

Walnut Shell Reinforced Composite: A Review

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Abstract

Natural fiber composite plays a vital role in aerospace and automobile industry. Owing to the advantage of easy availability and low weight natural fibers such as coir, flax, ramie, sisal, jute, banana, luffa cylindrica, bagasse etc. are often used. Natural fibers are light weight, renewable, non toxic, biodegradable, having high specific strength, low cost etc. In this review walnut shell powder is used to form a composite and its mechanical is discussed as the composition of the walnut powder is changed. Fiber and textile surface reinforced composite . materials are widely used in a broad range of usage fields. Defence industry, space industry, automotive industry, sea transport industry and sport materials are exemplary fields where composite materials are widely used.

Keywords – Composite, Walnut Shell powder, Specific strength, Elongation, Modulus of elasticity, Heat Flow, Stress, Strain.

1. Introduction

A Composite is when a superior and unique material is created by combining two different materials[1]. It can also be defined as the combination of a matrix and reinforcement, which when combined together gives property that is superior to the property of the individual components[2]. Van Suchetclan [3] defined composite as two or more solid phases heterogeneous material which are in intimate contact with each other on a microscopic scale. The reinforcement fibres can be cut, aligned, placed in different ways to affect the properties of the resulting composite. The matrix, normally a form of resin, keeps the reinforcement in the desired orientation. It protects the reinforcement from chemical and environmental attack, and it bonds the reinforcement so that applied loads can be effectively transferred. In ancient times composites were used for construction purposes, mud was mixed with straw. The mud acted as a binder whereas the straw provided the strength and structure. Now days plastic and structural fiber is used which is called 'Fiber Reinforced plastics' or FRP. The plastic polymer in FRP holds the fiber, the fiber provides the structure. The polymer matrix dramatically increases the overall mechanical strength of the composite material as compared to a simple polymer [4]. The boundary where these components meet is thus inherent to such materials and is greatly called interface and the region near this interface is generally referred to as

'interphase'. The interphase is a very small region over which the mechanical and physical properties change from the bulk properties of one component (glass) to the bulk properties of the other component (polymer). The load transfer from the matrix to the fibers occurs through the interphase region in Glass Fiber Reinforced Polyester (GFRP) composites. The primary reason composite materials are chosen for components is because of weight saving for its relative stiffness and strength. For example, carbon-fibre reinforced composite can be five times stronger than 1020 grade steel while having only one fifth of the weight. Aluminium is much nearer in weight to carbon-fibre composite, though still somewhat heavier, but the composite can have twice the modulus and up to seven times the strength.

1.1 Types of Composite

Basically there are three type of composites.

- a) **Ceramic matrix** –[5] Ceramic matrix composites (CMCs) are a subgroup of composite materials. They consist of ceramic fibers embedded in a ceramic matrix, thus forming a ceramic fiber reinforced ceramic (CFRC) material. The matrix and fibers can consist of any ceramic material. CMC materials were designed to overcome the major disadvantages such as low fracture toughness,

B) Metal matrix – [5] Metal matrix composites (MMCs) are composite materials that contain at least two constituent parts – a metal and another material or a different metal. The metal matrix is reinforced with the other material to improve strength and wear. Where three or more constituent parts are present, it is called a hybrid composite. In structural applications, the matrix is usually composed of a lighter metal such as magnesium, titanium, or aluminium. In high temperature applications, cobalt and cobalt-nickel alloy matrices are common. Typical MMC's manufacturing is basically divided into three types: solid, liquid, and vapour. Continuous carbon, silicon carbide, or ceramic fibers are some of the materials that can be embedded in a metallic matrix material. MMCs are fire resistant, operate in a wide range of temperatures, do not absorb moisture, and possess better electrical and thermal conductivity. They have also found applications to be resistant to radiation damage, and to not suffer from out gassing. Most metals and alloys make good matrices for composite application.

- b) **Polymer matrix** - Polymer matrix composites (PMCs) can be divided into three sub-types, namely, thermoset, thermoplastic, and rubber. Polymer is a large molecule composed of repeating structural units connected by covalent chemical bonds. PMC's consist of a polymer matrix combined with a fibrous reinforcing dispersed phase. They are cheaper with easier fabrication methods. PMC's are less dense than metals or ceramics, can resist atmospheric and other forms of corrosion, and exhibit superior resistance to the conduction of electrical current.

1.2 Composite Classification (On the basis of their shapes.)[6]

Metal matrix composites can be reinforced by strong second phases of three-dimensional shapes (particulate), two-dimensional shapes (laminar), or one-dimensional shapes (fibrous). All these three types differ in both the mechanical properties and the fabrication techniques.

a) Particle Reinforced Composite

Particles are used as binder includes ceramics and glasses such as small mineral particles, metal particles such as aluminium and amorphous material, including polymers and carbon black. Particles are used to increase the modulus of the matrix and to decrease the ductility of the matrix. units connected by covalent chemical bonds. PMC's consist of a polymer matrix combined with a fibrous reinforcing dispersed phase. They are cheaper with easier fabrication methods. PMC's are less dense than metals or ceramics, can resist

atmospheric and other forms of corrosion, and exhibit superior resistance to the conduction of electrical current.

b) Fibre Reinforced Composite

Generally fiber reinforced composites are made by fibers and a matrix. One of which have good strength and good strength as well, a binder or matrix which helps to hold the fibers and transfer stresses between the reinforcing fibers. Common fibre reinforcing agents include asbestos, carbon / graphite fibers, beryllium, beryllium carbide, beryllium oxide, molybdenum, aluminium oxide, glass fibers, polyamide, natural fibers etc. modulus of the matrix and to decrease the ductility of the matrix. Similarly common matrix materials include epoxy, phenolic, polyester, polyurethane, polyetheretherketone (PEEK), vinyl ester etc.

Fibers are a class of hair – like materials that are continuous filaments or are in discrete elongated pieces similar to pieces of thread. They can be spun or twisted into yarn such as cloth and can be converted into non woven fabrics, such as paper or felt. They can be used as reinforcement in composite materials. Fibers are of two types natural fiber and manmade or synthetic.

2. Walnut Shell composite

Material	Holocellulose (%)	Cellulose (%)	Lignin (%)	Ash (%)
Walnut shell	46.6	25.4	49.1	3.6

Table 1 Shows the composition of walnut shell[10]

Walnut shells are versatile soft abrasive media with unique physical and chemical properties. These properties make them ideal for a variety of applications, such as walnut shell blasting, tumbling, cleaning, polishing, filtration, non-skid flooring, as well as in soaps and cosmetics.

Walnut shells are meticulously crushed and ground to standard mesh sizes that range from abrasive grits to fine powders.

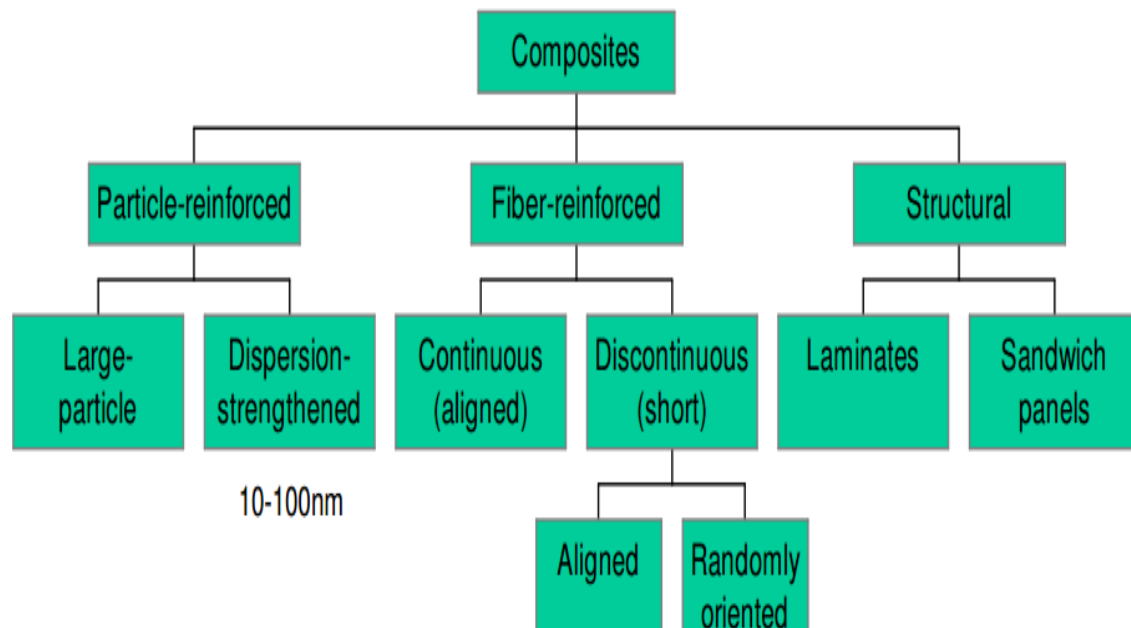


Fig.1. Types of composite[7]

2.1 Natural fibers in composites

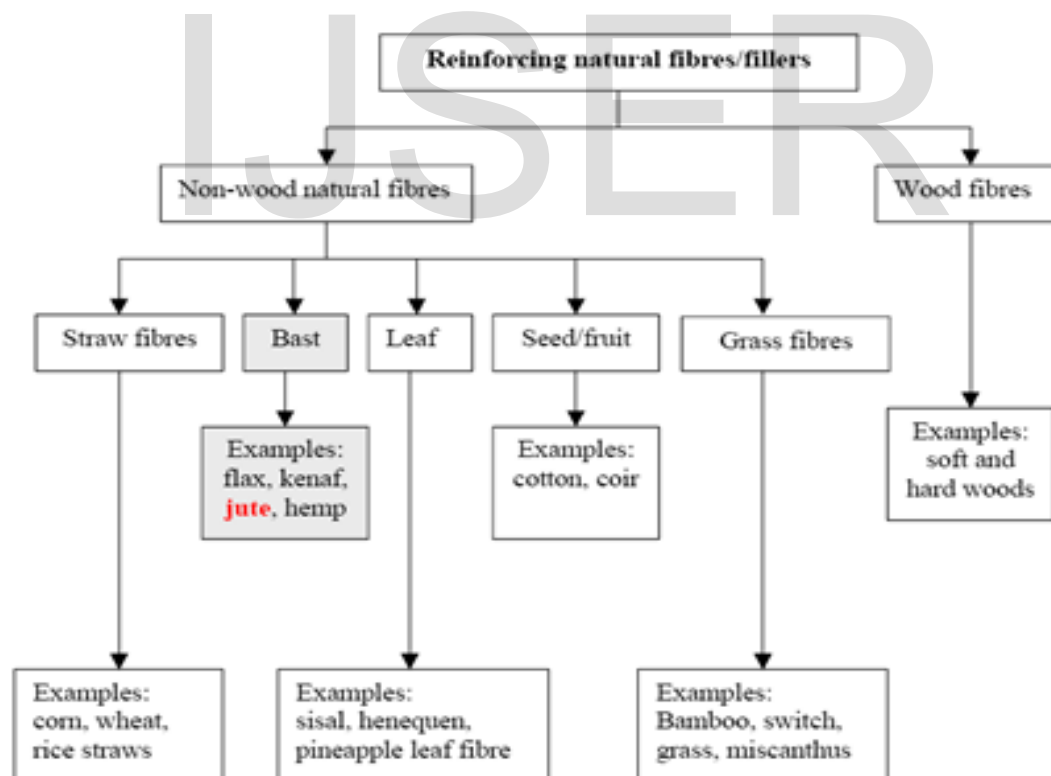


Fig. 2. Classification of Natural Fibers[8]

Properties	Fibre								
	E-glass	flax	hemp	jute	ramie	coir	sisal	abaca	cotton
Density g/cm ³	2.55	1.4	1.48	1.46	1.5	1.25	1.33	1.5	1.51
Tensile strength* 10E ⁶ N/m ²	2400	800 - 1500	550 - 900	400 - 800	500	220	600-700	980	400
E-modulus (GPa)	73	60 - 80	70	10 - 30	44	6	38		12
Specific (E/density)	29	26 - 46	47	7 - 21	29	5	29		8
Elongation at failure (%)	3	1.2 - 1.6	1.6	1.8	2	15 - 25	2 - 3		3 - 10
Moisture absorption (%)	-	7	8	12	12 - 17	10	11		8 - 25
price/Kg (\$), raw (mat/fabric)	1.3 (1.7/3.8)	- 1.5 (2/4)	0.6 - 1.8 (2/4)	0.35 1.5/0.9 - 2	1.5 - 2.5	0.25-0.5	0.6 - 0.7	1.5 - 2.5	1.5 - 2.2

Table 2 Shows the strength of various natural composite[9]

3. Literature Survey

Dinesh Kumar Rao[10] used 20 wt % of walnut shell particles and 10 wt % of coconut fibres were added as reinforcing material in epoxy resin CY 230 and hardener HY 951. Hardener was mixed in the solution at 400 C which were preheated to 1000 C and hold for 2 hours at 1000 C After curing, the composite sheet was used for tensile test to fulfil the objectives of the present investigation. A simple specimen shape according to ASTM D 790 is used for the flexural test. The thickness and width of the specimen are measured and recorded. This test is conducted using servo hydraulic universal testing machine (ADMET make). The force displacement curve for biocomposite (20 wt % walnut shell particle and 10 wt % coconut fibre)

and pure epoxy material. The flexural stress, strain curve for biocomposite (20 wt % walnut shell particle and 10 wt % coconut fibre) and pure epoxy material. The curve rises in non linear way until the maximum value reached where load drop suddenly. The non linear increase in the load demonstrates the ductile behavior of the material and this may be because of the use of short coconut fibre. The average values of ultimate strength of biocomposite and pure epoxy are 24.43 MPa and 44.93 MPa respectively. This shows that the ultimate strength of biocomposite is about 54.3% of pure epoxy. However the coefficient variance of biocomposite as compared to pure epoxy is about 6 times of the pure epoxy.

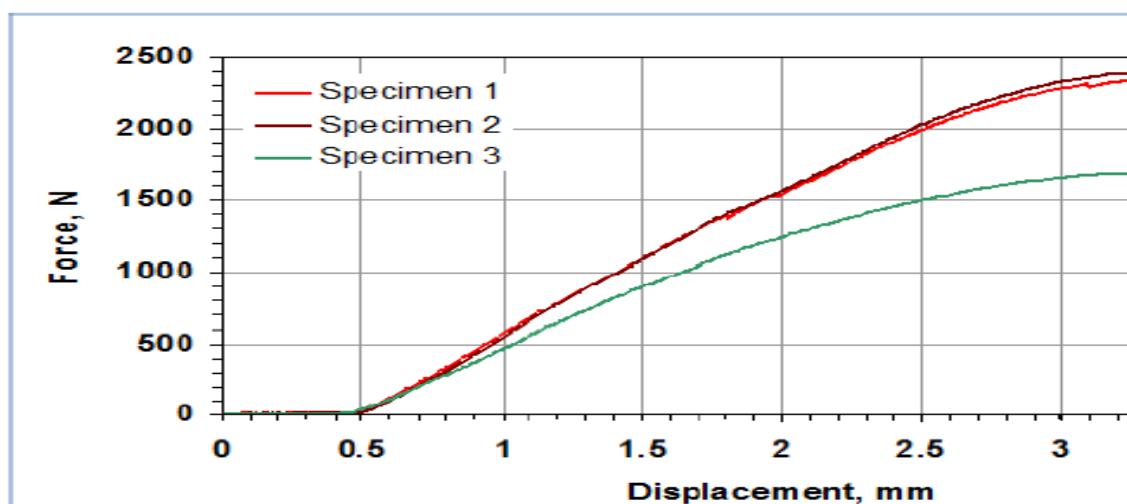


Fig. 3 Shows the force displacement curve for pure epoxy[10]

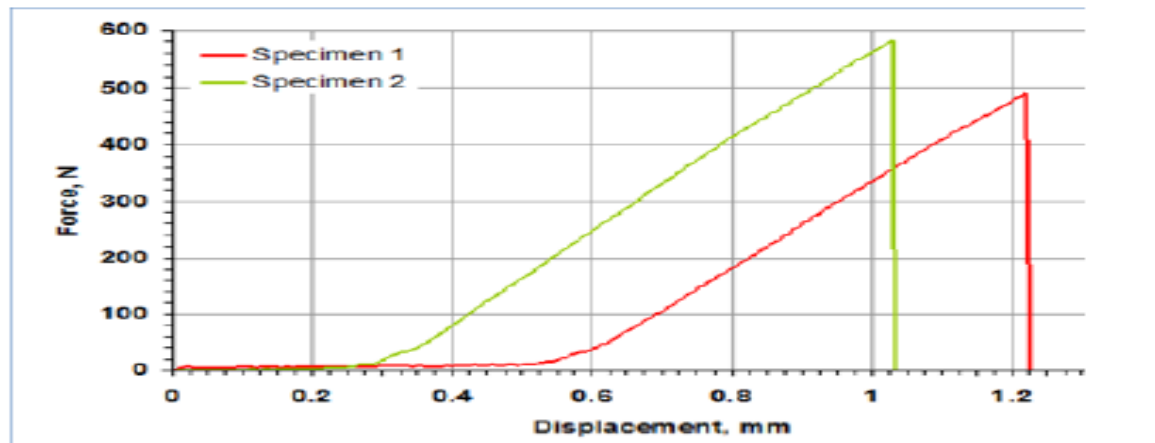


Fig. 4 Shows the force displacement curve for bicomposite with 20% walnut shell particle and 10% coconut fibre.[10]

S. No.	Walnut shell particle (10 wt%) (gm/cm ³)	Walnut shell particle (20 wt%) (gm/cm ³)	Walnut shell particle (30 wt%) (gm/cm ³)	Walnut shell particle (40 wt%) (gm/cm ³)
1	1.173	1.20	1.15	1.03
2	1.176	1.16	1.13	1.05
3	1.176	1.14	1.20	1.10
Mean	1.175	1.170	1.160	1.060

Table 3 Density of walnut shell particles reinforced composite[11]

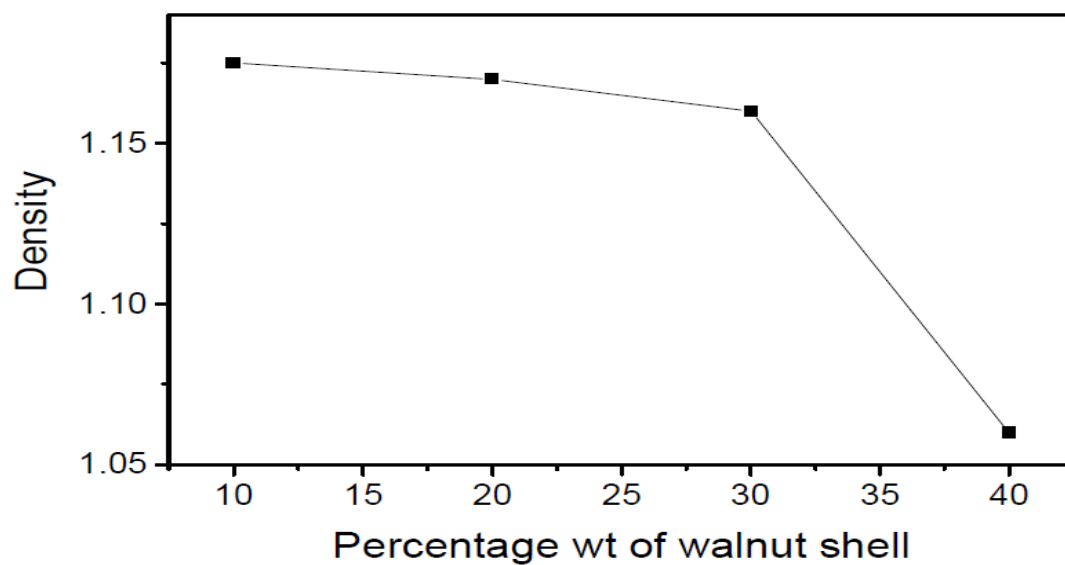


Fig. 5. Density variation with % of walnut shell particle[11]

S. Nitin [11] used walnut shell particles to improve the mechanical strength and wear properties. The walnut particles residue was widely generated in high proportions in the agro-industry by the grinding of the walnut shell. The particles were removed and the shell was crushed into smaller pieces manually. Thereafter the walnut shell powder was obtained by grinding the crushed shell in Willy's mill. The particle size of 1.00 mm was obtained using two sieves 0.5 mm and 1 mm successively. It can be seen that density decreases with increasing percentage of walnut shell particle. It can be further seen that there is a slow drop in density between 10 to 30 % of walnut shell particle

but there is drop in density between 30%wt to 40 %. Presence of Porosity/voids would be there which decreases the density because there was no pressure applied. Flow of material was properly maintained in mould required air removal for 30%wt reinforcement. The tensile stress-strain curve for unfilled epoxy resin and composite material containing 10 wt %, 20 wt %, 30 wt %, 40 wt % of walnut shell particle .All tests are conducted as per ISO in 100 kN servo hydraulic Universal Testing machine at different strain rates of 0.01 mm/min. The effect of particle reinforcement into epoxy resin matrix can be easily observed in the stress-strain diagram.

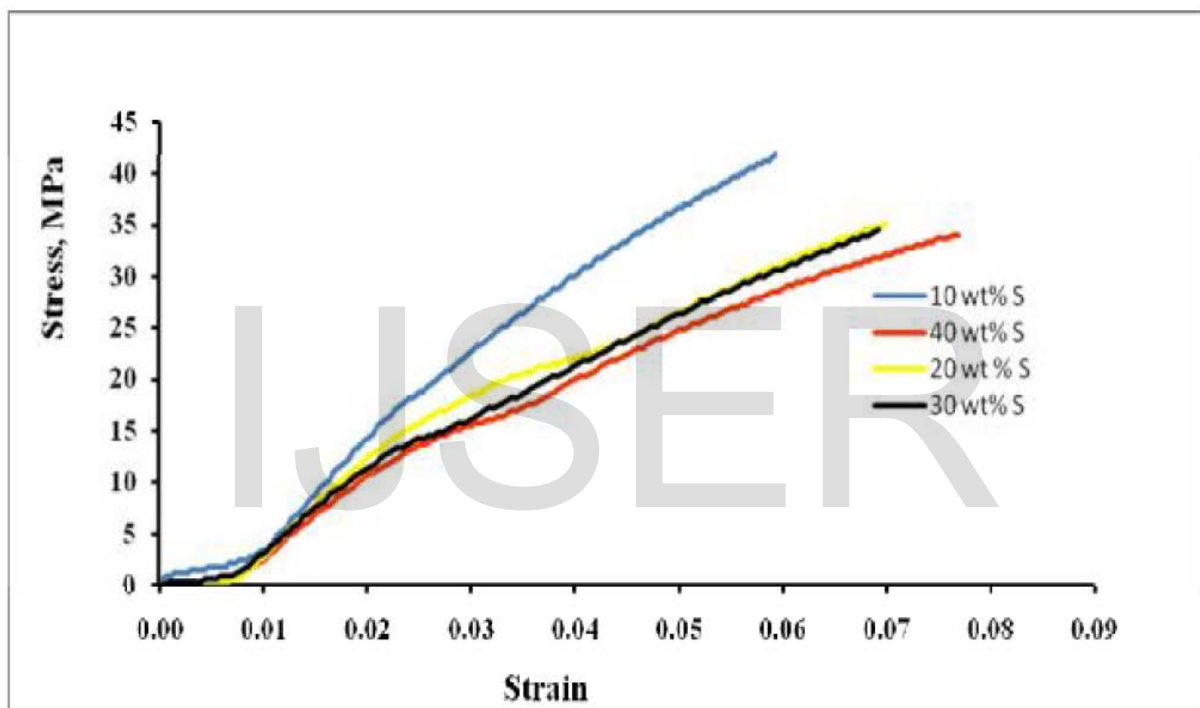


Fig. 6. Stress-strain diagram for different wt % of walnut shell particles.[11]

S.N	10 wt% S	20 wt% S	30 wt% S	40 wt% S
Ultimate Strength, MPa	41.818	35.151	34.545	33.939
Modulus of Elasticity, MPa	932.34	905.63	878.23	821.23
% Elongation	5.928	5.928	6.927	7.693

Table 4. Various mechanical properties for different wt% of walnut shell particles.[11]

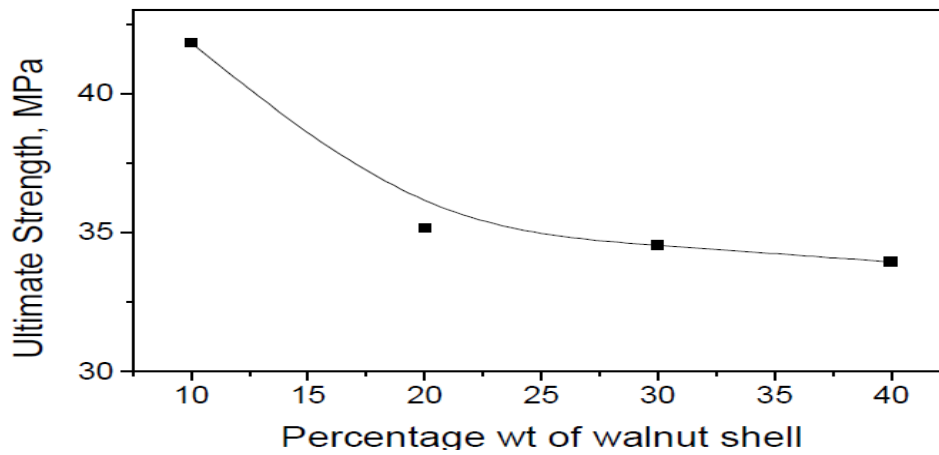


Fig .7. Ultimate strength variation for different wt % of walnut shell particles[11]

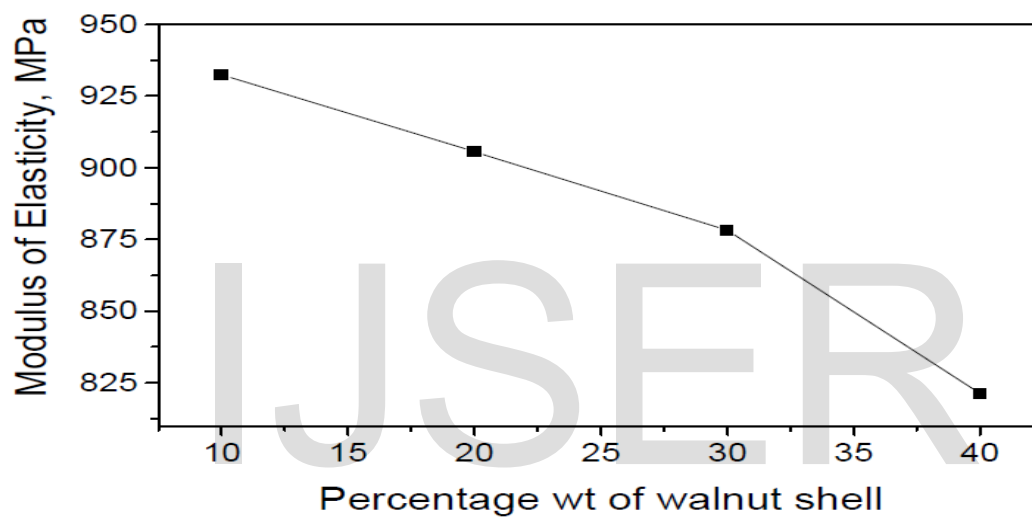


Fig. 8. Modulus of elasticity, E (MPa) different wt % of walnut shell particles[11]

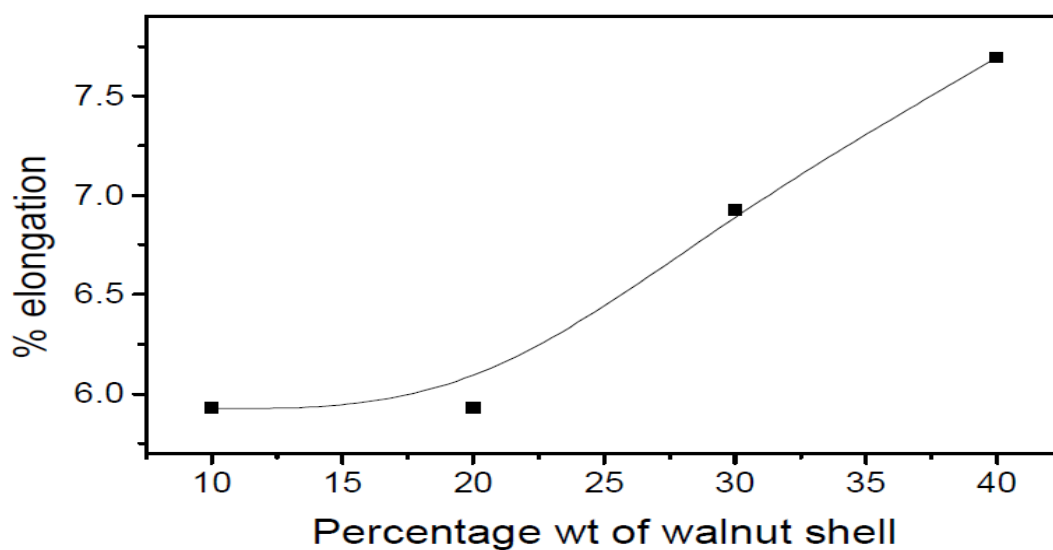


Fig .9. Percentage elongation for different wt % of walnut shell particle[11]

It can be stated that ultimate strength is highest for 10% walnut particle of 42.95 MPa and further drops abruptly at first up to 20% and then drops slowly further to a value of 34.0 MPa. The drop in tensile strength is due to porosity, poor adhesion and poor interfacial interaction between epoxy and shell particles. It can be seen from Fig.8 that there was drop in modulus of elasticity with increasing percentage of walnut shell particle and is maximum for the value of 932.34 for 10% walnut particle. This was due to increase in % elongation beyond 20%wt reinforcement. From Fig. 9. it is observed that percentage elongation is almost constant up to 20% wt of walnut particle and then rises sharply further up to 40%.

S. Nitin [11] observed that percentage elongation is almost constant up to 20% wt of walnut particle and then rises sharply further up to 40%. The density reduces with the increase of reinforcement of shell particles. But rate of increase is more beyond 30%wt reinforcement. Density obtained is very suitable for light weight applications. Tensile strength of 33-41 MPa achieved from these walnut shell particles reinforcement is sufficient for materials replacing wood.

Solmaz Saadat [12] Various forms of synthesized carbon nanomaterials, namely SWCNTs, MWCNTs, SWCNTs/Fe and CNFs, were tested to determine which was the most effective adsorbent for lead removal. The results showed that the SWCNT bundles were most capable of adsorbing Pb(II) ions. SWCNTs/WSh composite was successfully prepared by immobilizing SWCNTs onto RWSH. RWSH was used as the base medium for SWCNTs so as to keep the nanoparticles relatively fixed in aqueous media. Thus, it is possible to overcome the practical problems associated with the use of bare SWCNTs, and this in turn means that walnut shell-doped SWCNT can be effectively used in wastewater treatment. SEM images show clusters of SWCNTs dispersed properly on the surface of walnut shells. The immobilization of SWCNTs onto walnut shells increased its surface area from 118 m² g⁻¹ to 738 m² g⁻¹, hence improving its adsorption capacity. Batch adsorption studies showed that the synthesized adsorbent was effective in the removal of lead with relatively fast kinetics. Most of the adsorption happened within the first 30 min, and equilibrium was gradually reached within 400 min. Furthermore, it was found that the kinetic adsorption process can be described well by the pseudo second-order rate model. Kinetic experiments clearly indicated that the adsorption of lead on both SWCNTs/WSh composite and RWSH is a two-step process consisting of initial rapid adsorption of the metal ion followed by an almost flat plateau phase.

This was also confirmed by the intra-particle diffusion model. Equilibrium adsorption follows both the Langmuir and Freundlich isotherms, perhaps due to the truly heterogeneous nature of the surface sites involved in metal uptake. However, a greater R² value was obtained from the Langmuir model. The lead adsorption capacity of the novel adsorbent at pH 5 was 294.1 mg g⁻¹, which is higher than many other low-cost commercially available adsorbents. The adsorption process was affected by parameters such as time, pH, initial metal concentration, adsorbent dosage, and temperature. Removal efficiency rose as temperature increased, lending credence to the endothermic nature of the adsorption process. Under acidic conditions, the competition of heavy metal ions with hydrogen ions for the available sites resulted in a slight decrease in removal capacity. Conversely, the precipitation of heavy metal hydroxides led to a slight increase in lead removal under alkaline conditions. The pH experiments showed that maximum adsorption occurred at pH 5-6.

E.V. Mathias [13] aimed at the extraction and characterization of some important lignin compounds present in the walnut shell oil. The oil was extracted by a novel method in which the shells were roasted at 250–300 °C. The lignin breakdown compounds of the oil were then isolated by solvent extraction using petroleum-ether (60–80 fractions), separated by preparative TLC and were fully characterized by employing GC–MS and H NMR techniques. UV, FTIR and HPLC data was then used to confirm the structures. The shells were cracked and the nuts removed. The internal structure was removed and thoroughly scraped with a pairing knife to leave only the hardwoody part. The broken shells were then rinsed with deionized water, dried at 105 °C and then ground to coarse pieces of about 10mm in size using a mill. Fine pieces were avoided since the oil gets soaked in the powder itself making its isolation difficult. A quantity of 300 g of powdered shell particles was roasted to 250–300 °C in a stainless steel container over which was mounted a modified condenser. GC–MS and H NMR spectroscopy have been used in this work for the walnut shell oil and good results were obtained. By employing a series of methods to elucidate the structures, the results are more accurate and reliable than any other method of analysis carried out previously on the walnut shells and other lignocellulosic materials. Excellent resolution of the spectra has been obtained due to complete solubility of the biomass in petroleum-ether.

Ahmed J. Mohammed [14] studied mechanical properties of walnuts shells composites were

studied. The range of added walnuts shells has the values (0%, 2.5%, 5%, 10%, 15%, 20%, and 25%) of polyethylene weight and, the best fibers ratio was 10 % and 15 %. Obvious improvement in the mechanical parameters was recorded when adding walnuts shells with 10% weight ratio. The properties (LDPE /walnuts shells) composites were analyzed as a function of the powder amount. The research used polyethylene with low density (Low Density Polyethylene) as the basis of material and product by the General Company for Petrochemical Industries (Basra-Iraq) in the form of powder. Walnut shells fillers with polymer within the fillings natural organic were used Walnuts shells are mixed with LDPE using mixer 600 instrument attached to Haake Rheochard meter under following conditions; mixing time 15 minutes, mixing temperature 160 °C and mixing velocity 50 RPM., by using the cross section (mixer 400) with description 16 R.P.M, 60 °C for 10 minutes. The final mold product is introduced in a laboratory compress under 5 tons at 175 °C for 3 minutes in a square frame. The pressure then rises gradually up to 15 tons for 10 minutes and after this period the sample is cooled up to reach room temperature. Samples dumbbell in shape are prepared for measuring the mechanical properties by using Zwick Reil instrument. The elongation of the polymer begins at the percentage (0%) of the polymer pure (109 %) and then decrease when the percentage (2.5%) is (35.5 %) which is a polymer few flexibility and has a hardness high thereby acting shells powder Walnut to fill the spaces between the chains main polymer limited movement of the chains and thus less elongation and then increases until it reaches the maximum value to them when the ratio (10 %) is (44.2 %), and the polymer when this ratio high flexibility and low hardness, and then decrease when the percentage (20%) is (7.8 %) polymeric chains that are not constrained by any be free movement as a result of lack of homogeneity of the mixture, including the nature of the shells powder Walnut characterized by rigidity, which in turn increase the stiffness of the polymer and reduce elongation increased concentration of additive and worked to increase the density of the polymer.

Fig.11 shows the effect of shells powder Walnut on modulus of elasticity (Young modulus) which is known as a proportion of stress to elongation for solids only, shown in figure increase Young modulus progressively with increasing concentration of additive and this leads shells powder Walnut us to works elongation of the polymer, and probably explains the decline in the shells powder Walnut when the percentage (10%) of the additive to the heterogeneity of the model although the mixing models have been in the same circumstances, and this indicates that the polymer

has the recipe high flexibility and decrease in hardness at this percentage. Either when the percentage (15% and 25%) has a recipe polymer hardness and lack of elasticity.

Fig.12 represents the proportional limit with percentage added shells powder Walnut to the polymer, as we note that the highest value was when the proportion of the added polymer (15%) is 141 N as it will be at this rate homogeneity strong between shells powder Walnut with chains of polymeric polymer while less proportion limit of which 76.5 N at the percentage (20%), and probably explains the decline in the shells powder Walnut when the percentage (20%) of the additive to the heterogeneity of the model although the mixing models have been in the same circumstances.

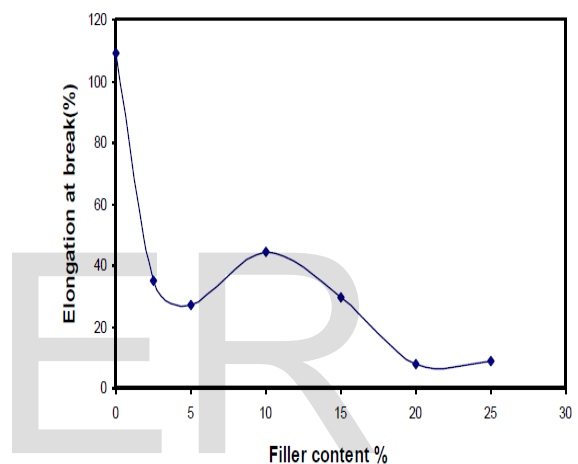


Fig.10. Elongation at break and shells powder walnut – LDPE Composites [14]

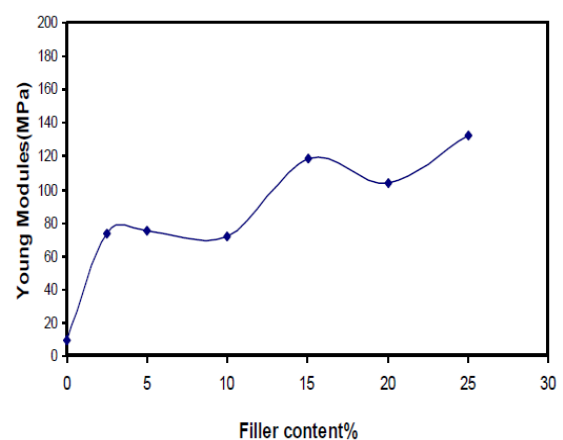


Fig.11. Young Modulus and and shells powder Walnut- LDPE composites [14]

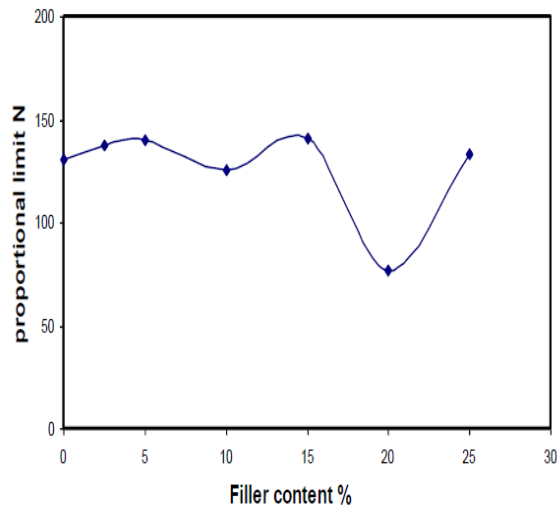


Fig.12. Relation between the proportional limit and shells powder walnut –LDPE composites [14]

Nadir Ayrimis [15] injection molded specimens were prepared from the walnut shell flour and polypropylene with and without maleic anhydride-grafted polypropylene at 40, 50, and 60% (weight) contents of the walnut shell. The bending and tensile modulus of the composites significantly increased with increasing the filler content while the bending and tensile strengths significantly decreased. Water absorption and thickness swelling of the composites increased with increasing filler content.

Significant improvement in the tensile modulus was observed with increasing the walnut shell flour content. The results of the tensile modulus test are similar to the results of the flexural modulus test; the composites with high walnut shell flour content and treated with the MAPP had better tensile modulus than the untreated ones. The tensile modulus of the polypropylene increased by 112% as 60 wt% walnut shell flour was incorporated to the polypropylene whereas the tensile strength decreased by 92%. The results of the tensile modulus revealed that the presence of the filler reduced the ductility of the polypropylene composite and increased its modulus. This is true for lignocellulosic filled thermoplastic composites in which filler added to a thermoplastic restrains the movement of its chains, thereby increasing its modulus.

The tensile strength of the specimens decreased gradually with increasing walnut shell content. The tensile strength values of the specimens filled with 40 and 50 wt% walnut shell flour were similar each other. The tensile strength of the specimens filled with walnut shell flour were significantly lower than that of the unfilled polypropylene composite

which was 27.8 MPa. Poor adhesion between fillers and polymer matrix is the main reason for the poor performance of tensile strength.

The result indicates that thermal stability of the polypropylene increased with increasing the filler content. The walnut shell flour absorbed more heat energy in the melting of the composites. The crystallinity of the polypropylene (X_c) decreased with the addition of the walnut shell flour. The crystallinity (X_c) of unfilled polypropylene was found to be 37.7%. As 40 wt% walnut shell flour was added into the polypropylene the X_c decreased 33%. The increment in the filler content up to 50 wt% did not significantly change the X_c (32.2%) of the polypropylene but further increment in the filler content (60 wt%) caused a noteworthy decrease in the X_c (28.2%).

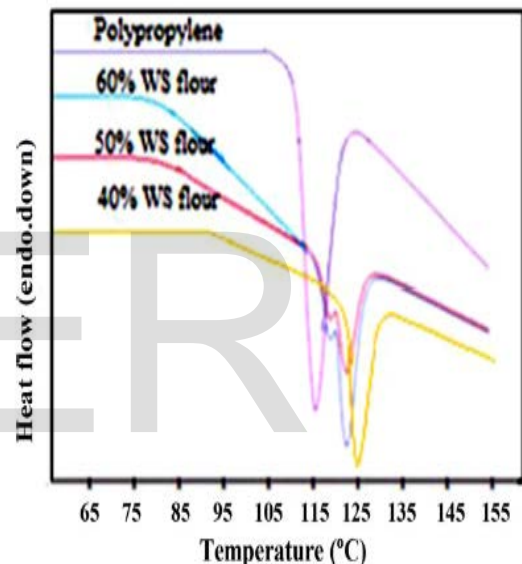


Fig.13. The crystallization peak temperatures of unfilled and walnut shell flour filled polypropylene composites. [15]

The flexural and tensile modulus of the polypropylene composites were noticeably improved by the addition of walnut shell flour while the flexural and impact strengths decreased. The thickness swelling and water absorption of the polypropylene composites increased gradually with increasing the walnut shell flour content, but generally lower than polypropylene composites filled with softwood and hardwood flours. The increment in the amount of the walnut shell flour decreased the melting temperature and degree of crystallinity of the unfilled polypropylene composite.

Ayhan onat [16] study, tests demonstrated that glass fiber based warp knitting and walnut shell reinforcements have impacts on mechanical and thermal properties of composite materials. Tests were applied to composite materials in 0° and 90° directions. Results of all mechanical tests are higher in 0° when compared to the results obtained in 90° direction. This difference of values results from different properties of fiber bundles forming the glass based biaxial fabric used in the production. Difference emerging between 0° and 90° directions as a result of these orientation properties is attributed to the biaxial glass based fabric. According to the results obtained from mechanical tests, a decrease in the particle size of the walnut shell used in the production of composite material yields better results. When the particle size is small, a better interface forms between matrix material and resin and, in turn, higher mechanical values were obtained. When heat conductivity results of composite materials were examined, it is observed that a higher heat conduction coefficient DT is obtained, as the particle gets bigger. It is understood from these results that when bigger walnut shells are used, produced composite materials isolate the heat more effectively. This better heat isolation can be attributed to the fact that more big walnut shell is found per unit area than small walnut shell as a result of the growth in particle size. In line with the results of this study, use of walnut shell that is a waste material in the composite materials in small particle sizes will make a positive contribution to mechanical strength. Use of big walnut shells yield better results in the fields of application where thermal isolation is sought.

4. Conclusion

In the present review paper we have discussed how the mechanical properties increased upon the addition of walnut shell powder as reinforcement. Different proportion of walnut shell powder corresponds to different mechanical properties. For example the tensile strength increases upon increasing the proportion of walnut shell powder but the water absorption property may decrease. Grain size of walnut shell powder may be varied for enhancing the mechanical properties of composite.

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