

# Thermoplastic polyurethane nanocomposites: effect of organoclay structure and hard segment concentration on morphology and properties

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## ABSTRACT

TPU nanocomposites were prepared by melt processing using a twin screw extruder. The effects of organoclay structure and hard segment concentration of the TPU matrix on mechanical properties and morphology of the nanocomposites were examined. Mechanical properties, transmission electron microscopy (TEM), and wide-angle x-ray diffraction (WAXD) data are reported. Specific comparisons of the structure of the organic treatment were made. The structural effects that produced the most significant enhancement in properties and morphology of TPU nanocomposites were the use of hydroxy-ethyl groups rather than methyl groups, one long alkyl tail instead of two, and a long alkyl tail in place of a short one. Higher degrees of exfoliation were obtained with a higher concentration of hard segments, as judged by TEM and WAXD.

**Keywords:** nanocomposites, thermoplastic polyurethane.

## 1 INTRODUCTION

Polymer layered silicate nanocomposites research has become of great importance in the last few years as a result of the superior properties that these materials exhibit over conventional composites. Numerous studies have shown that a very low percentage of layered silicates can lead to a significant enhancement in many properties; making these materials interesting prospects for a wide variety of applications, such as in automotive, electronics, food packaging, biotechnology, and many others.

The key to obtaining significant property enhancements is to disperse, or exfoliate, the individual silicate sheets within the polymer matrix. The affinity of the polymer with the surface of the clay and/or with the organic surfactant of the organoclay is essential to promote favorable interactions between these species and hence obtain a good exfoliation. An important aspect regarding the exfoliation process is the polarity of the polymer matrix. Recent studies from our laboratory show that a polar polymer such as Nylon 6 (PA-6), exhibits a higher level of exfoliation with an organoclay containing a one-tailed organic treatment, while nanocomposites made from non-polar polymers, such as PP, LLDPE, and PE ionomers showed completely opposite trends, i.e., a two-tailed organic treatment formed more exfoliated nanocomposites

than a one-tailed organoclay [1-3]. Since a one-tailed organoclay provides less coverage of the silicate surface than a two-tailed organoclay, these results suggest that PA-6 has a higher affinity for the polar surface of the clay than for the largely non-polar surfactant, while the opposite happens with non-polar matrices.

Thermoplastic polyurethanes (TPU's) are a polar type of polymer that has similar functional groups as PA-6 but a completely different repeat unit and structure.

The object of this study is to explore the structure-property relationship of TPU nanocomposites made from different types of organoclays. Mechanical properties and morphology characterization will be used to evaluate the performance and degree of exfoliation.

## 2 EXPERIMENTAL

Commercial grades of thermoplastic polyurethane (a medium-hardness polyester-based TPU from Dow Plastics, and a high-hardness polyether-based TPU from BASF) were chosen due to their high tensile strength, ductility and good processability. The medium- and high-hardness thermoplastic polyurethanes will be referred as M-H and H-H TPU's, respectively. A variety of amine based organoclays was donated by Southern Clay Products. The nanocomposites were prepared by melt blending the organoclays and the polymers in a Haake co-rotating, intermeshing, twin screw extruder at 180°C.

Specific comparisons were made between the structures of the organic treatment; these are i) one vs. two alkyl tails ( $M_3(HT)_1$  vs.  $M_2(HT)_2$ ), ii) unsaturated vs. hydrogenated tallow ( $M_3(HT)_1$  vs.  $M_3T_1$ ), iii) hydroxy ethyl vs. methyl alkyl chain ( $(HE)_2M_1T_1$  vs.  $M_3T_1$ ) and iv) length of the alkyl chain ( $(HE)_2M_1T_1$  vs.  $(HE)_2M_1C^*_1$ ). M stands for methyl, (HT) for hydrogenated tallow oil (saturated), T for tallow oil (predominantly  $C_{18}$  chains), (HE) for 2-hydroxy-ethyl, and C\* for coco oil (predominantly  $C_{12}$  chains).

The organoclays that produce the highest enhancement in mechanical properties will then be used to evaluate the effect of hard segment concentration by comparing M-H and H-H TPU nanocomposites.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of Organoclay Structure

Fig. 1 shows the modulus of the nanocomposites made from M-H TPU with the organoclays mentioned above. The addition of organoclay to the polymer matrix produces an increase in the modulus of all the materials even at low loadings. The modulus also shows that the one-tailed organoclay leads to higher stiffness values than the two-tailed organoclay while there is not much difference in the modulus of the saturated and unsaturated organoclays (Fig. 1a). Evidently the TPU matrix, like PA-6, interacts favorably with the silicate surface and, thus, a one tailed organoclay gives the best dispersion. Saturated and unsaturated organic treatments may provide almost the same amount of coverage of the clay surface, which may explain the similar modulus enhancement.

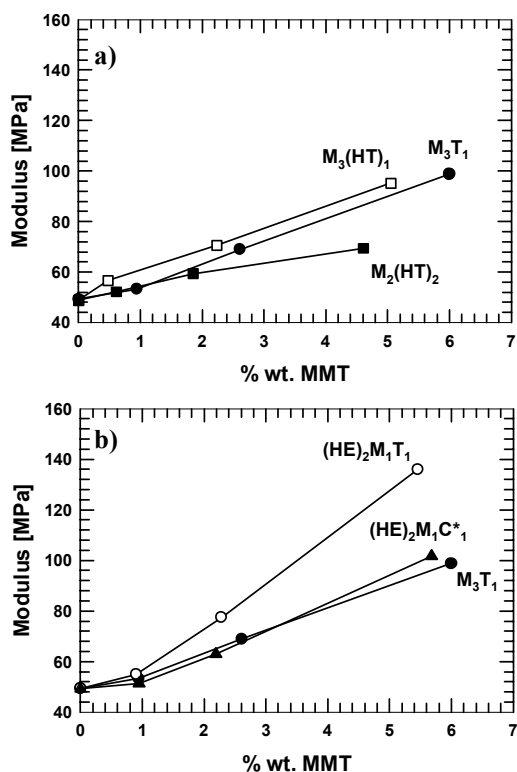


Figure 1: Modulus of M-H TPU nanocomposites. a) effect of number of tails and saturation of primary tail and b) effect of hydroxy ethyl and length of primary tail.

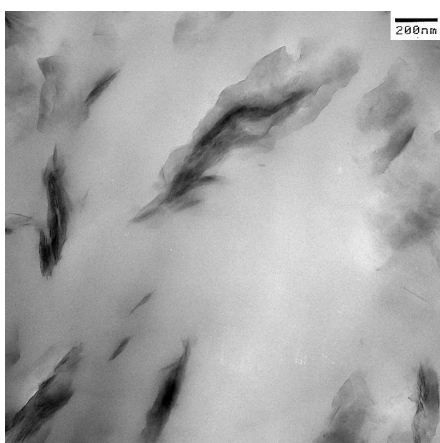
Figure 1b shows that the  $(HE)_2M_1T_1$  organoclay produces a higher reinforcement than both  $M_3T_1$  and  $(HE)_2M_1C^*_1$  organoclays. This may be due to the capacity of the hydroxy ethyl groups of the organic modifier to form hydrogen bonds with the TPU. The larger inter layer distance between the hydroxy ethyl short- and long-tailed organoclays may produce the difference observed in their properties.

X-ray diffraction patterns of the pure organoclays and TPU nanocomposites show an increase in the d-spacing of the nanocomposites, with respect to that of the pure organoclay, in all the samples except the ones made with  $(HE)_2M_1C^*_1$ . With regard to the effect of number of tails, there is a 1.1 nm increase in the nanocomposites made with the one-tailed organoclay, while there is only a 0.86 nm increase in the nanocomposites made with the two-tailed organoclay; this suggests a higher degree of exfoliation with the one-tailed organoclay. The nanocomposites made from the saturated and unsaturated one-tailed organoclays show almost the same increase in d-spacing from that of the pure organoclay (i.e. 1.1 nm vs. 1.2 nm increase, respectively). The nanocomposites formed with  $(HE)_2M_1T_1$  have an increase in d-spacing of 1.28 nm, which is the highest increase overall. These results indicate that the samples made with the  $(HE)_2M_1T_1$  organoclay have the highest degree of exfoliation, which is in agreement with the mechanical properties and will be shown next through TEM.

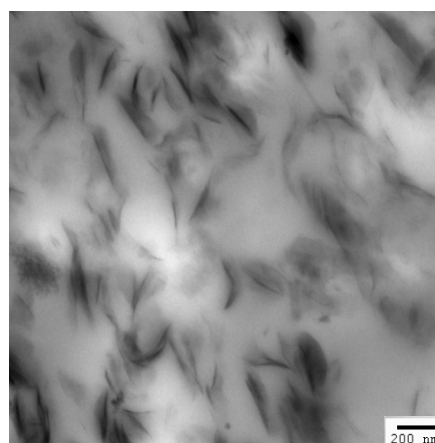
TEM micrographs are shown in Fig. 2 and 3. Regarding the number of tails comparison (Figures 2a and b) the particle density is much higher for the samples made from the one-tailed organoclay, which shows an intercalated structure. The two-tailed organoclay shows immiscible and intercalated structures. The unsaturated organoclay produces a similar structure than that obtained from the saturated one, but there seems to be more alignment in the nanocomposites made from the saturated organoclay (Figures 2b and 3c). Samples made with  $(HE)_2M_1T_1$  show the highest particle density and it reveals a larger number of single particles. The nanocomposites made from  $(HE)_2M_1C^*_1$  show a mixture of exfoliated and intercalated particles with some agglomerates.

Elongation at break is barely affected in these materials. The only sample that broke before the machine limit of 400% elongation was the highest concentration sample made from  $(HE)_2M_1T_1$ , this is reasonable considering that this sample is the one that showed the highest reinforcement. Reports in the literature show that the elongation at break increases with the addition of clay in TPU nanocomposites [4-6]. This behavior could not be explored due to machine limitations.

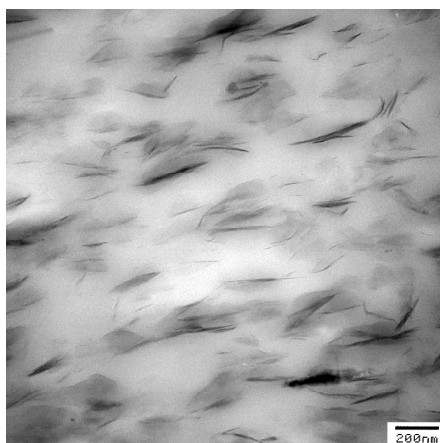
Organoclay studies performed on PA-6 show that  $M_3(HT)_1$  and  $M_3T_1$  organoclays produced a higher mechanical property enhancement and degree of exfoliation compared to  $M_2(HT)_2$  and  $(HE)_2M_1T_1$ , respectively; while they showed no significant difference between  $(HE)_2M_1T_1$  and  $(HE)_2M_1C^*_1$  [1]. On the other hand, studies performed on PE ionomers showed higher mechanical property enhancements and degrees of exfoliation on samples produced with  $M_2(HT)_2$  and  $(HE)_2M_1T_1$  versus  $M_3(HT)_1$  and  $M_3T_1$  and  $(HE)_2M_1C^*_1$ , respectively [3].



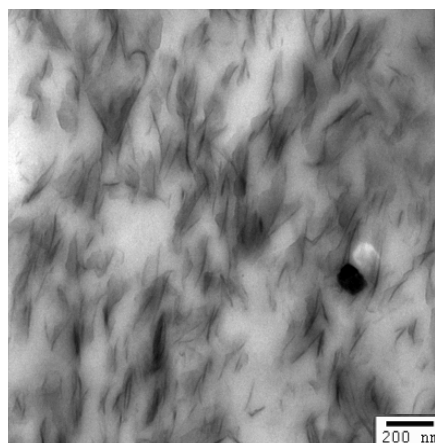
a)  $M_2(HT)_2$



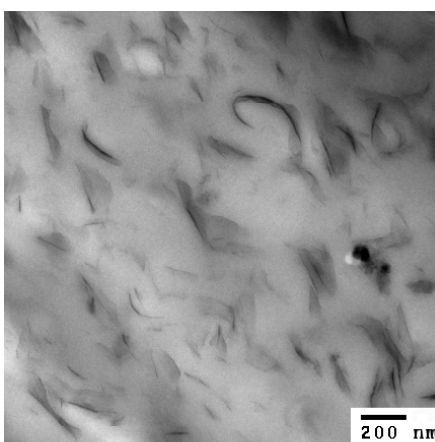
c)  $M_3T_1$



b)  $M_3(HT)_1$



d)  $(HE)_2M_1T_1$



e)  $(HE)_2M_1C^*_1$

Figure 2: TEM micrographs of a) two-tailed and b) one-tailed TPU nanocomposites.

One would expect that the organoclay study performed for TPU should produce results similar to those of PA-6, considering that TPU is also polar and that its functional groups are similar to those of PA-6. This study shows that the behavior of TPU nanocomposites is somewhat in between the behavior of the other two polymers.

### 3.2 Effect of Hard Segment Concentration

Reports in the literature have shown that the ratio of soft to hard segment concentration has an effect on the mechanical properties and increase of d-spacing on TPU nanocomposites [4-8]. With this in mind, a series of nanocomposites were made of a high-hardness TPU with  $(HE)_2M_1T_1$  and  $M_3(HT)_1$  organoclays. They were compared to the medium-hardness TPU samples used in the previous study to analyze the effect of the hard segment concentration. The high-hardness TPU had a Shore D Hardness of 73D, which corresponds to a 55 or higher percentage of isocyanates, while the medium-hardness TPU had a Shore D hardness of 58D, which corresponds to slightly more than 25% of isocyanates.

Figure 3: TEM micrographs of c) one-tailed unsaturated, d) hydroxy ethyl tallow and e) hydroxy ethyl coco TPU nanocomposites.

Figure 4 shows the modulus of the nanocomposites made from these two TPU's. Both TPU's have the same effect towards the different organoclay structures (i.e. a better reinforcement is obtained with the hydroxy ethyl organoclay), even though the modulus is much higher in the high-hardness TPU. The medium-hardness TPU shows a

high increase in modulus with increasing % wt. MMT, while the high-hardness TPU shows almost no enhancement up to 1 % wt. MMT with the hydroxy ethyl clay and almost no enhancement at all with the one-tailed organoclay.

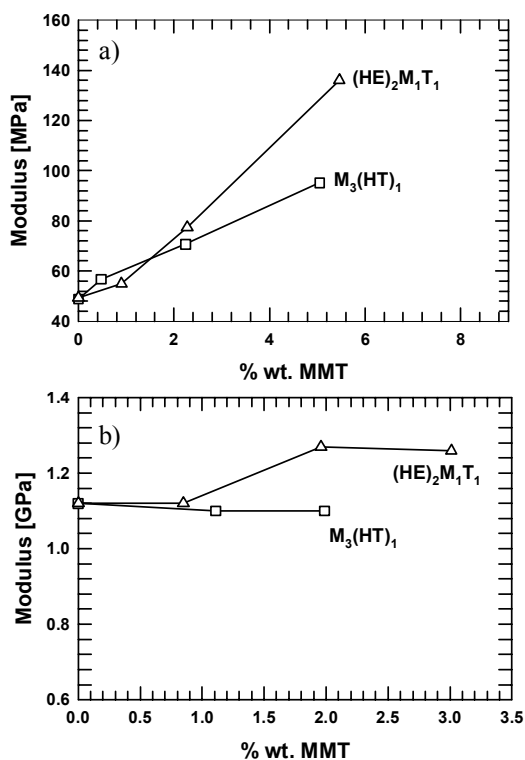


Figure 4: Modulus of modulus of a) medium-hardness and b) high-hardness TPU nanocomposites with (HE)<sub>2</sub>M<sub>1</sub>T<sub>1</sub> and M<sub>3</sub>(HT)<sub>1</sub> organoclays.

WAXD patterns give a good insight on the morphology of these nanocomposites. They show that the increase in d-spacing for the medium-hardness TPU, as seen before, is 1.28 and 1.1 nm for hydroxy ethyl and one-tailed organoclays, respectively; while the increase in d-spacing for the high-hardness TPU is 1.48 and 1.42 nm for hydroxy ethyl and one-tailed organoclays, respectively.

TEM micrographs show considerably higher particle density in the samples made with hydroxy ethyl organoclay. At low concentrations, there is a higher particle density on the H-H TPU nanocomposite samples.

The elongation at break also shows a difference regarding the two types of TPU's. The elongation at break of the high-hardness TPU is lower than the 400% machine limit. It remains almost constant for the one-tailed organoclay while it decreases significantly with the hydroxy ethyl organoclay. This is consistent with the higher level of reinforcement obtained with hydroxy ethyl.

As mentioned before, the higher driving force for intercalation into the hydroxy ethyl organoclay galleries may be due to the high potential for hydrogen bonding

between the hard segments of the TPU's and the hydroxy ethyl groups in the organoclay. This is also suggested by Finnigan et al. and Tien et al. [5, 8]. The difference in mechanical property behavior observed between the nanocomposites made from M-H and H-H TPU's may be related to their difference in chain mobility, with respect to the pure matrix. In the medium-hardness TPU, where there is a higher soft segment concentration, the clay particles may reduce the mobility enough to reinforce the composite, but not to hinder the elongation; while in the high-hardness TPU, where there is a smaller soft segment concentration, the clay may produce a lower reinforcement and reduce the mobility to a greater extent [5, 8].

## 4 CONCLUSION

TPU nanocomposites with different types of organoclays were prepared using a twin screw extruder. Overall, TPU nanocomposites prepared with (HE)<sub>2</sub>M<sub>1</sub>T<sub>1</sub> organoclay had a higher reinforcement and degree of exfoliation, as judged by mechanical properties, WAXD and TEM. The structural effects that produced a greater enhancement in properties and morphology of TPU nanocomposites were: the use of hydroxy-ethyl groups rather than methyl groups, one long alkyl tail instead of two, and a long alkyl tail in place of a short one. Higher degrees of exfoliation were obtained with a higher concentration of hard segments, as judged by TEM and WAXD. Although TPU is a polar matrix, some results show similar trends to polar, nylon 6 based nanocomposites, while others follow the ones observed in non-polar matrices. This might suggest that, even though the polarity of the polymer matrix is a key factor on determining the types of organic treatments that will produce a higher degree of exfoliation, some other factors like hydrogen bonding might also have an effect, especially if they determine the morphology and the properties of the polymer matrix like in thermoplastic polyurethanes.

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