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Development and characterization of walnut shell and date seeds powder in low-density polyethylene

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The demand for polymers in many applications has experienced steady growth over the years. This led to the evolution of different types of mixtures, blends, alloys, composites, and reinforced materials. Among the property-enhancing additives, fillers play a very prominent role. The aim of this study is to enhance the tensile and flexural strength of low-density polyethylene (LDPE) by incorporation of walnut shell powder and date seed powder. Both components added strength to the composite, and the combination often compensates for weaknesses in the individual components. Samples containing different weight fractions of the reinforcement were prepared through hot pressing by using a compression moulding process. Tensile strength resistance of an LDPE blend material to breaking under tension is decreased. So, the elongation decreases with fillers. Modulus resistance to flow, hardness and flexural strength are increasing in LDPE blend by adding fillers. There is no water absorption found neither by reinforcement nor by LDPE blend. So this composite can be used to make low-cost products or non-engineering products. As the prepared sample is biodegradable, it can be used in packaging material/disposable products.

Keywords: Low-density polyethylene; Walnut shell powder; Date seed powder; Moulding; Tensile strength; Flexural strength.

INTRODUCTION

In the world of polymers, composites have their charm and identity in connection with providing magnificent strength to the designed product. Moreover, when it comes to providing strength by reinforcing along with making the part cheaper, then what else would do better? A better way to explain this advantage is the strength to weight ratio. Distinctive materials have a diverse quality, that is, every material can take a diverse measure of the load for a similar volume (cross-sectional area) of the material [1].

The scope of this study is about a dispersion-strengthened composite using date seeds and walnut shell powder in the matrix phase of low-density polyethylene (LDPE). These two fillers are available in abundance and usually go to waste. Literature work shows that these natural fillers have a potential to provide strength to the material with which they are combined [1]. As LDPE is used in an enormous amount in the commodity to engineering applications, we can reduce its amount in the same part by reinforcing it with fillers, hence providing strength along with cost-effectiveness. A composite material is one made out of at least two components consolidated in a way that enables the materials to remain particular and recognizable. Van Suchetclan characterized the composite as at least two solid phases of heterogeneous material which are in close contact with one another on a microscopic scale. The strengthening fibers can be cut, adjusted plaud in various approaches to influence the properties of the subsequent composite [2, 3].

Numerous composite materials are made of only two phases: the first phase is a matrix and second is a dispersed phase. The phase in a composite is completely surrounded by the other phase. The intention is to transfer stress to different phases and defend the phases from the environment. Composite materials are normally grouped by the kind of reinforcement they use. This reinforcement is embedded into the matrix that holds it together. The reinforcement is utilized to fortify the composite [4, 5]. For example, in a mud block, the mud is the matrix and straw is the reinforcement. Most common composites include short-fiber or random-fiber reinforcement, long-fiber or continuous-fibre reinforcement, flake reinforcement, particulate reinforcement, filler reinforcement.

The particulate composite comprises a composite material in which the filler materials are generally round. For example; in unreinforced concrete, cement is the matrix and the sand serves as a filler; for lead particles in a copper matrix both the matrix and the filler are metals. The dispersion is strengthened when materials are in little particles (usually less than 0.1 μm) of a hard yet inert phase

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uniformly distributed within a load-bearing matrix phase [6].

The matrix is usually a form of resin that retains the reinforcement in the preferred orientation. It defends the reinforcement from environmental and chemical attack, and bonds the reinforcement by which the applied loads can be efficiently transferred. Many composites, dependent on the thermoplastic for use in inside and outside building components, are presently produced from polyethylene both virgin and recycled. The polymer matrix is generally chosen on its intrinsic properties, product requisite, accessibility, cost and the manufacturers' awareness with the material. The polymeric matrices incorporate both thermo-setting and thermoplastic resins [6].

Fillers are solid additives to any polymer or other materials to enhance their physical properties and also some chemical properties. Including a cost-effective filler in the polymeric matrix can only be viable if it does not significantly alter the main characteristics of the matrix like mechanical properties. The use of natural reinforcement continues to generate interest especially for use in the plastic industry, for it is a renewable material and a biodegradable resource. The use of natural fibers in thermoplastic composites serves to improve the toughness and strength of the plastic [7].

Dates have been stapled nourishment for the Middle East and part of south Asia for many years. Dates are oval or cylindrical with a diameter of 2-3 cm and 3-7 cm length, and the ripe range is dependent on the variety. The dates were also found to medicinal value; they cure a sore throat, cold, fever, and also can be used as cleansing powder. Dates are mostly consumed during fasting and other festivities. While the date is saturated with beneficial compounds for the skin, the effect of date seed particles reinforcement on the properties of polyester was discussed by Aleuo *et al.* They found out that as loading of the filler increases, tensile strength, impact strength and hardness increases while elongation decreases [8].

The effect of date seeds on the properties of natural rubber was also discussed by Abdullah *et al*. The results derived from their research were that tensile strength, hardness, density and Young modulus increases with increasing filler loading [9, 10]. The development and research activities in each country are mainly focused on the utilization of locally available resources of natural fibers. In general, the date palm plant consists of six distinctive potential sources of secondary waste that can be utilized for the production of natural fibers.

The effect of reinforcing date palm wood powder in LDPE based composites and its effect on the mechanical properties of composites was discussed by Marium *et al*. They found that with increasing filler content Young modulus increases, flexural strength is improved and the composite displays strong tendency to absorb water [9].

Walnut is an adaptable delicate rough medium with exceptional properties. It is ideal for a wide range of applications, like walnut shell blasting, cleaning, tumbling, filtration, polishing. It is also used in soaps and beauty care products. Walnut shells are fastidiously squashed and ground to standard mesh size that ranges from grainy grits to fine powder. The effect of walnut shell powder reinforcement in forming a composite was discussed by Rahul *et al.* They found a significant improvement in the tensile modulus and mechanical properties by adding walnut shell powder as reinforcement, a decrease in water absorption property. The grain size of the walnut shell powder can be diverse to enhance the mechanical properties [11].

METHODOLOGY

Powder LDPE grade FD0474 was obtained from Lotrene, Muntajat. Date seeds, walnut shells and their powders were bought from Pakistan. For making specimens for mechanical tests an injection molding setup arrangement of extruder is necessary for uniform mixing of (walnut shells+ date seeds) and LDPE powder. Date seeds and walnut shells powder were dried in an oven at 100^{o}C for 1 hour to remove the moisture content.

Development of Enhanced LDPE Composite

Polymer resin was brought in very fine powder form instead of pellets form and mixing was done manually in dry form as shown in Figure 1. For mixing we used a plastic bottle, then added a specific amount of powder LDPE, walnut and date seeds powder and the bottle was shaken very well to ensure good mixing. In the mixture equal proportions of date seeds powder and walnut shell powder were added. The reinforcement was about 30 wt.%, when 15 wt.% of date seeds powder and 15 wt.% of walnut shell powder were added and similarly for 10 wt.% and 20 wt.% reinforcement as shown in Table 1. Above 30 wt of fillers were not used because as we increased filler amount above 30 wt.%, the sample had a rough surface and was not stable enough under normal conditions. The preparation of composites with different proportions is shown in Figure 2.

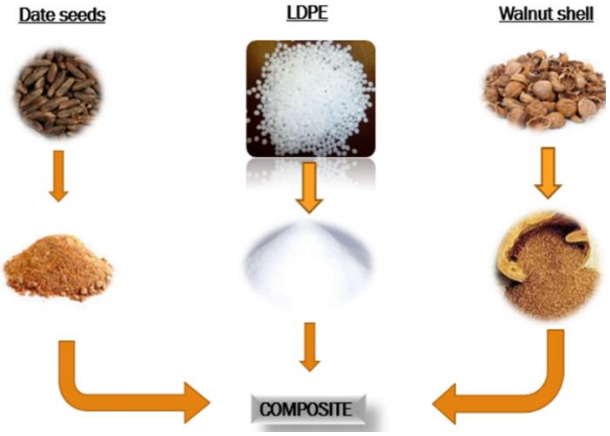

Fig 1. Mixing of LDPE with date seeds and walnut shells

Table 1. Different composition of composite

Samples	LDPE wt. %	Walnut shell wt.%	Date seed wt.%
1	100	-	-
2	90	10	-
3	90	-	10
4	90	5	5
5	80	10	10
6	70	15	15

Fig 2. Composite preparation with different proportions

Choose the type of mold that is tensile, compressive or flexural. Clean the mold surface to remove any film or grease particles. Then preheat the mold for about 5-8 min by placing it into the hot press machine jaws. After that fill the material manually with excess in order to have good flow behaviour so that there would be less number of voids. After filling the preheated mold, press it and again place in the hot press machine. Let the material remain in heating mode for about 5-10 min at a temperature of about 130 degree Celsius and 120 bar pressure. When the temperature is about 140 degree Celsius close the heaters and open the cooling water supply so that it may lose some heat and cool down. Allow the mold to be cooled for about 5 min. Before taking out the mold release the pressure that you have applied in order to make it air tight. After this open the jaws and take out the mold and with the help of gloves take out the samples as shown in Figure 3. After that, weigh the samples and send them for testing. The best samples are chosen and on them different testing procedures are performed.

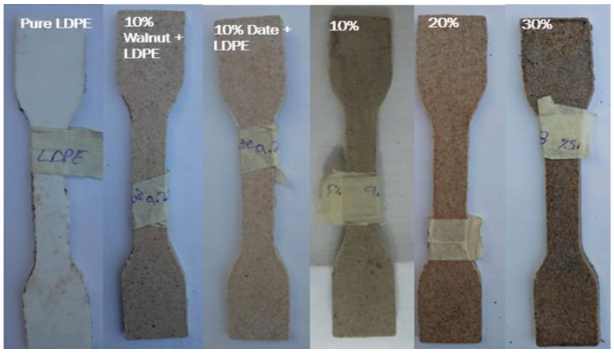

Fig. 3. Samples prepared of different composition

Characterization and Testing

The following techniques were used for characterization.

Stereomicroscopy test: The dissecting or stereoscopic microscope is an optical microscope modified for low magnification of a sample, usually using light mirrored from the surface of an object instead of transmitted through it [1]. Stereomicroscopy test was done to find out the dispersion of the particles in the matrix; this test gives enlarged pictures of the samples so that it could give us the dispersion of the particles. Take the sample which will be use for destructive testing. Place the sample under the microscope and adjust the height of the microscope. Fix the lens magnification according to the requirement and open the software and camera. Figure 4 shows the different composition of LDPE with walnut and date at 500× magnification.

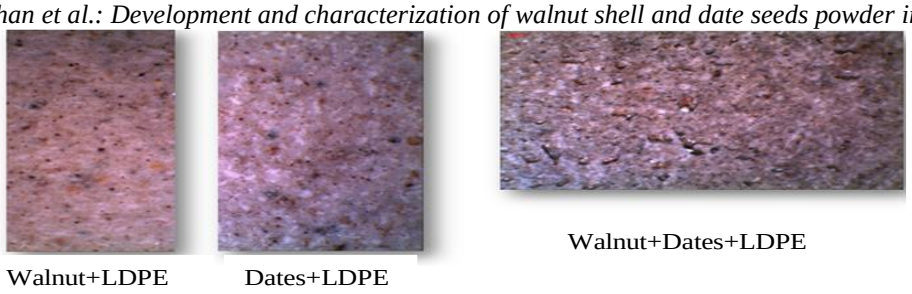

Fig. 4. Microscopic images of the samples

Tensile Test: The tensile test is an important test to check the properties of the composite. The tensile test gives us the mechanical properties of the composite materials. It is a destructive test which gives the maximum force which is composite can withstand under tensile loading and is determined by standard test method ASTM D638 [12]. The tensile test is performed on a dumbbell specimen. Universal testing machine is used for performing the tensile test. Cut or injection-mold the material into one of the five "dumbbell" shapes. The exact shape used will depend on material's thickness, and rigidity. Load the sample in the tensile grips. Begin the test by separating the tensile grips at a constant rate of speed (20 mm per min). The test ends after breaking of the sample. The tensile strength is calculated by Eq. (1)

$$Tensile\ strength = F/(L*W) \quad (1)$$

where, *F*= maximum applied load at failure, *L*= gauge length, *W*=width of gauge area.

Flexural Test: The flexural test estimates the force required to bend a beam under three-point loading conditions. The data are commonly used to select materials for parts that will support loads without flexing. Flexural modulus is utilized as a sign of a material's firmness when flexed. Flexural strength is expressed as modulus of rupture in PSI and is determined by standard test method ASTM D790 [13]. For the testing procedure a specimen of long rectangular shape is used. The load is applied to the centre by the loading nose producing three-point-bending at a specified rate. The test is stopped when the sample reaches 5% deflection or breaks before 5%. For ISO 178, the test is stopped when the sample breaks. If the sample does not break, the test is continued as far as possible and the stress at 3.5% is reported. The result of max force is recorded. The flexural strength is calculated by Eq. (2)

$$Flexural\ Strength = \frac{3PL}{2wT^2} \quad (2)$$

where; '*P'* denotes the load, '*L'* represents the length of span, '*w*' indicates the width of the specimen and '*T*' is for the thickness of the specimen.

Water Absorption Test: Water absorption test was done because the composite contains date seeds powder and walnut shell powder both of which absorb water [14]. This test will give us the result how much the composite is absorbing water, as shown in Figure 5. This test involves a water pot and a circularly shaped specimen. First, the specimen is weighed before dipping it into the water. The specimen is left in the pot for 24 h, then it is removed from the pot and again weighed. The difference between the initial weight and final weight of the specimen will tell us how much water is absorbed.

Fig. 5. Water absorption

Hardness Test: Hardness test is done on the sample to check how much the prepared sample shows resistance towards penetration, which gives us a guideline for defining the application of the samples by using the shore D hardness test. A formed circular disk-shaped sample is used, which has a good surface finish as shown in Figure 6 [15]. Place the sample on the testing plate, lower the plunger so that the pin can penetrate in the sample and reading is noted on the meter.

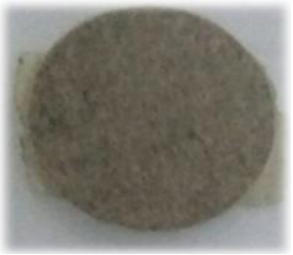

Fig. 6. Sample for hardness testing

Biodegradation Test: This test was conducted to check the biodegradation ability of the samples. We

conducted this test on different samples of varying filler loading [1]. This test takes 2 months to complete. Weigh the sample before putting it and place three samples of different filler loading in a pot. The pot must be filled with microorganism-rich soil and after about 2 months take out the sample from the pot and weigh it again as shown in Figure 7.

Fig. 7. Biodegradation sample placing

RESULTS AND DISCUSSION

Effect of Tensile strength, Modulus and Elongation in Enhanced LPDE Composite

Figure 8 shows a decrease in tensile strength with filler and this would be because of the poor interfacial bond between matrix and filler. Filler particles are just adhered on the matrix surface and work as a void weakening the sample. Moreover, when we use date seeds with LDPE the tensile strength decreases but when we use walnut shells with LDPE, its tensile strength decreases more than the first composition which shows that walnut particles have a weaker interfacial bond with LDPE [10]. Their max bearing force is also decreasing.

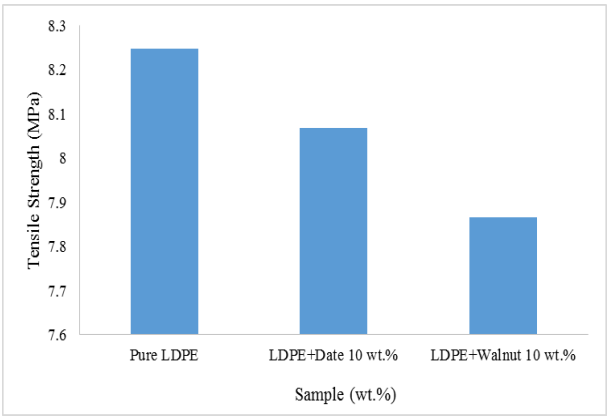

Fig. 8. Tensile strength of individual fillers

Figure 9 shows that by increasing the filler loading, tensile strength decreases. More the amount of filler, more voids are in the sample, which more weakens the sample. Drop in tensile strength is due to porosity, poor adhesion and poor interfacial interaction between both phases [16, 17].

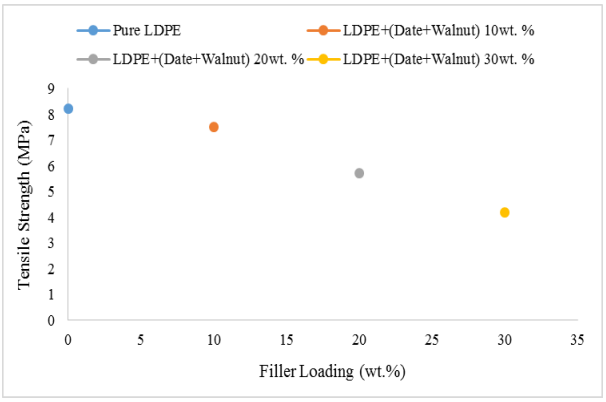

Fig. 9. Tensile strength of combined fillers

Figure 10 shows an increase in modulus with filler that would be due to the resistance shown by filler to LDPE chains to move. Walnut shells resist more than date seeds and this depends on particle size, shape and distribution in matrix [17].

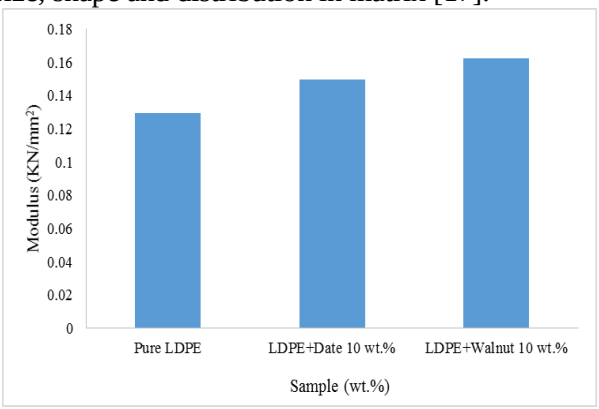

Fig. 10. Modulus of individual fillers

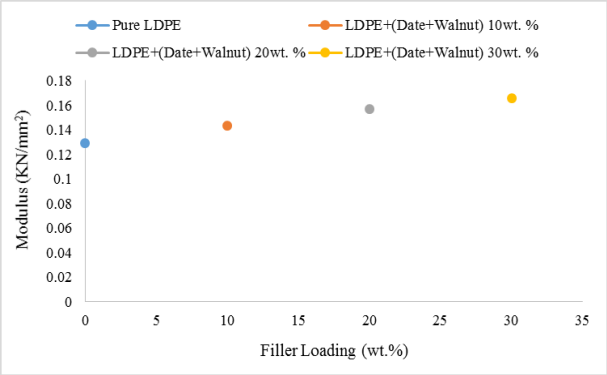

Fig. 11. Modulus of combined fillers

Figure 11 shows the increment in modulus as we increase the filler loading from 0% to 30% of both fillers. As modulus is a measure of the stiffness of a material, that is its resistance to extension. The higher the modulus of a material, the less it extends for a given force. This behaviour can be explained by the fact that adhesion occurred between the filler and the matrix which led to increased stiffness [17]. The LDPE with walnut shells and date seeds powder reinforcement displays a high elastic modulus. The highest value of the modulus was observed for the LDPE composites, attributable to higher strength, stiffness, and better interfacial bonding of fillers.

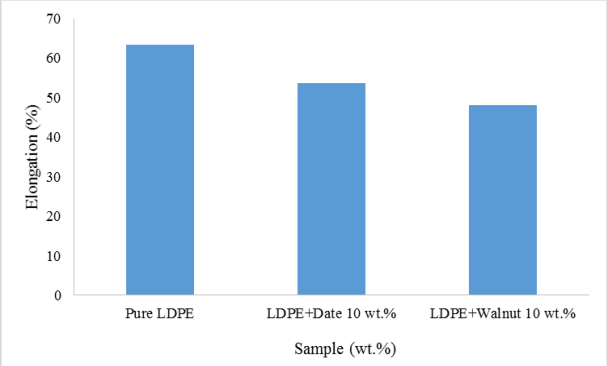

Fig 12. Elongation of individual fillers

Figure 12 shows that the elongation behaviour of LDPE decreases with date seeds and it decreases more with walnut shells due to the weaker interface existing among the composite components. That means, as we use a filler whether it is date seeds or walnut shells, it reduces the ductility of LDPE and moreover, makes the sample rigid [10, 18]. Elongation failure shows the ductility of materials, in other words, the amount of strain it can experience before failure in tensile testing and here the elongation decreases with fillers.

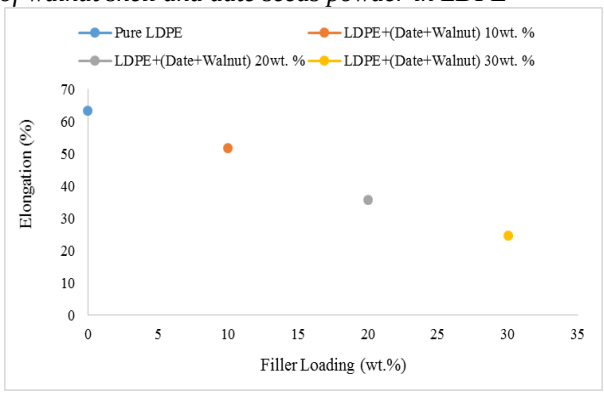

Fig. 13. Elongation of combined fillers

The elongation of the composite decreases with increase in particle concentration because there is adherence of the filler to the polymer phase which results in the reduction of the intermolecular bonds between the filler and matrix and it works for stiffening of the matrix chain. According to the literature, the percentage elongation decreases due to rigid fibres restraining matrix deformation persuading strength gain and brittleness of the resultant composites [17, 18].

Effect of Flexural Strength and Hardness in Enhanced LPDE Composite

As flexural strength expresses the rigidity of sample, in Figure 14 the flexural strength of LDPE increases with date seeds powder and it increases more when we take walnut shell powder with LDPE. This is happening because surface interaction increases due to flexural strength increase.

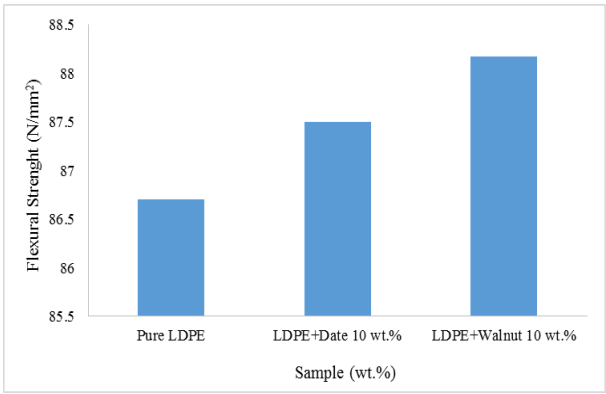

Fig 14. Flexural strength of individual fillers

Figure 15 shows an increase in flexural strength with increased filler loading as by the increase in the amount of filler the surface properties will increase due to good heat transfer at the surface of the mold. As a result, flexural strength and bending force increase. The reinforcement of both fillers in the LDPE led to a change in mechanical properties also depending on the temperature and running conditions. This is anticipated as a result of the high

modulus of both fillers [19]. However, all results proved that LDPE makes the interactions amongst the components stronger and this is proved by the solid-like behaviour of the composite at higher content of both fillers. The results obtained are in good agreement with previous literature concerning filler reinforced composite [19, 20].

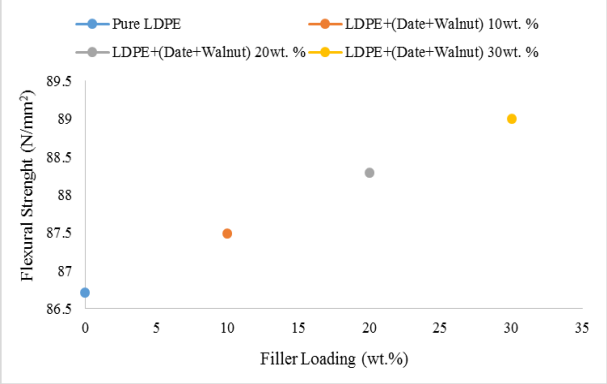

Fig 15. Flexural strength of combined fillers

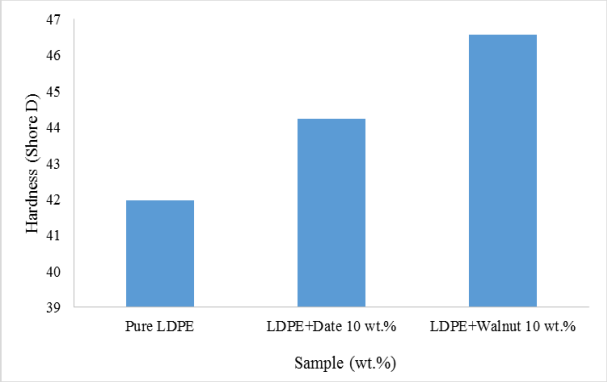

Fig. 16. Hardness of individual fillers

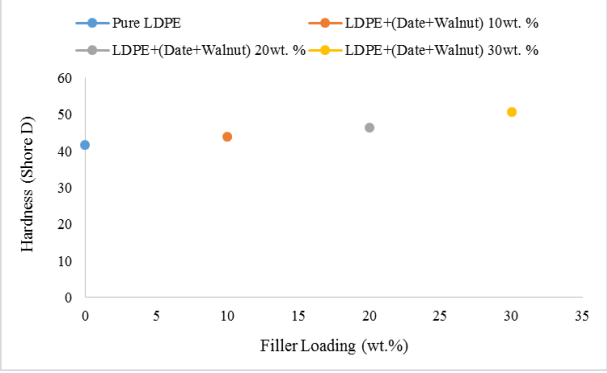

Fig. 17. Hardness of combined fillers

Hardness is a measure of material's resistance to surface indention. In Figure 16, hardness is increasing by adding filler in the LDPE matrix. Moreover, there is not much change in effect/results of whether we use date seeds or walnut shells [2].

By increasing the filler loading from 0 wt.% to 30 wt.% the hardness of the composite is increasing as the filler enhances the surface property of composite and resists deformation by penetration as shown in Figure 17. That means that combined reinforcement of date seeds and walnut shell powder increases the abrasion resistance of the sample, as well as the wear resistance (loss of material) [2, 21].

Effect of Water Absorption and Biodegradation in Enhanced LPDE Composite

As shown in Figure 18, both fillers are not water absorbing. They show negligible change in the water absorption test. Moreover, the change in weight would be because some water molecules adhere on the surface, as after drying the sample has the same weight as it had before the test. The date seeds (bio filler) can absorb the water a bit but here no change is seen that would be due to particle size or may be 24 h are not enough time to register water absorption. Whatever in this case, this composite hardly absorbs water which was also found in the literature [9].

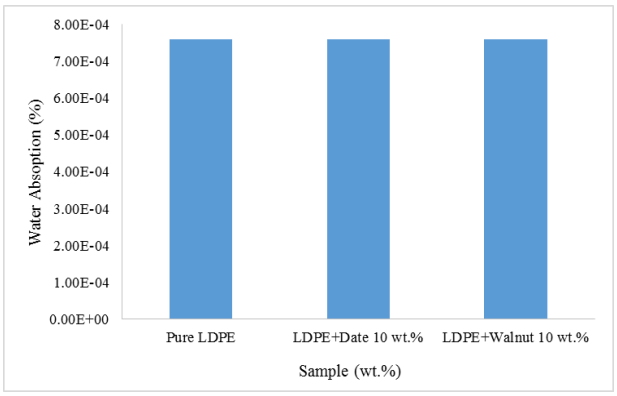

Fig. 18. Water absorption of individual fillers

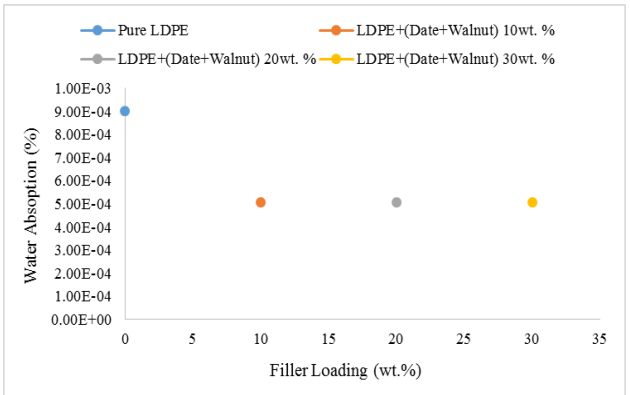

Fig. 19. Water absorption of combined fillers

Figure 19 shows that there is no difference in the weight of the sample before and after the test as there has been no water absorption by combined reinforcement of the composite even by changing the amount of fillers [9].

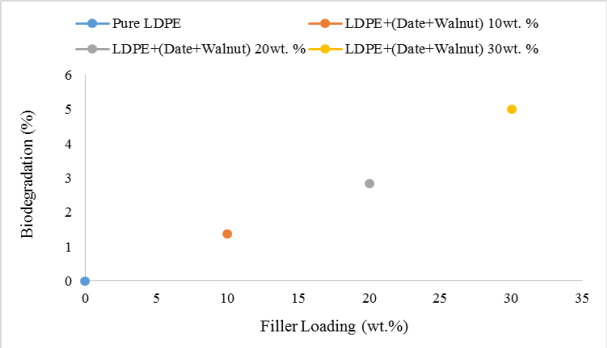

Fig. 20. Biodegradation of enhanced LDPE blend

Figure 20 shows the effect of biodegradation (deterioration) by reinforcement of date seeds and walnut shell powder. The use of biomass filler shows increased reduction in weight as biodegradation is the disintegration of reinforcement materials (date seeds and walnut shells) by bacteria, fungi, or other biological means [22]. Moreover, from 10 wt.% to 30 wt.% biodegradation increases. These are results of just 2 months. By increasing the time these results can be improved that means, biodegradation would increase.

CONCLUSION

The polymer matrix is generally chosen on its intrinsic properties, product requisite, accessibility, cost and manufacturers' awareness with the material. By increasing the proportion of dates and walnuts in LDPE, the tensile strength is getting decreased. On the other hand, the modulus shows a different trend, by increasing the proportion of both fillers, the trend goes high. The most appreciable results are related to the hardness of the composite, as the reinforcement is aiding in increasing the hardness of the composite with increased proportion. As both fillers used in the reinforcement are biomass fillers that is why the biodegradation test showed reduction in weight. So it is a huge advantage of using these fillers as reinforcing agents as they are making the sample biodegradable. There was no water absorption property found in the produced sample. So the sample will not absorb any moisture content. The future recommendation is to study combined reinforcement of walnut shells and date seeds in LDPE with a coupling agent and the effect of processing parameters.

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