CONTINUOUS MINERAL FIBRE - A REINFORCING ELEMENT FOR COMPOSITES

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SUMMARY: Properties of continuous mineral fibres and fibre reinforced composites compared to traditional fibreglass are analysed. These fibres have mechanical properties, comparable with S-fibreglass as far as E-modulus is concerned; a higher softening point than E- or Advantex glass and thermal stability up to 600°C. Introducing continuous mineral fibres into composite may cause a very great improvement in thermal and mechanical parameters. In unidirectional continuous mineral fibre reinforced composite on epoxy resin the data of E-modulus varies from 88 to 100 GPa. This makes them compatible with S-fibreglass or Aramid fibre reinforced composites. As a reinforced element of laminates continuous mineral fibres give the composite a more stable dielectric properties compared to E-glass fibres both under wet conditions and at temperatures up to 350°C.

KEYWORDS: mineral, basalt, glass, fibre, reinforcement, elastic modulus, laminate, rebar

INTRODUCTION

Mineral fibres are one of the oldest and most popular materials in the world used for different kinds of insulation, filtration, reinforcement of composites, etc. It may be produced as staple fibres, rockwool or superfine fibres based on eruptive rocks with or without additional components [1-2]. Continuous mineral fibres are about 30 years old and occupy a special place among mineral wool and traditional textile glass fibre due to the method of production and its properties. The idea of obtaining a mineral fibre in continuous form was attractive due to certain advantages in the properties of mineral wool such as thermal and chemical resistance, relative simplicity of mining and world-wide distribution of raw materials, as well as lower pollution and economical benefit. A lot of scientific groups have published and even patented results on production of continuous mineral fibres. In reality it was done either in a laboratory test using a single nozzle fibre forming unit or rock was mixed with other components to meet the requirements of classical glass fibre drawing technology [3, 4]. The first continuous mineral fibres on the base of pure rock were produced in the Ukraine and were brought from laboratory scale to commercial industrial production [5, 6]. At the present time industrial production of continuous mineral fibre is running in the Ukraine and Russia, supplying fibre all over the world. Some new small factories located in Georgia, Turkmenistan and Kazakhstan have already started production and are on the way to a commercial level. Short mineral fibres can be utilized as reinforcement of composites, apart from their main application in the field of insulation. Continuous mineral fibres may also be considered for use in the reinforcement of composites but more in those fields where continuous glass fibre is applied. This paper is a study of the properties of short and continuous mineral fibres compared to some kinds of textile glass fibres used for composites. It also outlines the results in the development of mineral fibre reinforced composites.

PROPERTIES OF MINERAL FIBRES

Continuous mineral fibres are produced without further correction of composition by additives from selected kinds of eruptive rocks such as basalt, diabase, porphyrite, andesite, gabbro, etc. They differ in the composition from short mineral fibres and glass based on them has different thermal-viscous constants, low tendency towards crystallization, fibirising region greater than 50°C, etc. The reason for this is the difference in the chemical and mineralogical composition, especially in iron oxide content. It puts continuous mineral fibres in between short mineral fibres and continuous glass fibres in terms of fibre forming properties. Moreover, mineral fibre properties depend on thermal „history“, and on chemical and phase composition of the initial mineral. Typical compositions useful for production of mineral and glass fibres are shown in Table 1.

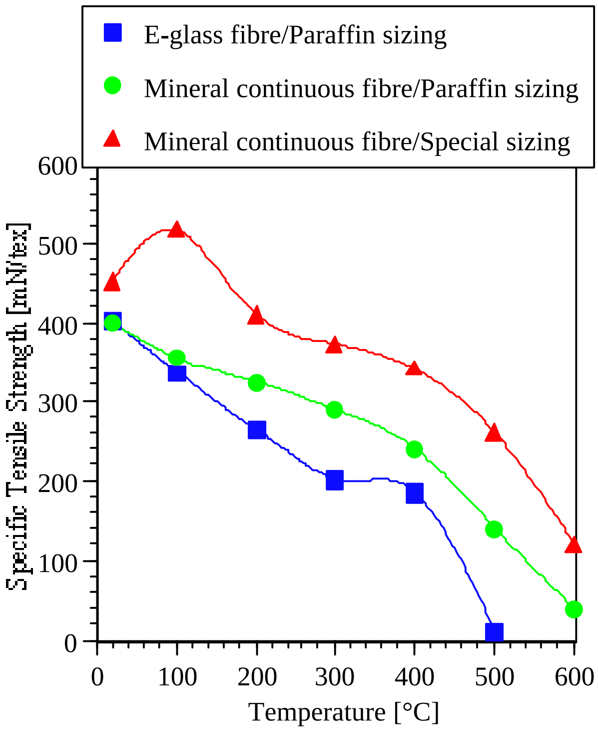
Table 1: Chemical compositions of mineral and glass fibres

Oxide	Basalt wool (Firm Deutsche Basaltsteinwolle)	Continuous mineral fibres (Ukraine)	E-glass [7]	S-glass [7]
SiO_2	46.2	52.43	55.2	65.0
TiO_2	2.3	1.19	-	-
Al_2O_3	13.6	18.33	14.8	25.0
B_2O_3	-	-	7.3	-
Fe_2O_3	12.1	8.97	0.3	tr.
FeO	-	1.56	-	-
CaO	10.1	7.68	18.7	-
MgO	9.3	4.04	3.3	10.0
Na_2O	3.4	2.88	0.3	-
K_2O	1.2	1.07	0.2	-
F_2	-	-	0.3	-
Others	1.8	1.85	-	-

Continuous mineral fibre is manufactured without boron or fluorine and the stage of batch preparation is absent. Therefore, its production needs a smaller furnace than glass fibre and creates no environmental pollutants at all.

Physical-chemical properties of continuous mineral fibres compared to standard glass fibres show an evident advantage especially regarding thermal resistance and mechanical strength (Table 2).

Mineral glass exhibits a higher softening point than E- or Advantex glass which may be advantageous for some applications. Mineral fibre treated in the temperature range of 20°C to 600°C has greater strength than E-glass fibre thread (Fig. 1, a). Mechanical and thermal properties of continuous mineral fibres depend not only on the method of production, but also significantly on the chemistry and nature of the fibre surface. For example, a sizing agent made with regard to the specificity of mineral fibres may improve tensile strength considerably (Fig. 1, a). Differences in the composition of the initial rock may also affect the mechanical properties (Fig, 1, b).



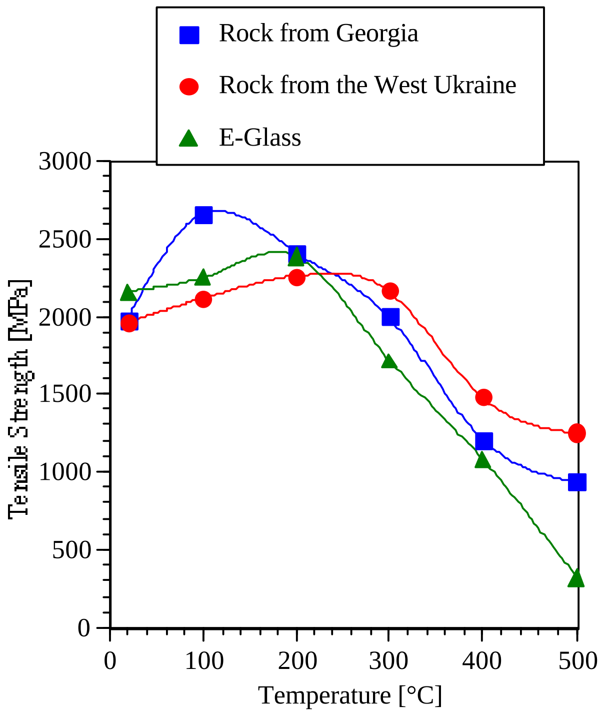


Fig. 1: Thermal dependence of tensile strength of commercially producing fibres (time of exposure-2 hours): a- with different sizing agents [12]; b- from different rocks

Pristine filament strength for mineral fibres produced on a laboratory scale varies from 3495 to 3565 MPa and is comparable to the data for E-glass fibres which have a strength of between 3427 and 3628 MPa. The elastic modulus of mineral fibre depends on the density of the mineral glass and drawing conditions. For mineral glass with a density of 3.05 g/cm^3 the elastic modulus is changed from 91.6 to 93.1 GPa compared with data for monolithic mineral glass equal to 96.7 GPa. Mineral glass with a density of 2.65 g/cm^3 has an elastic modulus equal to 87.3 GPa when it is monolithic glass and for fibres it varies from 82.2 to 83.9 GPa. E-glass has an elastic modulus equal to 82.6 GPa when it is monolithic glass and for fibres it is varied from 76 to 78 GPa. This shows that the tensile strength of continuous mineral fibres is better than or comparable to data for E-glass, Kevlar and Advantex fibres. The elastic modulus for continuous mineral fibre is well over that of E-glass and Advantex fibres and is comparable to that of S-glass fibres. Thermal properties of mineral fibres are promising due to the thermal-viscous nature of mineral glass, the development of corresponding sizing agents and the improvement of the drawing process. They have a decisive advantage over E-, S-fibreglass, Carbon and Kevlar fibre as far as usable temperature is concerned.

Table 2: Physical properties of glasses and continuous glass fibres compared to some advanced reinforcing fibres

Property	E-glass [7, 8]	Advantex [8]	S-glass [7, 8]	Mineral continuous	Kevlar 49 [9]	Carbon HS [10]
Density [g/cm^3]	2.55-2.62	2.62	2.46-2.49	2.65-3.05	1.44-1.45	1.76-1.8
Tensile strength [MPa]	3100-3800	3100-3800	4590-4830	3000-3500	2758-3034	2500-3500
Elastic modulus [GPa]	76-78	80-81	88-91	79.3-93.1	124.1-131.0	230-240
Elongation at the breaking load [%]	4.5-4.9	4.6	5.4-5.8	3.2	2.3-2.4	1.1-1.4
Thermal linear expansion, 20-300°C [°Cx10^6]	5.4	6	2.9	6.5	-	-
Poisson's ratio	0.22-0.24	-	-	0.24	-	-
T_g [°C] ($\eta=10^{13.3}$ dPa s)	640	-	-	660	-	-
Softening point [°C] ($\eta=10^{7.6}$ dPa s)	830-870	916	1056	960	-	-
Liquidus temp. [°C]	1140	-	-	1240	-	-
Fiberising temp. [°C] ($\eta=10^3$ dPa s)	1200	-	-	1340	-	-
Hydrolytic resistance (water) [class, ml 0.01n HCl]	Class 3 (0.27)	Class 3 (0.23)	-	Class 2 (0.18)	-	-
Highest usable temperature [°C][11]	350	-	300	650	250	500

A variety of studies have been performed to investigate and explain the chemical durability of mineral fibres where the test object was short mineral fibre or basalt/slag wool [13]. Particular attention has been given to biosolubility of mineral wool in connection with the suspicion that

it is, like asbestos, harmful to human beings [14, 15]. Continuous mineral fibre has no such problem and can substitute asbestos or mineral wool in certain demanding applications. The chemical composition of continuous mineral fibres and the morphology of its surface differ somewhat to mineral wool because it is produced via a drawing process instead of blowing, as with mineral wool. The surface of continuous fibres possesses fewer defects as well as continuous diameter and respective sizing agents make them more durable in the chemical medium applied. Chemical resistance of mineral fibres is better than for E-glass fibres both in acid and alkali medium. They show high durability in a saturated solution of $Ca(OH)_2$ and cement which may also be improved by selection of a suitable sizing agent.
Electrical properties of mineral glass are relatively low compared to E-glass, which was developed originally for dielectric purposes, but continuous mineral fibres may bring an improvement of dielectric constants when introduced into the composite laminate.

FIBRE REINFORCED COMPOSITES

The properties of textile glass fibres depend mainly on the chemical composition of the glass or initial material used for fibre production. The final properties of composites are also dependent on the chemical composition of fibres. During processing into composites mineral fibres could be treated applying the same procedure and facilities used for fibre glass. A number of composites reinforced with continuous mineral fibres have been developed. Some of them are shown in Table 3 compared to traditional composites.
Continuous mineral fibre shows a high elastic modulus of both filaments and especially as a unidirectional reinforced composite. The data are superior to those for E-glass and S-glass fibres, although tensile strength is slightly below that of S-glass fibre. Laminates based on fabric with simple weaving such as satin produced from continuous mineral fibres show better results. This is also valid for E- and S-glass fibre laminates. Compared to S-glass fibre and Aramid laminates mineral fibre laminates have higher tensile and flexural strength. This kind of advantage may suggest the possibility of applying continuous mineral fibres in the reinforcement of special vessels or elements working under high pressure, chemical and thermal stress and as an element of composites used for dielectric purposes.
As a reinforced element of composite for application in the production of printed circuit boards (PCBs) continuous mineral fibre gives a special stability of the dielectric parameters to fibre laminates. They may be made using various binder agents such as phenols, epoxy, polyimide resins, etc. (Table 4).

Continuous mineral fibre laminates [16]:

- are stable at high temperatures (Fig. 2);
- have the wetting angle (resins) at room temperature not more then 6-8°. This lowers porosity and water uptake of composites and increases strength, which remains even stable after conditioning under high humidity (Fig. 3);
- mineral fibre suppresses relaxation processes in the polymer (Fig. 4);
- combination of the properties of continuous mineral fibres and modification of resin composition lets the thermal conductivity of mineral fibre laminates increase by 20-25%, and thermal capacity by 40-60°C keeping dielectric properties stable. This makes possible to avoid the installation of cooling systems used to prevent the overheating of PCBs.

Table 3: Mechanical properties of fibre reinforced composites produced using epoxy resin*

Kind of material	Density [kg/m^3]	Tensile strength [MPa]	Tensile modulus [GPa]	Flexural strength [MPa]	Flexural modulus [GPa]
E-glass fibre unidirectional composite	1940	1380	51.7	-	-
E-glass laminate (E1581, Volan)	1800-1900	379-517	23-26	517-654	26.1
S-glass fibre unidirectional composite	1940	2070	51.7	1520	-
S-glass laminate (S7681, Volan)	1900	603.3	-	827.4	28.8
Aramid fibre unidirectional composite	1400	1930	82.7	-	-
Aramid laminate	1350	517	31	517	-
Continuous mineral fibre unidirectional composite	1800-1950	1100-1400	88-100	700-800	43
Continuous mineral fibre laminate	1800	430	39	560	-

* Data for E-, S-fibreglass, Aramid composites were taken from [8]

Table 4: Technical features of continuous mineral fibre laminates compared to a fibreglass product prepared under similar conditions

Properties	Copper-Clad Fibreglass	Copper-Clad Mineral fibreglass	
Binder	Epoxy resin	Epoxy resin	Polyimide resin
Tensile strength [MPa]	430	430	390
Bending strength [MPa]	540	560	480
Compressive strength [MPa]	400	440	380
Specific surface resistance* [Om·m]	$1 \cdot 10^{10}$	$5 \cdot 10^{11}$	$1 \cdot 10^{13}$
Specific volume resistance* [Om·m]	$1 \cdot 10^{10}$	$2.5 \cdot 10^{11}$	$1 \cdot 10^{14}$
Dissipation factor*, at 1 MHz	0.035	0.020	0.004
Dielectric constant at 23°C, 1MHz	5.5	5.5	4.5
Peel strength of Cu foil [N/3 mm]	60	120	120
Water absorption [mg]	20	7	8
Inflammability: - time of combustion [s] - length of burnt part [mm]	 10 25	 2 10	 - -

*After conditioning at 40°C under 93% humidity during 96 h

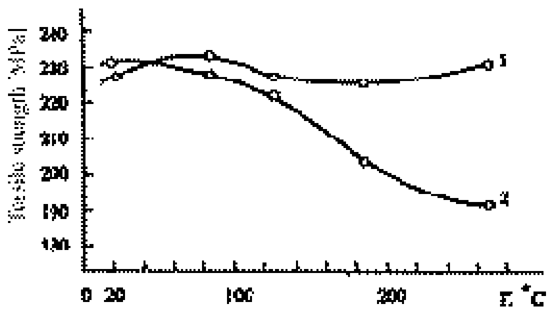


Fig. 2

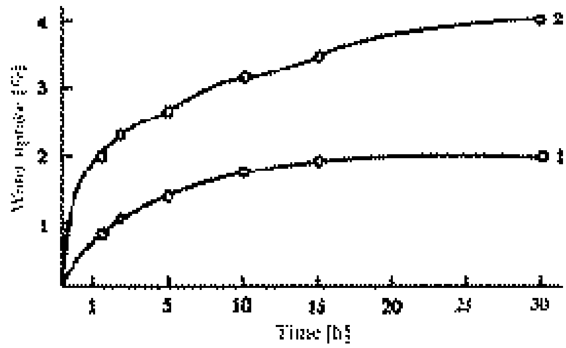


Fig. 3

Fig. 2: Tensile strength dependence on temperature: 1 - mineral fibreglass laminate (phenol-formaldehyde resin); 2 - E-glass fibre laminate (phenol-formaldehyde resin)

Fig. 3: Water uptake (weight increase) dependence on time: 1 - mineral fibreglass laminate (phenol-formaldehyde resin); 2 - E-glass fibre laminate (phenol-formaldehyde resin)

The improvement in the properties of mineral fibre laminates at high temperatures compared to fibreglass laminates cannot be explained completely from the physical-chemical point of view at the present time. One can only suspect that the Fe^{2+}/Fe^{3+} ratio in the mineral glass together with the morphology of the fibre surface creates special conditions at the interface for the interaction with sizing agent and binder. This could also be an explanation for the enhancement of elastic modulus of unidirectional mineral fibre composites. Experimental confirmation of this effect should be the key point for further investigations and may be helpful in the development of new composites based on continuous mineral fibres.

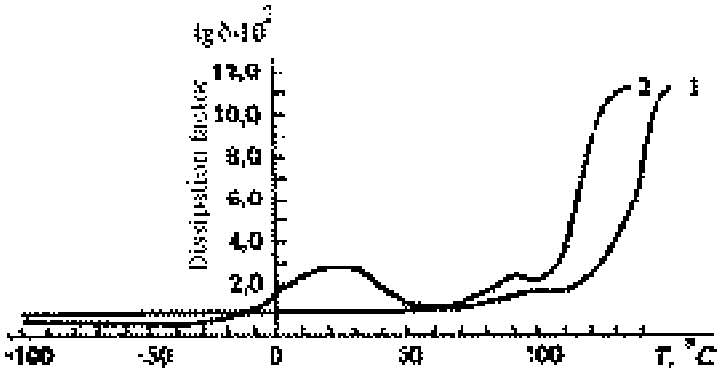


Fig. 4: Dissipation factor (tgδ) dependence on temperature at 1 MHz: 1 - mineral fibreglass laminate (epoxy resin); 2 - E-glass fibre laminate (epoxy resin)

The hardness of the initial mineral gives a remarkable stability of mineral fibres that may be considered as one of the most promising element for reinforcement of composites for friction application. Using asbestos or mineral wool for this purpose is questionable from the point of view of homogeneity of fibre distribution in the volume of composite and they are therefore well substituted by continuous mineral fibres (Table 5).

Table 5: Mineral fibre reinforced composites applied in friction materials

Property	Composite reinforced with asbestos	Mineral fibre composites reinforced or filled with		
		Superthin fibres [17]	Superthin + chopped roving[18]	Knitted fabric + Cu [19]
Brinell hardness, HB 10/500/30	30-44	40.2	34.2	-
Ultimate strength [MPa] shear	36.6	26.4	30-40	23-37
compressive	66.5	138.0	180-240	164-197
tensile	20.7	17.4	-	36.4-40.5
flexural	60.0	61.5	70-100	54.62
Friction coefficient	0.33-0.42	0.48	0.56-0.62	0.38-0.45
Water absorption [%]	0.36	0.08	0.01-0.018	0.26
Oil absorption [%]	0.27	0.08	0.04-0.06	0.18-0.27

Continuous mineral fibre as reinforcing element of friction material increases the friction coefficient and wear resistance as well as resistance to jamming in a wide range of operating pressures, they are useful for reinforcement of different kinds of pads and clutch plates for motorcycles, trams, trolleybuses, cars, etc.

This short overview of composites obtained from a base of continuous mineral fibres confirms how great potential these fibres hold for the development of composites with improved properties. Consideration of advantages of physical-chemical properties is always connected with the economic aspect. At the present time the price of continuous fibres lies between that of E-glass and S-glass fibres (Fig. 5). The price is brought up by the limited capacity of production facilities, newness of this kind of fibre, concentration of production only in the region of the former Soviet Union. Besides of that the distribution of the fibres around the world is sometimes carried out by suppliers which are not directly connected with the producing this fibre factories.

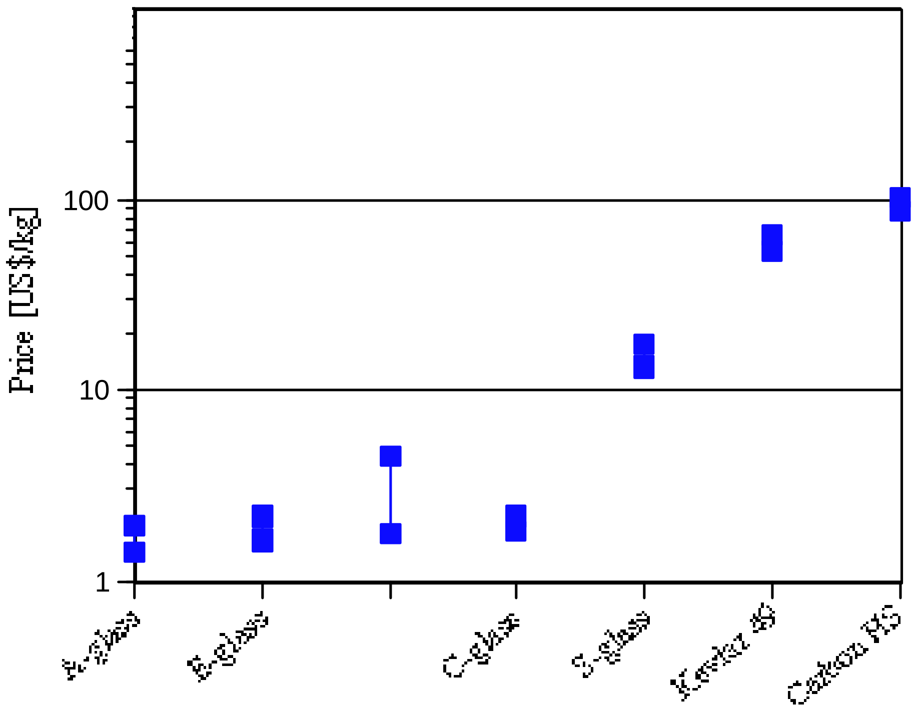


Fig. 5: Price distribution for reinforced fibres on the modern composites market [20]

Another factor that may influence the economic position of continuous mineral fibres is volume of production, which for the moment is not compatible with the volumes and facilities of glass fibre industry. This problem may be solved when the development of new composites based on continuous mineral fibres and fibre production technology keep pace with each other.

CONCLUSIONS

Continuous mineral fibre is an attractive kind of fibreglass possessing

- mechanical properties, comparable to S-fibreglass as far as E-modulus is concerned
- a higher softening point than E- or Advantex glass
- thermal stability up to 600°C.

When introduced into composites, continuous mineral fibres may greatly improve the thermal-mechanical and dielectric parameters. This makes them compatible with S-fibreglass or Aramid fibre reinforced composites.

Continuous mineral fibres have a wider spectrum of advantages in the field of application as textile glass fibre or reinforcement for composites. This is a basis for future investigations of these fibres and development of a new composite. If continuous mineral fibres produced in a small volume are already compatible with conventional glass fibres on properties and price, further investigations could bring important progress to help them to become an alternative substitution of some expensive materials on the composites market.

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