Unsaturated Polyesters / Layered Silicate Nanocomposites: Synthesis and Characterization

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Abstract: *Unsaturated polyester (PEs) / Egyptian bentonite nanocomposites were prepared. The bentonites used were chemically modified by cation exchange reactions with surfactant (quaternary ammonium salt). The prepared nanocomposites were characterized by morphology analysis using X-ray diffraction, transmition electron microscope, thermal analysis, mechanical analysis and electrical analysis. The results reported in this study revealed the improvement of the thermal and mechanical properties of the prepared nanocomposites. All modified clay-polyester nanocomposites displayed improved mechanical properties with organoclay content up to 7 wt % as compared with PEs filled with micrometer clay (40 wt %).Also the prepared nanocomposites show improvement of thermal stability and electrical conductivity .*
Keywords: *Unsaturated polyesters, Organoclay, Nanocomposites, Egyptian Bentonite (EB), Mechanical properties.*

I.   Introduction

Polymer matrix based nanocomposites have received enormous attention both in academia and industry over the past decades. Polymer/ clay nanocomposites are a new class of composites with polymer matrix in which the dispersed phase is the silicate constituted by particles that have at least one of its dimensions in the nanometer range (10^{-9}m). The excellent properties of nanocomposites are attributed to the large surface to volume ratio of the nanofillers **[1]**. Nanocomposites can, in principle, be formed from clays and organoclay in a number of ways including various in situ polymerization [2, 3, 4–10],solution [11,12], and latex [13,14] methods.

Much attention has been directed toward the preparation of unsaturated polyester (UP) / montmorillonite (MMT) nanocomposite. Two steps were used for preparing unsaturated polyester–layered silicate nanocomposite. In the first step, pre-intercalates of the unsaturated polyester and MMT nanocomposites, in other words, mixture of the UP and organophilic-treated MMT are prepared in the first step; a styrene monomer was then added to the pre-intercalates of UP/MMT with varying mixing time [15]. However the unsaturated polyester (UP)/organically modified clay (OMC) nanocomposites were prepared by multistep simultaneous mixing of UP oligomer chain, styrene (St) monomer, and OMC [16], the intercross-linked networks of unsaturated polyester (UP) toughened epoxy–clay hybrid nanocomposites have been developed. Epoxy resin (DGEBA) was toughened with 5, 10 and 15% (by wt) of unsaturated polyester using benzoyl peroxide as radical initiator and 4, 4′-diaminodiphenylmethane as a curing agent at appropriate conditions [17]. Dhakal et al, investigate the effect of various loading levels of nanoclay reinforcement on the nanomechanical properties of layered silicate nanoclay reinforced unsaturated polyester (UPE) nanocomposites using nano-indentation test method [18]. Various forms of organically modified montmorillonite (OMMT) were introduced in situ during the copolyaddition of epichlorohydrin, maleic anhydride and phthalic anhydride. The catalytic effect of OMMT containing quaternary ammonium ions was observed the introduction of clay leads to the increase in softening temperature, as well as melt or solution viscosity of unsaturated polyester [19]. The reaction between unsaturated polyester (UP) resin and styrene (St) is a heterogeneous free-radical chain-growth cross-linking copolymerization. Curing of the UP/St system in the presence of organically-modified nanoclay was studied by differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy. A mechanistic kinetic model based on the free radical copolymerization mechanism was developed to simulate the reaction rate and conversion profiles of UP/St resin mixtures with various nanoclay contents cured at low temperatures [20]. Unsaturated polyester (UP)/montmorillonite (MMT) nanocomposite was prepared by using hydroxylpropylacrylate (HPA) as a reactive diluent instead of conventional styrene monomer and the effect of polarity of reactive diluent on properties of nanocomposite was investigated [21]. The addition of a small amount of nanoclay (1–3 wt %) can provide excellent volume shrinkage control of unsaturated polyester (UP)/styrene (St)/poly (vinyl acetate) (PVAc) systems cured at room temperature. PVAc serves as the low profile additive (LPA) [22]. The reinforcing effect of both delaminated and intercalated clay nanoplatelets was theoretically evaluated with the Halpin-Tsai equations. It was evaluated that the aspect ratio of delaminated clay

nanoplatelets was approximately 150. The increase of the storage modulus below and above the glass transition temperature was achieved without reducing glass transition temperature and Izod impact strength with increasing clay content [23]. The bentonite used was unmodified and with different chemical treatments. The effects of these different chemical modifications (cation exchange reactions with quaternary ammonium and phosphonium salts) of this clay as well as the effect of clay content on the thermal, barrier (water absorption), mechanical (flexural) and dynamic-mechanical properties of unsaturated polyester matrix were analyzed. The results clearly show that the chemical modifications of the clay cause a desired effect on its final properties improving the performance of the nanocomposites. The enhancements could be directly related to the dispersion of the clay inside the matrix, as shown by transmission electron microscopy [24]. The thermal stability of nanocomposites based on unsaturated polyester resin (UP) and montmorillonite (MMT) clays was reported. The coefficients of thermal expansion (CTE) of both neat resin and nanocomposites with various concentrations of MMT were measured and it was found that the incorporation of clay particles reduced the CTE of the polyester resin [25]. The curing behavior of unsaturated polyester/modified montmorillonite nanocomposites was studied by Yan Zhou et al [26]. The results showed that their gel times increased markedly at the same cure temperature, and that the activation energy of the nanocomposites was higher than that of the pure unsaturated polyester. The effects of organic modifications of the pristine clay on the UV-curing behavior and structure of the nanocomposites system were investigated. The organic modifications of the clay affected considerably the UV-curing behavior and structure of the nanocomposite system [27]. The mechanical properties, the tensile modulus, tensile strength, flexural modulus, flexural strength and impact strength of the composites with modified montmorillonite were higher than the corresponding properties of the composites with unmodified montmorillonite. The tensile modulus, tensile strength, flexural modulus and flexural strength values showed a maximum, whereas the impact strength exhibited a minimum at approximately 3-5 wt% modified montmorillonite content. These results imply that the level of exfoliation may also exhibit a maximum with respect to the modified montmorillonite content. The level of improvement in the mechanical properties was substantial. Adding only 3 wt% organically modified clay improved the flexural modulus of unsaturated polyester by 35%. The tensile modulus of unsaturated polyester was also improved by 17% at 5 % of organically modified clay loading [28].

The objective of this study is to enhance the performance of polymer nanocomposites using the polyesters PEs based on maleic anhydride and dimethyl terephthalate with different concentrations of ethylene glycol EG with organo clay. Therefore, the present work investigates the mechanical properties and thermal stability of PEs-MMT nanocomposites. The results are supported by mechanical testing, X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermo gravimetric analysis (TGA).

II.   Experimental

1. Materials
Egyptian Bentonite Clay (EB), is supplied from south of El-Hamamm district, grinding through ball-mill and saving at 0.6 micron. ethylene glycol (EG), El-Nasr Pharmaceutical Co., Para toluenesulphonic Acid, Sigma Aldrich Co., Dimethyl Terephthalate (DMT), Sigma Aldrich Co., Maleic anhydride (MA), Sigma Aldrich Co., Octadecylamine (ODA) , Faluca Sigma Aldrich Co., Methyl Ethyl Ketone Peroxide (MEKP), Fluka Chemika,. Styrene, Sigma Aldrich, CO., Cobalt Octoate,El-Nasr Pharmaceutical Chemicals Co., and Hydroquionon, El-Nasr Pharmaceutical Chemicals Co. all chemical were used without further purifications.

2. Instrumentation
Morphology analysis . X-ray diffraction (XRD) patterns were obtained using a Rigaku X-ray diffractometer equipped with CuKa radiation and a curved graphite crystal monochromator. Samples were prepared by applying the pre-intercalated mixture and nanocomposite of UP-MMT in sheet form on a slide. All XRD data were collected with an X-ray generator (λ =1.5406 Å). Bragg's law (λ = 2d/SinΘ) was used to compute the crystallographic d-spacing. The TEM pictures were performed by TEM-1230 with an accelerating voltage of 100KV (JEOL Co.,Japan).

Thermal analysis: Thermal stability was determined by the thermogravimetric analysis (TGA) with Shimadzu TGA-50H thermal analyzer in nitrogen atmosphere and at a heating rate of 10°C/min from 800°C.

Mechanical analysis: Mechanical measurments (i.e tensile strength, elongation at break) were determined with an Instron 1026 testing machine, according to ASTM-D638, 08. The hardness of test specimens was measured with shore D durometer according to ASTM-D2240-05. All these tests were performed at room temperature (25 $\pm$ 1°C) and the reported results were averaged from a minimum of five specimens.

Electrical analysis: Electrical conductivity dc of the prepared cast sampels was performed using the Keilhley Electrometer Model 6517A/ High Resistance Meter by applying the following equation: Specific resistivity = (R.S)/ h where R is the electrical resistance measured directly by the used apparatus, h and S are the sample thickness and area, respectively.

3. Synthesis of different composites PEEG$_1$ and PEEG2
Synthesis of unsaturated polyester based on maleic anhydride PEEG$_1$

Dimethyl terephthalate (19.4 g,100 ml), maleic anhydride (9.8 g, 100ml), ethylene glycol (12.4 g, 200 ml) and p-toluensulfonic acid (0.21 g, 0.5% wt) as a catalyst were charged into a three necked round bottom flask 250 ml fitted with a Dean-stark tube, reflux condenser , thermometer and nitrogen inlet tube. The flask was heated slowly at 150 ^{o}C under a gentle nitrogen stream with continuous magnetic stirring for 30 min; the temperature was raised from 180 – 200°C for 6 - 8 hrs, to ensure that water was completely eliminated during this period. The resulted resin was dissolved in styrene monomer within 40 % wt of resin to introduced pale yellow polyester resin. Then hydroquinone was added as inhibitors to the resin.

Synthesis of unsaturated polyester based on ethylene glycol PEEG2

In 100 ml beaker (20 gm) unsaturated polyester prepolymer and 2 gm (10%) of ethylene glycol were sonicated at 30°C for 20 min, the new resin was poured in Petri dish then 0.05% of MEKP (Methyl ethyl ketone peroxide) was added as curing agent and cobalt octoate as initiator at room temperature to produce PEEG$_2$ film.

Preparation of Organo-Bentonite

The organo-bentonites were synthesized by cation exchange reaction between Na-bentonite and surfactant i.e octadecylamine (ODA)[29]. The surfactant was protonated by adding HCl. Aqueous suspension 0.5 wt% of Na-bentonite was prepared and heated at 80°C. The prepared alkyl ammonium salt solution was drop wise added to the Na-bentonite suspension and maintained at 80 °C for 12 h under vigorous stirring. Then the suspension was cooled to room temperature. Finally, the treated clay particles were collected by centrifugation and subsequently washed with deionized water several times until no halide were detected in the filtrate by AgNO3 test. The dispersion and washing was accomplished using a 50/50 ethanol/water mixture. The filter cake was then placed in a vacuum oven at 80 °C for 24 h. The dried cake was grind and screened with a 325-mesh sieve to obtain the inorganic-organophilic material ODA-B.

Preparation of PEEG1Composites

A series of PE / Egyptian Bentonite (EB) composites were prepared by sonicatore with the following molar ratio 3, 5, 7, 10, 20, 30, 40, 50, and 60 % wt.

In 100ml beaker (20 gm) unsaturated polyester prepolymer and (0.66 gm) of EB was sonicated at 30 ^{0}C for 40 min, the composite resin was poured in Petri dish then 0.05% of MEKP (Methyl ethyl ketone peroxide) was added as curing agent and cobalt octoate as initiator at room temperature to produce PEEG1 / EB composites.

Preparation of PEEG1 Nanocomposites

A series of PE / Organo-Bentonite (OB) nanocomposites were prepared by sonicatore with the following molar ratio 3, 5, 7, and 10 % wt.

In 100ml beaker (20 gm) unsaturated polyester prepolymer and [0.66 gm (3 %)]of OB was sonicated at 30 ^{0}C for 40 min, the nanocomposite resin was poured in Petri dish then we add 0.05% of MEKP (Methyl ethyl ketone peroxide) as curing agent and cobalt octoate as initiator at room temperature to introduced PEEG1 / OB nanocomposites.

Preparation of PEEG2 Composites

A series of PEEG2 / Egyptian Bentonite (EB) composites were prepared by sonicatore with the following molar ratio 3, 5, 7, 10, 20, 30, 40, 50, and 60 % wt.

In 100ml beaker (20 gm) unsaturated polyester prepolymer, [2 gm (10%)] of ethylene glycol (EG) and (0.66 gm) of EB was sonicated at 30 ^{0}C for 40 min, the composite resin was poured in Petri dish then add 0.05% of MEKP (Methyl ethyl ketone peroxide) as curing agent and cobalt octoate as initiator at room temperature to introduced PEEG2 / EB composites.

Preparation of PEEG2 Nanocomposites

A series of PEEG2 / Organo-Bentonite (OB) nanocomposites were prepared by sonicatore with the following molar ratio 3, 5, 7, and 10 % wt.

In 100ml beaker (20 gm) unsaturated polyester prepolymer, [2 gm (10%)] of ethylene glycol (EG) and [0.66 gm (3 %)] of OB was sonicated at 30 ^{0}C for 40 min. the nanocomposite resin was poured in Petri dish then add (0.05%) of MEKP (Methyl ethyl ketone peroxide) as curing agent and cobalt octoate as initiator at room temperature to introduced PEEG2/ OB nanocomposites.

III. Results and Discussions

In this study polyesters (PE) based on maleic anhydride and dimethylterephathalte with different concentrations of ethylene glycol EG were prepared to give two polyesters $PEEG_1$ and $PEEG_2$. A series of PEEG1, PEEG2 / Egyptian Bentonite (EB) composites were prepared by sonicatore with the following molar ratio 3, 5, 7, 10, 20, 30, 40, 50, and 60 % wt., also series of PEEG1,PEEG2 / Organo-Bentonite (OB) nanocomposites were prepared by sonicatore with the following molar ratio 3, 5, 7, and 10 % wt. to investigate the mechanical properties and thermal stability of the prepared composites.

Structure studies
Morphology Analysis

XRD pattern **Fig.1a,b** of the inorganic clay has a peak at a 2θ value of 7∘ and that corresponds to an intergallery spacing of 1.26 nm. The composites prepared with this clay also have this peak and that indicates the existence of clay as microtactoids and that leads to the formation of clay filled composites.
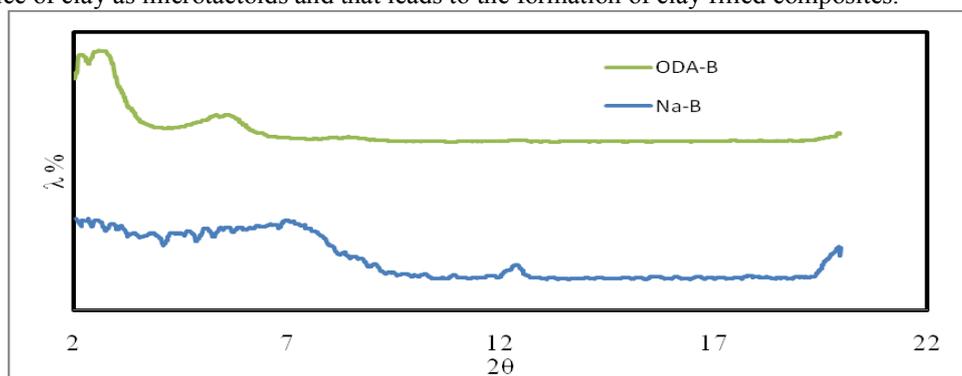
Fig 1a. XRD of Egyptian Bentonite (Na-B) & Organo Egyptian Bentonite (ODA-B).
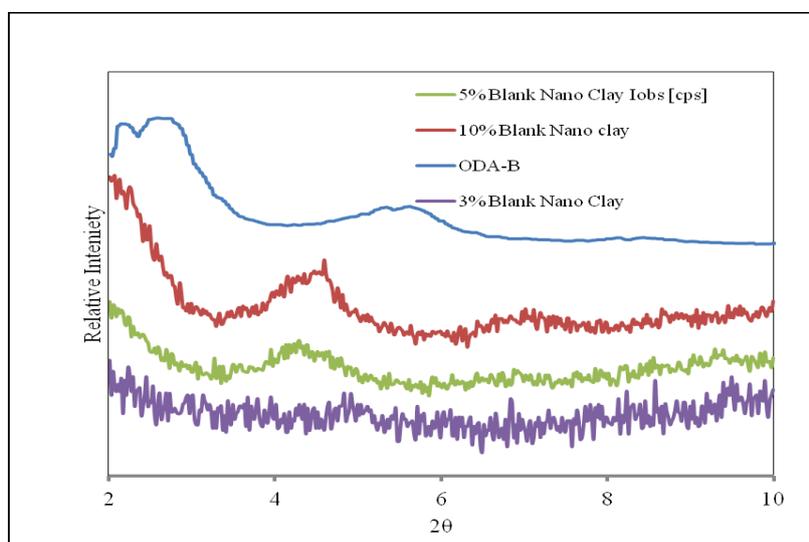
Fig 1b: XRD of different wt % of ODA-B. 3, 5, and 10% in PEEG1 matrix.

Organic clay has a peak at 2θ value of 2.9∘ and the corresponding initial intergallery spacing is 3.09 nm also another characteristic peak at 2θ = 5.7∘with intergallery spacing is 1.55 nm. This peak is not present in the nanocomposites prepared with organoclay **Fig.2.**
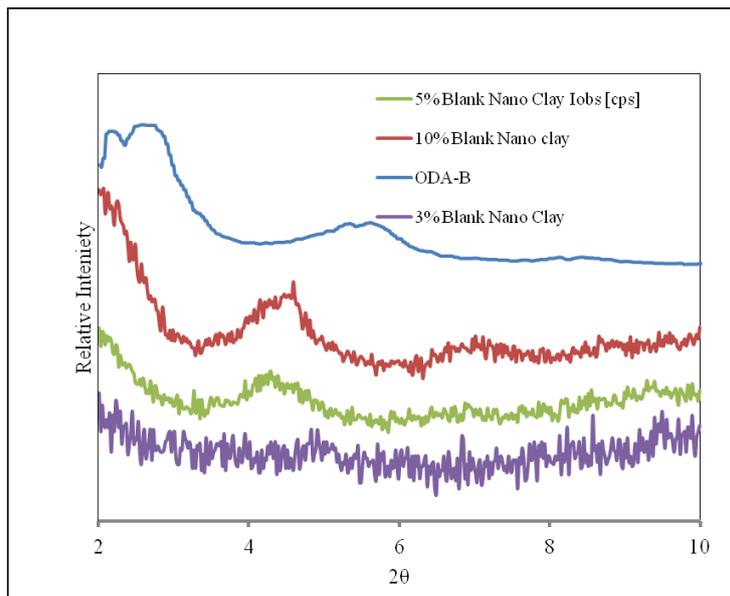
Fig 2: XRD of different wt % of ODA-B. 3, 5, and 10% in PEEG1 matrix .

During shear mixing, the polymer intercalates between the intergallery spacing of organoclay and makes the clay layers to move apart. On further mixing the nanosize clay platelets disperse fully in the unsaturated polyester matrix. The disappearance of peak indicates the separation of clay layers and the formation of exfoliated nanocomposite. For the organoclay content of 7 & 10 wt. %, there is a broad peak at 2θ value of 4.6◦and 4.6◦ the corresponding intergallery spacing is 19.12A° and 19.42A° respectively. This indicates the formation of intercalated nanocomposites.

On the other hand, TEM allows a qualitative understanding of the internal structure and can directly provide information in real space, in a localized area, on morphology and defect structures [30, 31]. Since the silicate layers are composed of heavier elements (Al, Si and O) than the interlayer and surrounding matrix (C, H and N), they appear darker in bright-field images. Therefore, when nanocomposites are formed, the intersections of the silicate sheets are seen as dark lines which are the cross sections of the silicate layers, measuring 1 nm thick. However, special care must be exercised to guarantee a representative cross-section of the sample [30, 32].

Fig 3a.b show the TEM micrographs obtained for an intercalated and an exfoliated nanocomposite. As already mentioned, besides these two well defined structures other intermediate organizations can exist presenting both intercalation and exfoliation. In this case, a broadening of the diffraction peak is often observed and one must rely on TEM observation to define the overall structure [33] so more direct evidence for the formation of a nanocomposite is provided by TEM

The TEM of image 3%ODA/PEEG1 in **Fig 3c** display individual silicate layers apparent as dark lines. However, the 5%ODA/PEEG2 in **Fig.3d** layers have some irregular dispersions of the silicate layer maintained their original ordering.
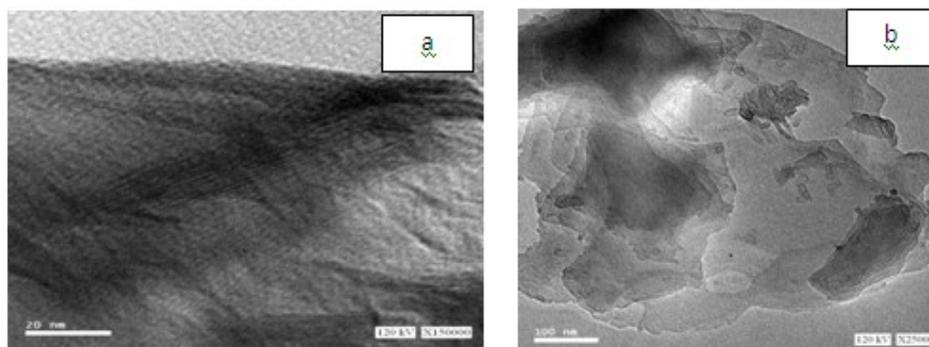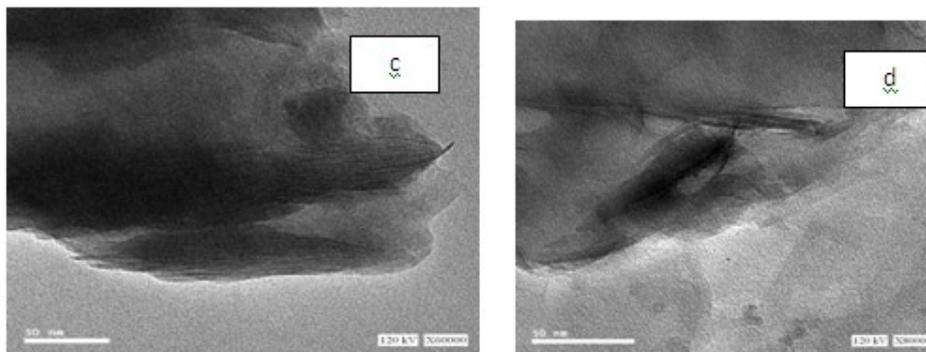
Fig 3: TEM of a) 3% Organo Egyptian Bentonite (ODA) in PEEG1 matrix, b) 5% Organo Egyptian Bentonite (ODA) PEEG1 matrix, c) 3% Organo Egyptian Bentonite (ODA) PEEG2 matrix, d) 5% Organo Egyptian Bentonite (ODA) PEEG2 matrix.

Thermal Analysis

The behavior of polymer/clay nanocomposites is complicated and many factors contribute to increase in thermal resistance. Due to characteristic structure of layers in polymer matrix and nanoscopic dimensions of filler particles, several effects have been observed that can explain the changes in thermal properties. The TGA thermogram **Figs 4,5** shows the effect of the clay content on the stability of PE nanocomposites where the char yield in PE was 4.8 while in case of 7% it becomes 8.6 as demonstrated in **Table 1**. The PEEG2 nanocomposites sampels have thermal stability and char yield more than the other samples, where the char yield was 7.6 and 11 in PEEG2 and 7% PEEG2 respectively.Where the particles with nanometer size restrict segmental motion near the organic-inorganic interface. This is a typical effect for the inclusion of clay in a polymer system.
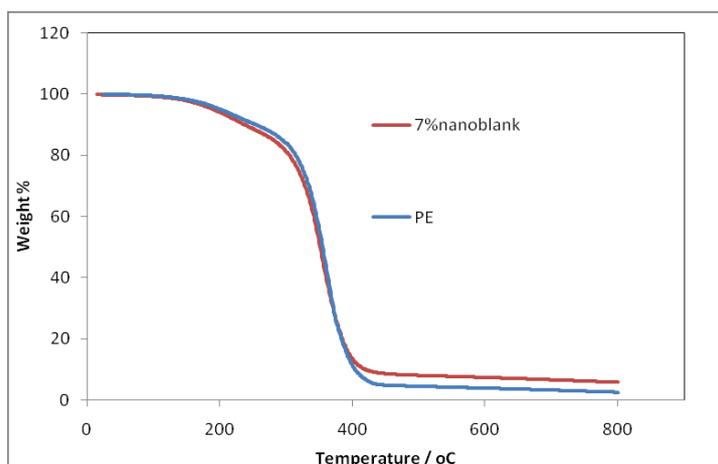
Fig 4: TGA of 7% ODA-B. in PEEG1 matrix
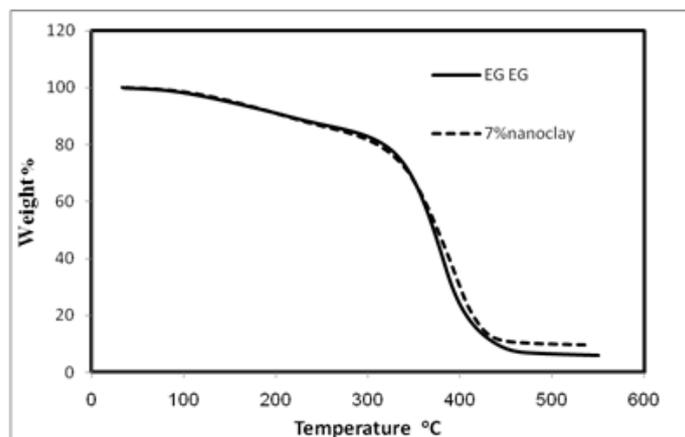
Fig 5: TGA of 7% ODA-B. in PEEG2 matrix

Table 1: properties of PEEG1/ODA & PEEG2/ODA nanocomposites.

Sample code	Formulation	Organoclay content / gm	Thermal properties TGA	Mechanical properties	
			Char yield %	Tensile N/nm²	Elongation %
PEEG1	DMT+EG+MA	0	4.8	3.1	65.6
PEEG1 / 3%	DMT+EG+MA	0.66	4.9	6.3	10
PE EG1/ 5%	DMT+EG+MA	1	5	11.4	14.8
PEEG1 /7%	DMT+EG+MA	1.4	8.6	15.3	21.8
PEEG1 /10%	DMT+EG+MA	2	8.5	14.4	19.2
PEEG2	(DMT+EG+MA) +EG	0	7.6	1.8	69.1
PEEG 23%	(DMT+EG+MA) +EG	0.66	8.1	3.8	36.3
PEEG2 5%	(DMT+EG+MA) +EG	1	8.4	7.7	38.2
PEEG2 7%	(DMT+EG+MA) +EG	1.4	11	10.2	42.8
PEEG2 10%	(DMT+EG+MA) +EG	2	8.9	9.8	40.2

Mechanical Analysis

In **Fig 6a, b**, the tensile strength of the PEEG2 nanocomposites is better than PEs nanocomposite owing to their higher degree of exfoliation and better adhesion at the PEEG1/ODA interface. Above 7% B-ODA content, the tensile strength starts to decrease with OMMT content increase in both types of nanocomposites, due to a lower degree of exfoliation and a lower degree of polymer–MMT surface interactions at higher B-ODA content. Also, the cross-link density might be lower with a higher Na-EB content, leading to a lower tensile strength i.e. indicating that the crosslinking density is inversely proportional to the degree of exfoliation [34].
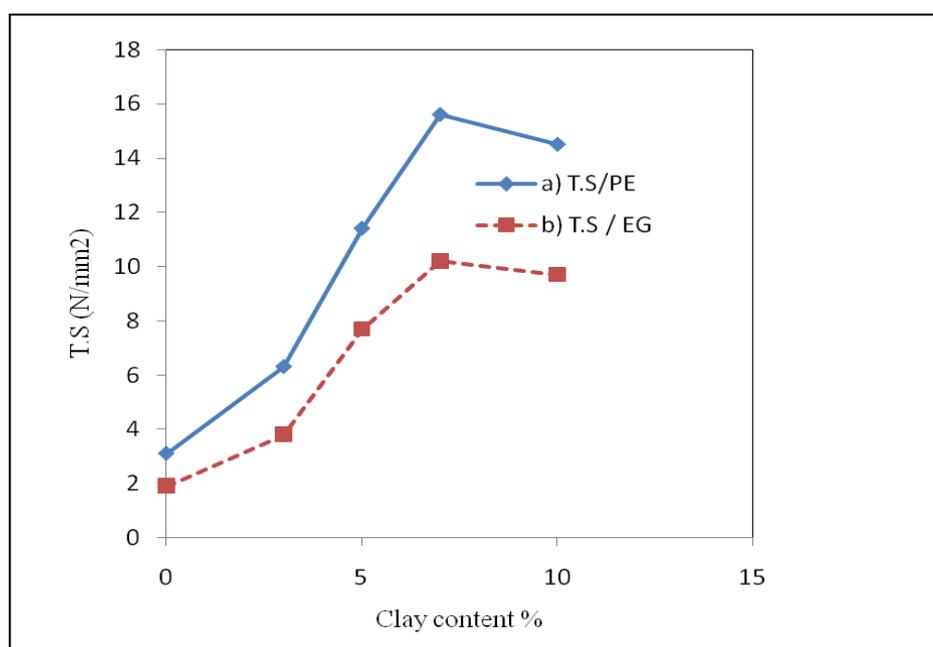
Fig 6: a) Tensile of different wt % of ODA-B.0, 3, 5, and 10% in PEEG1 matrix.
b) Tensile of different wt % of ODA-B.0, 3, 5, and 10% in PEEG2 matrix.

The increase in tensile strength associated with increases in EB-ODA content is demonstrated in **Table 1**. It was evident that with the addition of small amount of montmorillonite (3, 5 and 7%) to PEEG1, the tensile strength significantly increased. In **Fig 7a, b**, the elongation follows the same trend as tensile strength that is, increased with increasing EB-ODA contents up to 7%. The results indicated the reinforcing effect of EB-ODA to enhance the mechanical properties of the nanocomposite.
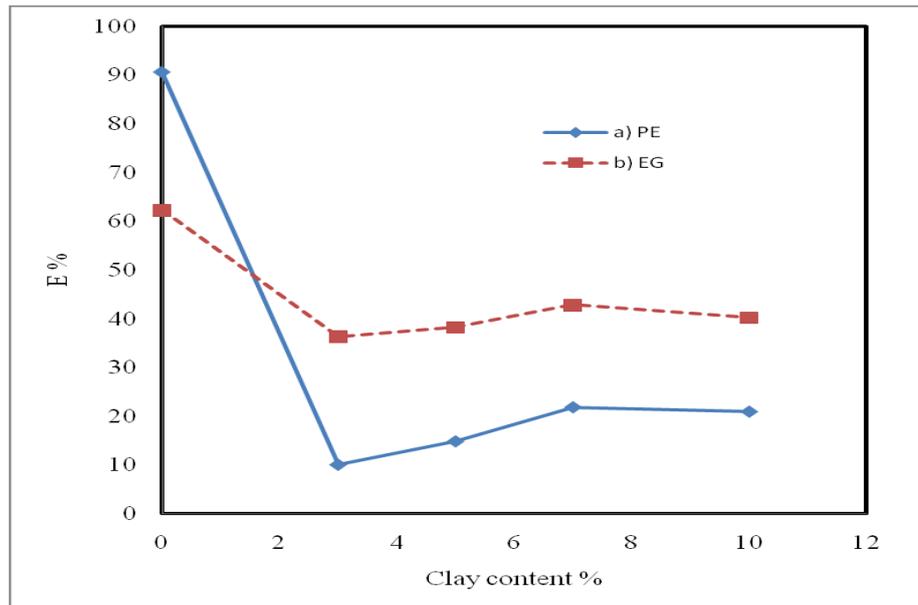
Fig 7. a) Elongation of different wt % of ODA-B.0, 3, 5, and 10% in PEEG1 matrix.
b) Elongation different wt % of ODA-B.0, 3, 5, and 10% in PEEG2 matrix.

The hardness of nanocomposites and conventional clay filled composites is shown in **Figs 8, 9.** There is an increase in hardness value of nanocomposites compared to the pristine polyester. The nanosize clay platelets uniformly distributed in the matrix system effectively restrict indentation. No further improvement in hardness is noticed at higher clay content (i.e. 7 wt. %). It may be due to the presence of porosity in the nanocomposites. During processing of nanocomposites at high clay contents, visually it was observed that the viscosity of the resin increases significantly. So the entrapped air during shear mixing finds very difficult to escape out of the matrix system and remains as micropores after curing. Another reason may be the formation of intercalated structure at high clay content, as is evident from the XRD results. This may lead to the formation of nanocomposite structure with two phases (hard phase where intercalated clay is present and soft phase where the matrix alone is present). There is no significant change in the hardness of conventional clay filled composites. The inorganic clay added just remains as microtactoids and does not contribute much on the hardness improvement.
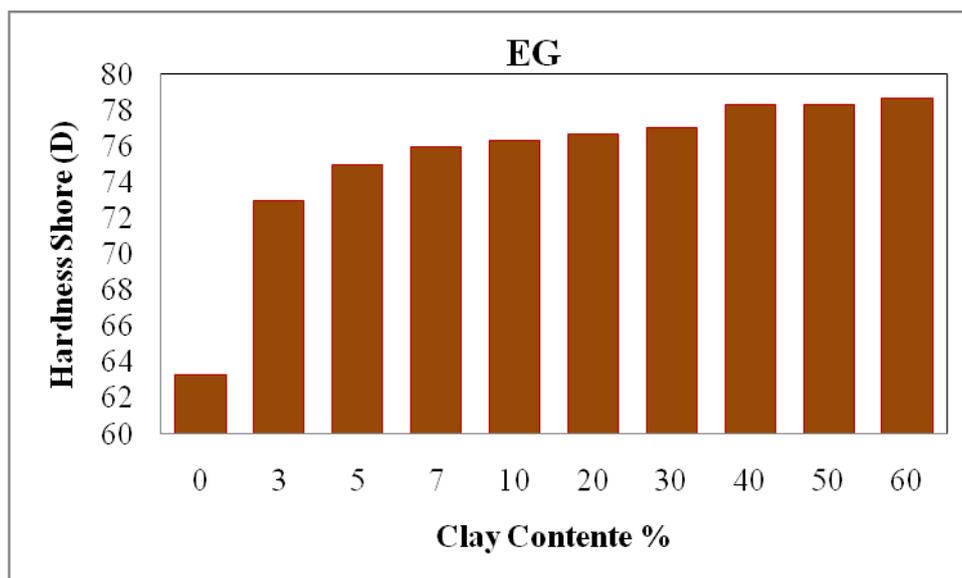
Fig 8: Hardness of different wt % of ODA-B.0, 3, 5, 7, 10, 20, 30, 40, 50 and 60% in PEEG2 matrix.
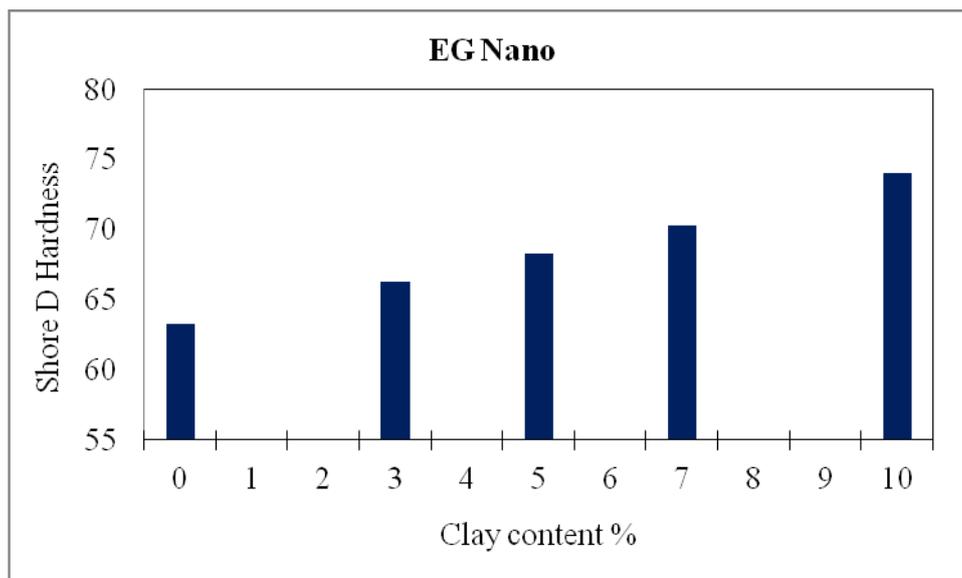
Fig 9: Hardness of different wt % of ODA-B.0, 3, 5, 7 and 10% in PEEG2 matrix

Electrical Analysis According to the common used classification of the electrical conducting materials,the materials with electrical conductivity r lower than 10^{-6} Scm^{-1} are treated as insulators, with electrical conductivity between 10^{-6} Scm^{-1} and 10^{2} Scm^{-1} as semiconductors, and consequently with r > 10^{2} S cm^{-1} as metals. Thus, the nanocomposites of PEEG1, PEEG2 with organo clay (EB-ODA) presented in this work belong to materials characterized as semiconductors. For comparison it should be mentioned that pure PE, with r = 10_16 S cm^{-1} belongs clearly to insulating materials.

IV. Conclusion

Polyesters (PEs) based on maleic anhydride and dimethylterephathalte with different concentrations of ethylene glycol EG were prepared to give two polyesters $PEEG_1$ and $PEEG_2$. Nanocomposites based on the prepared polyesters and organophilic Egyptian bentonite were prepared by sonicatore via in-situ procedure. The prepared organo-bentonite clay based on octadecylamine (ODA) was characterized with X-ray diffraction (XRD), and transmission electron microscopy (TEM). The results indicated that the intercalation of ODA within the clay layers. Organically modified clay was added in various contents (i.e. 3, 5, 7and 10 wt %) to the prepared polyesters matrices to study the effect of nanosilicate on morphology. Furthermore, the XRD analysis revealed exfoliated and intercalated structures for PEEG1and PEEG2 nanocomposites respectively. TEM images provided evidence of nanoclay-PEs interaction. The influence of the organoclay content relative to micrometer clay on the prepared nanocomposites was analyzed through mechanical properties (i.e. tensile strength, elongation at break percentages and hardness shore D), electrical conductivity and thermal stability. All the modified clay-polyester nanocomposites displayed improved mechanical properties, with organoclay content up to 7 wt % as compared with PEs filled with micrometer clay (40 wt %). The prepared nanocomposites exhibited improvement in conductivity and thermal stability. Beyond 7% wt organoclay deterioration in the properties of the nanocomposites takes place.

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