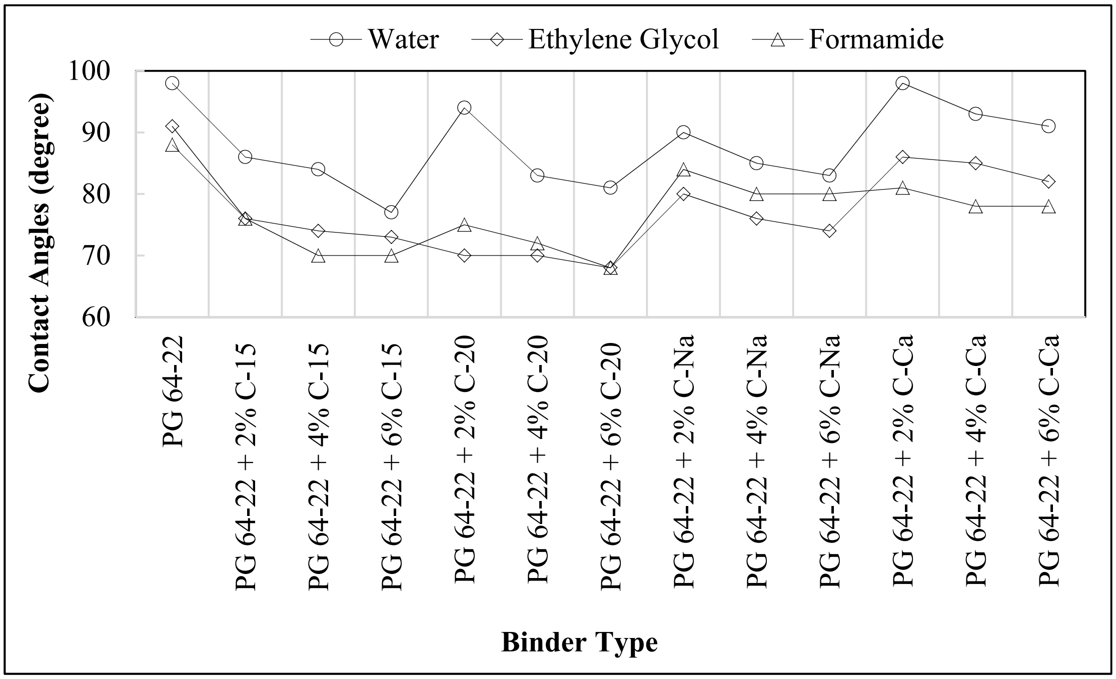
While preparing SD test samples, this study followed a technique recommended by Tarefder and Arifuzzaman (2011). In this process a glass slide with dimensions 57 mm x 70 mm x 1.5 mm was quickly run in a flame to ensure the glass slide is free from any dust. Then the glass slide was wrapped on all sides with tape and a drop of binder sample was dispensed on the remaining rectangular portion at the middle of glass slide. The liquid binder was leveled into a smooth surface by rubbing with another clean glass slide. The binder coated glass was then allowed to cool down and finally the tapes were peeled off as shown in Figure 2b. As described in Koc and Bulut (2014), the aggregate specimens were cut using a mechanical saw to create a flat surface with 2 cm in thickness and about 7 cm x 8 cm cross section. The plate shaped aggregate is then processed through repeated washing, grinding and polishing in order to prepare the OCA test sample of aggregate as shown in Figure 2c.

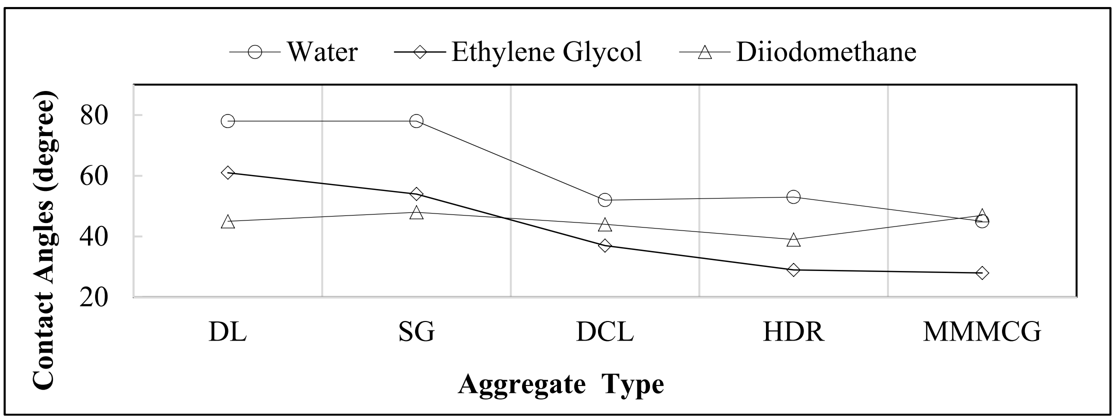
RESULTS AND DISCUSSIONS

Figure 3a shows the measured contact angles of various probe liquids on the binders and aggregates samples. Contact angle, the angle between liquid-vapor interface and solid-liquid interface, is a combined effect of cohesion, adhesion, and wettability. A contact angle of greater than 90^o indicates poor wetting, and the wetting ability increases when the contact angle decreases from higher value to lower value (Buddhala *et al.* 2012). It is seen that contact angle decreases with an addition of higher content of NCs in binder, indicating an increase of wetting ability of binder with NCs incorporation. Among four different NCs, C-20 showed highest value of contact angles, followed by C-Ca, C-Na, and C-15. This could possibly be due to the less dense particles in C-20 with a loose bulk density of 1.15 kN/m^3 and packed density of 2.13 kN/m^3 and lower moisture content (less than 2%) compared to the other tested NCs (Nuntrino, 2016). As contact angle is an inverse measure of degree of wetting or wettability, the obtained trend of contact angles indicates that C-15 has the highest wettability among these four NCs, followed by C-Na, C-Ca, and C-20. In regards of aggregates, DL showed the highest contact angle, followed by SG, DCL, HDR, and MMMCG (Figure 3b). In order to SFE estimation of NC-modified binders, SFE components of probe liquids have been utilized from Van Oss et al. (1998).

Figure 4 shows SFE components, total SFE, and W_C of all tested binders and aggregates. As shown in Figure 4a, Γ^{LW}values are significantly higher than Γ^+ and Γ^- values for all binder samples. Thus, Γ^{LW} is found most significant contributory component to total SFE, which is consistent with previous research (Little and Bhasin, 2006). An increasing trend of SFE components, total SFE, and work of cohesion is found with addition of NCs in the binder. Lu and Harvey (2005) illustrated that loss of cohesion is one of the reasons of premature failure of pavement due to presence of water. Thus, increasing trend of W_C primarily indicates an improved moisture resistance of NC-modified binders. A better understanding of the moisture damage is obtained though compatibility analysis, which is discussed next.



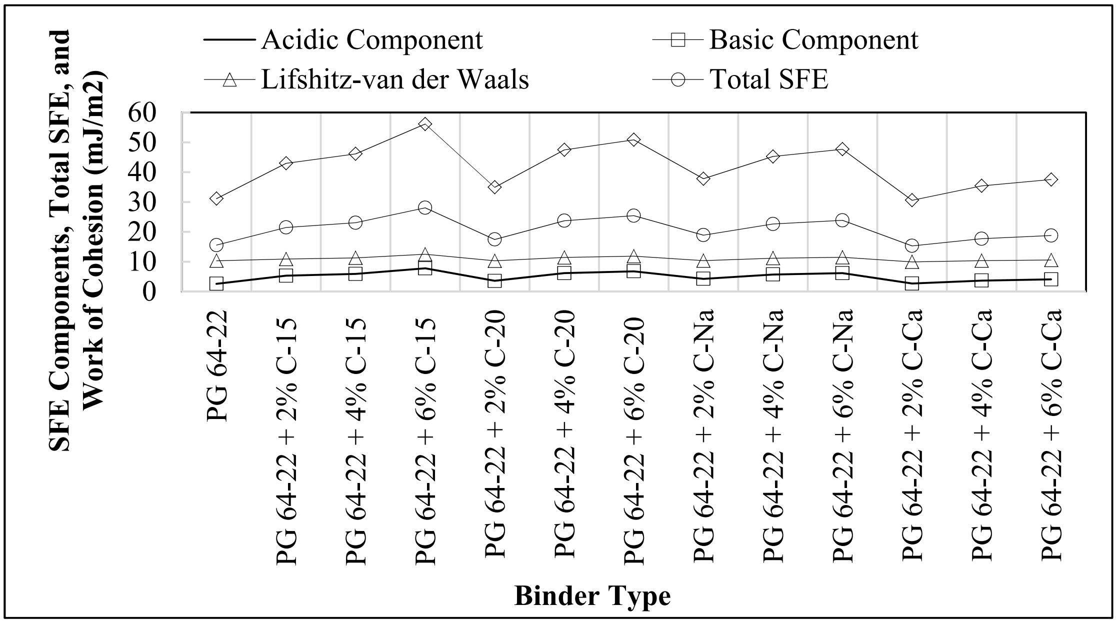
(a)



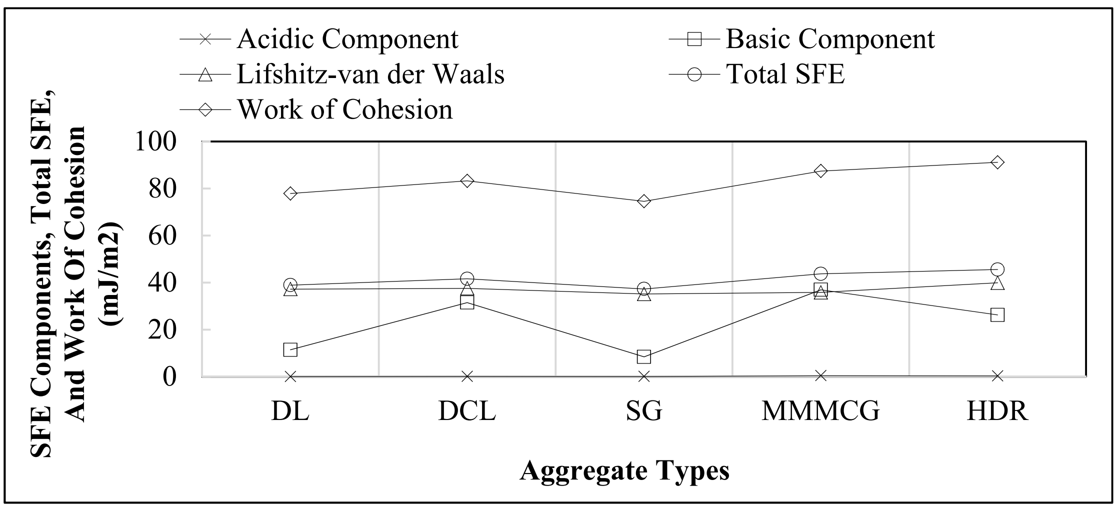
(b)

FIG. 3. (a) Contact Angles of Probe Liquids on (a) Binders, and (b) Aggregates.

The plot of ΔG^{ad}_{dry} and ΔG^{ad}_{wet} data (Figure 5) revealed that ΔG^{ad}_{dry} increases with the addition of higher content of NCs in cases of all aggregates, indicating an improved compatibility strength. Again, ΔG^{ad}_{wet} (negative value) decreased with an addition of higher content of NCs. The negative value of ΔG^{ad}_{wet} indicates the de-bonding energy at the binder-aggregate interface in the presence of water or a wet condition indicating the lower value of ΔG^{ad}_{wet} indicates a higher resistance to moisture damage of pavement. Thus, it appears that the addition of NC improves the adhesive energy between the aggregate and binder in both dry and wet condition, consequently provides more resistance to moisture damages.



(a)



(b)

FIG. 4. (a) SFE Components, total SFE, and (b) Work of Cohesion of Binders and Aggregates.

A CR analysis has been performed in order to determine the best performing binder-aggregate combination. Based on the CR guidelines found in Bhasin *et al.* (2006), moisture resistance increase with an increase of CR values and a CR value, when greater than 1.5, provides a desirable moisture resistance to pavement and. As shown in Table 1, NCs addition results in a significant increase of the CR value. It is also seen that all NC-modified binder shows a CR value greater than 1.5, which indicates that an addition of NCs provides the desired moisture resistance to pavement. Table 1 also shows that among four NCs, C-15 provides the most desirable moisture resistance and it was followed by C-20, C-Na, and C-Ca in both dry and wet conditions. Among five aggregates, MMMCG shows the most desirable adhesive energy with all binders, and it was followed by DCL, HDR, DL, and SG in both dry and wet conditions.

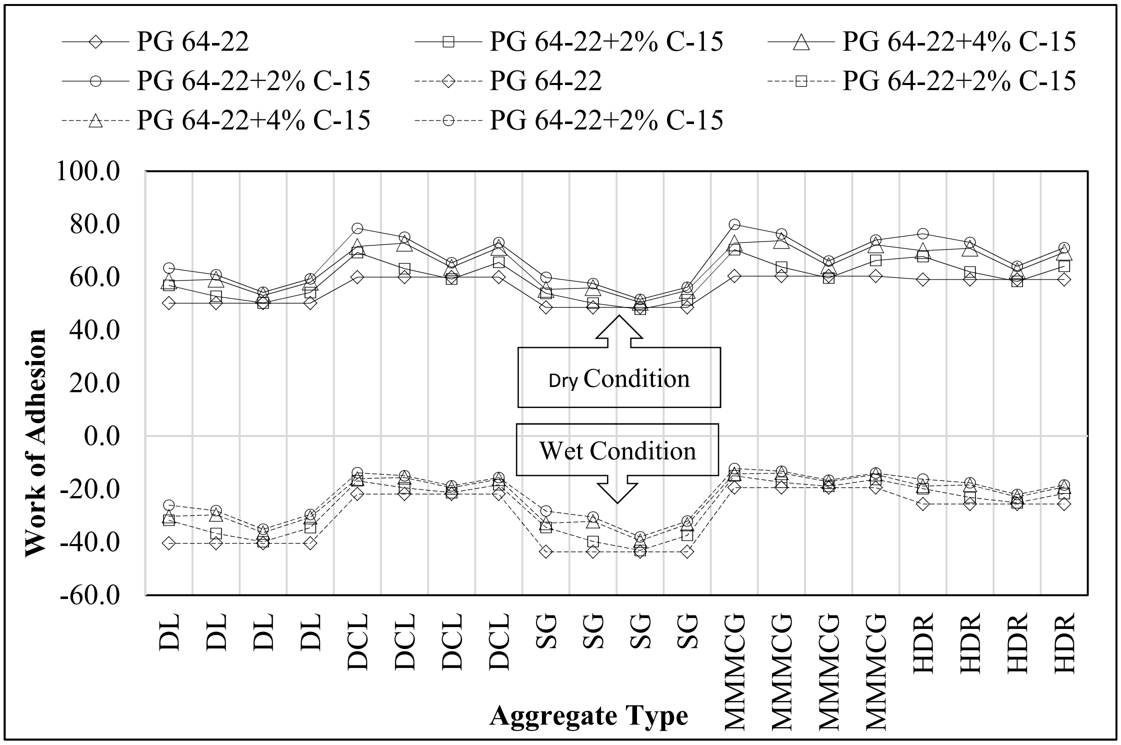


FIG. 5. Work of Adhesion of all Binder-Aggregate Combinations.

Table 1: Compatibility Ratio of All Binder-Aggregates Combinations

Types of Binder	Types of Aggregates				
	DL	DCL	SG	MMMCG	HDR
PG 64-22	1.2	2.8	1.1	3.1	2.3
PG 64-22+2% C- 15	1.8	4.1	1.6	4.7	3.4
PG 64-22+4% C- 15	1.9	4.5	1.7	5.1	3.7
PG 64-22+6% C- 15	2.4	5.7	2.1	6.5	4.7
PG 64-22+2% C- 20	1.4	3.2	1.3	3.7	2.7
PG 64-22+4% C- 20	2.0	4.7	1.7	5.3	3.9
PG 64-22+6% C- 20	2.2	5.0	1.9	5.8	4.2
PG 64-22+2% C-Ca	1.3	2.8	1.1	3.2	2.3
PG 64-22+4% C-Ca	1.5	3.3	1.3	3.7	2.7
PG 64-22+6% C-Ca	1.5	3.5	1.4	4.0	2.9
PG 64-22+2% C-Na	1.6	3.6	1.4	4.1	3.0
PG 64-22+4% C-Na	1.9	4.4	1.7	5.0	3.6
PG 64-22+6% C-Na	2.0	4.7	1.8	5.3	3.9

CONCLUSIONS

This study followed the surface free energy (SFE) approach to evaluate the moisture damage resistance of nanoclay (NC)-modified binders. To this end, four commercial NCs namely, Cloisite® 15 (C-15), Cloisite® 20 (C-20), Cloisite® Na^{+} (C-Na), Cloisite® Ca^{++} (C-Ca) were tested in laboratory. SFE data of five different aggregates namely, Davis Limestone (DL), Snyder granite (SG), Dolese-Cooperton limestone (DCL), Hanson-Davis rhyolite (HDR), and Martin-Marietta-Mill-Creek granite (MMMG) were used for a compatibility analysis. It is revealed that an addition of NC results in an increase in total SFE andwork of cohesion, which primarily indicates an improved moisture resistance of NC-modified binders. The compatibility analysis showed that an addition of NC also results in a significant increase of work of cohesion and compatibility ratio, which is desired for an asphalt mixes to be more resistive to moisture damage. Among five aggregates, MMMCG showed the highest compatibility strength with all binders and it was followed by DCL, HDR, DL, and SG. Among four NCs, C-15 exhibited highest compatibility with the aggregates, and it was followed by C-20, C-Na, and C-Ca.

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The Use of a Green Polymer Nanocomposite in Geo-Infrastructure

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Abstract

In recent years, there has been a great interest in using eco-friendly polymers in construction of geo-infrastructures to help in reducing their carbon footprint and enhancing their sustainability. Green polymers are one of these materials. Green polymers are polymers derived from plants that consist of starches, sugars, and cellulose. One of the green polymers that have received attention is polylactic acid (PLA). PLA is a hydrophobic, aliphatic polyester that can be extracted from most commonly from corn starches. This paper explores the use of PLA and PLA nano-composites as an alternative polymer to fabricate geosynthetics. To this end, PLA nano-composite materials were prepared using different carbon nanofibers contents. The mechanical properties of the produced nanocomposites samples were examined and compared to a geogrid material typically used in reinforcement of geomaterials in highway embankments and pavement structures. The results indicated that the carbon nanofibers enhanced the elastic modulus of PLA, but reduced its failure strain. Although the PLA carbon nanocomposites had higher tensile modulus than the geogrid materials tested in this study, they had lower tensile strength and strain. It is recommended that plasticizers used with the PLA nanocomposites to enhance their ductility.

INTRODUCTION

In 2012, the United States Environmental Protection Agency (EPA), recorded that 6,526 million metric tons of greenhouse gas (GHG) were emitted, with more than a quarter of those emissions generated from transportation structures (EPA, 2014). Carbon dioxide (CO_2) is one of the main greenhouse gases that its concentration has been significantly increasing due to human related activities such as the burning of fossil fuels. For example, in April of 2014, the average CO_2 concentration in the

Northern Hemisphere was higher than 400 parts per million (ppm) (Piccirillo, 2014). The increase in the CO_2 and other GHG emissions have contributed to constant thinning of the ozone layer and global warming, which is thought to increase the occurrence of natural disasters. As such there has been a growing interest in using construction materials that can reduce the carbon footprint of transportation structures.

Geosynthetics have been used extensively in the reinforcement of embankment and pavement layers during the past four decades. Different types of geosynthentics have been used such as geogrids and geotextiles. All of these types were fabricated from synthetic (petroleum and other oil based substances) polymers of polypropylene, polyester, or polyethylene. However, in recent years, chemists and engineers have searched for fruits and vegetables that they can potentially develop into bioplastics, better known as green polymers (Adeosun et al., 2012; Mülhaupt, 2014). Green polymers can most commonly be defined as polymers derived from plants that consist of starches, sugars, and cellulose (Mittal, 2011; Adeosun et al., 2012). One of the green polymers that have received attention in recent years is Polylactic Acid (PLA). PLA is a hydrophobic, aliphatic polyester that can be extracted from most commonly from corn starches (Henton et al., 2005; Jamshidian et al. 2010). PLA's have been found to be a very suitable alternative to petroleum based polymers in the construction of plastics (Jamshidian et al. 2010). PLA is abundant because of its close relationship to lactic acid, which can be derived by way of the hydrolysis and fermentation (Jamshidian et al. 2010, Misra et al., 2010, Gibson 2010). PLA has been found to be relatively strong, showing good stiffness which is of much importance with regard to civil engineering applications (Ozkoc and S. Kemaloglu, 2009).

The production of the PLA requires 20 to 50% less fossil fuel than that of oil based plastic resins; which means that up to 2 to 5 times more PLA can be produced within a given amount of fossil fuel than oil based plastics (Jamshidian et al. 2010, Henton et al, 2005). Likewise, the energy that is required to manufacture PLA is much lower than other synthetic polymers. PLA generates much less greenhouse emissions than conventional polymer. Figure 1 compares the greenhouse gas contribution to the environment for different plastic types. It is noted that the PLA can actually reduce greenhouse gases as it is produced from field wastes or other biomass. Thus, PLA currently serves as one of the most appealing green polymers for sustainable material alternatives.

Studies have been conducted during the past five years to investigate the use of different nano-fillers to improve the mechanical properties of PLA. To this end, PLA nano-composites developed with clay and cellulose fibers were prepared and evaluated (e.g. Kaci and Zaidi, 2012; Cheng et al., 2011; Jonoobi et al., 2010, Qu et a 2010). Jonoobi et al. (2010) conducted a study to evaluate the effect of cellulose nanofiber on PLA stiffness and strength properties. The PLA nanocomposites were fabricated using the extrusion method. Jonoobi et al. (2010) found that the PLA tensile modulus and strength increased by more than 20% when 5% by weight of the cellulose nanofibers were used. The dynamic mechanical analysis results showed that the storage modulus increased for all nano-composites compared to neat PLA. Kaci and Zaidi (2012) evaluated the effects of the loading rates on morphology and mechanical properties of PLA clay nanocomposites. Organically modified montmorillonite was introduced at various loading rates: 1, 3 and 5 % by weight. The nanocomposites were prepared by melt intercalation in a Brabender Plasticorder mixer. Their results showed a significant improvement in modulus, hardness, and tensile strength with the increase of the clay content.

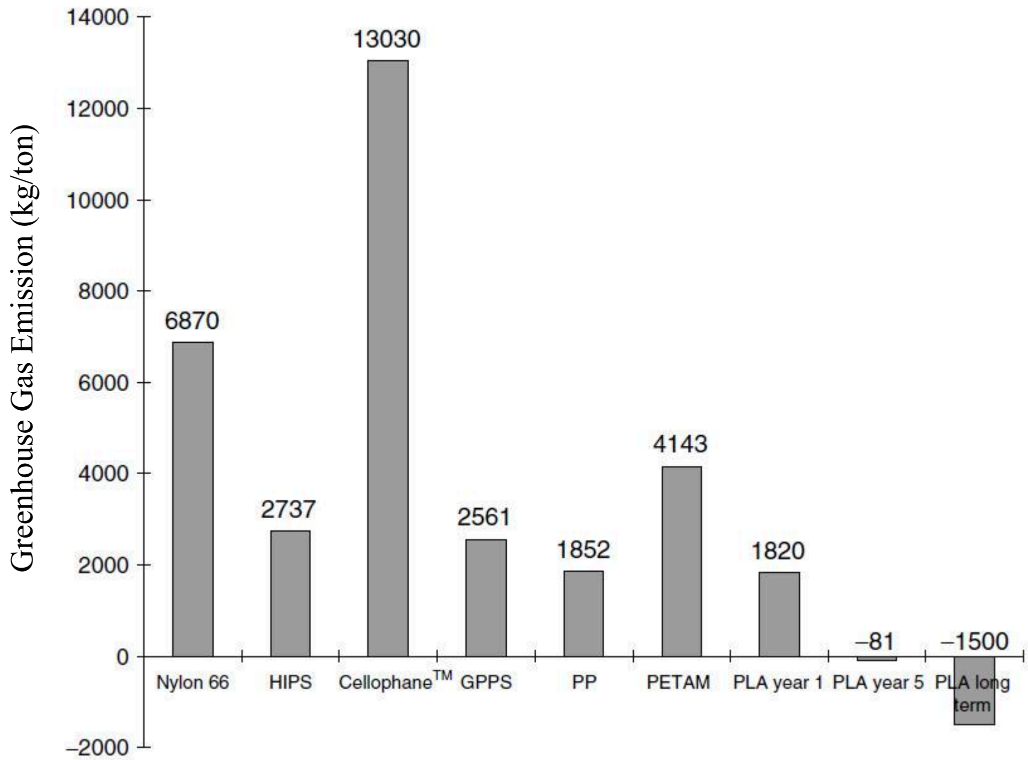

FIG. 1. Greenhouse Gas Emission for different types of Polymer (Henton *et al*, *2005*).

In this paper PLA nanocomposites were prepared my mixing carbon nanofibers using melt compound process. Three carbon nanofibers loading rates were used: 1%, 3% and 5% by weight. The tension properties were determined and compared to those of a geogrid material typically used in reinforcement of soil in highway embankment.

OBJECTIVES

The main objective of this paper is to investigate the use of PLA and PLA nano-composites as an alternative polymer to fabricate geosynthetics. Another objective of this paper is to evaluate the effect of using carbon nano-fibers on the mechanical properties of PLA.

LABORATORY TESTING PROGRAM

Materials

The PLA material used in this study was a Ingeo™ 3001D polylactide biopolymer, which was obtained from NatureWorks™ (Minnetonka, MN). Figure 2 presents a picture of the obtained PLA pellets. This type of PLA is designed for injection molding applications. Table 1 presents the main properties of the PLA used in this study. In addition a vapor-grown Pyrograf ®- PR-19-XT-LHT carbon nanofibers from Applied Sciences Inc. was used in this paper. Table 2 summarizes the properties of this carbon nanofiber (CNF). The PR-19-XT-LHT fiber is produced by heat-treating at 1500°C, which converts any chemically vapor deposited carbon present on the surface of the fiber to a short range ordered structure that increases the inherent conductivity of the fiber. This nanofiber was selected to enhance the mechanical as well as the electric properties of the PLA. The electrical conductivity of PLA nanocomposites was also investigated but not reported in this paper. Three CNF loading rates were used: 1, 3 and 5% by weight.

FIG. 2. Picture of PLA pellets used in this study.

Table 1. Properties of PLA Material Used in This Study

Property	Value
Thermal conductivity	0.160 J/m-°K-s (at 25 °C
Specific heat, Cp	25 °C 1.20 J/g °C
Glass Transition Temperature, Tg	55 - 60°C
Peak Melt Temperature, Tm	145 - 170°C
Specific Gravity, ρ	1.24 - 1.25 g/cc
Melt Density (200°C), ρ melt	1.12 g/cc
Pellet Bulk Density, ρ bulk	0.79 - 0.85 kg/liter (49 - 53 lb/ft^3)
Typical Flake Bulk Density, ρ flake	0.593 kg/liter (37 lb/ft3)