Swelling, Viscosity and Static-Mechanical Behaviour of Polyester Composites Based on Hybrid Filler System

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SUMMARY: Swelling and static-mechanical properties of fly ash/mica hybrid reinforced unsaturated polyester composites in cured state have been discussed with special reference to the effect of loading composition, nature of filler surfaces and surface treatment of fillers. Processing behaviour of the composites in uncured state was determined through the viscosity measurements. In terms of swelling behaviour of the composites, silanization of fly ash and mica surfaces causes a significant decrease in swelling compared to unsilanized counterparts. In cured state, addition of mica into fly ash polyester composition causes increase in tensile properties.

Introduction

Use of individual fillers in composites has well-known effects on the properties of components. For example, tensile strength can usually be improved by fibrous fillers, provided that adhesion is sufficient and rigidity can be improved by sheet-like fillers, and the improvement depends on the aspect ratio of the filler.[1] Multicomponent compounding, on the other hand, produces hybrid structures where the effects of two or more fillers with suitable particle shapes are combined.[2] Multicomponent compounding is also an effective way to reduce the amount of an individual component in a composite.

Investigations on composites having multicomponent compounding are mainly focused on elastomers and thermosets. Recently, the property optimization in nitrile rubber composites with carbon black/mica systems in polydimethylsiloxane composition with fumed silica/mica hybrid filler systems have been all discussed by our group.[3-5]

The effect of replacement of sand with fly ash on the tensile strength properties of polyester mortar (PM) using unsaturated polyester resins based on poly (ethylene terephthalate) has been evaluated by Rebeiz et al.[6]

In another study, properties such as cure time, flexural strength, and resistance to water absorption of unsaturated polyester based polymer concretes in the presence of fly ash and river sand were investigated by varying the level of fly ash.[7] A study on thermosetting resin molding compositions by using fly ash filler with carbon black filler with good tensile and physical properties has been patented.[8].

 CCC 1022-1360/00/$ 17.50+.50/0

The purpose of this study is to evaluate the effect of replacement of fly ash, finely divided coal combustion by-product resulting in environmental problems, with mica, whose crystals exhibit a high degree of basal cleavage, which allows them to be split into very thin sheets that are strong, flexible, chemically inert and transparent, in unsaturated polyester composites in terms of easy processability, optimum mechanical properties and minimum swelling in hydrocarbon media.

Experimental

Unsaturated polyester resin including 30% styrene was the product of Cam Elyaf A.Ş, Turkey, with a brand name of Neoxil-NX188. Muscovite mica (ca. 45 μm) was supplied from Sabuncular-Mica Trading Corporation of Turkey, Çine. Fly ash (ca. 0.1 μm) which has almost 17% hollow spheres by weight were supplied from Ferro-Chrome Production Plant of Antalya, Turkey. Methyl ethyl ketone peroxide (MEKP), which was in the form of 50% solution, as initiator and cobalt naphtanate (Co-naphtenate), which contains 6% cobalt, as promoter were purchased from Aldrich and used as received. The silane coupling agent, A-174, 3-methacryloxy propyl trimethoxy silane was supplied from Union Carbide, UK. Acetone was product of the Merck, Germany.

Silane coupling agent (4 per cent of filler, by weight) was added to the solution of distilled water and ethanol (20 per cent of distilled water, by weight) previously adjusted to pH 5.5. The filler was mixed with the coupling agent solution and stirred with a high shear mixer for 1 hour. The mixture was filtered on a Buncher filter. The treated filler was then dried at 120°C for 24 hours. The treatment was performed seperately for both fillers used.

All composites were prepared by using unsilanized and silanized fly ash and mica fillers in 0/40, 10/30, 15/25, 20/20, 25/15, 30/10, 40/0 compositions in unsaturated polyester resin which has 0.25%, by weight of resin, Co-naphtenate promoter and 30% by weight of resin, styrene in it. Total filler loading was kept constant in each composite (40% by weight of resin). After stirring the mixture with a high shear mixer, 2%, by weight of resin, MEKP initiator was added just before molding and mixed. Then the mixture was directly poured into glass molds having necessary dimensions for physical tests, let them there for 24 hours to complete curing reaction and give composites.

The following nomenclature is used. For example, the composition of polyester composite with 10 parts fly ash and 30 parts mica in total filler is indicated as PEC10FA30M. If silanized fillers are used, it is indicated as PEC10FAS30MS.

Viscosity measurement of unsaturated polyester resin solutions filled with fly ash and mica was conducted by a Haake Viscotester at 28°C, after mixing the solution at high shear for 15 minutes.

The swelling behaviour of the composites was followed with a travelling microscope (Geartner 7109-46). The samples dimensions of 2 mm x 5 mm x 2 mm were placed in acetone at room temperature for 34 hours. The swelling ratio, q, was defined as the ratio of the volume of the swollen to that of unswollen composites. The swollen lengths were measured at definite times with the help of the travelling microscope and 0.001 mm sensitivity. Two samples for each composite were studied to get average swollen length. The swelling ratio was obtained by the following equation[9]:

$$q = V / Vo = (L / L_0)^3$$

where Vo and V are the volumes of unswollen and swollen composites, respectively. Lo and L are the lenghts of unswollen and swollen composites, respectively.

Tensile stress-strain data were determined using a Zwick Universal Testing Machine (Model 1446) at room temperature with strips having approximately dimensions of 15 mm x 80 mm x 2 mm and at 50 mm / minute drawing rate.

Results and Discussion

Characterization of Fly Ash/Mica Hybrid Reinforced Polyester Composites in Uncured State

Use of fly ash and mica together in different weight fractions affects the viscosity hence the workability in mould. The variation of viscosity of uncured polyester composites as a function of filler composition is given in Figure 1.

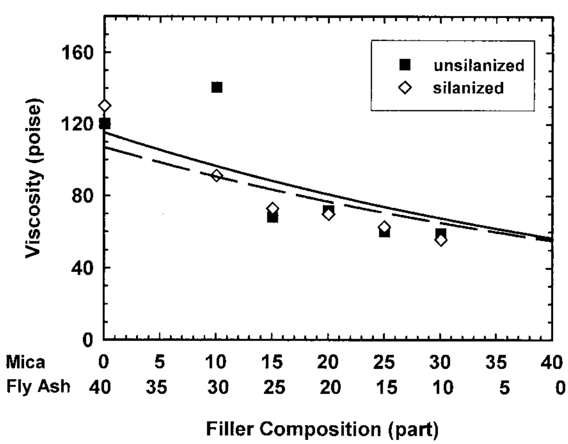

Figure 1. Variation of viscosity of uncured polyester composites versus filler composition.

It is clearly seen from the figure that as mica filler content in the fly ash reinforced composite increases, viscosity decreases. In the light of the results of viscosity measurement, the following theory could be postulated. Different fillers tend to move and orientate in different ways, and effect of particle size appears in the fact that fine grained particles are able to locate between the big particles and facilitate the flow. Thus, fly ash particles will be situated between the mica particles like small marbles causing increase in flow ability, hence lower viscosity. This orientational effect of mica resulting in decrease in viscosity of the composites was recently observed with infrared and birefringence measurement in different hybrid systems.[3-4]

On the other hand, silanization of filler surfaces causes a little decrease in viscosity for almost all composites probably due to the inhibition of the possible agglomeration of both fillers, particle to particle contact via silanization and providing perfect dispersion in the system.

Characterization of Fly Ash/Mica Hybrid Reinforced Polyester Composites In Cured State

In Figure 2, equilibrium swelling ratio values of composites was plotted as a function of both unsilanized and silanized filler compositions.

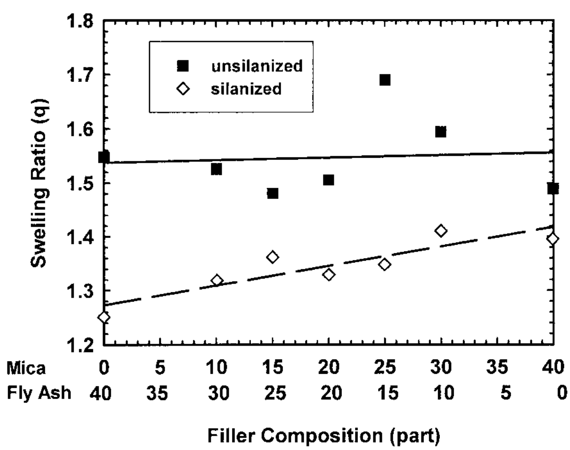

Figure 2. Variation of swelling ratio of polyester composites with filler composition.

It is clear from the Figure 2 that silanization of fly ash and mica surfaces leads to a significant decrease in swelling of each composite especially for the composite of PEC15FA25M whose swelling ratio decreases much more, almost 80 %, when fillers are silanized, PEC15FAS25MS. This can be explained by the mechanism as postulated before by which fly ash settled between the mica particles affecting the structure which then resulting in uniform distribution of crosslinker and effective crosslinking probably via providing the optimum packing. Such a significant decrease in swelling values indicates both enhanced polymer-filler interaction and improved dispersion of fillers in the system. The same results were obtained for the swelling behaviour of mica / carbon black reinforced nitrile rubber composites and mica/silica fume reinforced polydimethyl siloxane composites by Nugay et al.[3,5]

Figure 3 shows the variation of stress at break values of composites simultaneously reinforced with unsilanized and silanized fly ash and mica fillers.

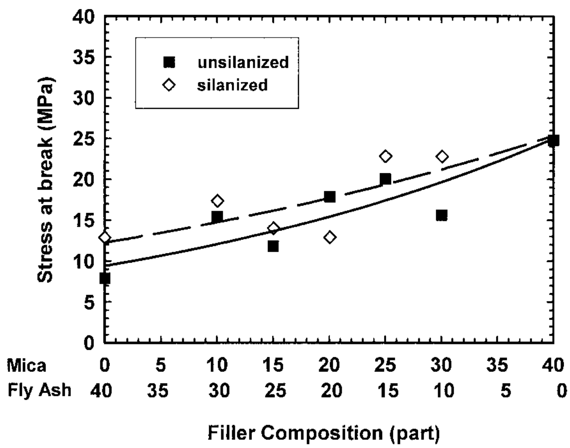

Figure 3. Variation of stress at break values of polyester composites as a function of filler composition.

The addition of unsilanized mica into unsilanized fly ash polyester composition causes an increase in tensile strength. On the other hand, the rise of stress at break values for the composites having increased mica content indicates both the ease of orientation of mica along the direction of applied force with the help of small fly ash particles showing somewhat solvent effect for platelet mica in the matrix which is also evident from the higher elongation values, illustrated in Figure 4. Especially, the composite of PEC15FA25M seems to be optimum filler composition whose tensile strength and elongation at break values are the highest.

Effect of silanization on reinforcement observed by small increase in tensile strength indicates improved dispersion and reduced the number of failure initiating stress concentrations. It is also well known and as mentioned before that if there is adhesion between polymer and filler, tensile strength of the composite increases. If there is no or weak adhesion, tensile strength decreases.[10] Silanization was found to have mostly effective on PEC15FAS25MS composition via minimizing the effect of voids which then leading to maximum tensile strength.

Addition of mica in fly ash reinforced polyester resin does not make the composite brittle as is evident from the higher percentage of elongation at break values of composite having increased mica loading (Figure 4).

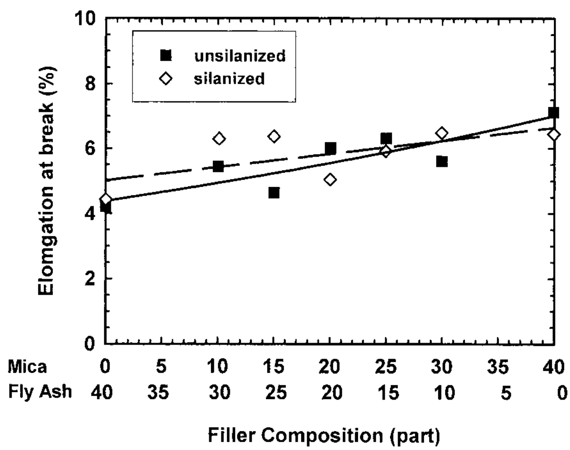

Figure 4. Variations of elongation at break values of polyester composites with filler composition.

By the surface coverage of fillers, a little decrease in elongation at break is observed for the compositions in elongation at break, which can be explained with higher crosslinking resulting from methacryl group of silane coupling agent, leading to less elasticity. This decrease in elongation is also in agreement with decrease in swelling ratio in terms of silanization for the same composite. (Figure 2).

It is well known that the area under stress-strain curves (work up to fracture) is a measure of the toughness and gives an idea about energy absorbed by the specimen to fracture or in short how the matrix dissipates energy in the case of damage or fracture of the composite. Work up to fracture values of the composites as a function filler composition is presented in Figure 5.

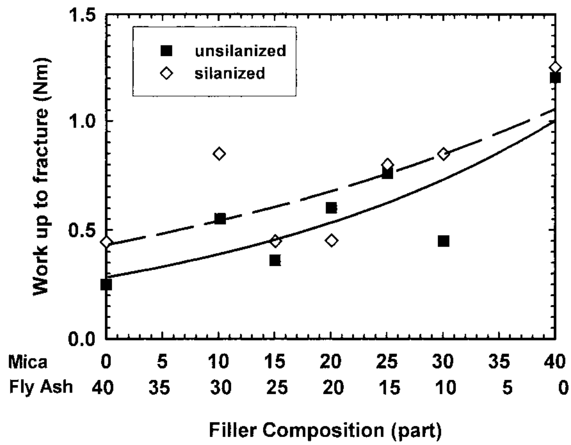

Figure 5. Variation of work up to fracture values of polyester composites with filler composition.

It is obvious here that the amount of energy absorbed by the specimen to break in other words toughness of the composites increases with the unsilanized and silanized mica replacement with fly ash particles and composite having 25 parts unsilanized mica in total filler (PEC15FA25M) exhibits the maximum toughness as an optimum unsilanized filler composition which is also in agreement with its high tensile strength and high elongation at break values, Figure 3 and Figure 4, respectively.

The composition, on the other hand having 10 parts unsilanized mica in total filler (PEC30FA10M) exhibits the one of the maximum toughness, but it has a high viscosity, which causes difficulties while working with moulds as a drawback.

Conclusion

In the use of fly ash and mica together, viscosity decreases as mica content in fly ash reinforced composite increases. Silanization of filler surfaces causes a little decrease in viscosity for almost all composites.

In terms of swelling behaviour of resultant composites, silanization of fly ash and mica surfaces causes a significant decrease in swelling especially for the PEC15FAS25MS composite whose swelling ratio decreases almost 80%.

Addition of unsilanized mica into unsilanized fly ash polyester composition causes an increase in tensile strength. The composite having 25 parts mica in total filler, PEC15FA25M seems to have optimum filler composition whose tensile strength and elongation at break values are the highest among the other composites having hybrid reinforcement.

Addition of mica in fly ash reinforced polyester resin does not make the composite brittle, which is evident from the higher percentage of elongation at break values of composites having increased amount of mica loading. Although the surface coverage of filler causes to a little decrease in elongation at break values the resultant elongation values were found to be still reasonable.

Toughness of the composites significantly increases with the unsilanized and silanized fly ash replacement with mica particles and PEC15FA25M composite exhibits the maximum toughness as an optimum unsilanized filler composition in agreement with its high tensile strength and high elongation at break values. The PEC30FA10M composition, on the other hand, also exhibits the maximum toughness, but it has a high viscosity leading to difficulties while working with moulds. Moreover, the composite of PEC15FAS25MS has the maximum toughness in silanized filler composition.

Acknowledgement: Support given by Bogazici University Research Foundation project no 99B507 is gratefully acknowledged.

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