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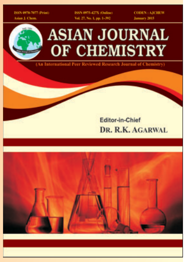

Effect of Surface Modification of Fumed-Silica on Mechanical Properties of Unsaturated Polyester Composites

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The aim of this study is to investigate the effect of surface modification of fumed silica *via* vinyltrimethoxysilane on mechanical properties of fumed silica-unsaturated polyester composites. Modified and unmodified fumed silica-unsaturated polyester composites were prepared with the inclusion of vinyltrimethoxysilane in different (0, 0.5, 1, 1.5, 2, 2.5, 3 wt %) contents. SEM images revealed dispersion and agglomeration of inorganic constituents throughout the fracture surface of the composites. FT-IR analysis confirmed succesful conduction of surface modification of fumed silica. Mechanical properties were evaluated *via* tensile and impact tests. Heat deflection temperature tests were also performed to evaluate thermal behaviour. The most obvious effect of modified fumed silica was seen in impact strength which showed two different trends.

Keywords: Vinyltrimethoxysilane, Fumed silica, Unsaturated polyester, Nanocomposites.

INTRODUCTION

Vinyl esters, epoxies and unsaturated polyesters are widely used in many areas from daily needs to high-tech applications. Their prominent features such as high glass transition temperature, specific strength and creep resistance provide them to be utilized in many composite applications. On the other hand, thermoset materials have low fracture toughness due to high cross-linking density. Poor resistance to fracture stems from ease of crack initiation and propagation. Hence, improvement of mechanical properties especially impact strength of thermoset composites is one of the major issues in this field. Therefore, intensive investigations have been performed with regard to the toughness improvement of thermosets[1].

In order to achieve improvement on mechanical properties of thermosets addition of rubber and some inorganic fillers are extensively utilized. However addition of fillers in micrometer scale do not provide better mechanical properties[2-6]. It is well known that fillers in macroscopic dimension results in deterioration of mechanical properties[2]. Nanomaterial filled composites, which are also called as nanocomposites, exhibit better mechanical properties compared to the composites filled with microscopic fillers. Recently, substantial improvements were obtained by using fillers in nanometer scale[6-12]. Due to that reason, nanofillers have attracted huge attention.

Nanocomposites can be classified mainly into three groups with respect to morphology. These are layered nanocomposites, whisker based nanocomposites and isodimensional nanocomposites. Layered silicates, carbon black or carbon nanotube and fumed silica are well known nanoscale fillers[13]. Among them, fumed silica used in enormous quantities in many applications such as adhesives and paints. However, fumed silica causes an increase in the viscosity of composite solution when used as received condition. The reason for the viscosity increase is the formation of hydrogen bonds between the filler and polymer matrix. Aso *et al.*[14] claimed that the inclusion of surface functionalized fumed silica improves the mechanical and thermo-mechanical properties of thermosets. They attributed improvements in mechanical properties to nanoeffect which increases the interaction between polymer matrix and inorganic filler interface. Specific surface area, increase in crystallinity of some polymer matrices and well dispersion of nanofillers within the matrix are the reasons for improvement in mechanical properties.

Although fumed silica has many advantages, compatibility between polymer matrix and fumed silica still remains as a major problem. It is important to note that materials having different surface properties have difficulties in coupling to each other without any surface modification. Thus, to overcome the compatibility problem, some chemical agents such as silane coupling agents are used as a compatibilizer providing better interaction between matrix and filler[15]. Prabhu and Alagar[16] and Chern *et al.*[17] used silane coupling agent to modify surface of inorganic materials and polymer structures. So, by attributing to their study, a mechanism was proposed to modify the surface of fumed silica to couple unsaturated polyester resin.

Hydrolysis reaction of vinyltrimethoxysilane (VTMS) was conducted in an acidic medium as a first step. In that case, VTMS was rendered to react with hydroxyl groups that take place on fumed silica particles. Subsequently, silane coupling agents were bonded to the silica particles as shown in Fig. 1. Then, the crosslinking reactions take place in the medium resulting in interpenetrating network structure. Cross-linking reactions occur between unsaturated polyester chains and VTMS modified silica nanoparticles. Basically, opening of double bonds leading to bridge between VTMS and unsaturated polyester was initiated by methyl ethyl ketone peroxide. Thus, silane coupling agent will provide chemical bonding between the unsaturated polyester resin and the fumed silica particles.

In this study, modified and unmodified fumed silica-unsaturated polyester composites were prepared with the inclusion of VTMS in different (0, 0.5, 1, 1.5, 2, 2.5, 3 wt %) contents. SEM images revealed dispersion and agglomeration of inorganic constituents throughout the fracture surface of the composites. FT-IR analysis confirmed successful conduction of surface modification of fumed silica. Mechanical properties were evaluated *via* tensile and impact tests. Heat deflection temperature tests were also performed to evaluate thermal behaviour. The most obvious effect of modified fumed silica was seen in impact strength which showed two different trends.

EXPERIMENTAL

The unsaturated polyester resin (orthophtalic) used in this study was provided by Poliya polyester in Turkey. Fumed silica (HDK-N20) is the product of Wacker. Vinyltrimethoxysilane (VTMS) (98 %), ethanol (99.8 %), HCl were purchased from Sigma-Aldrich. Methyl ethyl ketone peroxide (MEKP) as initiator and cobalt naphthenate as accelerator were supplied by Sigma Aldrich.

Surface treatment of fumed silica particles: The alkoxysilanes are a member of silane coupling agents' family. These chemicals have the capability to react with –Si-OH groups of silica, thereby forming –Si-O-Si- bonds without any requirement for prehydrolysis. However, silanes do not undergo the same reaction with the hydroxyl groups of inorganic material even at high temperatures. This has been attributed to the lower acidity of hydroxyl groups compared to silanol. Interaction between inorganic materials and silanes comes from the presence of –OH groups adsorbed on inorganic materials. Consequently, the silanol can react with the hydroxyl groups adsorbed on fumed silica or form three dimensional network in the surface of fumed silica in acidic media[18]. Besides, silane coupling agents have the capability to react with polymer matrix due to presence of C=C bonds or the other functional groups. Hence, silane coupling agents act as a compatibilizer to increase the compatibility between inorganic materials and polymer matrix by reacting with both. Xie *et al.*[18] proposed the operational mechanism of silane coupling agent as shown in Fig. 1.

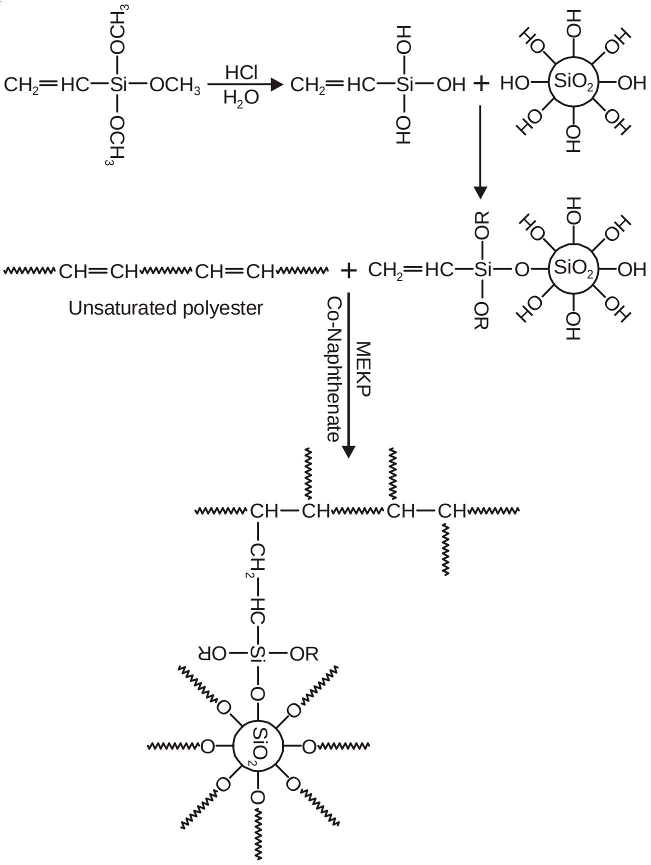

Fig. 1. Schematic diagram illustrating interaction of silane coupling agent with hydroxyl surface and croslinking reaction between modified silica and unsaturated polyester

In the light of this observation, modification of fumed silica was performed as explained below. 16 g of fumed silica was stirred in three-neck round-bottom reaction flask containing 300 mL ethanol. 32 g of VTMS was added drop by drop during 30 min. 7.77 g of distilled water was incorporated into solution to ensure r = 3 in reaction kinetic. In order for the reaction to proceed in a proper way, HCl was added till pH = 4 attained. Solution was stirred for 8 h by using mechanical stirrer to complete the reaction properly.

After completion of the reaction, fumed silica nanoparticles were precipitated by using Sigma Versatile Centrifuge - Sigma 3-16P in 9000 rpm at –5 °C during 20 min. Decantation of solution was followed by drying at 60 °C during 2 h. Finally, modified fumed silica was ready for inclusion into unsaturated polyester resin.

Preparation of nanocomposites: In order to produce surface modified fumed silica and fumed silica–unsaturated polyester composites, in appropriate weight, each type of fumed silica was added to unsaturated polyester resin and stirred manually. Vacuum (0.5 Bar) was applied and held at 50 °C for 1 h to remove air bubles and left to cool to room temperature. Methyl ethyl ketone peroxide (MEKP) (1.2 %) as a curing agent and cobalt naphthenate as promoter were added and the suspension was stirred manually. Thirteen different composites were produced containing seven different ratios (0, 0.5, 1, 1.5, 2, 2.5, 3 %) of each type of fumed silica. Finally these solutions were cast in to open molds made of Teflon.

Characterization: Mechanical properties of each type of fumed silica-polyester composite specimens were determined by ASTM D638 tensile test standard to measure the modulus (E), tensile strength (σ) and elongation at break (ε). Tensile strength experiments were performed at room temperature on a materials testing system Zwick Z010 with a load cell capacity of 10 kN, using a crosshead speed of 5 mm/min. To investigate fracture behaviour, Izod impact test according to the ASTM D256 test standart was conducted by using Zwick B5113.30 with 5.4 J Izod striker. Heat deflection temperature (HDT) test was performed on a Devotrans ZGT HV 2000 AC3. The samples (70 mm × 10 mm × 4 mm) were tested with 1.8 MPa bending force, heating rate 2 °C/min and heat deflection temperature was measured where the specimen deflects 0.25 mm. The infrared spectra of modified and unmodified fumed silica were analyzed using Fourier transform infrared (FT-IR) spectrum (Perkin Elmer Spectrum One FT-IR spectrometer) to identify whether VTMS bonded to the surface of fumed silica or not. Distribution and surface morphology of nanoparticles were examined under Zeiss EVO MA10 SEM at 15.00-20.00 kV. A tungsten filament was used to create the beam.

RESULTS AND DISCUSSION

Bonding of vinyltrimethoxysilane (VTMS) on the surface of the fumed silica particles was confirmed by the Fourier transform infrared spectra (Fig. 2) in which the peaks at 1650 and 1410 cm^{-1} are characteristic of the C=C bond of vinylsilane. The other peaks that appear around 2974 and 2896 cm^{-1} represent the C-H stretch resulting from VTMS vinyl and methyl groups. The presence of Si-C, Si-O and OH bonds were confirmed by peaks at 813, 875 and 3358 cm^{-1}, respectively[19].

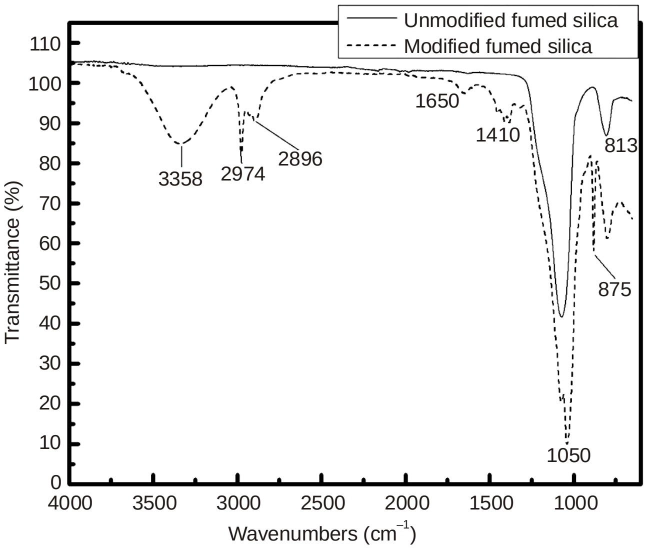

Fig. 2. FT-IR spectra of modified and unmodified fumed silica nanoparticles

SEM images of samples were given in Fig. 3. Schulte *et al.*[20] emphasized that incorporation of nanofillers even in low ratio affects polymer morphology by increasing crystallinity content in thermoplastics and cross-linking density in thermosets. They also proved that surface functionalized-nano fillers lead to more homogeneous dispersion of nanofillers within the polymer. It can be clearly seen from the SEM images that surface modification improved dispersion of fumed silica in polymer matrix. Surface modification of fumed silica resulted in better nanoparticle distribution compared to unmodified fumed silica added samples. On the other hand, VTMS inclusion worked well till a point exceeding 2.5 wt % nanoparticle content. Although VTMS modification was performed on fumed nanosilica particles, some microscopic scale nanoparticles can still be seen from Fig. 3f. This was attributed to the low dispersion limit of unsaturated polyester. This was thought to be the result of increased viscosity due to

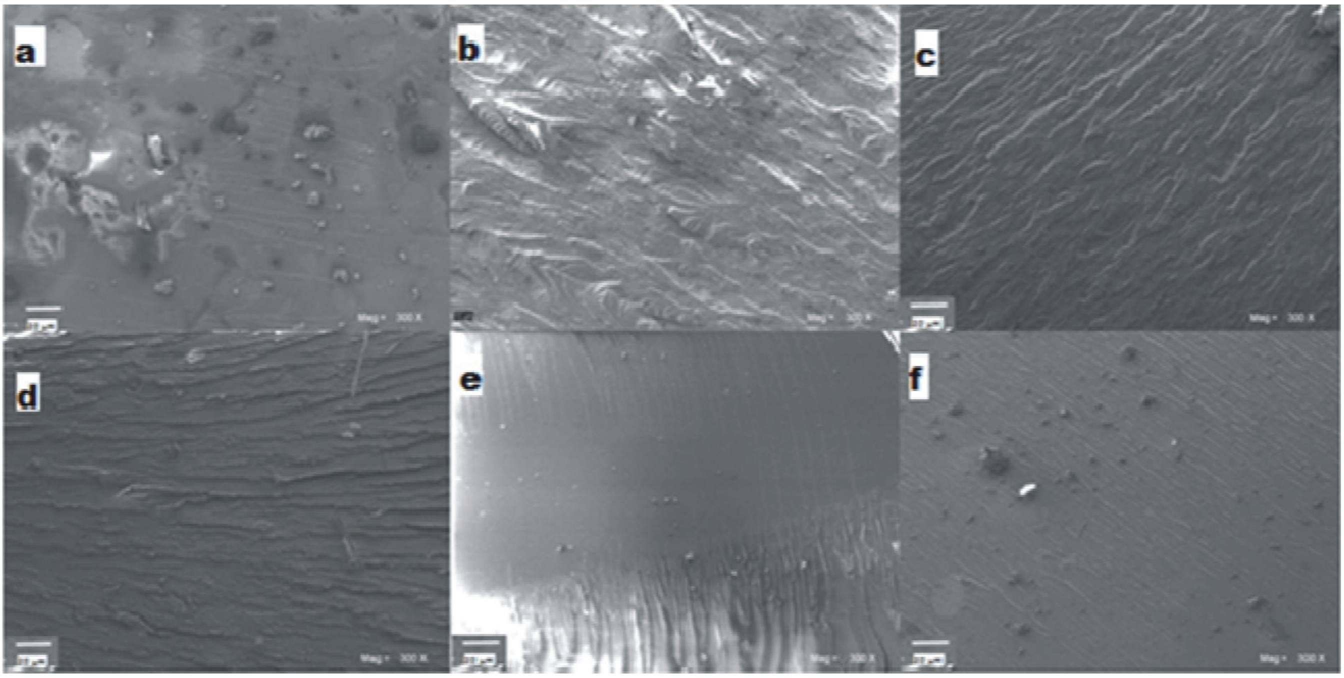

Fig. 3. SEM images of unsuturated polyester composite filled with a) 1 wt % unmodified fumed silica b) 2 wt % unmodified fumed silica c) 3 wt % unmodified fumed silica d) 1 wt % modified fumed silica e) 2 wt % modified fumed silica f) 3 wt % modified fumed silica

presence of fumed silica within polymer matrix. After exceeding nanoparticle dispersion capability of polymers, nanoparticles start to agglomerate forming agglomaretas in microscale. It was also observed that increasing the amount of filler caused a reduced miscibility leading to dispersion problems.

The most obvious effect of fumed silica on mechanical properties was observed on impact strength. As seen from Fig. 4, composites exhibited two different trends. Increasing silica content led to increase in impact strength until 1 wt. % for the unmodified fumed silica filled composite (UMFSC). Exceeding 1 wt. % loadings, impact strength values of UMFSC showed a decreasing trend, while modified fumed silica filled composite (MFSC) exhibited an increasing trend. Several mechanisms were proposed such as crack pinning, crack tip deformation, localized inelastic matrix deformation, crack deflection, void nucleation to identify the interaction between polymers and nanoparticles. However, two important challenges in nanocomposites are responsible for the inhibition of utilization of advantages of nanoparticles. One of them is low interfacial adhesion between polymer and nanofiller and the other one is low dispersion of nanoparticle in polymer matrix. Main advantages of nanoparticles come from their high specific surface area. However, aglomerations of nanoparticles cause to decrease in specific surface area and interaction between polymers and nanoparticles. It is also clearly indicated that functionalization of surface of nanoparticle facilitates distribution of nanoparticles[20-23]. Besides, interfacial strength has a key role for stress transfer. From this point of view, MFSC structures have higher interfacial strength and much more homogeneous distribution of nanoparticle compared to UMFSC. Due to that reason, MFSC exhibited higher impact strength than counterpart. In other words, modificiation of fumed silica provided inhibition of agglomeration of nanoparticles. Therefore homogeneous dispersion and improved matrix-filler interaction and enhanced cross linking density were obtained. Impact strength was 9,16 KJ/m^2 at the maximum for 2.5 % modified fumed silica filled nanocomposites. This corresponds to a 45 % increase in impact strength compared to neat polyester resin which has an impact strength of 6.3 KJ/m^2.

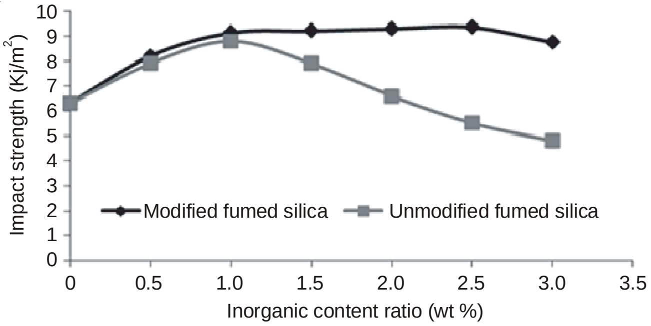

Fig. 4. Effect of inorganic content on the impact strength of composites

Sen and Nugay[5] pointed out that the addition of unsilanized mica into unsilanized fly ash reinforced polyester increases tensile strength and elongation ability of composites dramatically. This was attributed to the improved dispersion and reduced failure initiating stress concentration sites. Wichmann *et al.*[24] observed a slight decrease in young modulus and offered no explanation for this decrease. Sun *et al.*[25] modified fumed silica with dimethyl dichlorosilane and γ-methylacryloxypropyl trimethoxy silane. They observed increases in tensile and impact strengths compared to the unmodified counterpart. These increases were attributed to the improvement of stress transfer efficiency from matrix to inorganic particle. Wu *et al.*[26] reported that the addition of nanoparticles into Poliya polyester can bring in both reinforcing and toughening effects at filler contents as low as 0.5 vol %. Such a simultaneous improvement in modulus, strength and elongation-to-break is hard to be observed in conventional microsized particulate composites.

Fig. 5 shows the inorganic material content dependency of tensile strength. As seen from Fig. 5, inorganic content in polymer structure affected tensile properties slightly. However, tensile strength of the samples having 3 wt % unmodified fumed silica content affected remarkably. This can be the result of inhomogeneous dispersion. Modification process imparts easy dispersion of the particles within the matrix solution having 3 wt % inorganic material, thus preventing agglomeration. This result appears as enhanced tensile strength in 3 wt % modified fumed silica content.

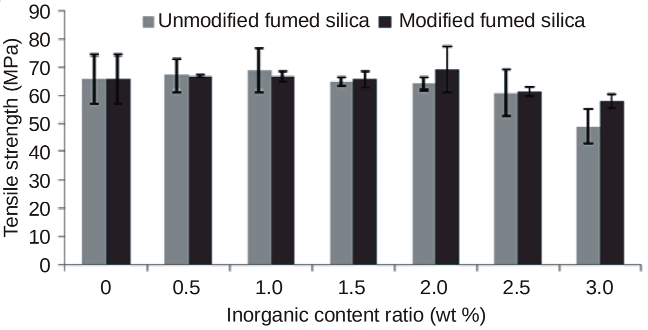

Fig. 5. Influence of inorganic fumed silica content on the tensile strength of composites

Increasing elastic modulus with increasing fumed silica content was given in Fig. 6. All elastic modulus values of fumed silica filled polyesters were higher than the neat polyester. 2.5 wt % unmodified fumed silica filled composite has the highest value for the elastic modulus. As seen in Fig. 6, modified fumed silica filled composites have higher values compared to the unmodified fumed silica values until 2.5 wt %. Modification of fumed silica surface enhances cross linking density that is why rigidness of samples are increased.

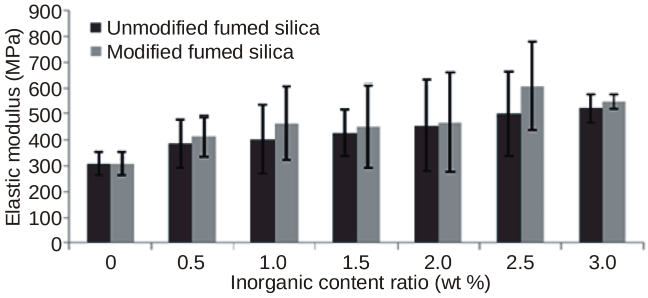

Fig. 6. Elastic modulus values of fumed silica composites

In Fig. 7, increasing modified fumed silica content increases elongation at break for all samples. Approximately 30 % increase in elongation was obtained. Unmodified fumed silica after 1.5 wt % content causes decrease in elongation. This can be attributed to agglomeration tendency of unmodified fumed silica. All elongation values of modified fumed silica composites were higher than that of unmodified fumed silica. Effect of surface modification of fumed silica on elongation was obvious.

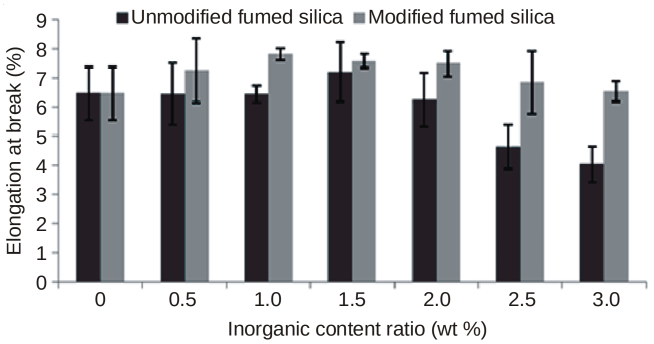

Fig. 7. Variation of elongation at break of fumed silica composites with inorganic content ratio

Heat deflection temperature values of modified fumed silica were approximately 1 °C higher (Fig. 8) than that of unmodified silica due to modification of fumed silica which improved nanoparticle distribution. Heat deflection temperature values varied from 50.6 to 56.65 °C. Maximum value was found for the sample having 2.5 wt % inorganic content. In filling rates exceeding 2.5 wt %, it was observed that agglomeration of nanoparticles plays an important role and leads to reduction in the uniformity of nanoparticle distribution. Thereby, deterioration in dispersion uniformity causes a reduction in polymer-matrix interaction. So lower heat deflection temperature values in the samples having 3 % inorganic content can be attributed to the reduction in particle-polymer interaction.

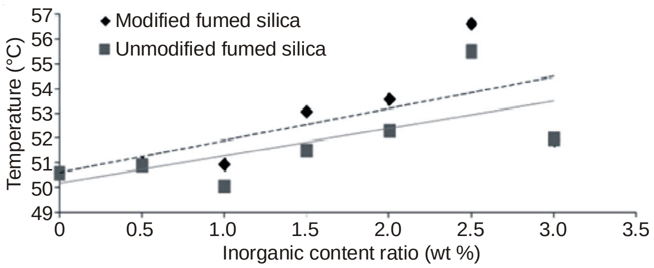

Fig. 8. Variation of heat deflection temperature with inorganic content

Conclusion

As it was observed from FT-IR analysis, modification of fumed silica by means of vinyltrimethoxy silane was successful. Heat deflection temperature values of modified fumed silica were approximately 1 °C higher (Fig. 8) than that of unmodified silica values because of having high crosslinking density. There is not any negative effect of both type of fumed silica on tensile properties except for 3 wt % fumed silica content which can be result of inhomogeneous dispersion caused by low dispersion of unmodified fumed silica in polyester matrix. All elastic modulus enhanced with both type of fumed silica and maximum was 2.5 wt %. The strongest effect was found on the impact strength. Modified fumed silica resulted in positive effect while unmodified fumed silica had negative effect on impact strength. Positive effect was due to homogeneous dispersion, improved matrix-filler interaction and increased cross linking density.

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