

DEVELOPMENT DESIRED PROPERTIES OF POLYSTYRENE NANO COMPOSITES BY ADDING POLYMERIC MODIFIERS

Sihama Issa Salih

Sihama_Salih@yahoo.com

Material Engineering Department, University of technology, Baghdad, Iraq

ABSTRACT

The introduction of polymeric blend-based nanomaterials has encouraged the development of flexible nanocomposites for structural applications in need of superior mechanical performance. In current research, three groups of polystyrene blend-based nanocomposites samples were fabricated by melting technique using a twin-screw extruder. These samples consist of polymer blend (polystyrene (PS): 1% copolymer (polystyrene (PS)-co- maleic anhydride (MA)): 3%ABS) as a matrix material, was strengthened by three different type of powders in nanometer size (silica (SiO₂), cement kiln dust (CKD) and Fly ash (FA)) individually, with selected weight ratio (0, 0.2, 0.4, 0.6 & 0.8 wt. %) for each of them. Experimental investigation was carried out for tensile properties and fatigue strength besides FTIR test and morphology analyzing of fracture surfaces by SEM. The results showed that tensile strength values and modulus of elasticity increased as the nanoparticle content in composite increased, but according to specific percentages of nanoparticle content in the composites samples, for three groups of the prepared nanocomposites samples. Moreover, the fatigue test revealed the super-improvement in the fatigue properties of the selected hybrid nanocomposites samples, as compared with neat polystyrene and polymer blend (PS: 1% (PS-co-MA): 3% ABS) and fatigue limit was apparent for all types of hybrid nanocomposites materials produced in this work. Morphology of the fracture surface was showed a homogeneous structure formation for optimal samples of each group of composites, indicating a good compatibility between the component materials of polymer blend and the reinforcement nanoparticles.

KEYWORDS: Fatigue properties, polystyrene, polymer blend, nanoparticles, hybrid composite.

تطوير الخصائص المرغوبة لمتراكبات البوليمرات نانوية عن طريق إضافة المعدلات البوليمرية

سهامة عيسى صالح

قسم هندسة المواد- الجامعة التكنولوجية

ان إضافة المساحيق النانوية إلى المواد البوليمرية حفزة العديد من الباحثين على تطوير متراكبات نانوية مرنة تستخدم في التطبيقات الهيكلية عالية الأداء الميكانيكي. في البحث الحالي ، تم تصنيع ثلاث مجموعات من المتراكبات النانوية المستندة على الخليط بوليمري بواسطة تقنية الصهر باستخدام باثقة ثنائية اللولب. يتكون الخليط البوليمري من البوليمرات كإضافة مواد بوليمرية توافقية أخرى :

(polystyrene (PS): 1% copolymer -co- maleic anhydride (MA)): (3%ABS polystyrene)

وتم تقوية الخليط بثلاثة أنواع من المساحيق النانوية المتمثلة ب (السليكا، غبار فرن الأسمنت والرماد المتطاير) بشكل انفرادي وبنسب وزنية محددة لكل منها (0,0.2,0.4,0.6,0.8% wt). تم إجراء اختبار تجريبي لخصائص الشد ومقاومة

الكلال إلى جانب الأختبارات التحليلية (SEM, FTIR). أظهرت النتائج أن قيم مقاومة الشد ومعامل المرونة زادت مع زيادة محتوى الجسيمات النانوية في المتراكب ، اعتمادا على نسب محددة من محتوى الجسيمات النانوية في العينات المتراكبة ، علاوة على ذلك ، كشف اختبار الكلال عن وجود تحسن الفائق في خواص الكلال لعينات المثلى من المتراكبات النانوية المختارة ، بالمقارنة مع قيم مادة لبوليسترين والخليط المحضر منه، كما ان حد الكلال كان واضح لجميع العينات المتراكبة النانوية المحضرة في هذا العمل. وأظهرت مورفولوجيا سطح الكسر تشكيل بنية متجانسة للعينات المثلى من كل مجموعة من المتراكبات ، مما يدل على وجود توافق جيد بين المواد المكونة للخليط البوليمر والجسيمات النانوية المضافة.

INTRODUCTION

Nanocomposites materials have a high interest in industrial applications However, the low in compatibility between matrix material and reinforcement materials, low degree of dispersion of the nanoparticles and weak interfacial interactions between polymer and fillers materials, which leads to low performance, limiting their use, to improve interactions between polymer and reinforcement material, a polymer functionalization and compatibilizers materials are required **Yu et al. (2006)**. The addition of polymer blends has encouraged the evolution of nanocomposites materials for structural applications that require high mechanical properties and high-performance materials. These polymeric nanocomposites materials exhibit significant structural performance with multifunctional properties by combining the properties of each element if correct proportions and inter-organization are achieved. For example, polystyrene is widely accepted material in many structural applications. However, sometimes lower mechanical characteristics arise to be incompatible with the field of their application. In contrast to fillers modification, Polymer modification seems to be a quick and effective way to provide interstitial adhesion between components of polymer composites **Sihama et al. (2015)**.

Reinforcement materials must possess distinct mechanical and physical properties that improve the properties of the base material. The synergy between composite components produces materials have properties unavailable in their constituent materials. So that, in order to provide good dispersion of nanoparticles in base polymeric material, added a third material that acts as a material compatible with the components of composite materials. There are many studies that emphasizes the role of compatibilizer substances in their function of dispersing inorganic nanoparticles within the base material and improving their properties **Pracella et al. (2006)**, **Asopa et al. (2015)**. From previous studies, the vinyl-modifier was used to prepared nanocomposites based on polymeric material, but the peel morphology not achieved above 3% ratio of nanofiller. And attributed this to the high steric impediment caused by the long chain hydrocarbon of the surfactant **Al-Sabagh et al. (2016)**. A others study, confirm that the organoclay is homogenously dispersed and peeled in the polymeric matrixes for both PS and PMMA, the study suggests that the thermal properties of the nanocomposites shows an increase in the decomposition temperature comparing to neat polymer **Ahmed et al (2017)**. Another way to improve the properties of polymeric composites through mutual interaction between more than one type of nanoparticle filler, by joining more than one reinforcing material to the same base material **Qiyan et al. (2017)**. Effect of compatibilization material of (alkylated-grafted-GO) on the morphologies and properties of polymer blend PP/PS with adding various ratios of modified GO were investigated. The results showed that an amendment for compatibilization between two of polymer blends PP/PS and an improvement of mechanical properties of composites **Yanping et al. (2017)**.

Recently, an improve in some mechanical properties of hybrid nanocomposites based on polymer blend, when adding two types of nanoparticles are silica, zirconia and woven carbon fibers in the ternary polymer blend (unsaturated polyester (UP) + 2% NR + 5% PMMA). The results have shown that the values of flexural modulus, impact strength and fracture toughness increase but flexural strength value decreases with the increase nanoparticles content in nanocomposite **Salih et al. (2018)**. Newly studying about the possibility using friction stir processing technique, to improving mechanical properties for polymeric surfaces by adding hybrid micro powders (graphite, Al_2O_3 , and Cu) to binary polymer blend. The results showed an enhancement in some mechanical properties, as compared with their values of control sample polymer blend **Sihama et al. (2018)**. In this study, three types of inorganic materials (silica, cement kiln dust and Fly ash) as nanofillers materials, and two types of organic are ABS and copolymer (PS-co-MA) as blending and compatibilizer materials respectively, where was employed according to their advantages functionality to improve the mechanical properties and morphology of nano composites that based on the polymer blend of (polystyrene : 1% copolymer (PS-co-MA): 3%ABS) as a matrix material, for used in structural applications.

MATERIALS AND EXPERRIMENTAL

Materials Used

Three types of the polymeric materials were used are polystyrene, Acrylonitrile-Butadiene-Styrene (ABS) and copolymer of (polystyrene (PS)-co-maleic anhydride (MA)). All polymeric materials were in the pellet's forms. and physical properties data and supplier names for each polymer is given in Table (1). Three different type of powders in nanometer size were used as reinforcement materials with selected weight ratio (0, 0.2, 0.4, 0.6 and 0.8 wt. %) for each of them which are: Silica (SiO_2) nanoparticles was supplied as partially stabilized particles from (China) with white color and particle size (24.29nm), cement kiln dust (CKD) nanoparticles obtained from the cement plants in Iraq/Kufa with Yellowish brown color and particle size of (84.23nm) and fly ash (nFA) class B obtained from the England with dark gray color and particle size of (64.94nm). Tables (2) and (3) show the chemical composition analyses of cement kiln dust and fly ash and respectively. Atomic Force Microscope (AFM) was used to measuring the average particle size of the nano powders, the results of particle size distribution for these nano powders are shown in Figure 1 (a, b and c) respectively.

Blend and Composites Preparation

Neat materials were weighed according to the selected ratios, to prepare an extrusion batches consisting of (polymeric pellets, nanoparticles (reinforcement materials) and 1% ratio of compatibilizer material (PS-co-MA)), they are mixed together in a dry condition, at room temperature for 20min, inside mill made from porcelain material. then the mixture was dried at 80°C for 8 hours in a vacuum drying oven. Then the mixture was melted in double screw extruder machine ((type: SJSZ20/40) made in China, L/D ratio of screw is 28:1 and the extrusion speed was 50 rpm with barrel temperature from the feeding zone to compression zone and metering zone are 195, 195 and 200 °C respectively, the melt was passed through a die to produce the plates with dimensions are (600×40×5mm). the plates were cutting according to international standard specifications for each test. fourteen models were

prepared, one for neat polystyrene, one for polymer blend (control sample) and twelve models for composites materials

Test Methods

Transformation infrared spectrum is used to obtain specific information about the chemical bonds and molecular structure of neat polystyrene, polymer blend and its composite. The FTIR test was done according to the international measurements (ASTM E-1252) **Annual book (2002)**, by using a spectrometer of the (Fourier infrared) manufactured by Bruker company type (SENSOR-27). Infrared spectrum was used in mid-IR source within range of (400- 4000) cm^{-1} . The tensile test was carried out by using a testing machine, model (WDW 200 E). according to ASTM D638 **Annual book (2003)**. The test was done at room temperature at the constant speed of crosshead of (5 mm/min). Fatigue test was performed according to (ADA Specification No.12, 1999), by using fatigue testing machine, type (HSM20), by an alternating-bending, carried out at room temperature **Roberts and Nigel (2001)**. The test was conducted on samples that had the best results for tensile testing. Morphology test was done for a fracture surface, by using SEM, type (TESCAN VEGA-SB), made in Belgium, the test was carried out for neat polystyrene sample, polymeric blend and optimal samples of nanocomposites. All samples were coated with gold to achieve good electric conductivity.

RESULTS AND DISCUSSIONS

FTIR Spectroscopy

FTIR spectral analysis made to determine the fully characteristic band of neat PS, polymer blend (PS: 1% (PS-co-MA); 3% ABS) and hybrid nanocomposites samples. Figure 2 (a) indicates the details of functional groups present in the neat polystyrene. The characteristic absorption bands of neat PS polymer that occur at 3059.27 and 3024.91 cm^{-1} due to the CH stretching vibration of aromatic side group, other peaks at 2922.50 cm^{-1} and 2849.69 cm^{-1} for asymmetric and symmetric of stretch bond of aliphatic CH respectively. The peaks at 1492.14 cm^{-1} and 1451.29 cm^{-1} are correspond to the aromatic C=C stretching. The peaks at 1027.51 cm^{-1} and 906.04 cm^{-1} due to out of plane bending vibration of =C-H of vinyl group **Samiksha et al. (2016)**. The styrene prominent peaks appear at 748.34 cm^{-1} of C-H deformation vibration band of benzene ring hydrogen and band refer to the ring deformation vibration are observed at 694.74 cm^{-1} due to out of plane bending vibrations of aromatic C=C. The assigned values are in agreement with that mentioned in the literature **Samiksha et al. (2016)**. The FTIR spectrum of polymer blend (PS: 1% (PS-co-MA): 3% ABS) is shown in Figure 2 (b). There is no shifting in peaks characteristic frequencies of polymer blend with respect to neat PS was observed. The characteristic absorption bands of polystyrene blend occur at 3029.26 cm^{-1} and 2921.20 cm^{-1} of aromatic and aliphatic C-H stretching, aromatic C=C stretching occurs at 1492.32 cm^{-1} and 1451.38 cm^{-1} . The peaks at 746.5 cm^{-1} and 693.6 cm^{-1} due to out of plane bending vibrations of aromatic =C-H and C=C respectively. The spectra of nanocomposites based on polymer blend (PS: 1% (PS-co-MA): 3% ABS) which was reinforced by three types of nanoparticles (silica (SiO_2), cement kiln dust (CKD)) and Fly ash (FA)) added individually and with different ratios (0.0, 0.2, 0.4, 0.6 and 0.8%), were shown in Figures 3, 4 and 5 respectively. It was observed there is no shifting in peaks of characteristic frequencies of nanocomposites with respect to neat PS. As well as, all the characteristics vibration bands of polymer blend (PS: 1% (PS-co-MA): 3% ABS) spectrum was present in the spectra for the three groups of nanocomposites specimens. In addition, from these spectra there are no other new peaks were appearing, or shifts in peaks are observed in the spectra of these nanocomposites' samples, this is may be due

to existence physical bond and no chemical reaction in these specimens. There is a clear rise in peaks intensity for all characteristic peaks of prepared samples with increasing the ratios of nanoparticles in composites samples, indicating that there is a good interaction between these nanoparticles and polymer blend matrix **Rosemal et al. (2010)**.

MECHANICAL TESTS

Tensile Test:

Figures (6), (7) and (8) shows the experimental stress-strain curves for base polymer blend (PS: 1% (PS-co-MA): 3% ABS) and three groups of hybrid nanocomposites, which was reinforced in different nanoparticles are silica, cement kiln dust and fly ash individually respectively. From these figures, it appears that at relatively low stress levels on the stress-strain curves, the samples behave elastically this is due to elastic deformation occurs in molecules chains in amorphous regions that elongating in the direction of the applied tensile stress, in this stage amorphous chains continue to align and become elongated without any bond rupture occur **W. F. Smith and J. Hashimi (2011)**, then the behavior changes to plastic deformation, in this stage, the chains become oriented in the direction of the tensile axis, thus, appreciable tensile deformation for polymer nanocomposites produces in highly oriented structure. So, when the load of stresses increased, the deformation of polymeric material will lead to rupture in their bonding and increased in growing cracks occur, the plastic deformation increased with increasing the stress load until the final failure occurs in hybrid nanocomposites samples, at this period, it could be predicted in a value of the tensile strength at break. As well as, it can be noticed, that from stress-strain curves, that the stress increase when increasing the weight percentages of nanoparticles, which refer to strengthening mechanism of nanoparticles, where the weight ratios content of these nanoparticles in the composite samples could influence in impede the movement of polymer chains. It can be observed from these figures that the increasing of nanoparticles fillers in polymer blend (PS: 1% (PS-co-MA): 3% ABS) leads to increase in the tensile strength values of polymer nanocomposites. As well as, there was increased in percentage of elongation at break occurs for composites specimens, therefore the behavior of base polymer blend transforms from (soft and weak) to (hard and toughness) when the nanoparticles fillers ratio in composite reaches to 6% wt for samples that reinforced by CKD and FA of nanofillers and at 4% wt when reinforced with silica nanofiller. The average data of the tensile properties test results, (tensile strength, elasticity modulus and elongation at break) as a function of weight percentage of nanoparticle content silica (SiO_2), cement kiln dust (CKD) and Fly ash (FA), was shown in Figures (9), (10) and (11) respectively. From these figures, it is appeared that the tensile strength, modulus of elasticity and percentage of elongation are increased with increasing the weight percentage of nanoparticle in all nanocomposites. The inclusion of nanoparticles of silica, CKD and Fly ash in individually form to polymer blend has raised the tensile strength (figure 9), where was the highest ratio increased in tensile strength values was reached to 114.5 % for the composite sample reinforced with a Fly ash at 6% ratio, which its value reached to 60.678MPa, compared to control sample of polymer blend (PS: 1% (PS-co-MA): 3% ABS) their value 28.267MPa, and for the composites samples reinforced with 6% of CKD nanoparticle the value of tensile strength has raised by 109.99%, and their value 59.358MPa, furthermore, the tensile strength has raised by 58.842%, for the composites sample reinforced with 0.4% silica nanoparticle and their value 44.9 MPa. This behavior may be attributed to good uniform distribution of nano powders, especially at specific percentage ratios of nanoparticles content in the nano-composites samples depending on the nature of the fillings, that may be led to reduces agglomeration of the nanoparticles and this reduced the concentration of internal stresses in nano-composites samples near the clustering of nanoparticles. So, such small internal stresses are not enough to break the

interactions at the region of interface **Sahai and Mahanwar (2015)**. Therefore, these small internal stresses can be easily transported from material of polymer blend to the nanoparticles, this permitting these nanoparticles to participate its high stiffness with polymer blend, so, the tensile strength of nanocomposites samples increased **Majid et al, (2014)**. As well as, this result is due to good bonding of the interface between the polymer blend constituents and the added nanoparticles, furthermore, the incorporation of hard nanoparticles powders into the polymeric matrix led to restricted the movement of polymer chains, and that improves the stiffness and reduces plastic deformation of the nanocomposites, accordingly, increases the tensile strength and elasticity modulus for nanocomposite material **Lanzhu et al. (2012)**. However, addition nanoparticles of the cement kiln dust and Fly ash individually to larger than 0.6% ratios, as well as, added of the silica nanoparticles to larger than 0.4% ratio led to decrease the tensile strength of nanocomposites, but the values remains higher than the control sample (polymer blend). This is could be related to the agglomeration and bad the wettability between polymer blend components and nanoparticles powders added (silica, cement kiln dust and Fly ash) especially at high concentrations. So that, in these high concentrations of nano fillings, the resultant composite materials have weak physical bonding between their components, this requires few values of tensile stresses for failure **Sahai and Mahanwar (2015)**. Moreover, from Figures 10 it is noticed that the samples of second group (polymer blend reinforced by cement kiln dust powder) have highest values of modulus of elasticity as compared with their counterparts of the other groups' samples (the first and third group) of the polymer blend that reinforced by nanoparticles of silica and fly ash respectively. This is related to the nature and constituents of the hybrid cement kiln dust powder (table 1) as compared with other nanoparticle powders of silica and fly ash (table 2). Moreover, there is a good compatibility between the constituents of nanocomposites based on the polymer blend, especially when incorporating with cement kiln dust nanoparticle, which plays an important role in the tensile behavior and load transfer. Generally, from Figure 10, it was noticed that, the value of modulus of elasticity of polymer blend (control sample) has been 11.194GPa, whereas, when incorporated a nanohybrid powder (cement kiln dust powder), with this blend, the highest values of modulus of elasticity reached to 18.98GPa when 0.8% ratio of the CKD. Obviously, there is a synergistic effect of hybrid cement kiln dust nano powder on the enhancement of the tensile properties of composites, this, may be concerning to the strong inter-atomic ionic bonding of nanoparticles LiO and CaO which form a components part of cement kiln dust (Table 2), and as is evident from Figure 10, the increasing trend is sharper as the CKD content grows from 0 to 0.8%. Accordingly, the reinforcement effect of CKD nanoparticles is more effective at a high content till to 0.8% of CKD **Gokule and Sidhu (2016)**.

Fatigue Test Results and Discussion

Fatigue test was achieved on the neat polystyrene, polymer blend (PS: 1% (PS-co-MA): 3% ABS) and the selected nanocomposites samples that gave the maximum properties in tensile test as optimal samples for comparison. The fatigue strength of polymer materials depends on the test frequency, loading mode and environmental conditions., Figure 12 describes the S-N curves, which was plotted from the 75% of maximum applied stress of each sample against the number of cycles for failure, with a stress ratio ($R = -1$) at room temperature and at the frequency test 3Hz, which was low enough to avoid self-heating of the specimen. The relationship of this curve was drawn by using the experimental data of fatigue test and apply power formula. The behavior of fatigue for all samples tests was represented by power equation and its relative correlation coefficient (R^2). It is noted that these equations have relatively high correlation coefficient which indicate that the experimental data are well explained by power

formula, assures the good representation of fatigue data. the results of the trend lines were summarized in Figure 12. According to this test, it was noticed that the fatigue limit (endurance limit) was apparent for all test samples, the values of fatigue limit which taken from fatigue stress at 10^6 of number of cycles loading, was shown in Figure 13. It was observed from Figure 12, that the polymer blend have the higher values of fatigue strength as compared with neat PS sample, this result may be related to the good compatibility between the components of polymer blend materials, moreover, the hybrid nano-composites samples have the higher values of fatigue strength as compared with polymer blend sample (control sample) this result related to a good interfacial adhesion between components of nanocomposites, which is indicating to the good wettability between the nanoparticles powders and the components of polymer blend materials **Bhagwan et al. (2012)**. This may be leading to inhibit crack initiation and impedes its propagation under the effect of cyclic load. such samples have a good physical bonding between their components, which requires higher stress for failure under the same number of cycles. Moreover, it was observed from Figures 12 and 13, that the maximum values of fatigue limit, about 26.3 MPa from fatigue stress was happened for the nanocomposite sample that reinforced with 6% ratio of fly ash under 10^6 loading cycle, as compare with other of nanocomposites sample reinforced with 6% ratio of CKD which were occurred at 20MPa of fatigue stress for the same loading cycle, and fatigue limit for sample which reinforced with 4% ratio of silica reached to 16.8MPa. On the other hand, all composites samples having the highest the fatigue limit, as compared with neat polystyrene and polymer blend which reached to 10.8MPa and 12.7MPa respectively. This behavior can be associated to the filler type of hybrid nanoparticle in the content of nanocomposites, this, may be concerning to the strong inter-atomic ionic bonding of nanoparticles (Al_2O_3 and SiO_2) are constituents of fly ash (Table 2), as well as, the nanoparticles (LiO and CaO) are constituents of cement kiln dust (Table 3), these particles depleting of energy required for the propagation of cracks. Furthermore, the strong bonding at the interfacial region between the polymer blend and constituents of nanoparticles powders of fly ash and dust of cement kiln, caused in formation of strong physical cross-links (supra molecular) bonding, which effect on the tensile strength and elastic modulus of composites materials. So that, the nanocomposite reinforced by fly ash nanoparticle has higher tensile strength compared with counterpart samples of the other groups of nanocomposites (figure 9), and as mentioned elsewhere, that the fatigue strength for polymeric materials is proportional to its tensile strength **Mallick (2008)**.

Morphological study

The photographs of scanning electron microscopy (SEM) were done on fracture surface for neat polystyrene, polymer blend (PS: 1% (PS-co-MA): 3% ABS) and the optimal samples of nanocomposites reinforced by nanoparticles (silica, CKD and fly ash) individually, at magnification (1000x), shown in Fig. 14 (a, b, c, d and e) respectively. The fracture surface morphology of the polystyrene material (Fig. 14 (a)) shows the appearance of large areas with smooth surfaces interspersed with some small cavities, indicating that the fracture nature of this material may tend to be fragile based on reference **Mohammed et al. (2016)**. While, both polymer blend (figure 14 (b)) and nanocomposite samples (figure 14 (c, d and e)) appear to have a co-continuous morphology and as a result it was difficult to identify the individual polymers in each of polymer blend and composites, moreover, two different of fracture surface morphologies appear depending on the nature of nanofiller in composites. In the case of a silica nanoparticles show weakly bonded filler, it can be seen some of separation between nanoparticles and matrix (figure 14 (c)), add 0.4% ratio of silica nanoparticle led to segregations and agglomeration some of these nanoparticle, due to weak interfacial adhesion between the components of polymer blend nanocomposite, and this caused the deterioration of

the mechanical properties of the composite samples reinforced by silica nanoparticle as compared with other of nanocomposites samples. However, in the case of nanoparticles of CKD and fly ash (figure 14 (d and e) respectively) show strongly bonded fillers, the nanoparticles are rigidly held within the matrix. So that, a less interfacial debonding occurred, most of nanoparticles are embedded inside the matrix material as an integral part of the base material structure, which indicates the improved interfacial adhesion between the components of nanocomposite. this denote a good compatibility between the matrix material and the reinforcement nanoparticles, this result was compatible with some previous studies **Bakar and Fauzi (2012) and Sihama et al. (2018)**. Thus, more energy is needed to break this interlink and start the fracture. Moreover, Fig.14 (d and e) show irregular fracture surface morphology with the dispersion of the reinforce material in a homogeneous manner, filling all the areas of composite material, especially with those reinforced with fly ash nanoparticle (figure 14 (e)). based on this morphology, the addition of the reactive compatibilizers (1% (PS-co-MA)) material with nanoparticle to polystyrene material, influenced enhancement of fillers dispersion, acceptable interfacial interactions and reduced pull-out phenomena for filler material and this consistent with that mentioned in the references **Mariano et al. (2010)**. Especially of nanocomposite samples reinforced individually by 0.6% CKD or 0.6% fly ash, indicated to high adhesion between the components of nanocomposites, which enhanced the mechanical properties of these nanocomposites.

Conclusions

From the tests results it can be conclusion the following:

- Tensile properties improved with adding nanoparticles (silica, cement kiln dust and fly ash) individually to a control sample of polymer blend (PS: 1% (PS-co-MA): 3% ABS).
- Hybrid nanocomposites sample reinforced by fly ash has the highest values of tensile strength. whereas, the hybrid nanocomposites sample reinforced by cement kiln dust has the highest values of elasticity modulus.
- Tensile strength and elongation ratio for nanocomposites samples increased with adding nano powders to certain loading levels depend on the chemical nature of the loading material
- The fatigue test revealed the super-improvement in the fatigue properties of the selected hybrid nanocomposites, where the S-N curve showed that fatigue strength increased with addition nanoparticles as compared with neat polystyrene and polymer blend (PS: 1% (PS-co-MA): 3% ABS). Moreover, the hybrid nanocomposite that reinforced with nanoparticles of fly ash have higher fatigue strength as compared with their counterparts of other groups composites that reinforced by nanoparticle of CKD or silica.
- The fatigue limit (endurance limit) was apparent for all test samples based on polystyrene.
- According to the results of fracture surface morphology analysis, added 1% of copolymer (PS-co-MA) enhanced the compatibility between the components of nanocomposites material, which show a homogeneous structure formation
- On the basis of what mentioned above it can be conclusion that the hybrid nanocomposites sample reinforced by 6%fly ash nanoparticles, is one of the promising materials to use in structural applications as high-performance material.

Table (1): physical properties and supplier names of the polymeric materials used.

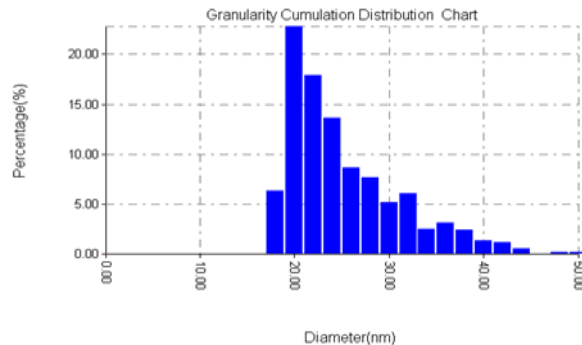
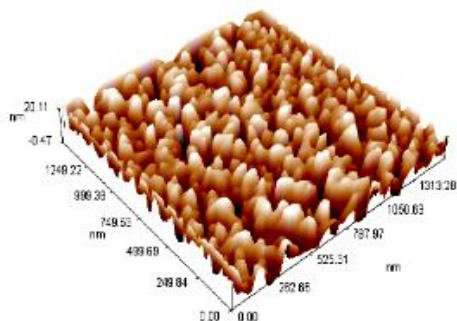
Polymer name	Melt flow index (2.5gm/10 min) at 200°C	Density (g/cm ³) at 23°C	Elongation at break	Supplier
PS	2.5	1.05	3%	Sabic Company
(PS-co-MA)	1.7	1.18	-	Sigma-Aldrich Company
ABS	26	1.05	5-25%	Basf Company

Table 2: Chemical Composition Analyses of cement kiln dust (CKD) used in this Research

Element Oxide	SiO ₂	Al ₂ O ₃	TiO ₂	MgO	K ₂ O	CaO	Fe ₂ O ₃	Mn ₂ O ₃	Na ₂ O	P ₂ O ₃	L.O.I
weight (%)	57.3	28.4	1.4	0.12	3.46	0.87	4.92	0.34	0.81	0.38	1.97

Table 3: Chemical Composition Analyses of fly ash used in this Research

Element Oxide	SiO ₂	Al ₂ O ₃	LiO	MgO	K ₂ O	CaO	Fe ₂ O ₃	L.O.I
weight (%)	13.1	3.52	30.34	3.92	1.27	37.6	2.81	7.4



(a) Sample: silica powder Avg. Diameter: 24.29 nm

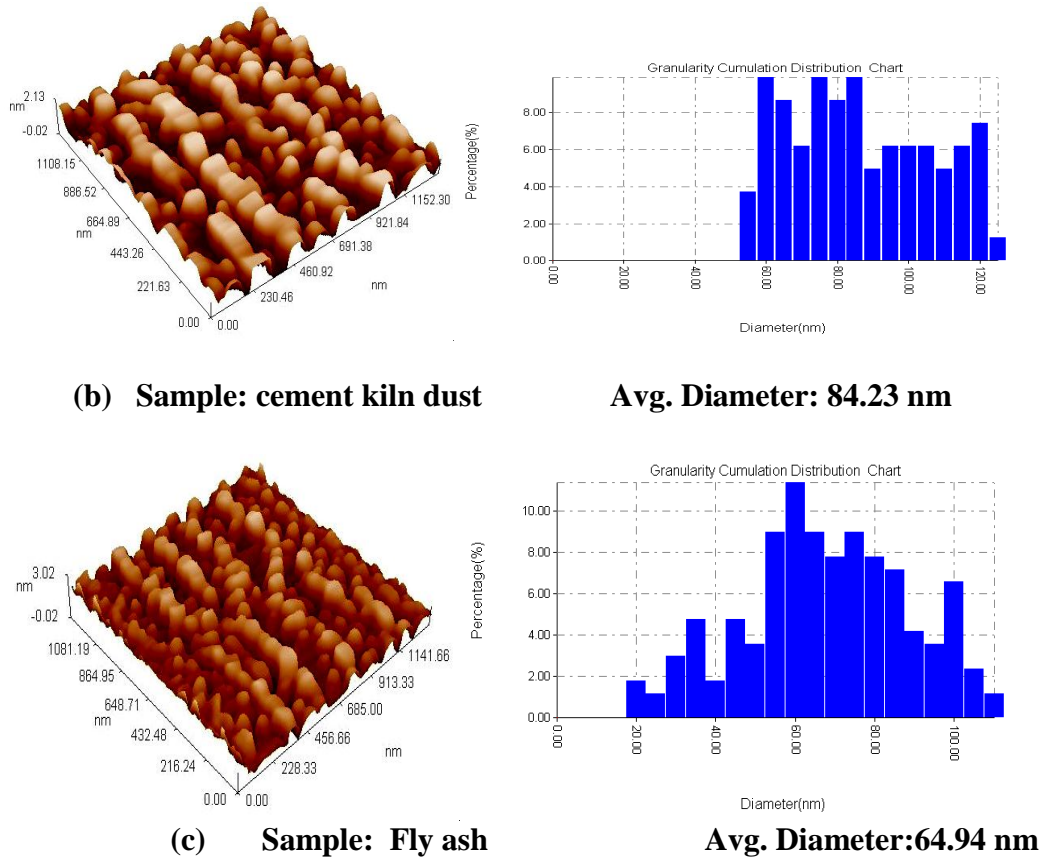


Fig. 1: Atomic Force Microscopy test for nano powders (a) Silica, (b) Cement kiln dust and (c) Fly ash

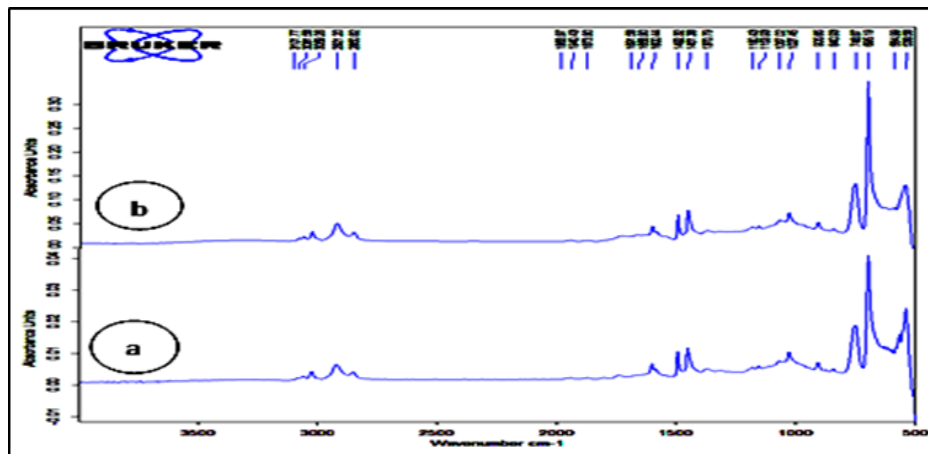


Fig. 2: FTIR analysis of (a): neat polystyrene and (b): polymer blend (PS: 1% (PS-co-MA): 3% ABS).

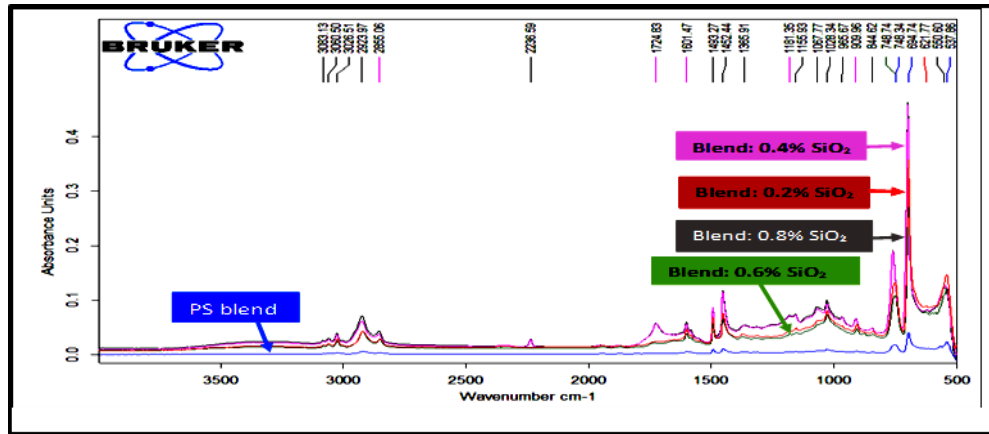


Fig. 3: FTIR analysis of polymer blend (PS: 1% (PS-co-MA): 3% ABS) and hybrid nanocomposite ((PS: 1% (PS-co-MA): 3% ABS): X% silica) as a function of silica content.

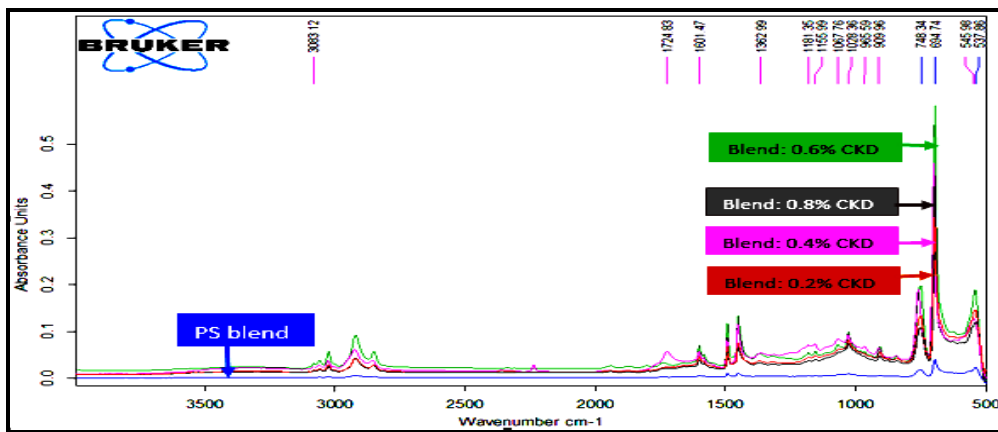


Fig. 4: FTIR analysis of polymer blend (PS: 1% (PS-co-MA): 3% ABS) and hybrid nanocomposite ((PS: 1% (PS-co-MA): 3% ABS): X% CKD) as a function of cement kiln dust (CKD) content.

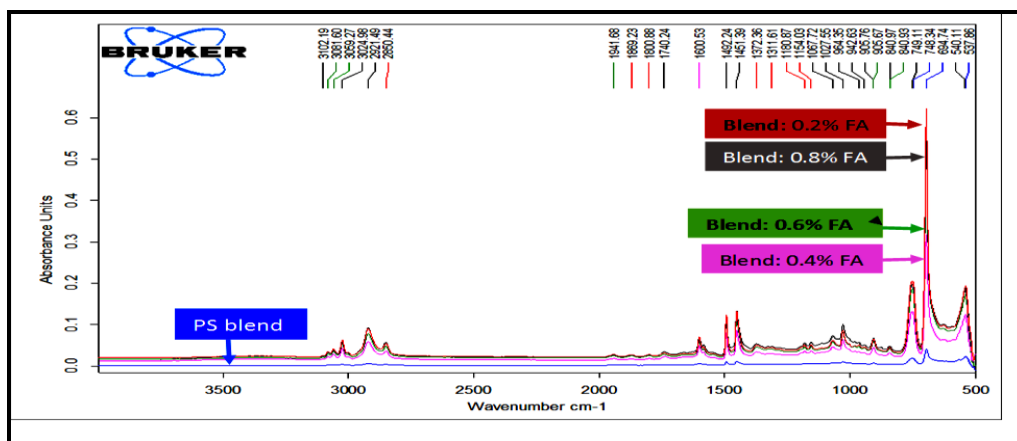


Fig. 5: FTIR analysis of polymer blend (PS: 1% (PS-co-MA): 3% ABS) and hybrid nanocomposite ((PS: 1% (PS-co-MA): 3% ABS): X% FA) as a function of fly ash content.

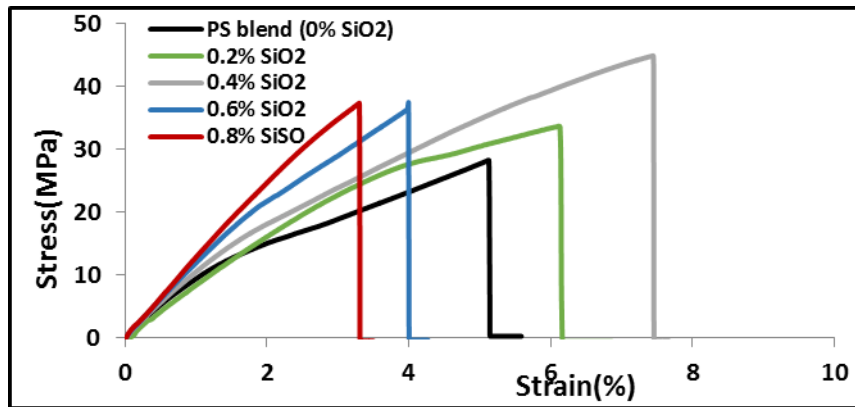


Fig. 6: Stress-strain curves of polymer blend (PS: 1% (PS-co-MA): 3% ABS) and hybrid nanocomposite ((PS: 1% (PS-co-MA): 3% ABS): X% SiO₂) as a function of silica content.

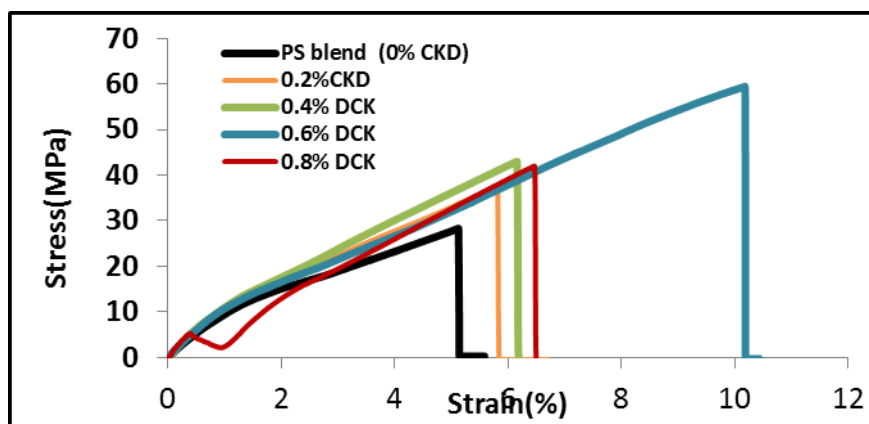


Fig. 7: Stress-strain curves of polymer blend (PS: 1% (PS-co-MA): 3% ABS) and hybrid nanocomposite ((PS: 1% (PS-co-MA): 3% ABS): X% CKD) as a function of cement kiln dust content.

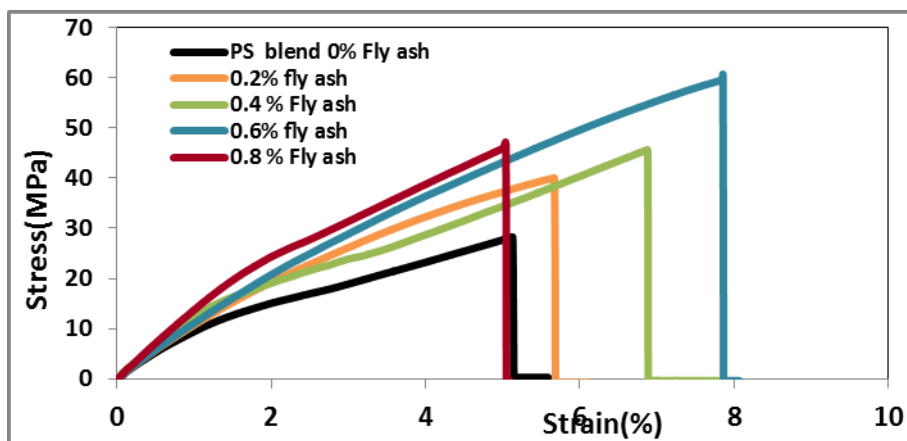


Fig. 8: Stress-strain curves of polymer blend (PS: 1% (PS-co-MA): 3% ABS) and hybrid nanocomposite ((PS: 1% (PS-co-MA): 3% ABS): X% FA) as a function of fly ash content.

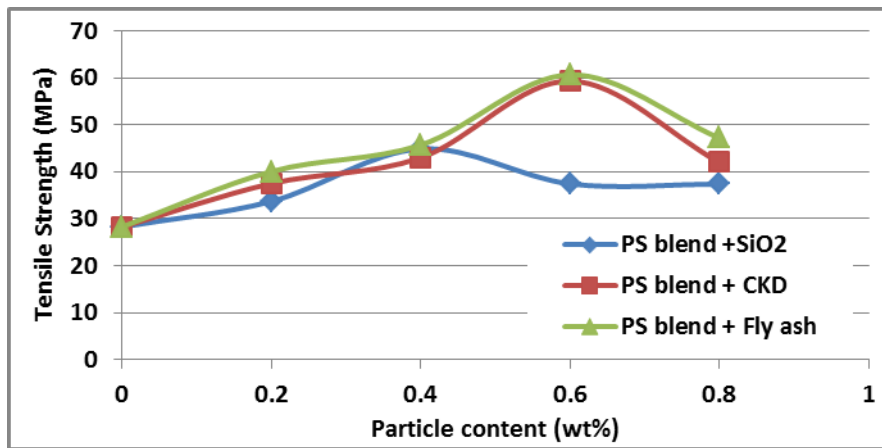


Fig. 9: The tensile strength for nanocomposites as a function of nanoparticles content (Silica, CKD and fly ash) in polymer blend matrix.

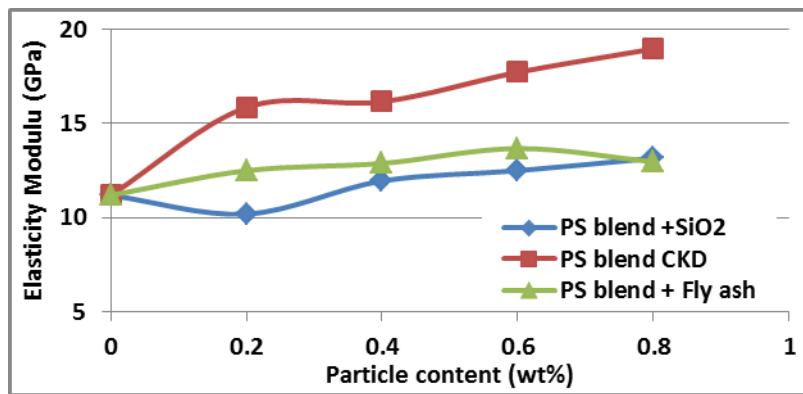


Fig. 10: The elasticity modulus for nanocomposites as a function of nanoparticles content (Silica, CKD and fly ash) in polymer blend matrix.

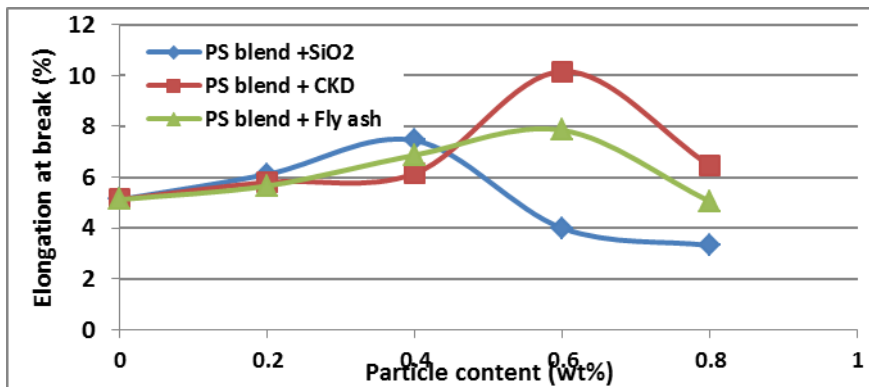


Fig. 11: The elongation percentage at break for nanocomposites as a function of nanoparticles content (Silica, DCK and fly ash) in polymer blend matrix.

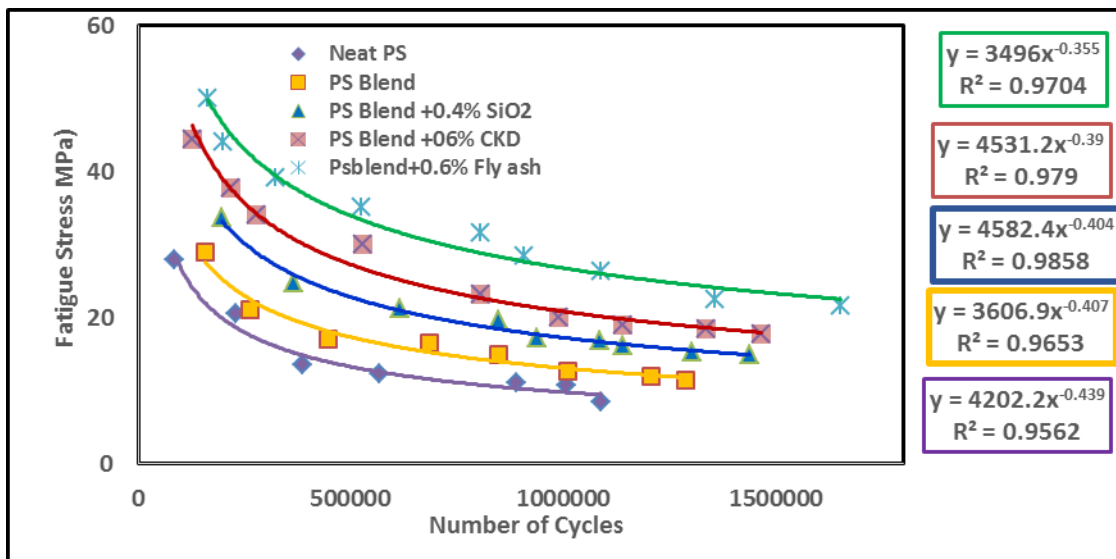


Fig. 12: (S-N) Curves of (a): Neat polystyrene, (b): Polymer blend (PS: 1% (PS-co-MA): 3% ABS), (c): (polymer blend: 4% SiO₂), (d): (polymer blend: 6% CKD) and (e): (polymer blend: 6% Fly ash).

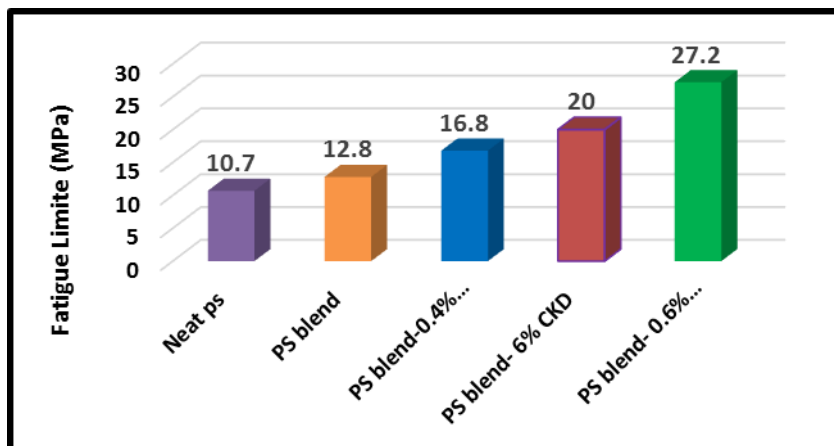


Fig. 13: Fatigue limit for: Neat polystyrene, Polymer blend (PS: 1% (PS-co-MA): 3% ABS), (polymer blend: 4% SiO₂), (polymer blend: 6% CKD) and (polymer blend: 6% Fly ash).

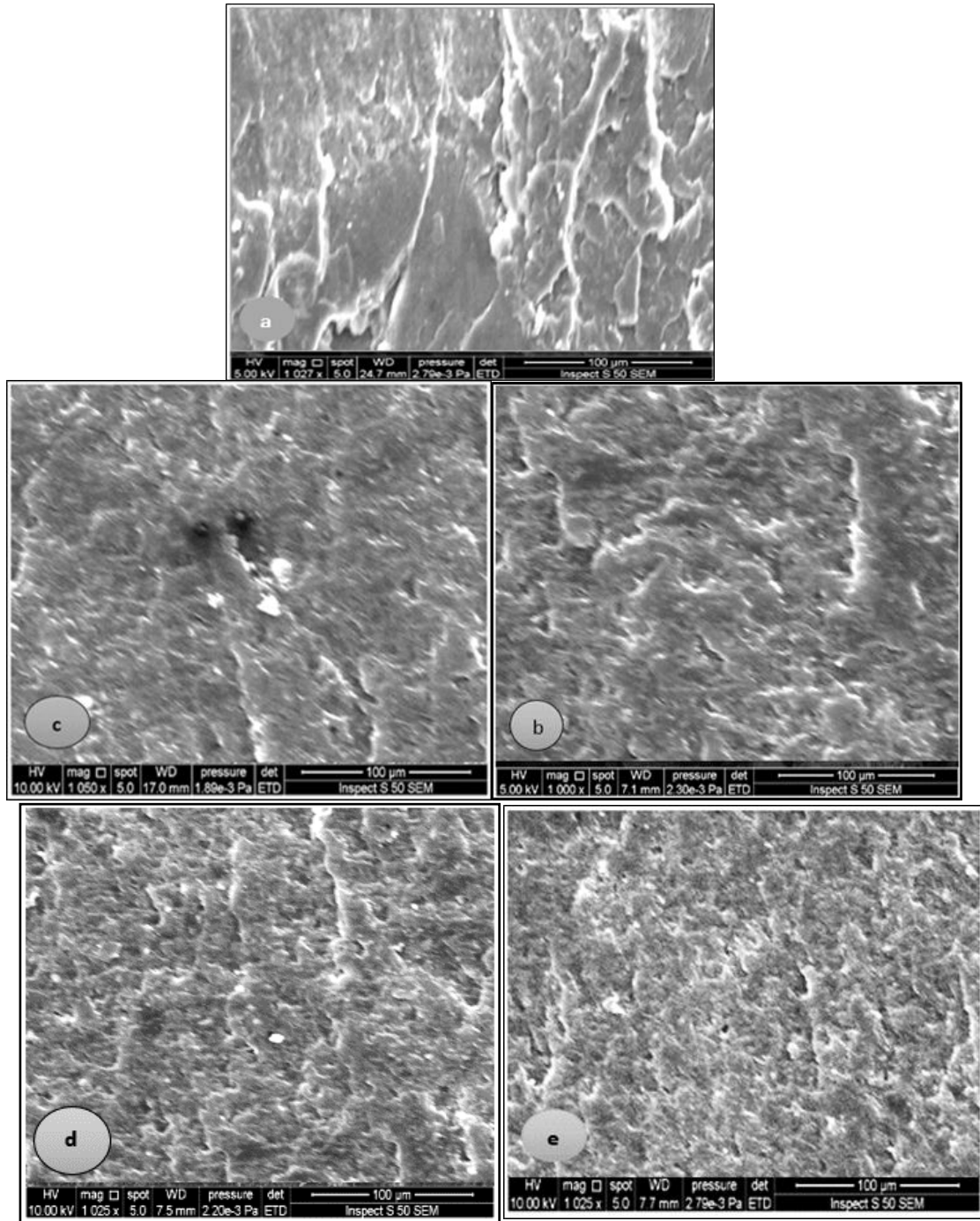


Fig. 14: SEM micrographs of fracture surface morphology, where (a) neat polystyrene, (b) polymer blend (PS: 1% (PS-co-MA): 3% ABS) (c) nanocomposites sample reinforced with 4% silica nanoparticles, (d) nanocomposites sample reinforced with 6% CKD nanoparticles and (e) nanocomposites sample reinforced with 6% fly ash nanoparticles. At (1000x) magnification.

REFERENCES

Al-Sabagh A. M, M. A. Betiha, D. I. Osman, A. I. Hashim, M. M. El- Sukkary and T. Mahmoud: ‘A new covalent strategy for functionalized montmorillonite poly (methyl methacrylate) for improving the flowability of crude oil’, RSC Adv., 6, (111), 2016, 109460–109472.

Ahmed Akelah, Ahmed Rehab, Mohamed Abdelwahab and Mohamed A. Betiha, “Synthesis and thermal properties of nanocomposites based on exfoliated organoclay polystyrene and poly(methylmethacrylate)”, Nanocomposites, VOL. 3, NO. 1, 2017, 20-29.

Annual Book of ASTM Standard, Standard Test Method for Tensile Properties of Plastics. 2003, D 638-03.

Annual Book of ASTM Standard. Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis. E 1252-98, 2002, 1-13.

Asopa V, Suresh S, Khandelwal M, Sharma V, Asopa SS, Kaira LS. A comparative evaluation of properties of zirconia reinforced high impact acrylic resin with that of high impact acrylic resin. Saudi J Dental Res. 6(2), 2015, 146–151.

Bhagwan F. Jogi, Mayur Sawant, Madan Kulkarni, Prakash K. Brahmkar," Dispersion and Performance Properties of Carbon Nanotubes (CNTs) Based Polymer Composites: A Review”, Journal of Encapsulation and Adsorption Sciences, Vol.2, 2012, 69-78.

Gokule V. G., J. S. Sidhu, “Mechanical Study of ZrO₂ & MoS₂ filled Epoxy Composites”, International Journal of Scientific Engineering and Research (IJSER), Volume 4, 2016, 18-

Lanzhu Zhang, Min Li and Hui Hu, “Study on Mechanical Properties of PEEK Composites”, Advanced Materials Research, Vol. 476-478, 2012, 519-525.

M. Rosemal, H. M. Harisa , S. Kathiresanb and S. Mohan, "FT-IR and FT-Raman Spectra and Normal Coordinate Analysis of Poly methyl methacrylate", Scholars Research Library, Der Pharma Chemical, Vol. 2(4), 2010, 316-323 .

Majid, S., Nabi, M. K. and Abbas, R., " An Experimental Investigation of HA/AL₂O₃ Nano Particles on Mechanical Properties of Restoration Materials ", Engineering Solid Mechanics , Vol. (2), No. (3), 2014, 173-182.

Mariano Pracella, Md. Minhaz-Ul Haque and Vera Alvarez, “Functionalization, Compatibilization and Properties of Polyolefin Composites with Natural Fibers”, Polymers, Vol. 2, 2010, 554-574.

Mohammed M Gad, Ahmed Rahoma, Ahmad M Al-Thobity and Aws Sar Rejaie, “Influence of incorporation of ZrO₂ nanoparticles on the repair strength of polymethyl methacrylate denture bases”, International Journal of Nanomedicine Vol.11, 2016, 5633–5643.

P.K. Mallick, "Fiber Reinforced Composites Materials, Manufacturing, and Design", by Taylor & Francis Group, LLC, 3rd edition, 2008.

Pracella, M.; Chionna, D.; Anguillesi, I.; Kulinski, Z.; Piorkowska, E. **Functionalization**, compatibilization and properties of polypropylene composites with hemp fibres. *Comp. Sci. Technol.* 66, 2006, 2218-2230.

Qiyang Z, Bo-Yuan Z, Zhao X G and Jian "Electrical Conductivity of Carbon-Black-Filled Ternary Polymer Blends by Constructing a Hierarchical Structure", *Polymers* 9, 404, 2017

R. Abu-Bakar and M. S. Fauzi, Natural Rubber-Grafted-Poly (Methyl Methacrylate): Influence of Coagulating Agents on Properties and Appearances" *Chem. Eng. Vol.6*, 2012, 962-966.

Roberts N. P. and Nigel R. Hart "Alternating Bending Fatigue Machine (HSM20), Instruction Manual", Hi-Tech Ltd. UK., 2001.

Sahai, R. S. N. and Mahanwar, P. A. "Effect of Particle Size and Concentration of Fly Ash on Mechanical Properties of Polyphenylene Oxide Composites ", *International Journal of Chemical, Environmental & Biological Sciences (IJCEBS)*, Vol. (3), No. (2), 2015, 64-168.

Samiksha Tiwari, Arunendra Kumar Patel, R. Bajpai, "Structural and Morphological studies on Fly ash Reinforced Polystyrene Composites," *International Journal of Current Trends in Engineering & Technology*, Vol. 2, No. 2 (2016) 277-281

Sihama Issa Salih, Jawad Kadhun Oleiwi, Rawaa Adnan Abdle Ameer, "Evaluation of addition ABS and EPDM effect on the mechanical properties of ternary polymer blends", *International Journal of Materials Science and Applications*. Vol. 4, No. 1, 2015, 39-46.

Sihama I. Salih, Jawad Kadhim Oleiwi, Sajid Abd Alkhidhir, "Comparative Study of Some Mechanical Properties of Hybrid Polymeric Composites Prepared by using Friction Stir Processing", *Jour of Adv Research in Dynamical & Control Systems*, Vol. 10, 2018, 1316-1326.

S.I. Salih, W.B. Salih and M.S. Mohammed, "Preparation and Investigation of Flexural Strength and Impact Strength for Nano Hybrid Composite Materials of the Tri-Polymeric Blend used in Structural Applications," *Engineering and Technology Journal*, Vol.36, Part B, No.1, 2018, 12-24. 2018.

W.F. Smith and J.Hashimi , "Foundation of Materials Science and Engineering ", Fifth Edition ,Mc Graw Hill , 2011

Yanping Hao, Xin Zhao, Jie Dong, and Qinghua Zhang, "The Compatibilization Effects of Alkylated-grafted-Graphene Oxide on Polypropylene/Polystyrene Blends" *International Journal of Polymer Science*, Volume , Article ID 2151205, 1-11.

Yu, L.; Dean, K.; Li, L. Polymer blends and composites from renewable resources. *Prog. Polym. Sci.* 2006, 31, 576-602.