Walnut Shell Particulates as Filler Material in Polymeric Matrix: A Review

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Abstract— Recently, natural fillers have become attractive and potential reinforcement material in polymeric matrix composites among the academic researchers and scientists all across the world. The reasons for such attraction are multiple which include low cost, large availability and easy processing as they are not as hard like synthetic fibers/fillers. But the main reason of interest is the environmental awareness and growing concern with the greenhouse effect. Natural filler or fiber has added advantage of being renewable and bio-degradable. Rigorous study has been conducted on different natural fillers. Among all the natural fillers explored by the researchers, it was found that relative less work has been conducted on walnut shell powder as filler material in polymer composites. Therefore, there is an ample opportunity available to explore this material as filler in different types of polymers. Hence, this study comprises of a background of recent work done on utilization of walnut shell powder as filler material to provide database to the researchers which may help them to progress their work in the specified direction.

Keywords— Natural filler, polymer composites, Walnut Shell Powder.

I. INTRODUCTION

Polymers have several advantages over other materialsmainly because of its unique combination of hydrogen and carbon atoms. This combination makes polymer very versatile and highly durable to heavy sunlight in summers, very low temperature in winters and humidity in rainy season. Also they are not affected by any microorganism and have a long life span. With all this properties, petroleum based plastics has been used in various applications especially where strength is not of much concerned [1]. But the widespread utilization of plastics has created severe environmental, economic and social problem. Finding disposal sites for plastic based material is of great challenge [2]. But still usage of plastic is not at all avoided as they had become the integral part of our life. Hence, lot of work has been done to reduce its consumption.

Also neat polymers have several limitations owing to its various properties. Hence they do not usually found practical application in different field. Therefore, proper reinforcing materials are added into the polymers to make them feasible for large number of diverse applications and also consumption of plastic will be reduced to a great extent. In general, earlier, different types of synthetic fibers like glass fibers, carbon fibers or aramid fiber were used as reinforcement in polymers. All this fibers successfully provides high stiffness with increases mechanical properties to polymers. Also, the reinforced polymer show high strength to weight ratio as compared to conventional material used for construction purpose like wood, steel and cement. Apart from various advantages, the usage of synthetic fibers declined as they are costly with high processing cost and added disadvantages of adverse effect on environment [3].

With this problem, there has been a renewed interest in natural fibers as a substitute for glass, carbon, andother synthetic fibers. Increased application of biodegradable materials in the form of fibers, particulates or their combinations as reinforcement material in polymeric matrix has been seen from last one decade. Natural fillers/fibers as discontinuous phase offer various advantages over other conventional or synthetic fillers and fibers. The various financial, technical and ecological benefits provided by natural fillers are low cost, easy availability, easy processing, high strength to weight ratio, biodegradability and eco-friendly nature [4]. Lot of studies has been reported on natural fibers which include jute fiber, sisal fiber, hemp fiber, kenaf fiber, coconut fiber, flax fiber and coir fiberfrom last so many years. Reinforcing potential of natural filler is also growing interest among the scientific community. Among the various natural filler, shell of edible nuts crushed in the form of powder has grown interest from past few years. In this contest, peanut shell, almond shell, coconut shell, hazelnut shell and walnut shell are of interest. Among the various shell powder used as filler material in polymeric resin, it has been found that walnut shell has been a less explored area. Hence, in this paper, a review of past research works on walnut shell as filler material in polymeric resin is reported.

II. WALNUT AND ITS SHELL

A walnut is an edible nut belongs to the Juglandaceae family. It belongs to the category of dry fruit and is mainly cultivated because of its edible kernel.The fruit of walnut consist of four main parts i.e. kernel, skin, shell and green husk. When walnut fruit is taken from the plant, it consists of all the parts. From the data available it was found that world walnut production is around 3.8 million tonnes per year. China is major cultivator of walnut and capture around 51 % of the total whereas United States, Iran and Turkey are another mass cultivator of walnut. Nutritional value provided by walnut is very high as kernel of walnut consists of 4 % water, 15 % protein, 65 % fat and 14 carbohydrates. It also contains 7 % of dietary fiber. In production center of walnut, skin and green husk is removed and the walnut is forwarded in the market for consumption after few processing. The husk part of the fruit has already been utilized which is compiled by Esfanlan et al. in one of their review work [5].The walnut shell is broken to take out the edible kernel and the shell remains is the waste product which is normally thrown away. The proportion of kernels to shell varies in between 45 to 55 %. It means a major part

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of walnut consist of its shell by weight. This walnut shell is tough, all natural and eco-friendly and is generally disposed as waste material in our household. This walnut shell is brown in color and has low specific gravity varies in between 1.2 to 1.4. It has flash point of 193 ^{o}C and free moisture content of 3-9 %. Hardness of this shell is in the range of 190 BHN, With this physical properties, the crushed shell has found wide variety of applications like in industrial blasting, parts cleaning, paint stripping, coating removal, deflashing, deburring, tumbling, filtration and cosmetics. But it has not been properly explored as filler material in polymeric composites. Utilizing the walnut shell as filler in the preparation of polymer composites is one of the possible uses that need to be further explored. The chemical composition of walnut shell fibers includes ash (3.4%), lignin (50.3%), hemicelluloses (22.4%), and cellulose (23.9%). Due to the lower quantities of hygroscopic components and greater quantities of hydrophobic components in walnut shells compared to wood, polymer-based composite materials containing walnut shell fillers have significant commercial benefits in outdoor products requiring high environmental resistance, such as flooring or fencing. Few works has been done using the powder of walnut shell as filler material and the same is discussed in next section.

III. WALNUT SHELL FILLER POLYMER COMPOSITES

The work performed by different researchers with combination of walnut shell powder as reinforcement in polymer matrix is discussed in this section. Walnut shell as filler material was first introduced by Nitin and Singh [6] in epoxy matrix. They used simple open moulding method for fabrication of composites. They incorporated maximum up to 40 wt. % of filler material in epoxy matrix. They evaluated the density, ultimate tensile strength, modulus of elasticity and percentage elongation before break in their study. From there analysis, they found that the density of the composite decreases with increase in filler content and this reduction is marginal for low filler content up to 30 wt. %. With further increase in the content of filler, they observed sharp decrement in the value of density. The minimum density observed in their analysis was 1.06 gm/cm^3. Tensile strength of the combination decreases with increase in the content of filler in their analysis and minimum value of 33.939 MPa is observed for maximum filler content. They explained the decreasing trend in tensile strength is because of the presence of porosity which increases with filler content and due to poor adhesion between the filler and matrix body. Similarly, modulus of elasticity also decreases with filler content where percentage elongation increases after the filler content increased beyond 20 wt. %.

On a similar note, Srivastava et al. [7] developed epoxy based walnut shell powder composites by open mould technique but they evaluated the water absorption behavior and compressive nature of the developed material. In their analysis they found that the water absorption capacity increases with increasing content of walnut shell particle. They observed such resultdue to the hydrophilic nature of the walnut shell. Compressive strength of the composite is a function of filler content in their analysis. With increase in filler content, compressive strength increases. They further observed that maximum increment in compressive strength is obtained when filler content increases beyond 20 wt. %. They reported that the ultimate compressive strength possesses the highest value of 50 MPa at 30 wt% of walnut particles.

Again, a walnut shell particle in epoxy matrix is further explored by V.K. Singh [8] where they studied the mechanical behavior of the combination. They fabricated four different sets of composites with 25 wt. % to be maximum. In mechanical behavior, they focused on almost all important mechanical properties which include tensile strength, compressive strength, hardness and flexural strength. In their analysis, tensile strength and modulus of elasticity drastically decreased when content of walnut shell particles increased. When filler content increases from 10 wt. % to 40 wt. %, a decrement of 36.2 % and 34 % is observed in tensile strength and modulus of elasticity respectively. Similar decreasing trend is observed for compressive strength as well where 48.2 % reduction is registered for similar content of filler. Though, modulus of elasticity under compressive loading situation increases by 51.5 %. Walnut shell being hard in nature increases the hardness of the composites when incorporated. They reported 59.4 % increment in the hardness which is an appreciable outcome. As far as flexural strength is concerned, it reduces with increase in filler content and decrement of 42.9 % is registered in their analysis.

Scichenget. al [9] studied the wear behavior of hybrid composite in which they used two reinforcing material, one is walnut shell powder and another one is jute fiber in phenolic resin. They fabricated the composites by keeping the content of jute fiber constant. They used alkali surface treatment of the filler material before incorporating it in matrix to improve the adhesion between filler and matrix phase. In their analysis, they found that the weight loss rate reduces with increases in walnut shell content. The behavior shows that walnut shell act as anti-wear element which reduces the wear rate of the composite body. The effect of walnut shell particles in friction formulations was proved to be very advantageous in stabilizing the coefficient of friction of studied friction materials, as well as improving wear resistance

Pashaei et al. [10] used polyvinyl ester as matrix material with walnut shell powder and fabricated the samples using in-situ polymerization technique. They studied the mechanical and sliding wear behavior of the fabricated samples. In their study they noticed that the tensile strength as well as the modulus of elasticity increases when the filler were incorporated. This proves that with addition of filler, there arises an effective and uniform stress transfer within the composite. Also, composite with 10 wt. % WSP loading indicated better tensile strength and modulus as compared to other composites. Also, with increase in filler loading, the hardness of the composites increases. The parameter used for studying sliding wear behavior was applied load, sliding velocity and the size of abrading. Wear study shows that the wear volume loss increases with increasing abrading distance/load. The increase in wear loss at higher load may be due to thermal softening. Furthermore, the observed wear loss decreases as the walnut shell powder content in the composites increases. It was found that WSP filled vinyl ester composites exhibit lower wear rate and higher coefficient of friction as compared to vinyl ester green composites. Composite with 10 wt. % filler has the lowest specific wear rate and coefficient of friction.

In their other analysis, Pashaei et al. [11] modified the walnut shell powder using silane coupling agent and fabricated the composite with polyurethane matrix. They studied the physical, mechanical and thermal behavior of the fabricated samples. From the analysis of mechanical results, they observed that incorporation of walnut shell powder component improves the surface hardness, tensile strength, elongation at fracture and tensile modulus of the resulting systems significantly. DSC analysis shows that glass transition temperature of the samples increases with increase in the content of the filler. From TGA thermo-grams of fabricated samples, it was found that filled composites are thermally stable at high temperature as compared to unfilled one.

In a more recent work, Lala et al. [12] used epoxy as base matrix with walnut shell powder as filler material. They studied the mechanical property of the developed material. After successful experimentation, they found that the highest value of tensile strength of 36 MPa was observed for 5 wt. % of filler content whereas maximum value of compressive strength of 130.13 MPa that is obtained when 10 wt. % of filler were added in epoxy. From there tensile and compressive analysis, they further evaluated the modulus of elasticity and observed 20 and 52 % improvement in modulus under tensile and compressive loading situation respectively. They also studied the water absorption behavior and found that the water absorption rate increases with increasing filler content where it is lowest for 5wt. % of filler and maximum for 20 wt. % filler. Finally on the basis of their analysis, they suggested that the improved composite may be use in the replacement of conventional wood products and plies.

In a most recent work, Salasinka et al. [13] again used a combination of epoxy and walnut shell powder. They studied the mechanical and thermos-physical behavior of the developed material. Under mechanical behavior, they studied tensile strength, impact strength and hardness whereas under thermos-physical study, they performed dynamic mechanical thermal analysis (DMTA) and thermo-gravimetric analysis (TGA). From the various experimentation done by them, they concluded that, stiffness and hardness of the composite increases with filler content, whereas, tensile and impact strength decreases with filler content. Dynamic mechanical thermal analysis showed a growth in the composite stiffness at elevated temperatures as a function of the increasing natural filler content. From TGA, it is clear that filled composites have much higher thermal stability as compared to unfilled one. It has been further found that the most encouraging filler content for developed walnut shell reinforced Epoxy composites was 30 wt. %.

IV. CONCLUSIONS

Research on walnutshell powder reinforced polymer composite is yet to be explored as till date very little work has been reported as seen from the past work. But in recent time, researcher started working on it as a lot of scope is available owing to its outstanding properties and environmental deliberations.

From the studies conducted so far by different researchers, it has been seen that inclusion of walnut shell powder enhance different properties of the polymeric composites. The various properties evaluated by different researchers are physical, mechanical, thermal and wear properties. It has been further observed that walnut has capability to substitute conservative materials or synthetic fillers as reinforcement in different types of polymer composites.Overall, the use of walnut shell powder reinforced composite can aid to produce professions in both urban and rural areas; in addition to help out to lessen waste, as well as providing to a better circumstance. Nevertheless, by observing at the future anxieties, further decisive studies are essential on manufacturing processes and product commercialization, particularly for bulky scale finish products.

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