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RESEARCH ARTICLE

STUDYING OF FACTORS INFLUENCING THE USE OF CELLULOSE-BASED NANOPARTICLES FOR REINFORCEMENT OF POLYMER COMPOSITES

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ABSTRACT

This study focuses on the use of cellulose-based natural fibers, extracted from date palm midribs in the form of nano particles, as reinforcement to Epoxy resin. Date palm midribs were first roughly broken to lengths of ~ 10mm in macro scale and then were chemically treated by two methods (Alkali treatment which is called Treatment1 and the other alkali and acetylation treatment which is called Treatment2). Further the material was milled down to nano scale, using a self-designed and constructed planetary ball mill, resulting in particles sizes ranging between 10.86 to 21.36 nm for Alkali treated fibers, and between 30.63 to 63.93 nm for alkali and acetylation treated fibers. Nanocomposites were prepared using a casting technique by ultrasonic dispersion method, where compounds of varying compositions (0.5 up to 5 wt% nanofiber reinforcement), were treated using Amino silane coupling agent, and finally specimen were poured into rubber molds of requested shape. Nanocomposites were oven-dried at 80°C for 2 hours. The mechanical performance of the composites was evaluated in terms of tensile, flexural and impact properties in addition to hardness. The results show that increasing palm midrib nano fibers content has significant effect on all mechanical properties as compared to the control sample. The results show that the alkali treatment is more suitable and provide better enhancing in all mechanical properties than the alkali and acetylation treatment.

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INTRODUCTION

Natural fibers have a weak fiber/matrix interface adhesion, high water absorption, and relatively lower durability. The weaker interfacial or adhesion bonds between highly hydrophilic natural fibers and hydrophobic inorganic polymer matrix, leads to considerable deterioration in the mechanical properties of the composites, which significantly inhibits their industrial utilization. However, several researches and schemes have been established to improve this deficiency in compatibility, including the introduction of coupling agents and/or various chemical surface modification methods (Kalia, 2009). The surface modification of the natural fibers can be performed by several techniques like physical, mechanical, and/or chemical treatments. The factors leading to better mechanical properties for composites are the homogeneous dispersion of the reinforcement material, orientation, good adhesion, and high aspect ratio. Nano-particles are now used as high-potential filler materials to improve the mechanical and physical properties of polymer composites (Njuguna, 2008).

As the nano scale fillers are free of defects, there is a growing trend for using them in polymer-based composites. Strong matrix-filler interfacial bonding and uniform dispersion of nanoparticles are responsible for changing relaxation behavior, as well as guaranteeing the mechanical, molecular mobility, and thermal properties (De Azeredo, 2009; Schadler, 2007). Generally, fillers, with nano size scale, are present in the minor zone, whereas only few of the micro scale particles participate in the plastic zone deformation. This gives the ability of the nanofillers to enhance fracture and mechanical properties of the matrix having brittle property. Nanofillers, which have greater aspect ratio are of wide interest, and, thus, provide better reinforcement for the nanocomposites production (De Azeredo, 2009). Nanofillers are generally incorporated on a weight basis for the nanocomposite development (Hari, 2011). The composite properties are greatly affected by the specific surface area of nano fillers, which appears uninterrupted influence. Nano fillers could belong to organic or inorganic nature. There are two types of fillers, the particles like silica ($SiO2$), titanium dioxide ($TiO2$), calcium carbonate ($CaCO3$), or polyhedral oligomeric silsesquioxane (POSS), etc., are known as inorganic fillers. However, the fillers, like coir nanofiller, carbon black and cellulosic nanofillers, and many others natural fibers known as organic nanofillers. Based on other researches (Benyahia, 2013; Meheddene Machaka, 2014; Anu Gupta, 2012; Wang, 2003; Rahul Shrivastava, 2015; Rakesh Kumar, 2011), the main aim of this study is to use suitable chemical modifications techniques for the natural fiber to maintain a good dispersion and interfacial adhesion between cellulose-based nanoparticles and the epoxy resin matrix which will provide improvements of mechanical properties.

MATERIALS AND METHODS

Materials: Palm Midribs were collected from Elkayat village, Eledwa province, Menya Governorate in October 2017. Date palm midribs were firstly roughly broken to lengths of ~ 10mm using a laboratory hammer mill and then chemically treated by two methods (Alkali treatment: 5% NAOH for 24h and the other alkali and acetylation treatment: 5% NAOH for 24h and then 10% Acetic acid for 48h). The material was further milled down to nano scale, using a self-designed and constructed planetary ball mill, resulting in particles sizes ranging between 10.86 to 21.36 nm for Alkali treated fibers, and between 30.63 to 63.93 nm for alkali and acetylation treated fibers. The size of nanoparticles has been measured using a JEOL JEM.1010 TEM electron microscope. These were oven-dried at 80°C for 24 hours and kept in a dry closed container up to further use to avoid moisture effect. The chemical composition of the used palm midrib is presented in Table 1.

Table 1. Chemical composition of date palm midribs

Constituent	Content (%)
NDF	68
ADF	55.31
ADL	7.54
Cellulose.	40.1
Hemicellulose	12.1
Lignin	8
Silica	Source: The chemical analysis has been conducted at the premises of Central laboratory, Centre of Agriculture Research, Cairo, November 2017). 0.8
NDF: Hemicellulose, cellulose, lignin, silica ADF: cellulose, lignin, silica ADL: lignin, silica	

Source: The chemical analysis has been conducted at the premises of Central laboratory, Centre of Agriculture Research, Cairo, November 2017).

For composite preparation a polymer-based matrix system has been considered. The epoxy-based resin, Biresin CR82 and its respective fast curing hardener Biresin CH80-2 (hardener mixing ratio 100:27 by weight) were supplied by Sika Deutschland GmbH. The utilized silane coupling agent is Dynasylan 1122 (3-triethoxysilylpropyl) amine which is the secondary aminofunctional ethoxysilane possessing two symmetric silicone atoms, and acts as an adhesion promoter between inorganic filler(glass, metals, natural fibers) and organic polymers (thermosets, thermoplastic) as a surface modifier and can be used for the chemical modification of substances. This Silane was supplied by Evonik Resource efficiency GmbH, Germany.

Sample preparation Method: Dried palm midrib nano fibers were added to the degased resin and stirred to a homogenous mix using a SONICS – Vibra cell sonicator for 20 minutes. Nano fibers were added in the ratio 0.5, 1, 3 and 5% of total resin weight. The silane coupling agent was added to the mixture and stirred using magnetic stirrer. Finally the hardener was then added to the resin-fiber mix and manually stirred slowly to avoid the formation of bubbles. The mixture was then degassed one more time for 30 minutes, after that it was poured into sample shape using rubber moulds.

Characterization

Tensile testing: Tensile testing was performed according to DIN EN ISO 527-2 with sample size 1BA, using an LRXPlus universal testing machine. Tests were conducted at a crosshead speed of 1 mm/min using a 2.5 KN load cell.

Bending Test: Bending specimens of 80x10x4 mm were supported at a span length of 64 mm and tested using an LRXPlus universal testing machine at a crosshead speed of 1 mm/min, in compliance with DIN EN ISO 178:2003.

Charpy Impact Test: Unnotched nanocomposite samples of 80x10x4mm were tested for their impact behaviour using a pendulum charpy impact tester in compliance with ISO 179-1: 2010, using a (1 J) hammer

Hardness Test: Shore D hardness of the nanocomposites under investigation was measured using a Zwick Roel hardness tester according to ISO 868: 2003.

SEM Microscopic Analysis : Scanning electron microscopy was conducted using a JSM-5500 scanning electron microscope, located at the Regional center for Mycology & Biotechnology (RCMBAZHAR), central laboratories sector to investigate the dispersion of the DPM nanofibres at different concentrations within the polymer matrix. The fracture surface of various tensile and bending test samples was sputtered with Gold for 15 minutes with a K550X sputter coater. Optical analysis further allows the observation of composite defects and interfacial morphology in addition to giving insight to a correlation between mechanical behaviour and composite structure.

RESULTS AND DISCUSSION

Figure 1 and figure 2 show the effect of NDPM content on the tensile strength and tensile Young's modulus of the nanocomposites under investigation. Results show that the tensile strength significantly increases with the addition of NDPM, according to one way ANNOVA test. The addition of palm midrib nano fibers causes an increase in tensile strength and modulus with respect to the pure epoxy resin. This lies in complete agreement with observations made by (Benyahia, 2013; Meheddene Machaka, 2014) emphasizing that the alkali treatment has led to high enhancement in the interfacial adhesion between NDPM and the Epoxy resin with respect to removing of waxes , oils, and impurities on the fiber surface. In addition other sources (Anu Gupta, 2012) proved that the alkali treatment in accordance with the use of silane treatment has led to the increase of the adhesion between the hydrophilic fibers and hydrophobic.

Figure 3 and figure 4 show the effect of NDPM content on the bending strength and flexural modulus of the NDPM composites. These results show that the bending strength and flexural modulus significantly increase with the addition of NDPM, according to one way ANNOVA test. These results were observed by (Kabir, 2011), where the surface treatment is essential to reduce the hydrophilicity of natural fibers, therefore increasing their adhesion with hydrophobic matrix. Chemical treatments include alkalization, silane, and acetylation. These treatments modify the structural constituents and surface morphology of the natural fiber and lead to significant improvements in bending strength and flexural modulus (Kabir, 2011).

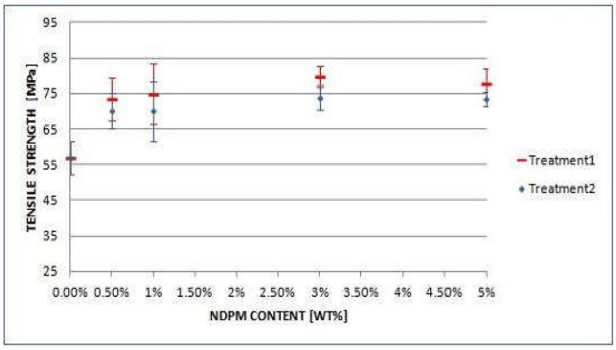


Figure 1. Effect of NDPM content on tensile strength

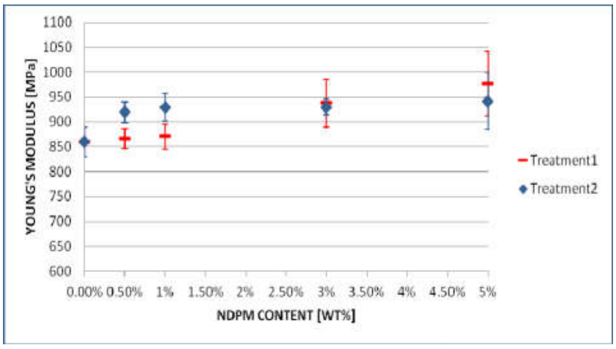


Figure 2. Effect of NDPM content on tensile modulus

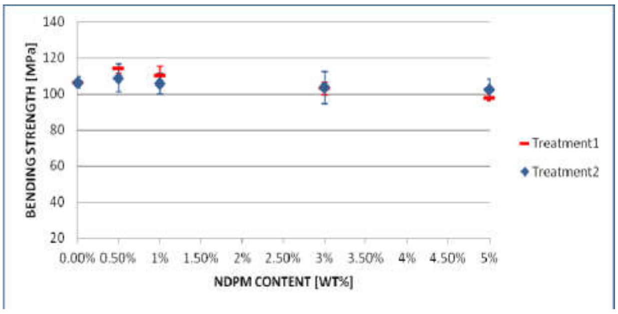


Figure 3. Effect of NDPM content on bending strength

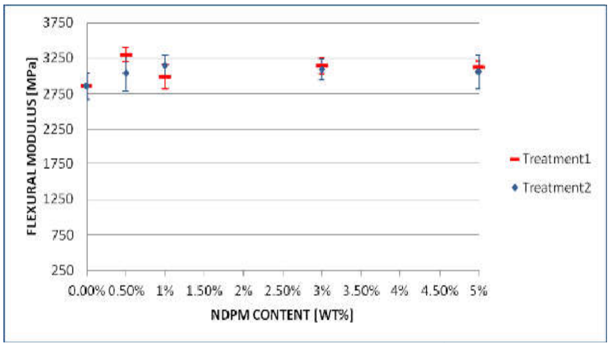


Figure 4. Effect of NDPM content on flexural modulus

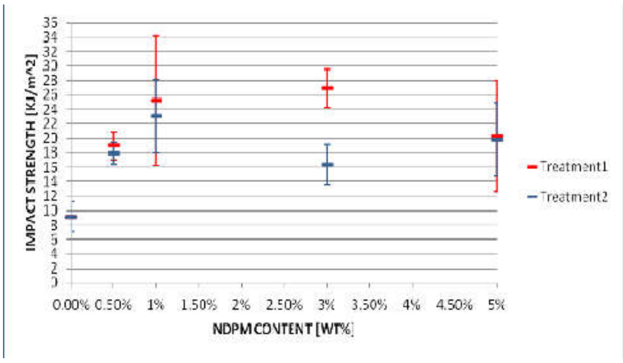


Figure 5. Effect of NDPM content on impact strength

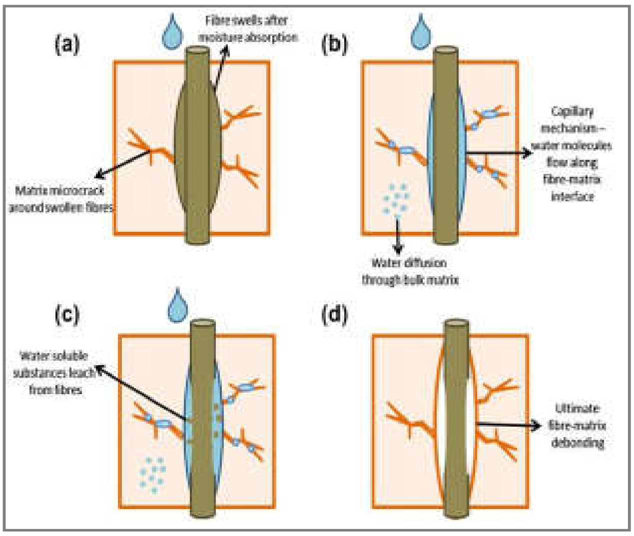


Figure 6. An illustration of the effect of moisture on fiber – matrix interface [14]

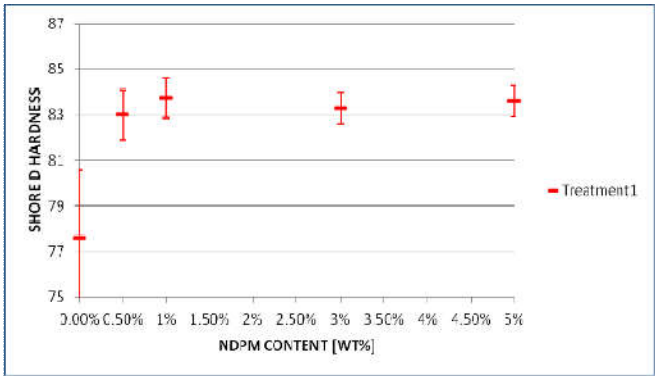


Figure 7. Effect of Alkali treated nanofiber content on shore D hardness

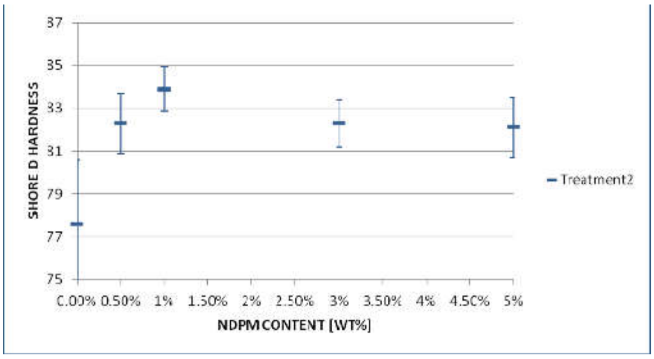
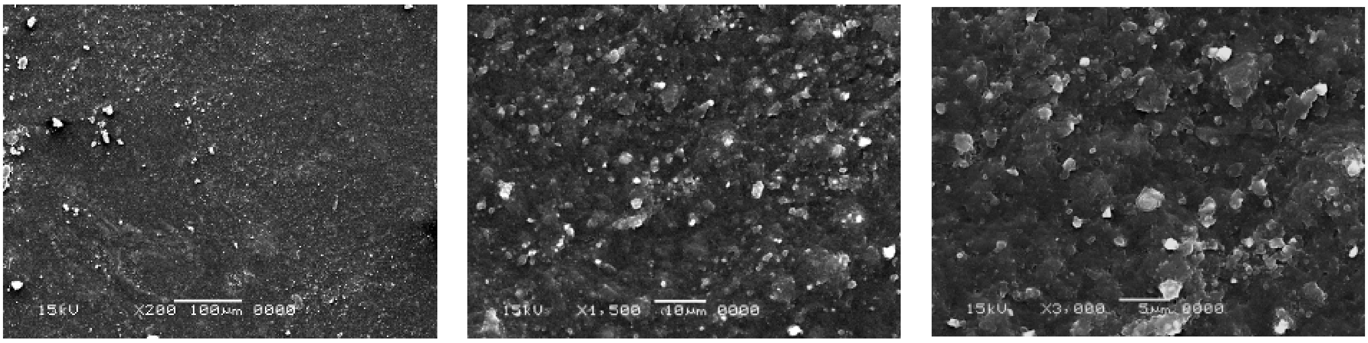
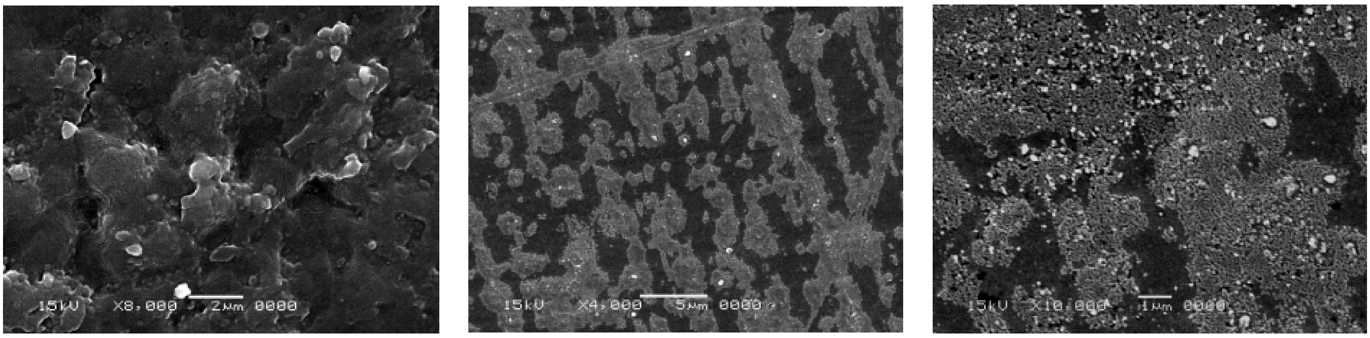


Figure 8. Effect of Alkali and acetylation treated nanofiber content on shore D hardness

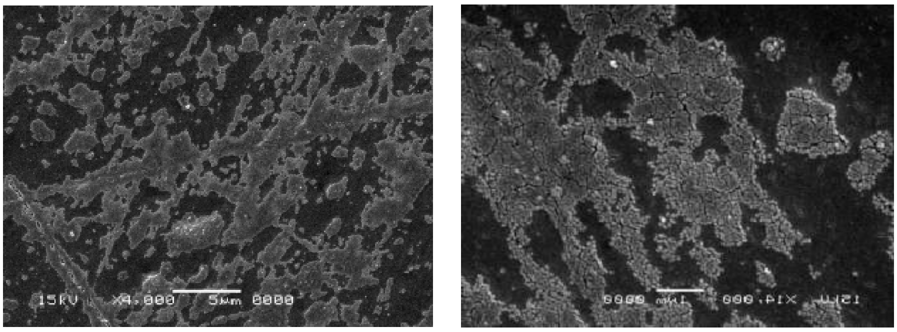
Other sources (Wang, 2003) observed that chemically treated natural fiber composites have better fiber-matrix interaction due to the good dispersion of fibers in the matrix, leading to the improvement of the mechanical properties. Figure 5 illustrates that the addition of nano fibers significantly increases impact strength of epoxy resin according to ANNOVA test. This lies in complete agreement with observations made by (Pearson, 1991; Ji-Fang, 2011), where the addition of nano fibers proved to be more efficient than large particles in producing a toughening effect. This can be related to the particle bridging mechanism, where nano fibers act as obstacles, thus hindering crack propagation (Micha Basista, 2006). Another research work (Rakesh Kumar, 2011) showed that silane coupling agents may reduce the number of hydroxyl groups in the fiber matrix interface. In the presence of moisture, hydrolysable alkoxy groups lead to the formation of silanols, which reacts with hydroxyl group of the fiber, forming stable covalent bonds with the fiber surface that lead to restraining the swelling of fiber and crack propagation. As illustrated in figure 6 (Rahul Shrivastava, 2015). However, other sources (Meheddene Machaka, 2014) proved that using high concentration of silane coupling agent caused deterioration of the interfacial adhesion between fiber and matrix leading to the decrease of the mechanical properties. The deterioration in impact strength at higher NDPM content is due to using the maximum recommended limit of silane coupling agent content in the nanocomposites, which may form the agglomeration of the nanoparticles. The effect of nanofiber content on the hardness of nanocomposites is presented in figure 7, and figure 8. The results show that the hardness increases with increasing of nanofiber content. The generation of dislocations leads to the Hall–Petch effect through the dislocation pile up mechanism or the dislocation density mechanism. In both mechanisms as the grain size is reduced, the yield stress increases resulting in higher hardness (Dave Maharaj, 2014). These results lie in agreement with the fact that hardness is a measure of resistance to penetration. Nanoparticles act as obstacles to penetration, where a reduction in inter-particle distance with increasing particle loading in the matrix results in increase of resistance to penetration. These results lie in a complete agreement with the observations made by (Elmadania, 2018; Nabil, 2004; Sreejith, 2015) showing that the hardness of nanocomposites increase by addition of nanofiller and using aminosilane with adequate concentration which helps in good dispersion of nanofillers into matrix and increases the interfacial adhesion between nanofiller and the matrix.



a) Magnification of 200X **b) Magnification of 1500X** **c) Magnification of 3000X**

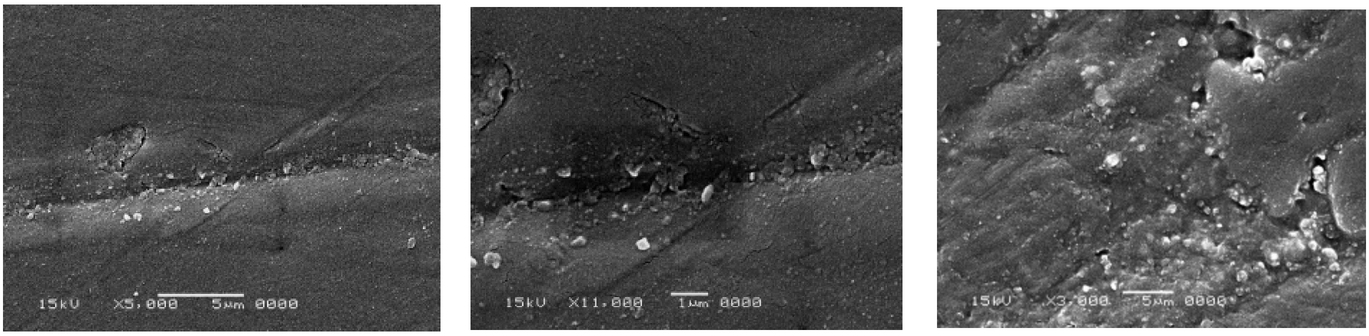


d) Magnification of 8000X **e) Magnification of 4000X** **f) Magnification of 10000X**

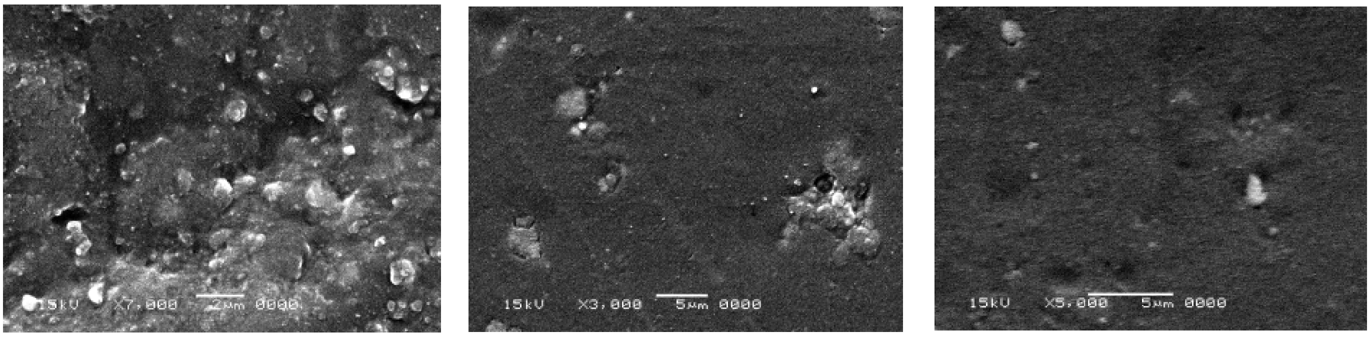


g) Magnification of 4000X **h) Magnification of 14000X**

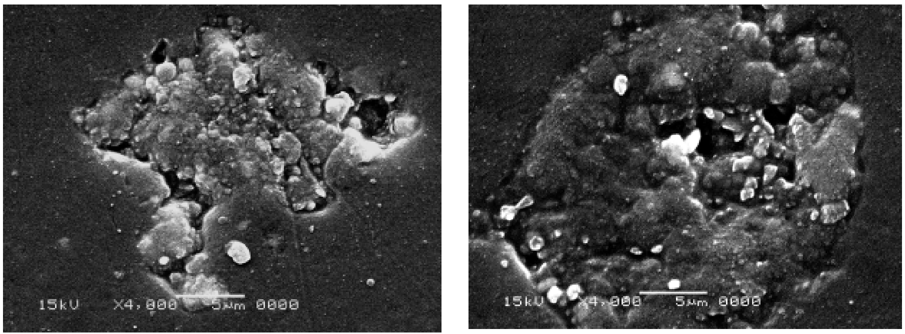
Figure 9. SEM micrographs illustrating the fracture surface of 1, 3 and 5 % reinforced epoxy composites using NDPM which alkaline treated with 5% NAOH (a) 0.5% (200X), (b) 0.5% (1500X), (c) 1% (3000X), (d) 1% (8000X), (e) 3% (4000X), (f) 3% (10000X), (g) 5% (4000X), and (h) 5% (14000X)



a) Magnification of 5000X b) Magnification of 11000X c) Magnification of 3000X



d) Magnification of 7000X e) Magnification of 3000X f) Magnification of 5000X



g) Magnification of 4000X h) Magnification of 4000X

Figure 10. SEM micrographs illustrating the fracture surface of 1, 3 and 5 % reinforced epoxy composites using NDPM which treated with (5% by wt) NAOH solution and then neutralized by (10% by wt) (a) 0.5% (5000X), (b) 0.5% (11000X), (c) 1% (3000X), (d) 1% (7000X), (e) 3% (3000X), (f) 3% (5000X), (g) 5% (4000X), and (h) 5% (4000X)

SEM Analysis: SEM analysis was conducted on the fracture surfaces of various tensile and bending test specimens to provide a deeper analysis for the distribution of NDPM, with two different chemical treatment, as reinforcement in the epoxy resin matrix and the failure mechanisms of the composites under investigation. In most cases, the SEM micrographs confirm the above discussions. Figure 9 shows the SEM micrographs of the fracture surface of 1, 3 and 5 % reinforced epoxy composites using NDPM which alkaline treated with (5% by wt) NAOH solution. It can be well observed that at low NDPM content, there is a good dispersion of nanoparticles individually, which is responsible of high result values of bending strength and flexural modulus (Figure 9 a-d). And also, at the case of increasing NDPM content to 3 and 5% results in the good dispersion of nanoparticles as groups which illustrates the particle bridging mechanism, where nano fibers act as obstacles, thus hindering crack propagation and lead to increasing of impact strength and tensile properties as can be well depicted in (Figure 9 e-h). Figure 10 shows the SEM micrographs of the fracture surface of 1, 3 and 5 % reinforced epoxy composites using NDPM which treated by alkaline and acetylation chemical treatment, treated with (5% by wt) NAOH solution and then neutralized by (10% by wt) acetic acid solution. It can be well observed that at low NDPM content, there is a good dispersion of nanoparticles individually, which increases the bending and impact properties as shown in (Figure 10 a-d). However, the increasing NDPM content to 3 and 5% results in a lower level of dispersion for nanoparticles and appearing of voids and some notches which responsible of deterioration of some mechanical as can be well depicted in (Figure 10 e-h).

Conclusion

- The use of alkali treated NDPM as a reinforcement of epoxy resin (3% loading) has increased the tensile strength by an amount of 40%.
- The use of alkali and acetylation treated NDPM as a reinforcement of epoxy resin (3% loading) has increased the tensile strength by an amount of 29.74%.
- The use of alkali treated NDPM as a reinforcement of epoxy resin (5% loading) has increased the tensile Young's modulus by an amount of 13.6%.
- The use of alkali and acetylation treated NDPM as a reinforcement of epoxy resin (5% loading) has increased the tensile Young's modulus by an amount of 9.5%.

- The use of alkali treated NDPM as a reinforcement of epoxy resin (0.5% loading) has increased the bending strength by an amount of 7.2%.
- The use of alkali and acetylation treated NDPM as a reinforcement of epoxy resin (0.5% loading) has increased the bending strength by an amount of 2.83%.
- The use of alkali treated NDPM as a reinforcement of epoxy resin (0.5% loading) has increased the flexural modulus by an amount of 15.36%.
- The use of alkali and acetylation treated NDPM as a reinforcement of epoxy resin (1% loading) has increased the flexural modulus by an amount of 9.93%.
- The use of alkali treated NDPM as a reinforcement of epoxy resin (3% loading) has increased the impact strength by an amount of 196%.
- The use of alkali and acetylation treated NDPM as a reinforcement of epoxy resin (1% loading) has increased the impact strength by an amount of 153%.
- The use of alkali treated NDPM as a reinforcement of epoxy resin (1% loading) has increased the Shore D hardness by an amount of 8%.
- The use of alkali and acetylation treated NDPM as a reinforcement of epoxy resin (1% loading) has increased the Shore D hardness by an amount of 8.1%.
- -The alkali treatment provides better enhancement for mechanical properties than alkali and acetylation treatment.
- -The silane coupling agent enhanced the mechanical properties of nanocomposites by increasing of interfacial adhesion between NDPM and matrix.

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