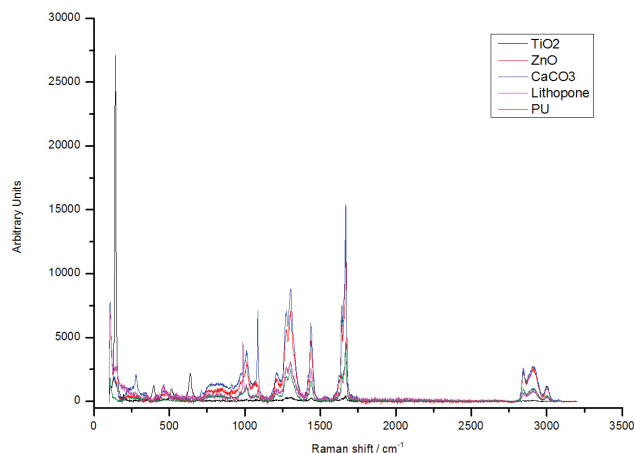

Figure 3: Raman spectra of microcomposites of elastomeric PU with different mineral fillers and neat PU.
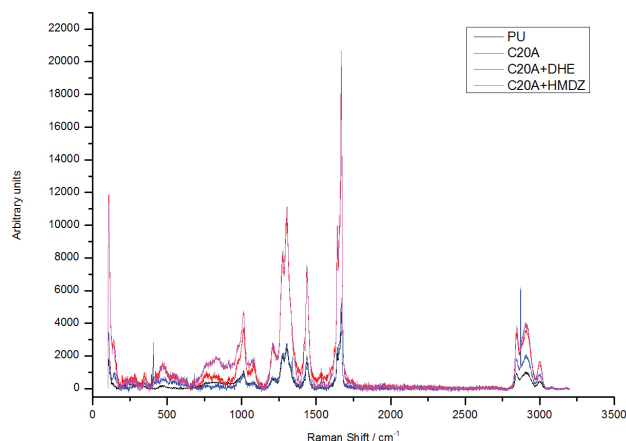

Figure 4: Raman spectra of nanocomposites (NPU) of elastomeric PU with nanoclay and modified nanoclay. PU: neat sample without nanoclay; NPU with C20A 5%; NPU with C20A + HMDS and NPU with C20A+Dantocol DHE.

w/w). Nanoclay creates crosslinking of polymer matrix by strong interfacial interaction with the polymer chain and limiting the mobility of surrounding chains, thus increasing modulus [37, 38]. However, silanization with HMDS did not improve mechanical resistance, although it a significant increase in elasticity (elongation a break) respect to both micro and nanocomposites was seen. The NPU obtained could be a useful material for special applications demanding very high elasticity.

In general, it is expected that fillers act as nucleating agents for polymers, inducing the formation of crystallites. Among the mineral fillers tested, all increased tensile strength respect to unfilled PU (0,5 MPa, not in Table) and to TiO$_2$-filled microcomposite. It was observed that Carbon Black increased significantly modulus, almost

Table 1: Mechanical properties of microcomposites (PU) with different inorganic mineral fillers [20% (w/w)] and nanocomposites (NPU) with Cloisite 20A nanoclay [5% (w/w)].

Sample	Young Modulus (MPa)	Elongation at break (%)
TiO$_2$	1,08	1000
ZnO	1,81	240
BaSO$_4$-ZnS (Lithopone)	1,68	250
CaCO$_3$	2,17	260
Carbon Black	2,82	200
PU nanocomposites		
Cloisite 20A	3,3	280
Silanized Cloisite 20A	0,5	1200
Cloisite 20A+Dantocol DHE	1,27	370

Figure 5: Thermal properties of polyurethane microcomposites with different mineral fillers studied. Curves (from top to bottom): CaCO$_3$, Lithopone, ZnO, TiO$_2$ and Carbon black.

augmenting three-fold tensile strength. Addition of Carbon Black to HTPB-TDI system provided a ten-fold increase in tensile strength and a three-fold increase in elongation while generally improving other properties [39]. However, we consider not convenient its utilization as liner for composite propellants because of excessive generation of combustion gases and pyrolysis products when exposed to high temperatures. In general, properties of elastomeric filled materials mainly depend on the dispersion condition of filler particles and their principal relevant properties: particle size, surface area, aggregate structure, surface activity, and rubber-filler interactions [40].

The following figure depicts the thermograms of microcomposites with mineral fillers under study:

Carbon black microcomposite higher temperature peak was split in two exotherms. In a PU system based on HTPB-IPDI filled with Carbon Black, main exotherms were also found at 370 °C and 500 °C [3]. Sample with calcium carbonate decomposed completely 6.4 °C higher than sample with titanium dioxide. This could be due to the aragonite-type structure of calcium carbonate which shielded hard segments better than TiO$_2$ from high temperatures. Thermal properties for the three PU nanocomposites (NPU) prepared with 5% C20A nanoclay, silanized 5% C20A with 5% hexamethylene disilazane (HMDS) and 5% C20A plus bond promoter Dantocol DHE at 5% were not different from microcomposites with mineral fillers (exotherms were found at 375 and 500 °C for these three samples). This indicated that silanization and addition of bonding agent did not affect thermal properties of NPU with C20A nanoclay, and that the main improvement of nanoclay in thermal properties is due to their barrier properties.
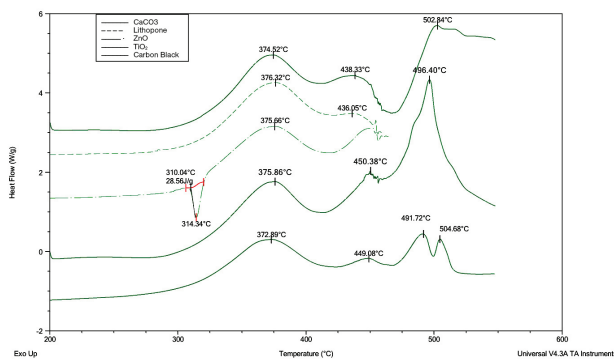
Microstructure morphology of a nanocomposite sample was studied by atomic force microscopy (AFM). The stronger penetration of the AFM tip in the softer region relative to the harder urethane region allowed visualization of different phase-components. In the following figure, the left hand side image corresponded to the PU liner without nanoclay. The hard and soft domains were clearly seen, indicating segregation of these structures. The high modulus hard domains and the low modulus soft blocks appeared as light and dark regions, respectively [41]. White clear dots (left hand-side) were impurities after film sample preparation by spin coating.

Right hand-side image corresponded to C20A-NPU. Nanoclay could be seen as dark coloured aggregates. The AFM micrograph showed that the clay agglomerates were broken into smaller tactoids, which are then intercalated/exfoliated in HTPB [42, 43].

4 Conclusions

We have shown that NPU with C20A nanoclay improved the mechanical properties significantly, when compared to microcomposites with conventional mineral fillers. This improvement in mechanical properties is well-known and thoroughly reported in the bibliography. Surface modification of nanoclay-HTPB by incorporation of HMDS silane was shown by FTIR. Elongation at break was increased by four-fold with respect to NPU with C20A, and was almost the same as with TiO$_2$-filled microcomposite. With respect to the thermal properties, neither nanoclay silanization nor addition of hydantoin-bonding agent produced any effect on thermal properties of NPU compared to NPU with C20A, as main improvement
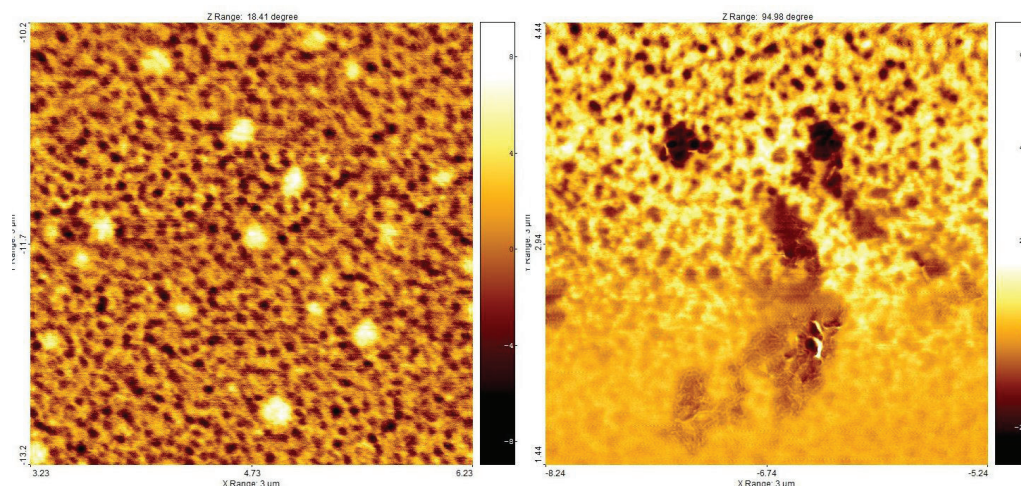
Figure 6: Atomic Force Microscopy of polyurethane liner without C20A nanoclay (left) and with C20A nanoclay (right).

is due to platelet barrier effect of nanoclay. The materials obtained with silanized C20A were very soft compared to NPU with C20A, probably because of the increased compatibilization of nanoclay with hydrophobic HTPB segment. Silanization impeded the segregation of hard and soft domains, then rendering the nanocomposite very soft in comparison with C20A nanocomposite. These materials are potentially useful for high elasticity applications. Dantocol DHE-NPU did not show any particular advantage with respect to thermal and mechanical properties compared to the microcomposites studied. Morphology of nanocomposite with C20A was analyzed by AFM, evidencing PU hard and soft domains and nanoclay incorporation. However, it has to be kept in mind that properties of nanocomposites depend on several factors acting simultaneously. Anticipated behavior due to the combined effect of particle size, surface area, aggregate structure and polymer-filler interactions detailed behavior needs to be further investigated.

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