

Assessment of changes in plasticity and mechanical properties of polystyrene fatty acid-based neem seed oil blends

Salihu, Takuma. ^{*}, ² Mamza, Paul .A.P and ³ Siaka, Abdulfatai. A.

Received 18 November 2019/Accepted 12 December 2019/Published online: 30 December 2019

Abstract In order to assess changes in plasticity and mechanical properties of polystyrene fatty acid-based neem seed oil blends, the value added product was developed. The effect of loading on the mechanical and thermal properties of polystyrene and the nature of interaction in the blend were investigated. Neem seed oil was epoxidised at 60 °C and at a pressure of 1 atm for 5 hours. Fourier transform infrared (FTIR) spectroscopy was used to identify the unsaturation and epoxy group in the neem oil and in the epoxidised neem oil. The infrared spectrum indicated that the absorption band at 3012 cm⁻¹ was absent in the blend and that a new band was formed at 943 cm⁻¹, which supported epoxidation. The mechanical performance of the various composites (95/5, 85/15, 75/25, 65/35, 45/55, and 35/65) were tested using tensiometer. Comparison of mechanical properties such as elongation at break, tensile strength and tensile modulus revealed apparent compatibility domain for 95/5 polystyrene/epoxidized neem seed oil (8.70±0.08, 24.40±0.02 and 37.0±1.0. Viscosity measurements revealed that miscibility occurs between the compositions 95/5, 85/15, 45/55 and 35/65 while phase inversion and phase separation occur in the 65/35 and 75/25 blends, indicating immiscibility and incompatibility.

Keywords: *Polystyrene, epoxidised neem seed oil, blend, mechanical performance, interaction*

*S. Takuma

Department of Chemistry, Federal College of Education (Tech),
Gusau, Nigeria
Email: salihutakuma2@gmail.com

P. A. P. Mamza

Department of Chemistry, Ahmadu Bello University,
Zaria, Kaduna State, Nigeria

S. A. Abdulfatai

Department of Applied Chemistry,
Federal University Dutsin-Ma,
Katsina State, Nigeria

1.0 Introduction

Over the past few decades, most polymers used are derived from petroleum products that are non-biodegradable and non-renewable. The increase in environmental problem resulting from greenhouse gas emission and diminishing fossil resources has attracted global concerns that has enhanced the development of green polymer composite which are environmentally friendly and biodegradable (Chiang *et al.*, 2013). Polystyrene (PS) is one of most durable and widely studied thermoplastic polymers because of its linear structure and ease of processing. It is used in a wide range of products due to its versatile properties. It is a widely applied polymer that has excellent properties including optical, chemical, heat insulation and the ease of facile synthesis. Despite these desirable features, the high brittleness of PS can limit its mechanical applications (Wunsch, 2000). Therefore, considerable efforts have been made to modify its structure for enhanced mechanical properties by employing plasticizers. Commonly used plasticizers are petroleum based, which suffers from meeting stringent environmental requirements. Therefore, the present study is aimed at epoxidized neem seed oil as a biodegradable plasticizer to enhance the mechanical properties of polystyrene (Cataldo *et al.*, 2013). Vegetable oils are derived from plants and are chemically composed of different triacylglycerol, i.e., esters of glycerol and fatty acids (Tan and Man, 2002). Neem seed oil are attractive raw materials for many industrial applications as

they are derived from renewable resources, biodegradable, environmentally friendly, easily available (Lligadas *et al.*, 2013). Neem seed (*Azadirachita Indica*) oil is a favourable vegetable oil because it is cheap, less toxic and easily available as a sustainable agricultural resource. It is a product of the seed of neem trees, one of the economical perennial non edible oil crops in Nigeria and belongs to the family *meliceae*. Epoxidized neem seed oils have been reportedly used as plasticizers, stabilizers and additives to many polymers (Groud *et al.*, 2006). In this study, epoxidized neem seed oil was used as plasticizer to polystyrene via solution casting technique. The aim of this study is to modify plasticity and mechanical properties of PS using neem seed oil. The raw neem seed oil shall be modified and the effect of plasticizer loading on the mechanical properties of polystyrene shall be investigated.

2.0 Materials and Methods

A commercial grade of polystyrene (molecular weight = 280 999 g/mol) was obtained from Steeve Moore Chemical store, Zaria, Kaduna state, Nigeria. Raw neem oil was obtained from National Research Institute of Chemical Technology (NARICT), Zaria, Kaduna state, Nigeria.

The epoxidation of neem seed oil was carried out with the use of per acid generated directly in the environment as a result of the reaction of 30 weight % solution of hydrogen peroxide and formic acid (98%). The FTIR spectra of raw and epoxidized neem oil were recorded using Fourier Transform Infrared spectrometer (Agilent Technologies Cary 630 series, made in Germany) equipped with a universal attenuated total reflectance (UATR) accessory. The spectra were recorded between 4000 cm^{-1} and 500 cm^{-1} frequency ranges.

The PS/ENO blends were prepared by solution casting technique using chloroform according to the procedure described by Ashraf *et al.*, (2007).

Casting of PS/P ENO films was done following the method described by Folaranmi and Zayyan, (2002). The tensile properties were tested using Monsanto Tensometer 9875 (type `w`) series. The samples were cut in dumbbell shapes following ASTM D638 standard as described by Imran *et al.* (2010).

3.0 Results and Discussion

3.1 Fourier Transform Infrared (FTIR) Analysis of RNO and ENO

FTIR spectroscopy is a technique that is sensitive to intermolecular interactions. Infrared spectrum helps to reveal the structure of a new compound by telling us what groups are present or absent in the molecule formed. A particular group absorbs light of certain frequencies which is useful in characterizing or identifying a given functional group. FTIR spectroscopy was used to correlate shifts in absorption band (hence functional groups) in raw neem oil and epoxidized neem oil. The FTIR spectra of raw neem oil and epoxidized neem oil are presented in Fig. 1 as (a) and (b) respectively. The two spectra have C—O link on the carboxylic acid functional group around 1159 – 1170 cm^{-1} , carbonyl functional group around, 1714 – 1744 cm^{-1} and C—H (Sp^3) around 2855 2922 cm^{-1} . However, the remarkable difference in the two spectra is the C=C stretching peak around 3011 cm^{-1} (Fig. 1a) which is absent in the spectrum of epoxidized neem oil (Fig. 1b) indicating that epoxidation has taken place with the appearance of C=C (Espinoza *et al.*, 2009; Kouroosh *et al.*, 2012). Also, the broad hydrogen bond absorption band around 3418 cm^{-1} due to hydrogen bond acceptance of the epoxy oxygen (with the available moisture in the system) was also formed (Pim-Pahn *et al.*, 2008; Kouroosh *et al.*, 2012). Also, the epoxidized spectrum displayed a unique characteristics peak that corresponded to C—O—C stretching in oxirane at 943.0 cm^{-1} which is often found within the range, 850 – 950 cm^{-1} (Ahmad *et al.*, 2001; Silveraja *et al.*, 2012; Prema and Chhibber, 2013; Boung *et al.*, 2014). The relative instability of concentrated hydrogen peroxide in air is attributed to the inability of obtaining 100% conversion as reported in similar literatures (Pim-Pahn *et al.*, 2008; Silveraja *et al.*, 2012; Boung *et al.*, 2014).

3.2 Plasticization effect of ENO on the tensile properties of PS.

Table 1 presents mechanical parameters for various composition of PS/NO blends. These include force (N), area (mm^2), change in length (mm), tensile stress, (MPa), tensile modulus (MPa), strain and elongation (%) etc.



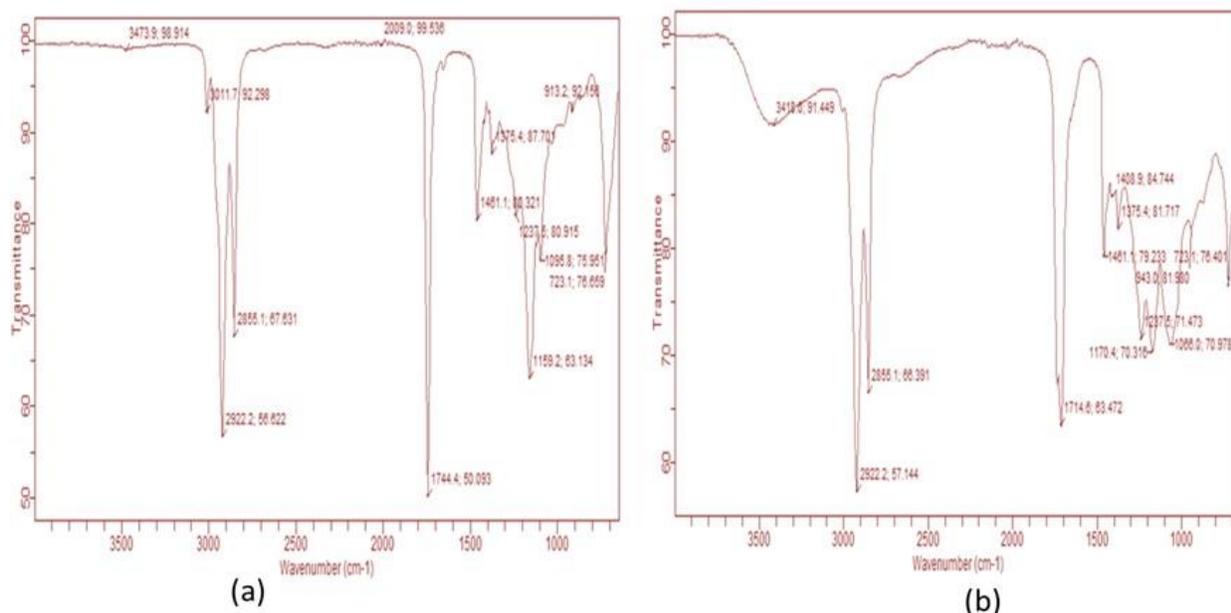


Fig 1: FTIR spectra of (a): neem oil (b): epoxidized neem oil.

Table 1: Tensile Strength Test for Percentage Composition of PS/ENO Blends

% PS/ENO	Force (N)	Area (mm ²)	Lo (mm)	ΔL (mm)	Tensile Stress (MPa)	Strain	Tensile Modulus (MPa)	Elongation (%)
35/65	25.5	11.62	10	1.60±0.03	2.20±0.08	0.16±0.01	10.38±0.02	16.0±1.0
45/55	21	11.62	10	1.80±0.03	1.80±0.08	0.18±0.01	9.70±0.02	18.0±1.0
65/35	49	11.62	10	1.60±0.03	4.20±0.08	0.16±0.01	33.80±0.02	16.0±1.0
75/25	39.2	11.62	10	1.40±0.03	3.40±0.08	0.14±0.01	34.30±0.02	14.0±1.0
85/15	70.5	11.62	10	1.80±0.03	6.10±0.08	0.18±0.01	27.20±0.02	18.0±1.0
95/5	101	11.62	10	3.70±0.03	8.70±0.08	0.37±0.01	24.40±0.02	37.0±1.0
100/0	118.17	11.62	10	2.50±0.03	10.20±0.08	0.25±0.01	38.60±0.02	25.0±1.0

Percentage elongation sometimes called strain percent measures the ductility, which is related to the toughness of a material. Fig. 2 shows the effect of ENO loading on the elongation at break of PS/ENO blends. The elongation at break of PS/ENO blends with 5, 15, 25, 35, 55 and 65 wt % ENO are 37, 18, 14, 16, 18, 16 percent, respectively. Pure PS (100 % PS) exhibited an elongation at break of 25 %. It has been observed that elongation at break of the blends increases significantly at the rate of 5 % per ENO loading before decreasing (after a certain critical value) as the weight % ENO loading

increases. The increase indicates that ENO at this composition reduces the intermolecular forces and increase the mobility of the PS chain, thus enhancing the flexibility and extensibility of the blend at this weight percent composition (Diez-Pascual *et al.*, 2009). Further addition after this point, as stated before, causes the blends to be more harder and brittle. This could be due to poor intermolecular interaction between the plasticizer (ENO) and polymer (PS) molecules. This can also lead to antiplasticization which may be attributed to the bulky group (aromatic ring) in the backbone of



PS chain and the non-polar nature of PS, (which can also makes the PS/ENO blend more rigid and stiffer). Several theories have been proposed to explain the mechanism and action of plasticizers on polymers. Among those theories, lubricity theory and gel theory have been widely accepted to describe the effect of plasticizers on polymeric networks. According to Lubricity theory, the plasticizer acted as a lubricant to reduce friction and facilitates polymer chain mobility over one another and consequently reduces deformation. The Gel theory extends the Lubricity theory and suggests that plasticizer disrupts and replaces polymer-polymer interactions (hydrogen bonds, van der Waals or ionic forces etc.) that hold polymer chains together resulting in reduction of the polymer gel structure (Puyou *et al.*, 2016)

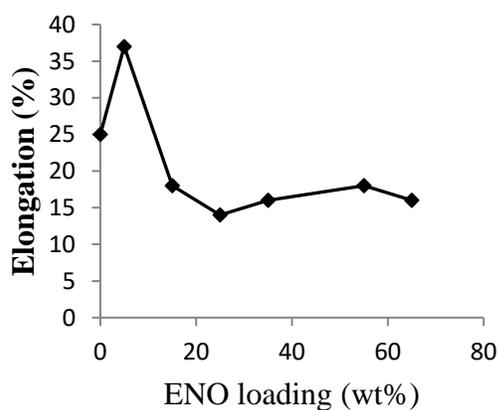


Fig. 2: Elongation (%) versus ENO loading (wt %)

Tensile strength is a unique property of plastic materials that can be used to explain the inherent strength of a material. It is dependent on the molecular structure and the orientation of the polymer with a particular sample, and on the presence of filler or reinforcement that may be incorporated into the polymer. Fig. 3 shows the effect of ENO loading on the tensile strength of PS/ENO blends. A significant influence in the values of the tensile strength of PS/ENO blends was observed due to the addition of different content of ENO. The tensile strength decreases with increasing amount of ENO until it eventually loses at about 7 % of its strength (9.65 MPa) after 5 wt % increment in ENO (9.02 MPa). However, the increase was 481 % (1.66 MPa) with 65 wt % ENO Fig. 3). The observed increase is in accordance with the common

rule that the plasticizer can decrease the tensile strength of the polymer. Generally, plasticization of a polymer forces solid to undergo a change from hard and tough to soft and tough. Therefore, a drop in tensile strength may be caused by the formation of plasticizer-plasticizer interaction which dominates at higher ENO contents and leads to a phase separated structure. In addition, at higher plasticizer (ENO) loading, only part of the plasticizer was located in the interfacial area, while the remaining was dispersed in the PS matrix. This might have influenced the homogeneity and caused the drop in tensile strength of the blends (Silveraja *et al.*, 2012; Bounq *et al.*, 2014; Puyou *et al.*, 2016). The reduction in tensile strength above 5 weight % ENO content may also be attributed to agglomeration and subsequent poor interaction at the interphase (Diez-Pascual *et al.*, 2009; Silveraja *et al.*, 2012).

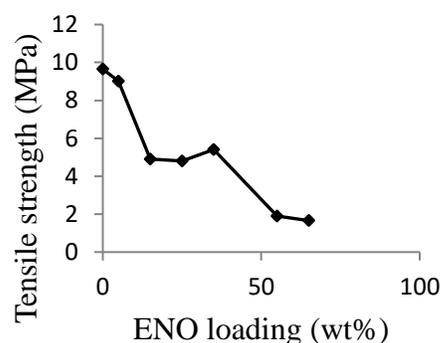


Fig 3: Tensile strength (MPa) versus ENO loading (wt %)

The observed changes in tensile strength with loading of ENO is also in agreement with some other works. In 2013, Orathai and his coworkers stated that every solution casting blend (based on chloroform, benzene and carbon tetrachloride) showed a tensile strength drop and then rise again at the point at which phase inversion is possible.

Tensile modulus (E) also called modulus of elasticity or young modulus is a measure of material stiffness and rigidity. Fig. 4 presents the effect of ENO loading on the tensile modulus of the PS/ENO bends. The addition of ENO to pure PS decreases the tensile modulus of the blend losing up to 58 % at 5% increase in ENO (24.4 MPa). This was succeeded by a rise in tensile modulus after further increase in ENO loading (15, 25 and 35 weight %). Beyond 35 weight % ENO loading the tensile



modulus values dropped (9.7 and 10.38 MPa for 55 until 65 weight % ENO loading). The drop in tensile modulus may be due to the presence of excess ENO in the blend which reduces the stiffness and rigidity of the PS molecular chain. Moreover, increasing ENO content above 5 weight % might have contributed to the occurrence of empty voids in the blends and influences the local stress acting on the material (Park *et al.*, 2010; Silveraja *et al.*, 2012).

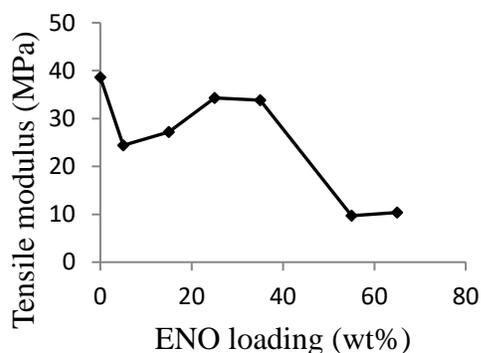


Fig 4: Tensile modulus versus ENO loading

4.0 Conclusion

The epoxidation of neem oil was performed using a conventional method. The successful development of value added product from sustainable resource has been demonstrated as confirmed by FTIR analysis. A possible side reaction was the epoxy ring opening that produced hydroxyl functional groups. The results and findings of this study confirmed that the addition of epoxidized neem oil to PS produces softer and more flexible material which were attributed to disruption or weakness of secondary valence bonds. The behaviours of PS/ENO blends can be assessed through the effect of their composition on percentage elongation, tensile strength and tensile modulus and there was a significant and favourable changes in these parameter as a result of blending. Therefore, the epoxidized neem oil (ENO) can be used as a plausible plasticizer to increases interaction at the phase boundaries and improve overall properties of polystyrene polymer.

5.0 Acknowledgment

A profound gratification goes to Tertiary education trust fund (Tetfund) and the management of Federal College of Education Technical Gusau, for granting a study fellowship that gave birth to this research.

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