Reduction in HDPE Geomembrane Thermal Expansion using Nanoclay Particles

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ABSTRACT

This study investigates the use of nanoclay particles to reduce high density polyethylene (HDPE) thermal expansion for application in geotechnical engineering. Nanocomposite samples were prepared with various ratios of nanoclay and the addition of various amounts of four different compatibilizing agents. The coefficient of linear thermal expansion was measured using a dynamic mechanical analyzer. It was computed between 35 and 50°C. The degree of exfoliation of the nanoclay particles in the samples was assessed by transmission electron microscopy on specimens prepared with an ultramicrotome. A more or less significant reduction in HDPE thermal expansion was obtained depending on the compatibilizing agent. On the other hand, the compatibilizing agents tested did not appear to produce an exfoliation of the nanoclay particles, which remained in an intercalated configuration.

Keywords: thermal expansion, nanoclay, high density polyethylene, compatibilizing agent

1 INTRODUCTION

Polymer membranes have progressively replaced traditional building materials like concrete, soil and, bituminous products to perform waterproofing functions and control the advective migration of pollutants in civil engineering structures [1]. Either during deployment or in service, geomembranes, 50% of which are made of HDPE, may sustain large temperature variations. Yet, polymer materials generally display very high thermal expansion coefficients. This has been resulting in various problems with geomembranes, in particular the formation of interconnecting wrinkles leading to increased risk and extent of leakage [2].

The addition of nanoparticles has been proposed as a way to reduce thermal expansion in polymers. Interesting data for polyolefins have been reported with graphene, silica, carbon nanofibers, and various types of nanoclay for example [3-19]. The effect is attributed to a reduction in the mobility of polymer chains trapped in nanoscale zones formed between the nanoparticles [3]. Surprisingly, very few results have been published on HDPE, and none with nanoclay. Yet, a preliminary assessment revealed the potential of nanoclay for reducing the thermal expansion of HDPE [20]. In this study, a more thorough investigation is conducted involving the use of several types of compatibilizing agents.

2 METHODS AND MATERIALS

HDPE nanocomposite membrane samples were prepared with various ratios of nanoclay (0, 0.5, 1.5, 2.5, 5, and 10% of 50% organo-modified montmorillonite / LLDPE masterbatch, Nanocor Inc., IL) dispersed in a geomembrane-grade HDPE (Pétromont, QC).

A series of olefin-based polar compatibilizing agents were selected for the study. Polyethylene-grafted maleic anhydride (PE-g-MA) was used in our previous work with LLDPE and HDPE [20]. Two PE-g-MA products are included in this study, one provided by DuPont Packaging & Industrial Polymers, DE (0.94 g/cm^3, labelled PE-g-MA #1), and the other obtained from Honeywell, NJ (0.92 g/cm^3, labelled PE-g-MA #2). In addition, polypropylene-grafted maleic anhydride (PP-g-MA) was purchased from Sigma-Aldrich, MO, and oxidized ethylene-vinyl acetate (OE-VA) from Honeywell, NJ.

Two percentages of each compatibilizing agent were used in the study: 5 and 10 wt%. For comparison purposes, samples without any compatibilizing agent were also prepared and characterized.

The pellets were premixed manually and fed in a twin-screw extruder heated at 195°C. The extruded blends were water-cooled and pelletized. The pellets were further homogenized in a two-roll mill heated at 180°C. Finally, 1.8-mm thick plates were prepared by compression molding at 177°C.

The coefficient of linear thermal expansion was measured using the standard test method ASTM E831 and a dynamic mechanical analyser (DMA). Tests were conducted at 1°C/min with 6.25 x 30 mm rectangular specimens. The thermal expansion coefficient was computed between 35 and 50°C. A correction was made for the thermal expansion of the DMA grips.

A complementary characterization of the degree of exfoliation of the nanoclay particles in the samples was conducted by transmission electron microscopy (TEM) on specimens prepared with an ultra-microtome.

3 RESULTS

Figures 1-4 show the variation of the thermal expansion coefficient normalized by the value for pure HDPE as a function of nanoclay content for samples without compatibilizing agent and with 5% and 10% of the four compatibilizing agents. Each data point is the average of at least two measurements.

For samples without compatibilizing agent (see Fig. 1 for example), a peak in the coefficient of thermal expansion is observed at 0.5% nanoclay followed by decrease with further increase in nanoclay content. The origin of that initial peak has yet to be understood. The reduction in thermal expansion at 10% nanoclay is 12% compared to the value for pure HDPE.

For samples with PE-g-MA #1 (Fig. 1), a 17% drop in thermal expansion is observed between 0 and 0.5% nanoclay both for 5% and 10% PE-g-MA #1. Then the decrease is more limited upon further increase in nanoclay content. However, the compatiblizer agent itself appears to negatively affect the sample thermal expansion, maybe by facilitating the mobility of HDPE chains. As a result, at a given nanoclay content, the coefficient of thermal expansion of PE-g-MA #1-containing samples remains higher than or equal to that of samples without compatibilizing agent.

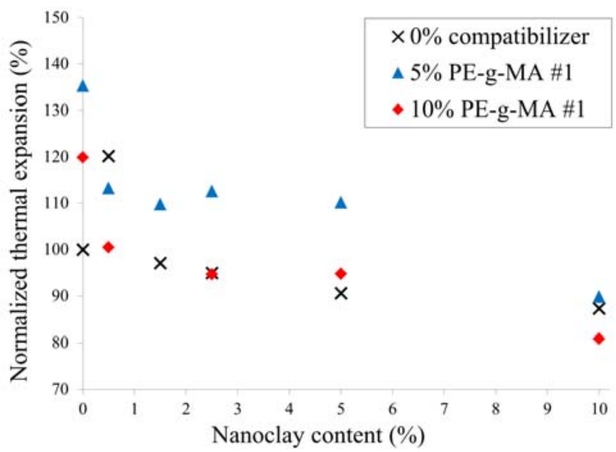

Figure 1: Normalized thermal expansion as a function of nanoclay content without and with 5% and 10% of PE-g-MA #1 compatibilizing agent.

In the case of PE-g-MA #2 (Fig. 2), a strong decrease in the coefficient of thermal expansion is observed with increasing nanoclay content. With 5% PE-g-MA #2, the reduction in thermal expansion reaches 44% at 10% nanoclay. In addition, the negative impact of the compatiblizer agent itself that has been observed with PE-g-MA #1 is absent with 5% PE-g-MA #2. As a result, a reduction in the coefficient of thermal expansion of up to 36% is obtained at a given nanoclay content compared to the condition without compatiblizer agent.

With PP-g-MA (Fig. 3), the coefficient of thermal expansion first increases with nanoclay content; it reaches a maximum at about 1.5% nanoclay content for 5% PP-g-MA and 2.5% for 10% PP-g-MA before decreasing with a further increase in nanoclay content. The reduction in thermal expansion at 10% nanoclay is around 30%. However, the negative impact of the compatiblizer agent itself on the coefficient of thermal expansion is observed once again. As a result, except at 10% nanoclay, the coefficient of thermal expansion of PE-g-MA-containing samples is higher or equal at a given nanoclay content compared to samples without compatibilizing agent.

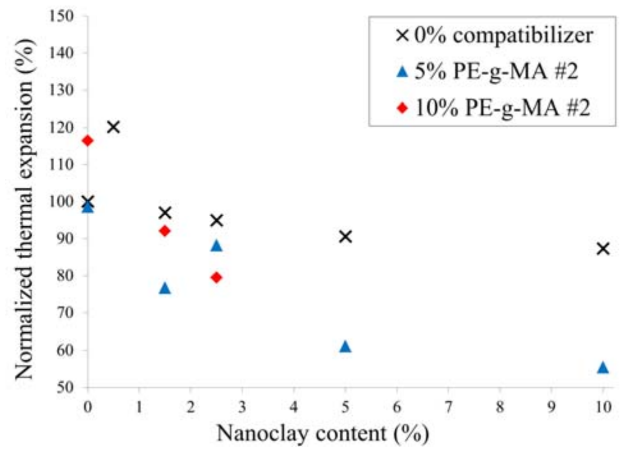

Figure 2: Normalized thermal expansion as a function of nanoclay content without and with 5% and 10% of PE-g-MA #2 compatibilizing agent.

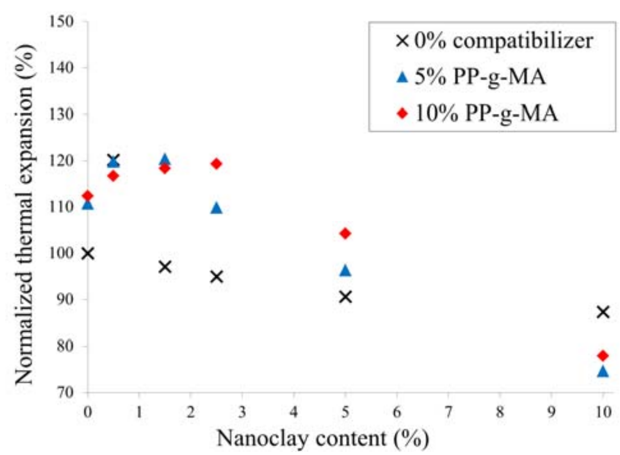

Figure 3: Normalized thermal expansion as a function of nanoclay content without and with 5% and 10% of PP-g-MA compatibilizing agent.

Finally, a similar situation prevails for EO-VA samples (Fig. 4), i.e. the negative impact of the compatilizing agent itself on the coefficient of thermal expansion is too strong to be offset by the larger decrease in thermal expansion with nanoclay content associated with the presence of the compatilizing agent. As a result, at a given nanoclay content, the coefficient of thermal expansion of EO-VA-containing samples remains higher than or equal to that of samples without compatibilizing agent.

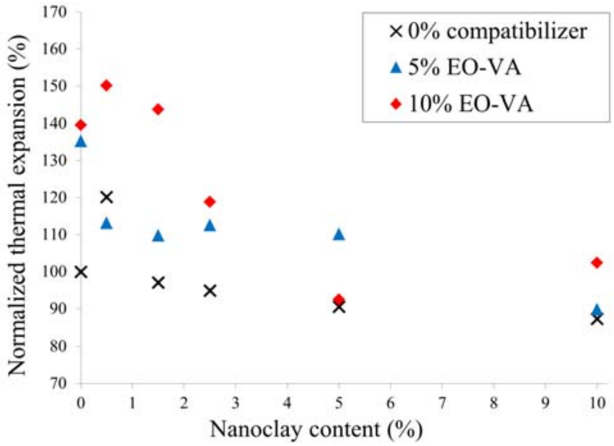

Figure 4: Normalized thermal expansion as a function of nanoclay content without and with 5% and 10% of EO-VA compatibilizing agent.

The degree of exfoliation of the nanoclay particles in the samples was investigated by TEM. As shown in Figure 5 for a sample containing 10% nanoclay with no additional compatibilizing agent, the nanoclay particles exhibit an intercalated configuration, which persists when the different compatibilizing agents are added in the formulation (Figures 6-8 with 10% nanoclay and 10% PE-g-MA #1, PE-g-MA, and EO-VA, respectively).

Figure 5: TEM picture of sample with 10% nanoclay and no compatibilizer.

4 DISCUSSION

Except in some instances at low nanoclay content, the addition of the compatibilizing agent appears to enhance the extent of the reduction in thermal expansion induced by the nanoclay particles dispersed in HDPE, even if the compatibilizing agents tested prouved unable to promote the exfoliation of the nanoclay particles, which remained in an intercalated configuration.

However, with the exception of PE-g-MA #2, that effect was cancelled by the negative impact of the compatibilizing agent itself on the coefficient of thermal expansion and no benefit of the addition of the compatibilizing agent on thermal expansion was provided. Only PE-g-MA #2 was able to provide a reduction in thermal expansion larger than that obtained without compatibilizing agent. That reduction reached 45% at 10% nanoclay compared to pure HDPE. Further research is still needed to understand the phenomena at the origin of this success of PE-g-MA #2 in reinforcing HDPE/nanoclay thermal stability.

In addition to thermal stability, geomembranes have to meet a series of other engineering performance requirements to ensure proper operation in service. These properties may also be affected by the nature and amount of compatibilizing agent in the formulation [21]. Formulations should thus be carefully optimized considering all the requirements.

5 CONCLUSION

The reduction in HDPE thermal expansion produced using nanoclay particles was generally enhanced in the presence of the compatibilizing agents tested. However, a negative impact of the compatibilizing agent itself on thermal expansion was also sometimes observed. Only one of the compatibilizing agents tested was able to provide a reduction in thermal expansion compared to the condition without compatibilizing agent.

A better understanding of the mechanisms involved in the action of the nanoclay particles and compatibilizing agents on HDPE thermal expansion, and the achievement of full nanoclay exfoliation should allow further improvements in HDPE thermal expansion reduction. This solution offers great promises for geotechnical applications, in particular for geomembranes.

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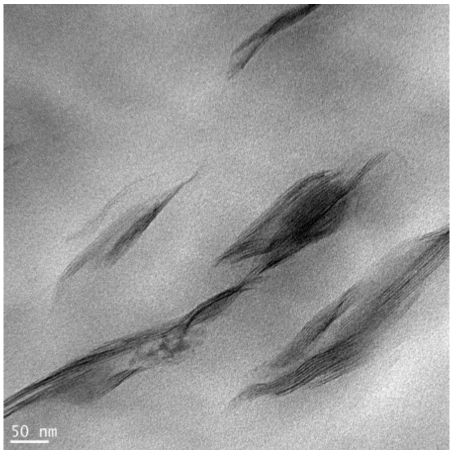

Figure 6: TEM picture of sample with 10% nanoclay and 10% PE-g-MA #1.

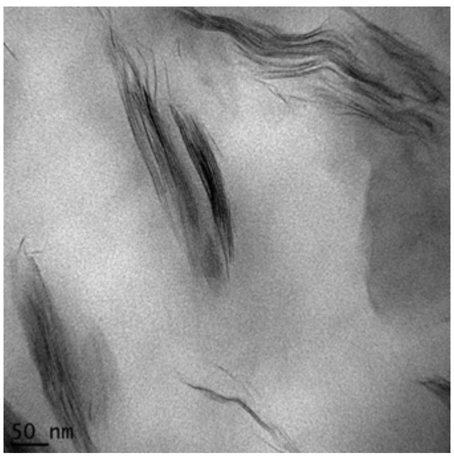

Figure 7: TEM picture of sample with 10% nanoclay and 10% PP-g-MA.

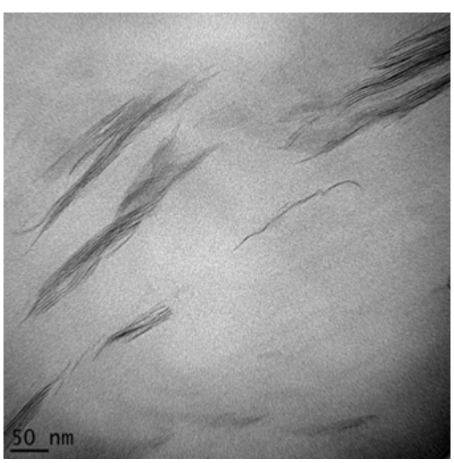

Figure 8: TEM picture of sample with 10% nanoclay and 10% EO-VA.

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