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ARAŞTIRMA MAKALESİ / **RESEARCH ARTICLE**

CHARACTERIZATION OF COMMERCIALLY AVAILABLE ALKALI RESISTANT GLASS FIBER FOR CONCRETE REINFORCEMENT AND CHEMICAL DURABILITY COMPARISON WITH SrO-Mn_2O_3-Fe_2O_3-MgO-ZrO_2-SiO_2 (SMFMZS) SYSTEM GLASSES

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ABSTRACT

According to the relevant literature, the utilization of different kind of glass fibers in concrete introduces positive effect on the mechanical behavior, especially toughness. There are many glass fibers available to reinforce concretes. Glass fiber composition is so important because it may change the properties such as strength, elastic modulus and alkali resistance. Its most important property to be used in concrete is the alkali resistance. Some glasses of SrO–MgO–ZrO_2–SiO_2 (SMZS) quaternary system, such as 26SrO, 20MgO, 14ZrO_2, 40SiO_2 (Zrn glass), have been found to be highly alkali resistant thanks to their high ZrO_2 and MgO contents. Previous researches on these glasses with MnO and/or Fe_2O_3 partially replacing SrO have been made with the aim of improving the chemical resistance and decreasing the production cost.

The main target of the present study, first of all, was to characterize commercially available alkali resistant glass fiber for concrete reinforcement and then to compare its alkali durability with those of the SrO-Mn_2O_3-Fe_2O_3-MgO-ZrO_2-SiO_2 (SMFMZS) system glasses. For such purposes, XRF, Tg-DTA, alkali resistance tests and SEM analysis conducted with EDX were employed. According to the alkali endurance test results it was revealed that some of the SMFMZS system glass powders are 10 times resistant to alkali environments than the commercial glass fibers used in this study. Therefore, they can be considered as alternative filling materials on the evolution of chemically resistant concrete structures.

Keywords: Glass fiber, Alkali resistance, Reinforcing agent, Concrete, Characterisation.

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BETON TAKVİYESİNDE KULLANILAN ALKALİ DAYANIMLI TİCARİ CAM FİBERLERİN KARAKTERİZASYONU VE $SrO-Mn_2O_3-Fe_2O_3-MgO-ZrO_2-SiO_2$ (SMFMZS) SİSTEM CAMLARI İLE ALKALİ DAYANIMLARININ KARŞILAŞTIRILMASI

ÖZ

Yapılan literatür çalışmalarına göre, beton içerisinde çeşitli türde cam fiber kullanımı, mekanik özelliklerde, özellikle toklukta, pozitif etki sağlamaktadır. Beton takviyesinde kullanılabilecek çok sayıda cam fiber mevcuttur. Cam fiber bileşimi o kadar önemlidir ki, mukavemet, elastik modül ve alkali dayanımı gibi özellikleri değiştirebilmektedir. Böylesi katkıların betonda kullanımına yol açan en önemli özellik alkali dayanımıdır. 26SrO, 20MgO, $14ZrO_2$, $40SiO_2$ (Zrn camı) cam bileşiminin yüksek miktarda ZrO_2 ve MgO içermesi nedeniyle alkali dayanımının yüksek olduğu tespit edilmiştir. Böylesi camlarla ilgili önceden yapılan çalışmalarda MnO ve/veya Fe_2O_3'in kısmen SrO'in yerine kullanılmasıyla kimyasal dayanımı arttırma ve üretim maliyetini azaltma hedefi gerçekleştirilmiştir.

Bu araştırmanın amacı, her şeyden önce, beton takviyesi için piyasada bulunan alkali dayanımlı cam fiberlerin karakterizasyon çalışmalarını gerçekleştirmek, ardından da $SrO-Mn_2O_3-Fe_2O_3-MgO-ZrO_2-SiO_2$ (SMFMZS) sistem camları ile alkali dayanımını karşılaştırmaktır. Bu amaçla, XRF, Tg-DTA, alkali dayanım testleri ve EDX destekli SEM analizleri yapılmıştır. Alkali dayanım testleri sonuçlarına göre bazı SMFMZS grubu cam taneciklerinin bile kullanılan ticari cam fiberden 10 kat daha fazla alkali dayanımı sergiledikleri görülmüştür. Dolayısıyla, kimyasal dayanımlı beton yapıların geliştirilmesinde alternatif dolgu malzemesi olarak kullanılabilecekleri belirlenmiştir.

Anahtar Kelimeler: Cam fiber, Alkali dayanımı, Takviye malzemesi, Beton, Karakterizasyon.

1. INTRODUCTION

Concrete reinforcement has been a focused area for years. Reinforced concrete is the one, in which some materials such as bars ("rebars"), grids, plates or fibers have been used for reinforcement. Ferro Concrete means; concrete that is reinforced with iron or steel. Also other materials like organic and inorganic fibers, as well as composites in different forms, can be employed for such a purpose. For a strong, ductile and durable construction the reinforcement must have high strength, high tensile strain, good bond to concrete, thermal compatibility, resistance in the concrete environment. Steel rebars mostly have been employed to reinforce concrete, adding strength to the body (Yaprak et. al., 2004; Tuncan et al., 2004).

Glass fibers with high alkali resistance are perfect candidates for reinforcing concrete. The nature and chemical structure of such fibers incorporated into concrete [Glass Fiber Reinforced Concrete (GFRC)] is a key for designing and controlling the final desired properties expected from the composite structure. For instance, it is well known fact that when small amounts of alkali resistant glass fiber are doped into concrete matrix, the chemical resistance, crack resistance and flexural strength of the resulting GFRC are considerably improved (Tuncan et al., 2004; Enfedaque et al., 2010). The SMZS glasses have been studied in detail and their melting behaviour, physical and thermal properties, chemical resistance and crystallisation mechanism were reported (Karasu et al., 2000; Arslan et al., 2009; Karasu, 1994; Karasu, 1999; Karasu, 2002; Karasu et al., 2002a; Karasu et al., 2002b). It was found that when SiO_2 level was reduced to 40–45 wt. %, the melts became very fluid at the lowest melting temperatures used. It has been also mentioned that the glasses could not be made with SiO_2 contents lower than 40 wt. % and there were maximum levels for ZrO_2 and MgO. Most importantly, the glasses containing this level (40 wt. %) of SiO_2 were found to produce the highest chemical resistance against alkali attacks. The most durable glass of this group was Zrn glass ($26SrO.20MgO.14ZrO_2.40SiO_2$ in wt. %). It was pointed out in the previous studies that chemical resistance was impaired by the release of Sr^{2+} ions into the attacking alkali solution and cracking of the protective layer took place (Karasu et al., 2000; Arslan et al., 2009; Karasu, 1994; Karasu, 1999; Karasu, 2002; Karasu et al., 2002a; Karasu et al., 2002b). With replacing strontium by iron or iron plus manganese in the reference Zrn glass composition new glasses being considerably more durable than the Zrn one were produced. Among these, Fe11 glass with $40SiO_2.14ZrO_2.15SrO.11Fe_2O_3.20MgO$(wt. %) exhibited the highest chemical resistance. The experiments, thus, showed that iron and manganese interact in some particularly interesting way to increase the proportion of ferric iron and to reduce Mn^{3+} to Mn^{2+}. These glasses could be important for cement and concrete reinforcement. It is suggested that the production cost of Zrn glass can be effectively lowered by incorporating appropriate levels of transition metal oxides into glasses (as in case of Fe6, Mn3Fe3, Mn5.5Fe5.5 and Fe11 glasses) and the alkali resistance can also be improved.

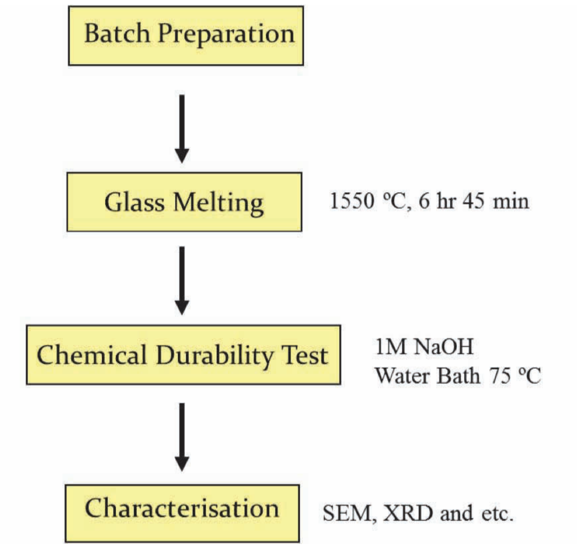
Accordingly, it is clearly stated that the proper choice of the glass fibers, before starting to produce GFRC, is the most significant parameter. Therefore, in the current research, commercially available glass fibers generally used in GFRC structures were characterized in detail to indicate whether or not they were convenient as reinforcing materials through XRF, XRD, DTA-TG, FTIR and SEM-EDX techniques as well as chemical (alkali) resistance test. The overall results obtained exhibited that why a highly alkali resistant system, like the $SrO-Mn_2O_3-Fe_2O_3-MgO-ZrO_2-SiO_2$ one, was really required to produce glass fibers for the evolution of reinforced concrete structures (Karasu et al., 2000; Arslan et al., 2009; Karasu, 1994; Karasu, 1999; Karasu, 2002; Karasu et al., 2002a; Karasu et al., 2002b).

2. EXPERIMENTAL PROCEDURE

During the current research, experimental procedure of which is shown aside, first of all, the chemical composition and surface morphology of commercial glass fibers, and then structural changes after conducted chemical resistance test were determined by using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis.

In the alkali resistance test beside commercially available glass fibers some bulk glasses of the SMFMZS system, in powder form, were investigated by placing the samples in inert sieve pockets and then immersing them into plastic bottles with a 250 ml capacity containing 1 M NaOH solutions with a pH of 14. They were held in a continuously stirred bath at 75 °C. The weights of the samples and the pH values of the attacking solutions were recorded at weekly intervals. Measurements confirmed that the pH value remained at 14 until the end of the alkali resistance tests, which were stopped after eight weeks. The exposed samples were analysed by X-ray fluorescence (XRF Rigaku ZSX Primus), scanning electron microscope (SEM, Zeiss Supra 50 VP at 20 kV) and energy dispersive X-ray spectrometer (EDS; Oxford Instruments, Inca Energy model 7430 with an ultra thin window), to determine whether any kind of crystallisation has occurred, what kind of surface reaction layers formed during chemical resistance testing, and whether any undissolved raw materials remained in the glasses as produced.

The flow chart of experimental procedure:



3. RESULTS AND DISCUSSION

The chemical analysis results obtained by XRF of the commercial glass fibers are presented in Table 1. The compositions of SMZS (Zrn) and SMFMZS system glasses were given in other publications (Karasu et al., 2000; Arslan et al., 2009; Karasu, 1994; Karasu, 1999; Karasu, 2002; Karasu et al., 2002a; Karasu et al., 2002b). The low-magnification secondary electron (SE) SEM image acquired from the commercial fiber was presented in Fig. 1.

Table 1. The chemical composition of commercial glass fibers (wt. %)

SiO_2	57.27
ZrO_2	16.17
Alkali Oxide (Na_2O)	17.84
Earth Alkali Oxide (CaO)	5.70
B_2O_3	0-2
Al_2O_3	0.05
TiO_2	0.09
F_2	0-2

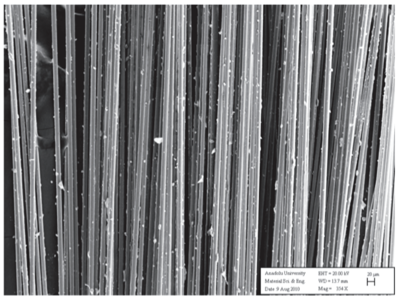


Figure 1. The low magnification SEM secondary electron (SE) image of the commercial glass fibers.

When Fig. 1 examined, at a first glance, it could be seen that the fibers' width was around 10 µm. However, for the sake of the clarity of the fibers' width, SEM-SE image was obtained at a higher magnification and indicated in Fig. 2.

Based on Fig. 1, the commercial glass fibers' width was around 14 µm, and it surface smoothness was determined to have a quite good quality. The results of SEM-EDX analysis carried out with the aim of determining the chemical composition of the commercial fibers are given in Fig. 2 and Table 2.

When Fig. 2(a-b) considered, the commercial glass fiber composition is found to contain O, Na, Mg, Ca, Si and Zr elements. Therefore, based on Fig. 2 (b), the quantities (%) of the relevant elements were calculated as presented in Table 2.

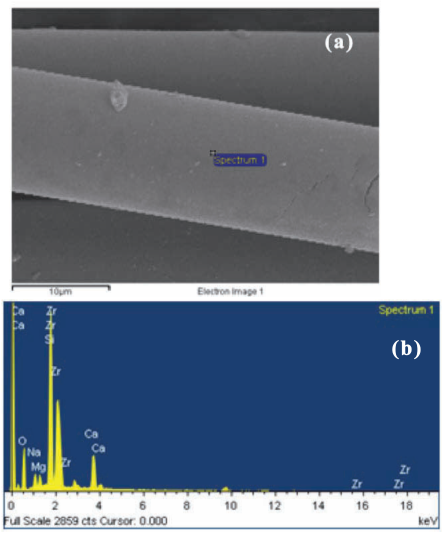


Figure 2. (a) SEM-SE image indicating where EDX point chemical analysis was acquired from the commercial glass fiber, (b) EDX spectrum obtained from the point labeled.

Table 2. % semi-quantitative concentration values of EDX analysis results acquired from a specific point shown in Fig. 2 (a)

Element-Characteristic X-ray Line	Wt. %	Atomic %	Compound %	
Na-K	2.73	3.12	3.68	Na_2O
Mg-K	1.82	1.96	3.01	MgO
Si-K	19.79	18.50	42.34	SiO_2
Ca-K	8.07	5.28	11.29	CaO
Zr-L	29.37	8.45	39.68	ZrO_2
O-K	38.22	62.69		
Total	100.00			

In Fig. 3, based on a function of time, the chemical resistance test results of the commercial glass fibers and the SMFMZS system glass powders depict the linear changes in weight losses.

Considering the results presented in Fig. 3, the polymer coated fiber indicated the highest weight loss values. In other words, it is concluded that the fiber composition exhibiting the worst chemical resistance is un-heat treated fiber. In addition, when heat treatment was applied to the same fiber, no significant change in chemical resistance was observed. This may be explained by high alkali content in the glass composition (11-21 wt. %) (Table 1). It is very well known fact that if high amounts of alkali are incorporated into silica-based glasses, bonds between Si and O are broken and networks are loosened, most probably deteriorating the chemical resistance of the glass (Sinton et al., 2001). In previous studies conducted by Karasu et al. (Karasu et al., 2000; Arslan et al., 2009; Karasu, 1994; Karasu, 1999; Karasu, 2002; Karasu et al., 2002a; Karasu et al., 2002b), Fe and Mn-containing SMFMZS system glasses were reported to possess very high alkali resistance. When a comparison is made between E-glass (Jones et al., 1986) composition and those of the SMFMZS system glass powders, although the former seems to have satisfactory chemical resistance, it displays relatively weak behavior with respect to transition metal, e.g., iron and manganese oxides containing SMFMZS system glasses.

Therefore, the chemical resistance analysis results not only confirmed the findings of previously done studies (Karasu et al., 2000; Arslan et al., 2009; Karasu, 1994; Karasu, 1999; Karasu, 2002; Karasu et al., 2002a; Karasu et al., 2002b), but also strengthened that the SMFMZS system glasses, being free of sodium especially Fe11, Mn5.5Fe5.5 ones, even in the powder form, have ten times higher alkali strength than that of commercial fiber. Optimum amounts of Fe and/or Mn ion additions to the relevant system enhance alkali resistance because of their field strength. The changes in surface morphology and chemical composition of polymer coated and uncoated glass fibers after durability test were determined by a combination of SEM-EDXS.

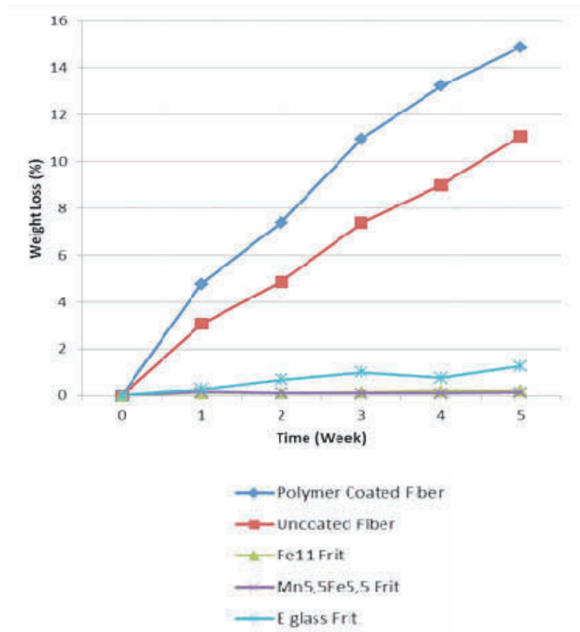


Figure 3. The chemical resistance test results of glass fibers and powders in different compositions.

For this purpose, firstly, SEM-SE images were obtained from the polymer coated commercial glass fibers after alkali resistance test and given in Fig. 4, presenting that the removal of ions from glass fiber due to the severe alkali attack during 6 weeks. Dominantly Na ions leave the body with the reaction given below and the pH level of the solution increases (Shelby, 1997). At the same time by the dissolution of Na ions the weight of glass fiber decreases. This can be more if the composition includes Ca. According to the pH of the environment either pH level rises or dissolution increases, so do the weight losses.

$$Na^{+} + 2H_2O \rightarrow H_3O^{+} + NaOH$$
$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Also, more corrosion in polymer coated glass fiber indicates that the polymer-based coating material on the glass fiber surface is very sensitive against alkali attacks and dissolved in a short time like glass fiber itself as mentioned above. It can also be said that some phase formations on the fiber surface occurred. Similarly, the separation on the fiber surface after chemical resistance test of the uncoated glass fiber (Fig. 5) is an evidence of severe alkali attack, pointing out that the commercial glass fiber was corroded by OH^- ions and the increase in silicon and sodium concentrations on the glass surface shows the dissolution of the glass network (Fig. 5 and Table 3).

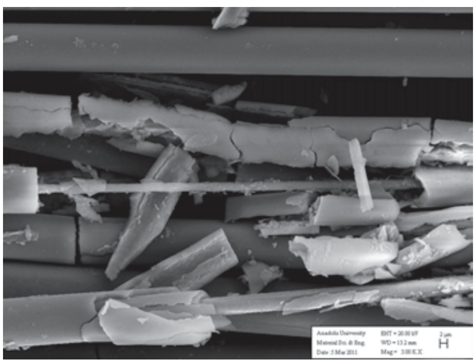


Figure 4. The SEM-SE image of polymer coated commercial glass fibers after alkali test.

Considering Fig. 5 and Table 3 together, the chemical composition of glass fiber, after chemical resistance test, was found to change significantly. Fig. 6 indicates that the layers occurred on the fiber surface after 6 weeks durability test. Each layer exhibits the thickness formed in alkali medium in one week.

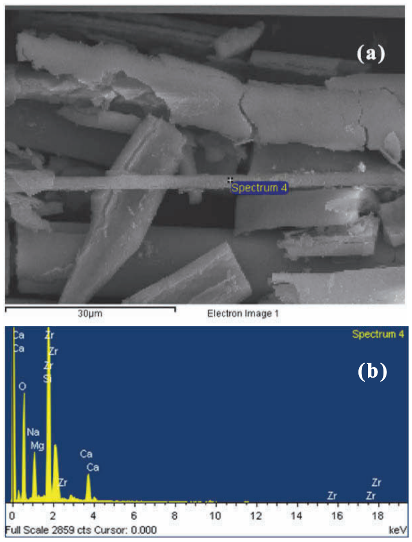


Figure 5. After chemical analysis, (a) SEM-SE image depicting where EDX point chemical analysis was acquired from the commercial glass fiber, (b) EDX spectrum obtained from the point labeled in Fig. 5 (a).

Table 3. The EDX analysis results acquired from a specific point shown in Fig. 5 (a)

Element-Characteristic X-ray Line	Wt. %	Atomic %	Compound %	
Na-K	9.26	9.55	12.49	Na_2O
Mg-K	0.36	0.35	0.60	MgO
Si-K	25.31	21.35	54.14	SiO_2
Ca-K	5.39	3.19	7.54	CaO
Zr-L	18.68	4.85	25.24	ZrO_2
O-K	41.00	60.72		
Total	100.00			

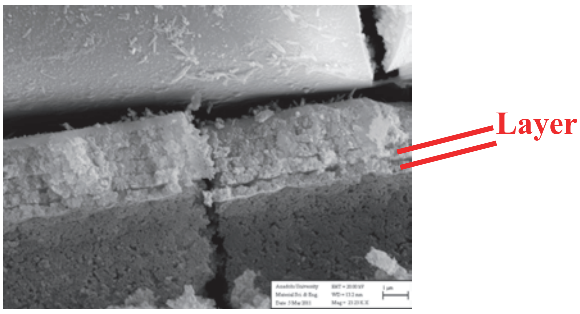


Figure 6. The SEM-SE image presenting the layers occurred after chemical resistance test.

4. CONCLUSIONS

Characterization of commercially available glass fibers revealed that they consist of high amount of Na_2O (17.84 %) in their chemical compositions and also polymer coating of fiber surfaces worsens the alkali durability. Consequently, the SMFMZS system glasses without alkali content show better resistance. Hence, even their powders exhibit more endurance than that of the commercial glass fiber. Finally, it is concluded that the SMFMZS glasses, especially in the fiber form, are thought to be potential candidates for reinforcing the concrete matrix.

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