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A Review on Mechanical and Tribological Properties of Epoxy Resin, SiO₂, TiO₂, BaSO4, Al₂O₃, CaO, MgO, K₂O, Na₂O, Fe₂O₃ Reinforced with Basalt Fibres

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Abstract: In modern years, both industrial and academic world are focussing their attention toward the development of sustainable composites, reinforced with natural fibres. In particular, among the natural fibres that can be used as reinforcement, the basalt ones represent the most interesting for their properties. The aim of this review is to illustrate the results of research on this interesting subject. In the introduction, mechanical, thermal and chemical properties of basalt fibre have been reviewed. Moreover, its main manufacturing technologies have been described. Then, the effect of using this mineral fibre as reinforcement of different matrices as polymer for thermoplastic and thermoset, metal and concrete has been presented. Furthermore, an overview on the application of this fibre in biodegradable matrix composites and in hybrid composites has been provided. Finally, the studies on the industrial applications of basalt fibre reinforced composites have been reviewed.

Keywords : Basalt fibre, epoxy resin, reinforcement, fillers, tensile strength.

1.Introduction

Natural fibres are now considered as a serious alternative to glass fibres for use in composite materials as reinforcing agents. The advantages of natural fibres over glass fibres are their low cost, low density, high strength-to-weight ratio, resistance to breakage during processing, low energy content and recyclability [1]. Since they are waste, the utilization of natural fibres as reinforcement for polyester composite is a best ecoreusing technique [2]. Natural fibres can be divided into two groups: natural fibres, which are available in a fibre form, and fibres with a natural origin that are artificially produced from natural raw materials. Currently, glass fibre is the typical reinforcing material for polymer composites. Carbon fibre is used when there are more specialised and greater requirements (e.g., space technology, the aircraft industry, military applications and sports). However, carbon fibre's production costs are one order of magnitude greater than those of glass fibre, and adhesion between carbon fibres and the matrix is also more diffi- cult to achieve [3]. Natural fibres like flax, sisal, coir, hemp, etc. are becoming more popular because it has satisfactory strength properties along with a relatively low price and good biodegradability. A disadvantage of these fibres is that the consistency of the fibres cannot be guaranteed; they are sensitive to the moisture content of the environment, and they do not adhere well to a polymer matrix under moist conditions [4]. Considering that the fibre market is very competitive and that the economic and environmental requirements imposed on plastic structural reinforcing elements are increasing, the applicability of newer fibres is being examined in leading research institutes throughout the world. Basalt fibres which extracted from common volcanic rock could be a good option for reinforcing with polymer matrices [5]. Its chemical composition is closely similar to glass; its basic components are SiO2, Al2O3, CaO, MgO, K2O, Na2O, Fe2O3 and FeO [6]. Thus, over the last few years, intensive research has begun on the applicability of basalt fibre as a reinforcing material for polymers. Its melting temperature ranges between 1350 and 1700 C. When cooled slowly, basalt solidifies as a partially crystalline structure. Basalt fibres can be used from 200 to 600 C without any significant loss of mechanical properties [7,8]. To enhance fracture toughness, basalt fibres were introduced into concrete composites by Dias and Thaumaturgo [9]. Sim investigated the durability and mechanical properties of basalt fibres strengthening structural concrete [10]. Studies on the use of basalt fibres as reinforcements of polymer composites have focused mainly on polypropylene and epoxy resin matrix composites [11–16]. The polyester resin could be used for reinforcement due to its advantages like cost effective, easiness in processability, lower density, etc. Generally, surface modifications enhance the mechanical properties of fibres. In the past, there have been few studies on the surface modification of basalt fibre; however, the good chemical durability of basalt fibre has been mentioned in several articles. Most researches focus on the applicability, mechanical performance and interfacial properties of basalt fibre reinforced polymer composites [9, 11–14] but pay little attention to surface modifications.

Hybridization is a commonly used procedure to obtain properties, which are intermediate between the two originating materials. Dealing with polymer composites, hybridization may result in a compromise between mechanical properties and cost to meet specified design requirements, as one of the reinforcements is usually cheaper than the other one. A number of studies have been performed recently, which suggest that mechanical properties can be possibly tailored using hybridization based on glass or basalt fiber laminates and including other natural (aiming at a more sustainable material) or synthetic fibers. In particular, with respect to plant fibers, which equally show thermal and acoustic insulation properties, the higher specific weight of basalt fibers (around2700 kg/m³) is widely compensated by their higher modulus, excellent heat resistance, good resistance to chemical attack and low water absorption. This suggests that hybrid laminates, based on basalt fibers and plant fibers, and/or glass–plant fiber hybrid laminates, the latter being particularly studied when it comes to the need for sufficient impact resistance, may have some interest. This would possibly result in a more sustainable end-of-life scenario without substantially affecting the structural performance of the laminates.

As a matter of fact, hybridization of basalt fibers has been attempted with ceramic fibers, to provide improved hot wear resistance to friction materials, with high tensile strength fibers, such as carbon and aramid, and with glass fibers. In these cases, basalt provided an impact and environmental resistance superior to that provided by the corresponding hybrids with glass fibers, coupled with a substantial reduction in costs, with respect to carbon and aramid fiber composites. In the case of basalt/Nylon fibers hybrid laminates, low tensile modulus of Nylon is improved by adding basalt fibers, whilst Nylon provides conversely a higher impact resistance. Also basalt hybridization with glass fibers has been attempted, which is based on the use of two fibers, which are chemically not very different. Basalt fibers possess good tensile strength [17]. The Figure1 shows the basaltfiber



Figure 1.Basalt Fiber

Though Basalt fibers tensile strength is higher than other fibers but still increase in basalt fiber's tensile strength will give more applications to basalt fiber like post-earthquake strengthening, bridges, underground tunnels etc. Moreover reducing the wear resistance, friction coefficient, and increasing the hardness also gives more applications to basalt fiber. Thus to increase its tensile strength we are adding Titanium oxide and Aluminium oxide to basalt fiber in proportion of 5% weight [19]. We are also adding Barium sulphate to basalt

fiber in 5wt%, we are also adding Silicon carbide in 5wt% to increase the hardness [18] and we are also adding 2wt% of graphite to reduce coefficient of friction [20].

Basalt originates from volcanic magma and flood volcanoes, a very hot fluid or semifluid material under the earth's crust, solidified in the open air. Basalt is a common term used for a variety of volcanic rocks, which are gray, dark in colour, formed from the molten lava after solidification. Basalt rock-beds with a thickness of as high as 200 m have been found in the East Asian countries. Russia has unlimited basalt reserves. There are large deposits of these rocks in the Ural, Kam, chatka, Far East, Sakhalin, Kola Peninsula, Northwest Siberia, and the Transcaucasia. Basalt fiber is a material made from extremely fine fibers of basalt, which is composed of the minerals plagioclase, pyroxene, and olivine. Plagioclase is an important series of minerals within the feldspar family. The pyroxenes are a group of important rock-forming inosilicate minerals found in many igneous and metamorphic rocks. In silicates (from Greek, fiber), or chain silicates, have interlocking chains of silicate tetrahedra with either SiO3, 1:3 ratio, for single chains. Igneous rock is formed through the cooling and solidification of magma or lava.

Metamorphic rock is the result of the transformation of an existing rock type, the protolith, in a process called metamorphism, which means "change in form". The mineral levels and chemical makeup of basalt formations can differ significantly from location to location. Moreover, the rate of cooling, when the original flow reached the earth's surface, also influenced the crystal structure. Its ready availability from mines and open-air quarries around the world, only a few dozen locations contain basalt that has been analyzed and qualified as suitable for manufacture of continuous thin filaments. Basalt formations in the Ukraine are particularly well suited to fiber processing.

2. Mechanical Properties

The effect of basalt fibre on physical and mechanical properties of concretes was also evaluated by several authors. To this aim, ten mixtures were prepared by incorporating different amounts and sizes of basalt fibres. The mechanical characterization showed that improvements of flexural strength, fracture energy and abrasion resistance can be obtained by using basalt fibre even at low contents. The inclusion of basal fibre in concrete resulted in a decrease of the compressive strength. It was shown that the flexural modulus of the composites depends on their composition according to a rule of mixture, while an important synergistic effect is detected for the ultimate flexural properties. Moreover, the Charpy impact tests evidence a strength increase with increasing of basalt and glass fibres content. In particular, the hybridization with basalt fibres promotes an increase of the adsorbed impact energy due to an enhancement of the fracture propagation component.

Basalt Rock fibers have no toxic reaction with air or water, are non-combustible and explosion proof. When in contact with other chemicals they produce no chemical reactions that may damage health or the environment. It has good hardness and thermal properties, can have various application as construction materials. Basalt is a major replacement to the asbestos, which poses health hazards by damaging respiratory systems. Basalt base composites can replace steel as light weight concrete can be get from basalt fiber. As it is made of basalt rock is really cheap and has several excellent properties[21-23]. The major advantages of Basalt fiber are

- 20-25% higher tensile strength than E-glass [24]
- 10-15 % higher tensile modulus than E-glass [25]
- Better chemical resistance than regular E-glass
- Extended temperature range up to 580°C
- Environmental friendliness and easy recycling/disposal of basalt-fiber-reinforced plastics (BFRP) compared to GFRP [26]

Basalt is a natural material that is found in volcanic rocks originated from frozen lava, with a melting temperature comprised between 1500 and 1700 C [27-28]. Its state is strongly influenced by the temperature rate of quenching process that leads to more or less complete crystallization. Perhaps 80% of basalts are made up by two essential minerals; i.e. plagiocene and pyroxene. Analyzing the chemical composition it is possible to observe that SiO2 is the main constituent and Al2O3 is the second one [27, 29, 30]. Several authors reported the typical composition, as identified by Militky et al. [27] and Deak et al. [29].

Basalt fibre, which was developed by Moscow Research Institute of Glass and Plastic in 1953e1954, is a high-tech fibre invented by the former Soviet Union after 30 years of research and development, and its first industrial production furnace that adopted 200 nozzles drain board combination oven bushing process was completed in 1985 at Ukraine fibre laboratory [31]. The base cost of basalt fibres varies in dependence of the quality and type of raw material, production process and characteristics of the final product. As the cost, the chemical and mechanical properties depend from the composition of the raw material. Differences in terms of composition and elements concentration give difference in thermal and chemical stability and more or less good mechanical and physical properties [32].

Overall, the manufacturing process of this kind of fibre is similar to that of glass fibre, but with less energy consumed and no additives, which makes it cheaper than glass or carbon fibres. Using a natural volcanic basalt rock as raw material, basalt fibre is produced by putting raw material into furnace where it is melted at 1450-1500 °C. After this, the molten material is forced through a platinum/rhodium crucible bushings to create fibres. This technology, named continuous spinning, can offer the reinforcement material in the form of chopped fibres or continuous fibres, that can be used in the textile field manufacturing process and have a great potential application to composite materials. In addition to the ability to be easily processed using conventional processes and equipments, the basalt fibres do not contain any other additives in a single producing process, which makes additional advantage in cost [33].

Blowing melt technologies are proposed for the production of short and cheap basalt fibres characterized by poor mechanical properties [29]. Continuous basalt fibres are produced by spinneret method similarly to glass fibres. Recently, Kim et al. [34] proposed melt-spinning method based on dielectric heating in order to produce fibres on laboratory scale.

Even if asbestos and basalt fibres present similar composition, basalt seems to be safe, because of different morphology and surface properties avoid any carcinogenic or toxicity effects, which are presented by asbestos instead [35,36]. In particular, Kogan et al. [37] made rats inhale air containing asbestos and basalt fibres for 6 months. Similar surveys were conducted by McConnell et al. [38] and they also concluded that basalt fibres pose no risk to human beings.

It is known that the fibrous fragments with diameter (d) of 1.5 mmor less and length (l) of 8 mm or greater should be handled and disposed of using the widely accepted procedures for asbestos. Fibres falling within the following three criteria are of concern [39] fibres with diameters lower than 1.5 mm remain airborne and are respirable; fibres with an length to diameter aspect ratio higher than 3 do not seem to cause the serious problems associated with asbestos; fibres durable in the lungs do not cause problems if they are decomposed in the lungs. Since most of nonpolymeric fibres have diameter significantly higher than 3.5 mm but break into long thin pieces, emission of particles, including fibres, occurs during handling. For simulation of these phenomena, the abrasion of basalt weaves was made [27]. The experimental results showed that, because the mean value of fibre fragment diameter is the same as diameter of fibres, no splitting of fibres during fracture occurs. The aspect ratio l/d of basalt fibre fragments is equal to 20.8, higher than the critical value.

Overall basalt fibres show several advantages, which make them a good alternative to glass fibres as reinforcing material in composites used in several fields such as marine, automotive, sporting equipment, civil, etc. In particular, basalt fibres have mechanical properties similar to those of glass ones.

3. Thermal Stability of Basalt Fiber

The good thermal stability of basalt fibres allows applying an additional heat treatment such as partial pyrolysis in nitrogen at high temperatures to a polymer matrix composite, which yields a ceramic matrix composite with enhanced resistance to oxidation. To this aim, polysiloxane resins acts as matrix precursors in several recent works.

Moreover, basalt fibres are non-combustible, they have high chemical stability [30,40], and good resistance to weather, alkaline and acids exposure. Moreover, basalt fibres can be used from very low temperatures about 200°C up to the comparative high temperatures (i.e. in the range 600e800 C) [41-42].

The thermal stability that depend from the composition of the raw material and the presence of a large amount of micro-pores that prevent convection and thermal radiation of the air are reasons to think to use basalt fibres fabrics in thermal insulation and passive fire protection applications [43,44]. In particular, the thermal gravimetric analysis performed by Hao and Yu [44] shows that the mass loss occurs in the temperature range of 250-350° C for both basalt and glass fibres However, the basalt fibre has better thermal stability than glassfibre. The main factor determining the heat temperature stability of basalt fibres is their crystallization behaviour. Crystallization ability primarily depends on fibre chemical composition as well as heat treatment conditions.

In particular, due to its high content of iron oxides, crystallization in basalt fibre begins with oxidation of ferrous cat ions and formation of spinel structure phase on the fibre surface: i.e. divalent cations diffuse from the interior to the surface where they react with environmental oxygen forming nanocrystalline layers likeCaO, MgO, Mg,Fe₃O₄. Moreover, with increasing temperature the crystallization of pyroxene phases takes place on the spinel crystals, which act as nucleation sites. The crystallization of continuous basalt fibre during heat treatment was discussed in details [45,46]. It is worth nothing that the crystallization ability of basalt fibre can be selectively controlled by doping with other elements: for instance, the effect of zirconium oxide on the crystallization and thermal stability of basalt fibres was studied[47].

For the first time, the chemical durability of basalt fibre was studied by Ramachandran et al. as early as 1981 [48]. The authors stated that this fibre has excellent resistance to alkaline attack, but it has poor resistance to acids. The better mechanical behaviour of the basalt fibres than glass ones after corrosion treatments was discussed[49].

4. Manufacturing Methods

The manufacturing methods of basalt fiber is described below[50]

- 1. The major component of basalt fiber and Epoxy Resin.
- 2. Hardener HY951 is used for hardening and support.
- 3. Resin + Hardener are mixed in the ratio of 10:1 and the mixture made up is called
- a. MATRIX.
- 4. Tool is prepared by standard method.
- 5. Apply the matrix on glass cloth which is wrapped around the mandrel.
- 6. Ensure proper weighing is done.
- 7. Clamp the tool die for 2 hrs at ambient temperature condition.
- 8. The sample is then furnace heated at 100celcius for 2 hrs for hardening.
- 9. Take out and cool the specimen until room temp. is achieved.
- 10. Flash is removed from the sample.
- 11. Demoulding i.e. clamp is removed from the specimen.
- 12. Cut to appropriate dimension as per experimental needs
- 13. Emery paper of grade 60 is used to provide necessary surface finish.

5. Tribological Properties

The friction coefficient and wear rate of the pure and filled basalt fabric composites sliding against GCr15 metal disc are compared. It can be seen that the friction coefficient and wear rate of the filled basalt fabric composites decreased compared with that of the unfilled one. It is clear that graphite was more beneficial than nano-SiO2 in decreasing the friction coefficient and increasing the wear resistance of the composites when they were incorporated singly. Besides, it is well worth noting that the further addition of TiO₂, BaSO₄, SiC and graphite to epoxy resin composites can enhance the friction–reduction and anti-wear properties of the basalt fabric composites to a greater extent, which may be ascribed to the positive contribution of nano-SiO2 to the development of a thin and uniform transfer film and the formation of better adhered transfer film on the counterpart steel disc during sliding.

Compared with pure basalt fabric composites, the friction coefficient of Basalt fiber filled with TiO₂, BaSO₄, SiC and graphite decreased. Based on the above results, conclusions can be made that the simultaneous addition of graphite and TiO₂, BaSO₄,SiC effectively improved the friction-reduction and anti-wear abilities of basalt fibre composites owing to the synergistic effects between them

Variations of the friction and wear behaviour of the filled and un- filled basalt fabric composites with load. As is seen obviously, the combination of graphite and TiO₂, BaSO₄SiC was the most effective in

modifying the friction and wear behaviour of the basalt fiber composites under all the tested loads, although the tribological properties of the different composites varied with the loads in different manner. The friction coefficient of the unfilled basalt fabric composites increased with increasing load up to 9 Kgf[51-53]. With the increase in load, more basalt fibers dropped out from the matrix during the friction process, which led to a severe abrasive wear and resulted in a higher friction coefficient. When the load was beyond this range, the friction coefficient decreased owing to the micro-melting and mechanical deterioration caused by friction heat under a higher load. The wear rate of the unfilled basalt fabric composites increased from 3 Kgf to 9 Kgf. With the increase in load, the adhesion between the fiber and matrix deteriorated resulting from the increased flash temperature, which rendered the pulverized basalt fibers pulled out or peeled off easily and the wear resistance of the composites decreased. It also can be seen that the friction coefficient and wear rate of the TiO_2 , BaSO₄SiC filled basalt fabric composites increased when the load was larger than 6 Kgf. In the case of graphite filled basalt fabric composite, its friction coefficient and wear rate decreased remarkably with the increase of load. When TiO₂, BaSO₄SiC and graphite were added simultaneously, the friction coefficient and wear rate of the composites were decreased. With the increase of applied load, adhesive wear took adominant place, which was generally less dangerous for polymer composite sliding surface. The transfer films on the counterpart surface may be of higher quality at higher load compared to that formed at lower load. With the formation of higher quality transfer films, the plowing and scuffing will be abated, and the tribological behaviour was improved [54-56]. Besides, the forming rate of transfer films may be enhanced at higher load, which can shorten the running-in period and is favorable for improving the tribological properties of polymer composites. With further increase of applied load, the newly formed wear debris would come into being a more integrated but thinner layer on the worn surface, which played an important role in improving the tribological properties.

Based on the above experimental results, the BFC/Gr/SiO2 composites were chosen to study the effects of sliding speed on the tribological properties of BFC composites further. It is clearly seen that the composites registered lower friction coefficient and wear rate under high sliding speed than low speed. At high sliding speed, there was not enough time to produce more adhesive points owing to the decreased surface contact time. As a result, the friction force component from adhesion can be greatly reduced and the transfer film can easily form and difficult to rupture. Moreover, the reduction in friction coefficient and wear rate can be contributed to the surface softening caused by frictional heat. It is assumed that, under a small load, the interfacial temperature is a crucial factor determining the tribological characteristics of polymer composites.

Conclusions

Basalt fibres can be considered environmentally friendly and non-hazardous materials. It is not a new material, but its applications are surely innovative in many industrial and economic fields, from building and construction to energy efficiency, from automotive to aeronautic, due to its good mechanical, chemical and thermal performances. Hence, basalt fibre has gained increasing attention as a reinforcing material especially compared to traditional glass fibres.

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