Naman Jain*, Vinay Kumar Singh and Sakshi Chauhan

Review on effect of chemical, thermal, additive treatment on mechanical properties of basalt fiber and their composites

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Abstract: Basalt fiber is emerging out the new reinforcing material for composites. To overcome some of the disadvantages of fibers such as poor bonding to polymers, low thermal stability and high moisture absorption fiber characteristics are modified with chemical, thermal and additive treatments. Chemical treatment corrosive resistance to alkali and acid were investigated which were used to clean and modify the surface of fiber for higher bonding with resins. To improve the thermal stability and reduce moisture uptake thermal treatment such as plasma and non thermal plasma were used which increased the surface roughness and change the chemical composition of surface of basalt fiber. Additive treatment is used to improve the mechanical properties of fibers, in basalt fiber additive treatment was done with SiO_2 additive because of its chemical composition which contains major content of SiO_2. In present investigation review on the effect of different treatment such as chemical, thermal and additive were studied. Effect of these treatment on chemical composition of the surface of basalt fiber and corrosion to acidic and alkali solution were studied with their effect on mechanical properties of basalt fiber and their composite.

Keywords: additive treatment; basalt fiber; chemical treatment; thermal treatment.

1 Introduction

Due to increase in the environmental issue, there was increase in development of biodegradable [1] or green material/composite. Green/bio-composite [2, 3] materials are obtained when both reinforcing material and matrix/resin are biodegradable. Matrix/resin is an adhesive which used to bind the reinforcing material which may be in a different forms such as particle, flakes and fiber. The biodegradable resin is classified as natural (polysaccharides, proteins, polyesters etc.) and synthetic (poly imides [4], poly anhydrides, poly amide-enamines, polyvinyl alcohol etc.). On the other end natural fibers are classified into three basic categories such as vegetable fiber (bast, leaf, seed, wood and grass stem), animal fiber (wool, hair and silk) and mineral (asbestos, basalt and other) as shown in Figure 1. First we extract fiber and polymer from plant then polymerization process to produce synthetic polymer after that composite is manufactured through a different process which has different application after its useful life they are dumped and decompose by the action of microorganisms into form of H_2O and CO_2. In past years, demands of biodegradable composite has been increasing due to environmental impact. In recent year demands of basalt fiber as reinforcement materials was increasing because it is cheaper than glass fiber and has many advantages such as high mechanical strength, high thermal stability, flame retarding and light weight.

Basalt is eco-friendly naturally occurring inorganic fiber obtained from igneous rock in dark color which was developed by rapid cooling of volcano lava. The processing of basalt rock is affected by pressure, temperature and mineral composition. The major study in the field of basaltic magma was done from year 1960. In 1960 Kuno [5] was first to propose that depth of generation control the chemical compositions of different primary magmas [6]. In 1962 Yoder and Tilley [7] experimentally verified the effect of pressure on basaltic composition. The application of basalt rock was been traced from the roman age where it had been used as building and paving material. In 1911 Ribbe [8] get US patent on application of basalt in manufacturing of industrial object. In 1923 Dhe [9] was first to get US patent on extrusion of basalt fiber. US and USSR around 1960 started investigation on basalt fiber for military purpose. There are wide ranges of application of basalt fiber depending upon its properties such as high heat insulator used as thermal shielding, used in storage of radioactive nuclear material as do not absorb radiation, because of high anti-corrosion and anti-frictional it can be used

***Corresponding author: Naman Jain,** Department of Mechanical Engineering, G. B. Pant University of Agriculture and Technology, Pantnagar, India, e-mail: namanjainyati@gmail.com
Vinay Kumar Singh and Sakshi Chauhan: Department of Mechanical Engineering, G. B. Pant University of Agriculture and Technology, Pantnagar, India

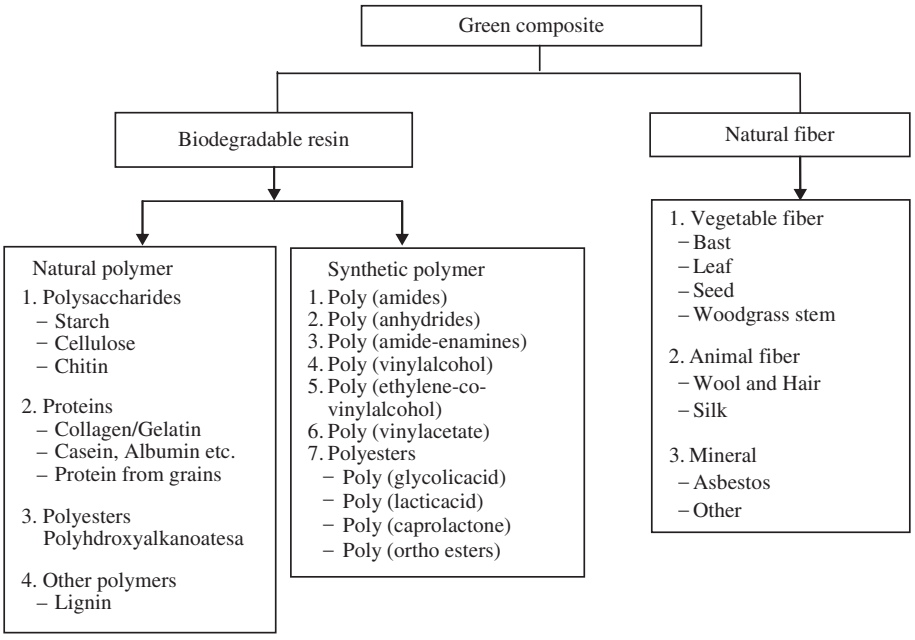

Figure 1: Classification of biodegradable resin and fiber.

for casting equipment and because of high mechanical properties used for structural components etc.

1.1 Chemical composition

Molten stage of basalt rock is obtained between 1350 and 1700°C [10]. Glassy amorphous phase is obtained when cooled rapidly and partially crystalline structure when cool slowly. Basalt rock is silicon-aluminum oxides having major components Mg_2SiO_4 and Fe_2SiO_4 in olivine, and $CaSiO_3$, $MgSiO_3$, $FeSiO_3$, $NaFe^{3+}$ Si_2O_6, $NaAlSi_2O_6CaTiAl_2O_6$, $CaAl_2SiO_6$, and $MgAl_2SiO_6$ as per the studied of Kushiro and Kuno [11]. Classification of igneous rock is based on total alkali silica (TAS) recommended by International Union of Geological Sciences (IUGS) in which igneous rock are classified on the basis of SiO_2 content as basalt (45–52%), andesitic basalt (52–57%) and andesite (57–63) [12]. The major classification of basalt rock is done on the basis of SiO_2 content as acidic basalt (Tholeiites) when SiO_2 content higher than 46% this magma is developed at shallow depth at ocean floor and island arc or continental arc. Mildly acidic basalt SiO_2 content is 43–46% this magma developed at intermediate depth. Alkaline basalt SiO_2 content up to 42% (nepheline basalt) this magma developed at greater depth. In 2016 Chen et al. [12] studied the chemical composition different types of basalt rock shown in Table 1. Comparison of chemical composition of basalt fiber and glass fiber is also shown in Table 1.

2 Chemical treatment

To overcome some of the disadvantages of fibers such as poor bonding to polymers, low thermal stability and high moisture absorption chemical, physical and additive treatments to modify the fiber characteristics. Alkali treatment, acetylation, organic silane coupling and isocyanates are most commonly treatment. In alkali treatment based on NaOH used to clean and modify the surface of fiber. In acetylation acetic anhydride substitute the hydroxyl group in fiber and reduce moisture uptake. Silane and isocyanates are used as coupling agent to improve the interfacial adhesion in natural fiber composite. Different researcher had studied the effect of alkali, acidic and H_2O. On comparing the chemical composition from Table 1 the basic difference is the high percentage of Fe_2O_3 and FeO in basalt as compare to glass fiber which results in density and color (brownish appearance) distinction between glass and basalt fiber, better solubility characteristic, high temperature stability and low heat conductivity.

2.1 Alkali treatment

Resistance to alkali medium depends on the dissolution of SiO_2 network [14] which is effect by hydroxyl group of solution as shown in Equation 1. Alkali treatment on basalt fiber had been studied by different researcher. To

Table 1: Comparison between chemical composition of basalt and glass fiber [12, 13].

Compound	Chemical composition of tholeiite and alkali basalt (wt.%)		Chemical composition of E and S glass	
	Tholeiite basalt	Alkali basalt	E-glass	S-glass
SiO_2	49.64–51.79	47.09–46.45	52–56	64–66
Al_2O_3	13.18–16.54	16.13–16.39	12–16	24–26
CaO	5.35–8.37	8.14–8.99	16–25	0–0.3
MgO	3.61–5.6	7.16–7.94	0–5	9–11
Na_2O	2.24–3.49	6.12–6.6	0.8	0–0.3
K_2O	0.75–1.79	2.04–2.2	0.2–0.8	–
Fe_2O_3	2.78–4.95	8.3–9.13	Less than 0.3	Less than 0.3
B_2O_3	–	–	5–10	–
FeO	4.4–7.11	1.75–0.76	–	–
Other	4.36–7.48	0.39–0.41	–	–

study alkali effect the basalt fiber was pre-treated with acetone then fibers were boiled at different content of NaOH. Scheffler et al. [15] studied the alkali resistance behavior of basalt fiber with time and temperature parameter. Five percent NaOH solution was taking with temperatures 20, 40, 60 and 80 whereas time was varied from 1 to 15 days. A brittle layer of constant thickness was observed as shown in Figure 2 which was partially and completely peeled off in some area. The brittle layer was mainly composed of high content of iron and aluminum oxide. In 2010 Wei et al. [16] study the effect of NaOH on mass loss ratio and strength maintenance ratio by treating basalt fiber with 2 mol/l NaOH solution for 0.5–3 h at boiling temperature. The maximum mass loss occurs at 2 h was near about 7% whereas tensile strength ratio decrease sharply and reaches below 20% after 0.5 h. In 2012 Mingchao et al. [17] studied the effect of alkali treatment on mechanical properties of basalt fiber. In order to determine the corrosion resistance basalt fibers were treated with 2 mol/l NaOH solution for 3 h at boiling temperature. Mass loss is about 4.3% whereas strength of the basalt fiber is decreased by

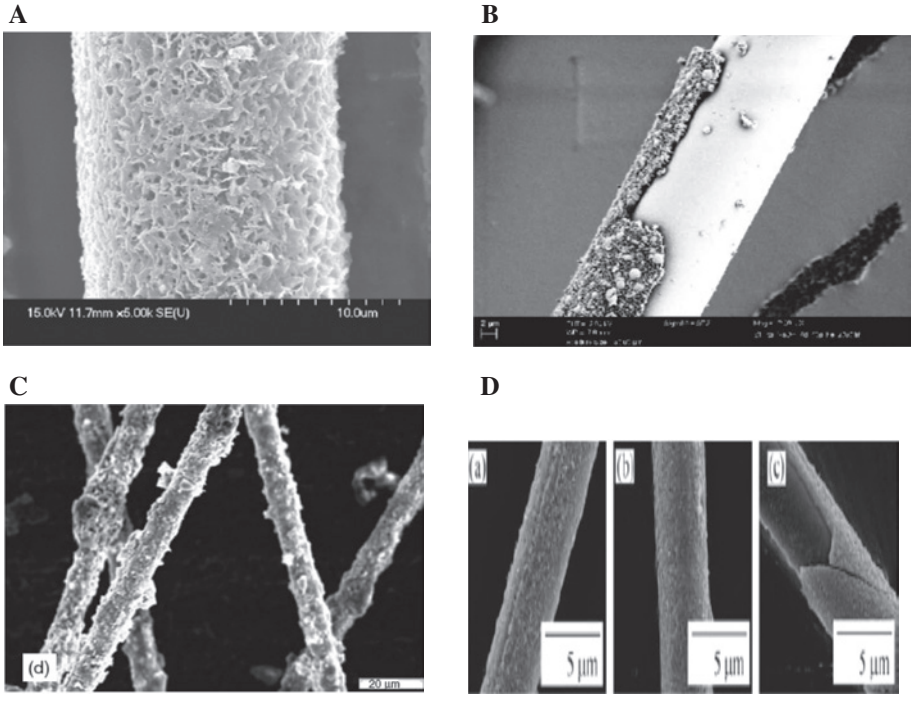

Figure 2: SEM image of basalt fiber after alkali treatment. (A) Treatment with NaOH [16], (B) Treatment with 5% NaOH [15], (C) Boiled with 2 mol/l NaOH [17], (D) 2 mol/l NaOH solution after 1 h, 6 h and 24 h [18].

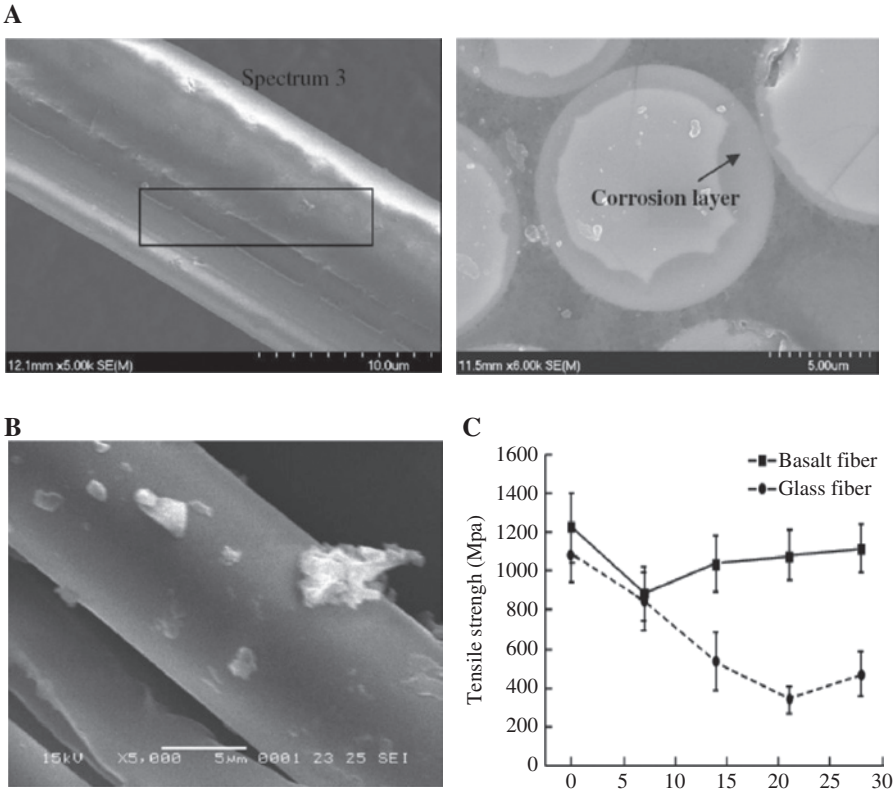

Figure 3: SEM image of basalt fiber treated with acidic solution. (A) Treatment in HCl for 3 h [16], (B) H_2SO_4 treated basalt fiber [19], (C) Strength of basalt fiber after HCl treatment [18].

19.4%. Shuni and Xiaodong [18] treated the basalt fiber in 1 and 2 mol/l NaOH solutions at room and 100°C temperature for different time period. There is about 6% and 8% weight loss occurs for 1 and 2 mol/l NaOH solutions at 100°C, respectively due to dissolution of Si-O and formation of Si-OH gel on surface of basalt fiber. The strength of basalt fiber first decreases rapidly for 1 h, then become constant up to 6 h and then increases for 24 h as shown in Figure 2 for 1 mol/l NaOH. Decreases in strength occur due to leaching of potassium, aluminum and sodium from the surface by NaOH solution whereas magnesium, iron, titanium and calcium were increased.

$$\equiv \text{Si-O-Si} \equiv + \text{OH}^- \rightarrow \equiv \text{Si-OH} + \equiv \text{Si-O}^- \quad (1)$$

2.2 Acidic treatment

Acidic corrosion resistance of basalt fiber is better as compare to alkali treatment because -Si-O- structure is inert to acid. In 2010 Wei et al. [16] studied the acidic resistance behavior of basalt fiber with 2 mol/l HCl acid for 0.5–3 h. The mass of the basalt fiber decrease sharply before 0.5 h and maximum loss was near about 10% and same trend was been shown for strength. The basalt fiber surface was badly affected with acid after 1 h as shown in Figure 3 extension of crack along the longitudinal direction. The concentration of Na, Mg, Al, K, Ca, Ti and Fe is decreases whereas Si content increases from 26.9% to 52.5% after 3 h. Due to increase in percentage of Si the strength of the fiber increases after 1 h. Manikandan et al. [19] in 2012 studied the effect of 1 N H_2SO_4 on basalt fiber and mechanical strength of basalt fiber reinforced unsaturated polyester composite. In acidic treatment the Fe_2O_3 react with sulfuric acid to form ferric sulfate $[Fe_2(SO_4)_3]$ which result in increased in the tensile strength of the composite by 24.15%. As per Shuni and Xiaodong [18] when basalt fiber are treated with 1 mol/l HCl result in replacement of H^- with metals ions of fiber, alkalis such as Ca^{2+}, Al^{3+}, Na^+, K^+ etc. are attracted toward acid as shown in equation 2. Total weight loss was about 4% whereas there was very little decrease in tensile strength of fiber as shown in Figure 3.

$$\equiv \text{Si-OM} + \text{H}^- \rightarrow \equiv \text{Si-OH} + \text{M}^+ \quad (2)$$

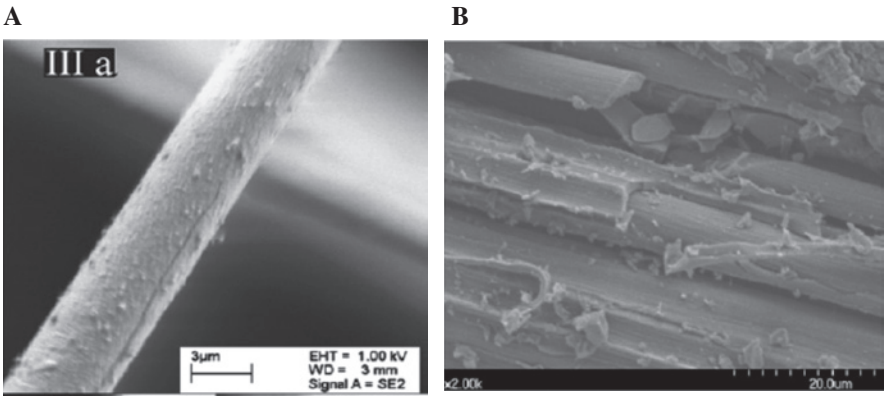

Figure 4: SEM image of basalt fiber after water treatment. (A) BF after water age for 4 weeks [20], (B) BF treated with seawater for 90 days [21].

2.3 Water treatment

Water absorption of basalt fiber is very negligible and exchange of alkali ions was occurs as shown in equation 3. In 2007 Lund and Yue [20] studied the crystallization and surface morphology of BF by chemical gaining in water and humidity environment. After 4 weeks aging as shown in Figure 4 there was relatively increase in some element such as K, Al, Mg and Na as compared to Si. Very small shift in crystallization peak occurs about 12 and 9 K. Wei et al. [21] in 2011 studied the BF degradation in seawater. Mass gain of sample was occurred due to absorption of

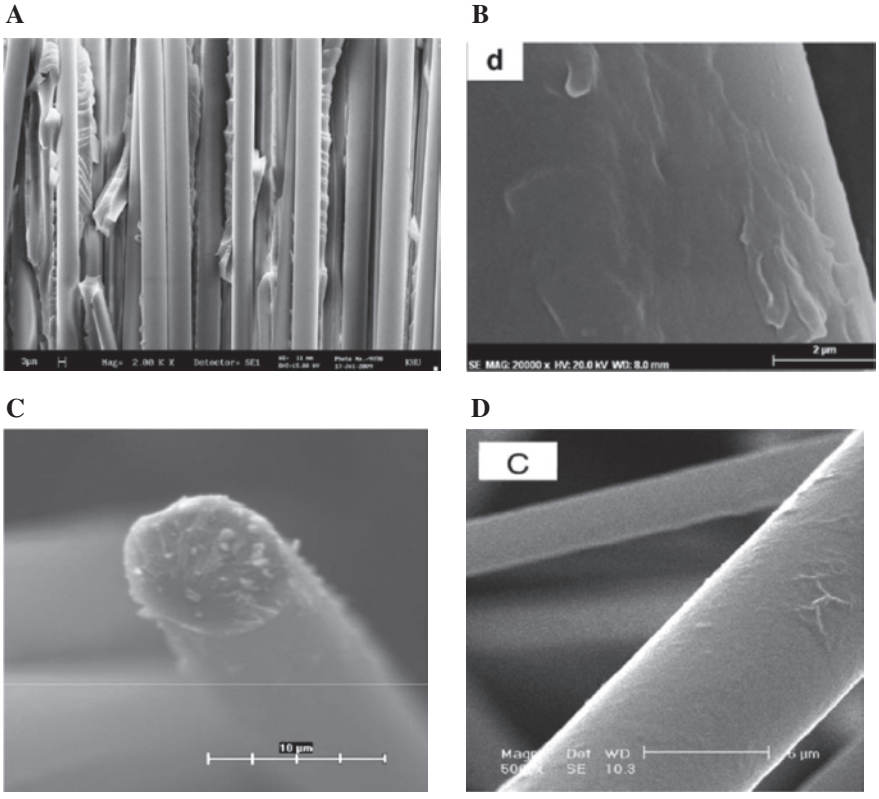

Figure 5: SEM image of basalt fiber and their composite after thermal treatment. (A) Fracture surface after oxygen plasma treatment [24], (B) BF after 4.5 min plasma polymerized [26], (C) BF failure surface treated with 250°C for 60 min [22], (D) BF surface after 10 min plasma treatment [23].

water molecules whereas some compound were extracted by seawater. After 90 day treatment a basalt fiber reinforced plastic (BFRP) decreased as shown in Figure 4. Tensile strength of BFRP composite decreased with increase in treatment time. Color and pH value of BFRP changed from black to ivory-white and 7.1–7.4, respectively. Molecules such as O_2, CO_2 and H_2O and ions such as Cl^- and Na^+ penetrates result in formation of voids and formation of iron oxide by reaction of Fe^{2+} ions with Cl^-, OH^- and O_2. Hydrated layer was formed by compounds such as Ca, Mg, K and Al which was leached out from BF.

$$\equiv \text{Si-OM} + H_2O \rightarrow \equiv \text{Si-OH} + M^+ + OH^- \quad (3)$$

3 Thermal treatment

Thermal treatment such as plasma and corona discharge is been used to increase the surface roughness to improve the bonding [18]. Hydrothermal treatment is used to improve the thermal stability and reduce moisture uptake. Now a day's plasma both thermal and non thermal are used to increase the surface roughness for higher bonding of fiber with polymers. Miliky et al. [22] studied the effect of temperature treatment on failure of basalt fiber and observed that when basalt fiber treated with 250°C for 60 min nonhomogeneities occurs in cross section which was the main reason for failure as shown in Figure 4. In 2007 Wang et al. [23] studied the surface modification of basalt fiber with non thermal plasma (at atmospheric pressure) of oxygen, hydrogen, argon and mixture gases of nitrogen and hydrogen to improve the interface adhesion of fiber with polymer. The different structure units such as $[SiO_4]^{4-}$, $[Si_2O_5]^{2-}$ and $[Si_2O_6]^{4-}$ were obtained with active functional group $-NN_2$, -NH, etc. Kim et al. [24] studied the low temperature oxygen plasma (at atmospheric pressure) treatment of basalt fiber and same structure units ($[SiO_4]^{4-}$, $[Si_2O_5]^{2-}$ and $[Si_2O_6]^{4-}$) were observed as in case of Wang et al. whereas the fracture toughness of basalt/epoxy woven composite was increased by 16%. Gutnikov et al. [25] studied the effect of H_2/Ar atmosphere at 650 and 700°C on basalt fiber. Observation shows that ferric ions were converted into ferrous. The initial ratio of Fe^{2+}/Fe^{3+} was 36/64 and after treatment was 16/84. This result in decrease in glass transient temperature by 12–17°C and crystallization temperature by 57°C. Kurniawan et al. [26] studied the polarization of basalt fiber through atmospheric pressure glow plasma discharge in presence of acrylic acid and their effect on strength of basalt fiber/polylactic acid composite. Result obtained show that surface of basalt fiber gets smoother with increase in APDG plasma and result in formation of ppAA (plasma polymer

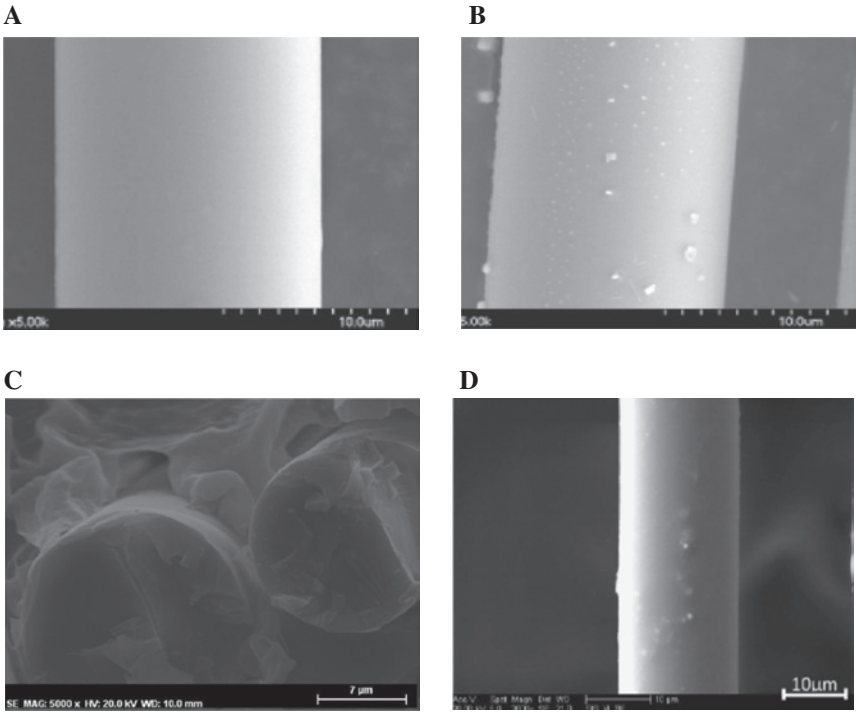

Figure 6: SEM image of basalt fiber after additive treatment. (A) BF untreated (left) and (B) treated (right) with SiO_2 [29], (C) BF/PLA after silane treatment [30], (D) BF treated with 5% SiO_2 [28].

acrylic acid) by shifting in the peak of C=O in FTIR as shown in Figure 5. The strength of composite decreases with increase in plasma time whereas Young's modulus remains constant.

4 Additive treatment

Additive treatments involve solvent exchange or infusing monomer into fiber and polymerizing them in-suit using a catalyst, heat or radiation. The strength of the fiber is increased by interacting it with compatible materials/polymers. In 1993 Jung and Subramanium [27] studied the effect of Al_2O_3 on strength of basalt fiber. The powder of basalt is mixed with Al_2O_3 at 800°C. The mixture was melted at 1325°C and single continuous filament was drawn. The strength of fiber with 2 wt.% alumina additive was higher by 26.18%. Wei et al. [28] strengthen the basalt fiber with SiO_2 and epoxy coating as shown in Figure 6. 5 wt.% concentration of SiO_2 was taken and to studied the interfacial adhesion composite with epoxy was fabricated. The results show that tensile strength of fiber is increased by 30%. Kurniawan et al. [30] studied the effect of silane [γ-glycidoxy-propyltrimethoxysilane (GPS)] on mechanical properties of BF/PLA composite. Treatment was done through diluting GPS in water or methanol based solution. Maximum tensile strength of composite was increased by 25.7% when treated with GPS and water solution for 15 min. increase in strength occur due to formation of more Si-O-Si bonds and reaction of carbonyl group with silane. In 2011 Wei et al. [29] studied the SiO_2 additive treatment on BF and effect on mechanical properties of BF/epoxy composite. Nano-SiO_2 was prepared by stober method. From FTIR analysis it was found that chemical bonding was occurred in SiO_2 and epoxy. Strength of BF increases by 15% at 5% SiO_2 content then decreases again. During treatment, silicon hydroxyl group (Si-OH) reacted with nano-SiO_2 to form -Si-O-Si- result in improvement in network structure which helps in stress transfer and hence strength was improved with increase in SiO_2 results in negative effect by clustering of nano-SiO_2.

5 Conclusion

Alkali and acidic treatment have been done to change the chemical composition of surface so that compatibility of basalt fiber with different resin increased. To improve bonding with matrix surface roughness of basalt fiber has been done by thermal treatment. To prove strength to the basalt fiber additive treatment with SiO_2, Al etc has been done. A review on thermal, chemical and additive treatment has been done to study the interface bonding of basalt fiber. This paper provides an overview on effect different treatment on basalt fiber to improve mechanical, thermal and water absorption properties of basalt fiber and its composites.

References

[1] King MFL, Srinivasan V, Purushothaman T. *Middle-East J. Sci. Res.* 2014, 22 (2), 308–312.
[2] Rahman MM, Netravali AN, Tiimob BJ, Rangari VK. *ACS Sustain. Chem. Eng.* 2014, 2 (10), 2329–2337.
[3] Satyanarayana KG. *J. Bioprocess Biotech.* 2015, 5, 1–12.
[4] Sazanov YN. *Russ. J. Appl. Chem*. 2001, 74, 1253–1269.
[5] Kuno H. *Geol. Soc. Am. Bull.* 1950, 61, 957–1020.
[6] Webber GR. *Earth Planet. Sci Lett.* 1966, 1, 183–184.
[7] Yoder HS Jr, Tilley CE. *J. Petrol.* 1962, 3 (3), 342–532.
[8] Ribbe F. Manufacture of industrial objects from volcanic or other fusible rock, US 1108007 A, 1911.
[9] Dhe P. Filament composed of basalt, US 1438428 A, 1921.
[10] Deák T, Czigány T. *Text. Res. J.* 2009, 79 (7), 645–651.
[11] Kushiro I, Kuno H. *J. Petrology* 1963, 4 (1), 75–89.
[12] Chen X, Zhang Y, Hui D, Chen M, Wu Z. *Compos. Part B* 2017, 116, 53–60.
[13] Jamshaid H, Mishra R. *J. Text. I.* 2015, 107, 923–937.
[14] Friedrich M, Schulze A, Prosch G, Walter C, Weikert D, Binh NM, Zahn DRT. *Mikrochim. Acta* 2000, 133, 171–174.
[15] Scheffler C, Förster T, Mäder E, Heinrich G, Hempel S, Mechtcherine V. *J. Non-Crystall. Solids* 2009, 355, 2588–2595.
[16] Wei B, Cao H, Song S. *Mater. Des*. 2010, 31, 4244–4250.
[17] Mingchao W, Zuoguang Z, Yubin L, Min L, Zhijie S. *J. Reinf. Plast. Compos.* 2008, 27 (4), 393–407.
[18] Shuni Y, Xiaodong Z. *J. Wuhan Univ. Technol. Mat. Sci. Edit.* 2013, 28 (3), 560–565.
[19] Manikandan V, Jappes JTW, Kumar S, Amuthakkannan P. *Compos. B* 2012, 43, 812–818.
[20] Lund MD, Yue YZ. *J. Non-Cryst. Solids* 2008, 354, 1151–1154.
[21] Wei B, Cao H, Song S. *Corros. Sci*. 2011, 53, 426–431.
[22] Militky J, Kovacic V, Rubnerov J. *Eng. Fract. Mech.* 2002, 69, 1025–1033.
[23] Wang GJ, Liu YW, Guo YJ, Zhang ZX, Xu MX, Yang ZX. *Surf. Coat. Technol*. 2007, 201, 6565–6568.
[24] Kim MT, Kim MH, Rhee KY, Park SJ. *Compos: Part B* 2011, 42, 499–504.
[25] Gutnikov SI, Manylov MS, Lipatov Ya V, Lazoryak BI, Pokholok KV. *J. Non-Cryst. Solids* 2013, 368, 45–50.
[26] Kurniawan D, Kim BS, Lee HY, Lim JY. *Compos: Part B* 2012, 43, 1010–1014.
[27] Jung T, Subramanian RV. *Scripta Metall. Mater.* 1993, 28, 527–532.
[28] Wei B, Song S, Cao H. *Compos. A* 2011, 42, 22–29.
[29] Wei B, Song S, Cao H. *Mater. Des.* 2011, 32, 4180–4186.
[30] Kurniawan D, Kim BS, Lee HY, Lim JY. *Polym.-Plast. Technol. Eng*. 2013, 52, 97–100.