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Synthesis and Polymerization of New silane Coupling Agent and Used it as Impact Modifier of Silica Filled Unsaturated Polyester

Widad S. Hanoosh
Department of chemistry,College of Scince, University of Basrah
Basrah-Iraq
Email: whidadhanoosh [AT] yahoo.com

ABSTRACT---- ***The aim of this study was to prepare vinyltriallyloxysilane (VTAS) through the reaction of allylalcohol and vinyltrichlorosilane, this monomers was polymerized free radically by using peroxide initiator. The monomer and polymer were characterized by FTIR,TGA and DSC technique. The result shows that the polymer has high decomposition temperature. On the other hand composite of unsaturated polyester filled with untreated and treated silica have been prepared .The surface modification of the silica was done by using the prepared silane coupling agent (SCA), the effect of this treatment of filler particles in the polymer matrix was evaluated by mechanical analysis. The result shows that the tensile strength, elongation and impact resistance were improved.***

Keywords----VTAS, Silica particle, commercial unsaturated polyester(UP),filled composites, thermal and mechanical properties.

INTRODUCTION

Unsaturated polyester resin are the most commonly used in a variety of application due to their excellent properties, such as thermal stability, mechanical response, low density and electric resistance(1,2).For ages polymers were reinforced with a variety of particles to form polymer compsites , these particles which include silicates (mica, talc, silica and fiber glass), metal oxides (titania, alumina) ,calcium carbonate and carbon black(3,4).

Composites are made from combination of two or more materials present as separate phases and combined to form desired structures, so as to take advantage of certain desirable properties of each components(5).The constituent can be on organic or inorganic inform of particles ,roads,fibers,plates ,this additional variable often provides greater latitude in optimization for given application such as physically uncorrelated parameters like strength density, electrical and coast. In composites weak adhesion may result from the lack of stress transform from polymer matrix to the load bearing fillers (6),so the interfacial bond can enhanced and the mechanical properties of the composites will be improved by suitable surface treatment (7).Most of fillers are pretreated before they are used as secondary phases in composites material ,as typical surface treatment for polymer matrix composites ,we often used the silane coupling agents (SCA) (8-10). SCA are generally has the following formula $RSi(X)_3$ where silicon atom is the centre of silane molecule, which contains an inorganic functional group R (ex: vinyl,amine,chloro,epoxy and mercapto), with a(X) (ex: alkoxy group). The functional group (R) will attach to an organic resin while the functional group (X) attaches to an inorganic material or substrate to achieve a coupling effect.

SCA are predominately used as mediators , binding organic material to inorganic materials as aresult, silanes will improve the properties of composites. The aim of this study to report the results on the effect of surface treatment by SCA on the properties of silica powder reinforced unsaturated polyester composites.

EXPERIMENTAL PART

Materials

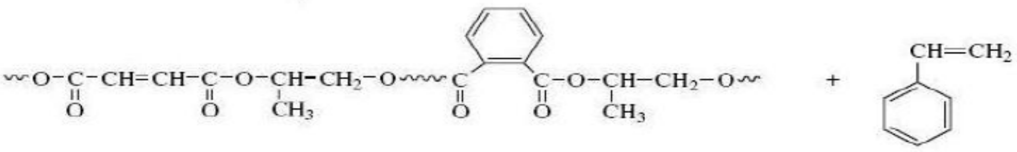
1-Allyl alcohol , vinyltrichlorosilane,aceton,xylene, tolune,hydrochloric acid were supplied from Merck company.

2- Sodium bicarbonate,ethylmethylketone peroxide were supplied from fluka company.

3- Silica particles (Novacite 1.207 A^0) having an average dimeter of 5 micrometer, were obtained from Malvern Minerals .

4- Unsaturated polyester was supplied from Revertex (Malaysia) with the following specification :

SI.No.		Properties
1-	Appearance	Clear
2-	Specific gravity	1.12 @ 25C^0
3-	Acid value	28-30 (mg KOH/ g)
4-	Gel time	20-25 minutes @25C^0
5-	Volatiles	35-40%
6-	HDT	55 C^0 ISO; 75/1974
7-	Water absorption	30 mg ISO ;62/1980
8-	Viscosity	550-700 (cps) @ 25C^0



Chemical structure of Unsaturated poly ester and styrene used in this study

SYNTHESIS

Synthesis of vinyltriallyloxysilane

The reaction was carried out in 100 ml three necked flask fitted with stirrer,dropping funnel and gas out let tube. The reaction vessel was charged with 26.8 g (0.17 mol),Then allyl alcohol 29.0 g (0.15 mol) was added drop wise over aperiod of 90 min.At the end of addition time the mixture was transferred to the boiling flask and heated gently to get rid of the dissolved hydrogen chloride (about 2 hrs). The residual hydrogen chloride was neutralized by sodium hydrogen carbonate,filtered.dried over anhydrous magnesium sulphate,finally distilled under reduce pressure to yield slightly yellow oily product (88% yield, b.p 198-200 C^0, density 1.011 gm/ccm , refractive index 1.43624 at 25 C^0). The product was characterized by FTIR & CHN analysis.

Polymerization of vinyltriallyloxysilane

The unsaturated silane monomer was polymerized by ethyl methyl ketone peroxide (1 wt%) in the presence of cobalt octaote as accelerator. The components were reacted together by efficient mixing on clean and dry glass mold for 2 min. at room temperature and the mixture was lifted over night to cure,complete curing was done by heating the product in an oven at 100 C^0 for about 4-5 hrs,finally post cure at 130 C^0 for 3hrs.The slightly yellow polymer was obtained and characterized by FTIR, TGA & DSC.

Silylation of silica(11)

The silica particles were immersed in a 1% hydrochloric acid solution for 8 hrs at room temperature to remove contaminates, followed by washing and immersing in diionized water for 1hr. to clean and hydrolyze the surface. The particles were then filtered and dried at 110 C^0 to remove the excess of surface water, then the hydroxylated particles were silylated in excess solution of 10 % vinyltriallyloxysilane using co-solvent of methanol and demonized water with the ratio of (80/20 wt%).The silylation reaction was performed in aslurry batch reactor equipped with reflux condenser for 3 hrs. The silylated particles was dried at 110 C^0 for 1 hr, followed by 24 hrs at room temperature.

Preparation of composites

The untreated and treated silica were uniformly dispersed separately in the unsaturated polyester resin along with the accelerator (0.5% w/w) ,following which the free radical initiator was added on weight basis, on parts per hundred grams of resin (phr), i.e 2.5 phr would refer to 2.5 grams of filler per 100 grams of unsaturated polyester resin. The composition was then deaerated to remove any entrapped air and poured in a Teflon mold maintained at 30C^0. The cure cycle was 30C^0/24 hr and 100C^0 /6 hrs ,finally 120C^0/2hrs for post cure. The composites had a thickness of 3mm± 1%.The composites were machine cut into the respective shapes for testing.

Testing of composites

The composites were tested for their tensile ,compression and impact properties. The tensile strength and elongation were determined according to ASTM D638 with a universal testing machine model Instron 3366 equipped with load capacity of 10 kN at a deformation rate of 5 mm/ min and a gripping length of 100mm. Azod impact on notched specimens of dimensions (67x12.7x3.2 mm with a 1mm notch). Was carried out on an Avery Denison Impact tester using 2.7 J skriker with astriking velocity of 3.46 m/s in accordance with ASTM D256.Tests were carried out on five samples and the average have been reported as the test result. Water and toluene absorption were studied using three 1x1x0.3 cm chips and suspending them separately for a period of 7 days in 100 ml solvent at 30 C^0.After the required amount of time the sample were removed and gently dried using filter paper to remove water or solvent adhering to its surface. The increase in weight was then estimated and the percentage increase in water or solvent was reported.

Thermal test

Thermal Gravimetrical Analysis (TGA) & Differential Scanning Calorimeter (DSC) tests were performed concurrently using the TGA model Q20 TA Instrument in basrah university ((at heating rate 50 C^0/ min. under nitrogen atmosphere)) while DSC on model Q20 TA American technique present in Misan university ((at heating rate $10C^0$/min. also under nitrogen atmosphere to prevent oxidation)). Sample mass for each experimental was chosen between 6 and 20 mg.

RESULTS AND DISCUSSION

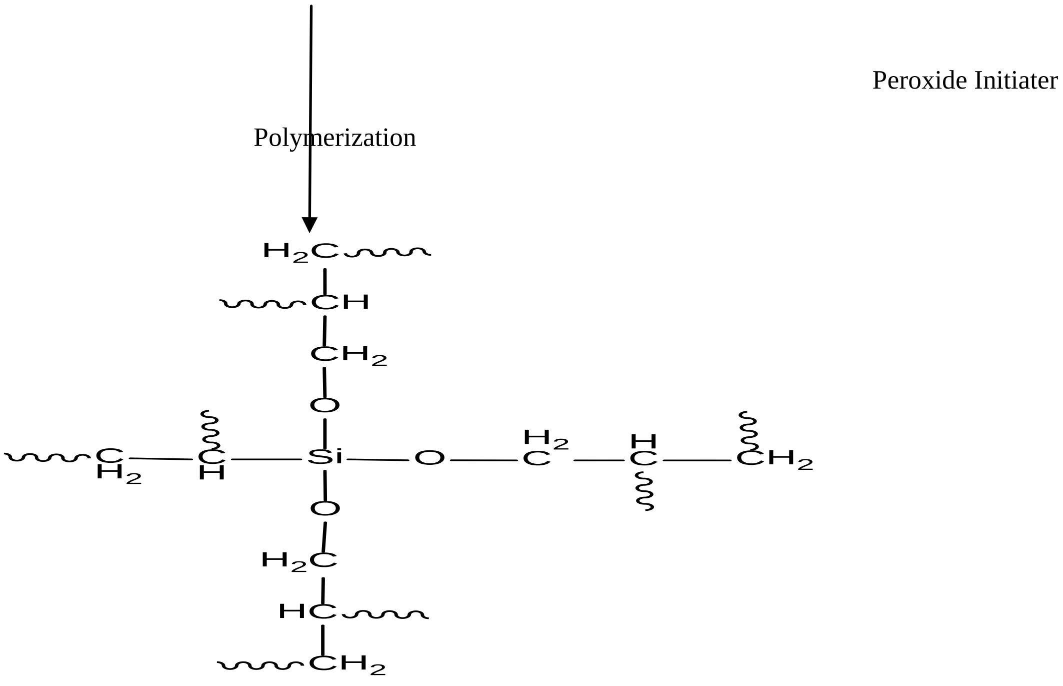
Reaction schem

Vinyl triallyloxy silane was prepared througth the reaction of vinyltrichlorosilane with allyl alcohol according to the reaction below :

$$CH_2{=}\ CH\text{- }Si\ Cl_3\ \ +\ \ CH_2 = CH\text{- }CH_2\ OH \rightarrow\ CH_2 = CH – Si\text{- }(O\text{-}CH_2CH{=}\ CH_2\ )_3\ \ + 3\ HCl$$

While the curing of the prepared monomers were initiated by ethyl methyl ketone peroxide in the presence of accelerator. The curing reaction takes place according to free radical mechanism at the double bond presence in the allyl group and vinyl group, as shown in the following expected equation:

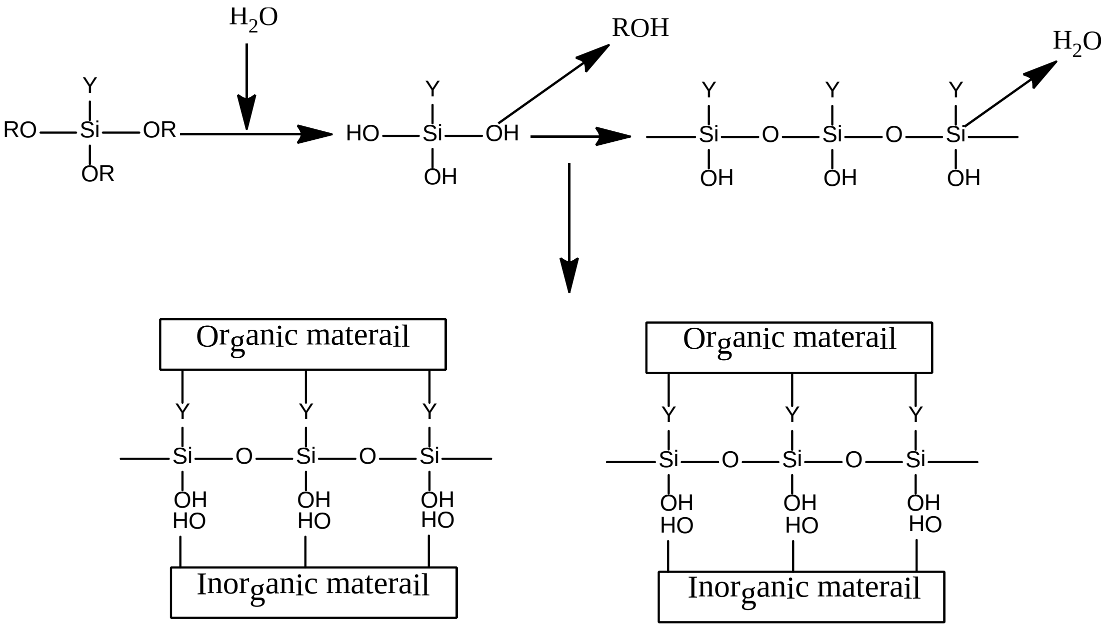
$$CH_2 = CH – Si\text{- }(O\text{-}CH_2CH{=}\ CH_2\ )_3$$



Net work structure of silicone resin prepared from silane monomer

Silylation reaction

Scheme (1) shows the reaction mechanism of asilane coupling agent. As shown asilane is composed of alkoxy group (OR) and (Y) group. Y group is the vinyl group it is selected according to unsaturated polyester resin, the alkoxy group become hydroxyl group after hydrolysis and react with hydroxyl group presented at the surface of silica in ordre to bonded to the inorganic material , while the vinyl group (Y) of the silane coupling agent bonded to the unsaturated polyester through the double bond after the addition of peroxide (i.e. polymerization) leading to good adhesion of filler to the resins and prove the properties of the composites.



Scheme (1) : Reaction mechanism of silane coupling agent with silica and resin

FTIR study

The FTIR spectra of the silane monomer and the polymer were recorded as thin film over NaCl and KBr disc.The spectra are shown in Figs (1,2) respectively, the monomeric silane showed strong absorption bands in the region (1030-1080) cm^{-1} attributed to the stretching vibration of the Si-OC, other bands were also observed in the region 850 and 910 cm^{-1} due to the stretching vibration of the alkoxy group ,where R is the allyl group.There is also two distinguished bands , first in the region (3020-3090) cm^{-1} related to the stretching vibration of the olefin protons and the other in the region (1620-1630) cm^{-1} related to the stretching vibration of C=C of the allyl and vinyl group.

Figure (1) : FTIR spectrum of vinyltriallyloxysilane monomer.

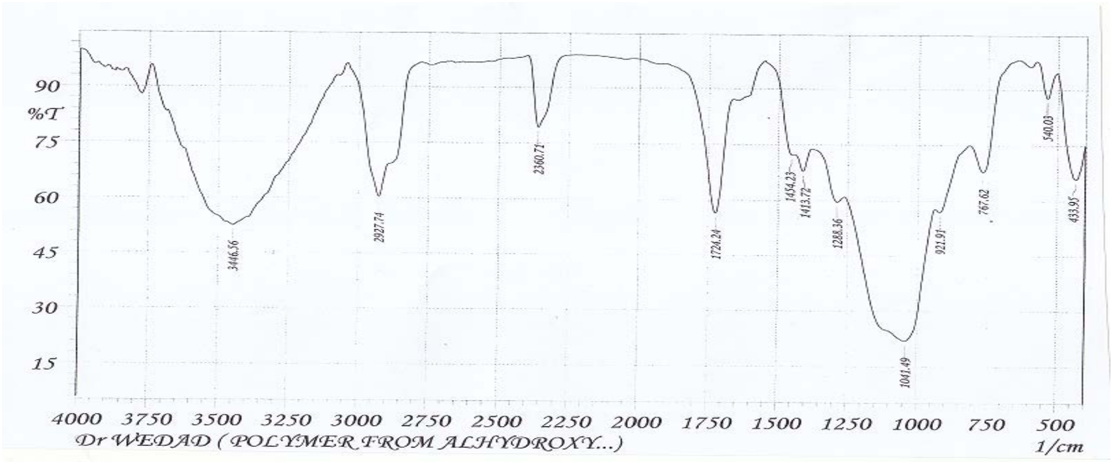
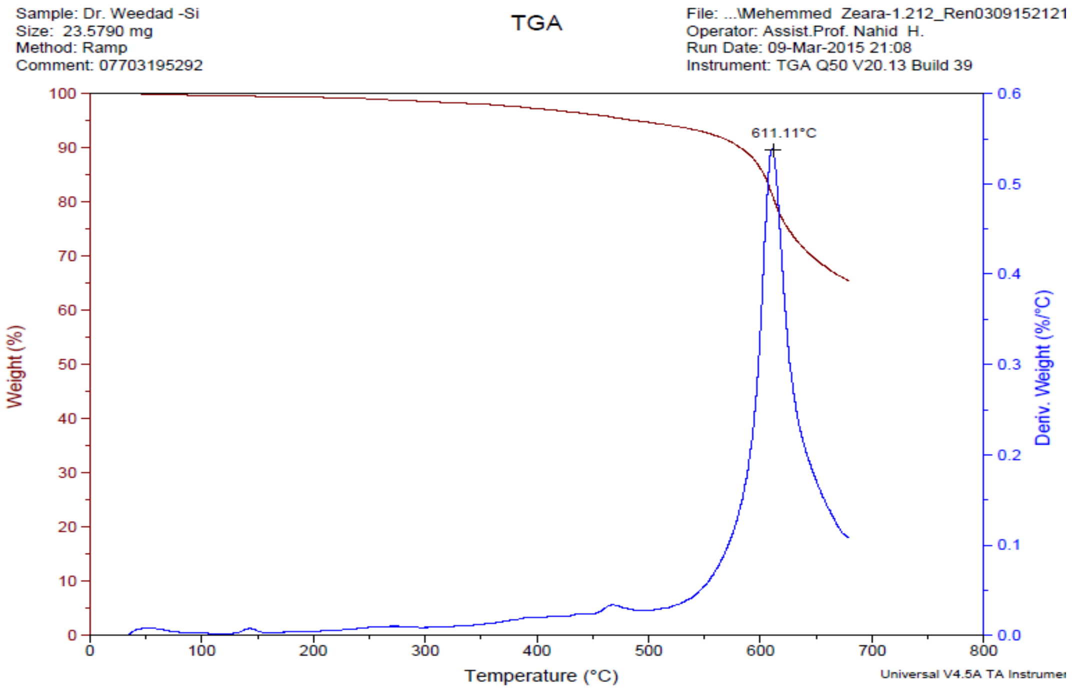


Figure (2) : FTIR spectrum of poly (vinyl tryallyloxy silane)

Thermal study

TGA& DSC thermograms of the polyallylxyvinylsilane (which prepared from the polymerization of the vinyltriallyloxy silane) are shown in Figs (3,4) respectively . The DSC thermogram shown exothermic peak at 145 C^0 due to the curing of remaning double bond presence in the polymers ,another endothermic peak at 181 C^0 due to the melting of the polymer.While the TGA thermo gram of the polymer show high decomposition temperature at 611 C^0 with high char content 66% at $700C^0$ and low rate of decomposition (0.048% / min.).This means that the polymer is thermal stable polymer due to the presence of Si-O bond which have more bond energy than C-O bond.



.Figure (3) : TGA &DTGA Thermograme of polyallyloxyvinyl silane

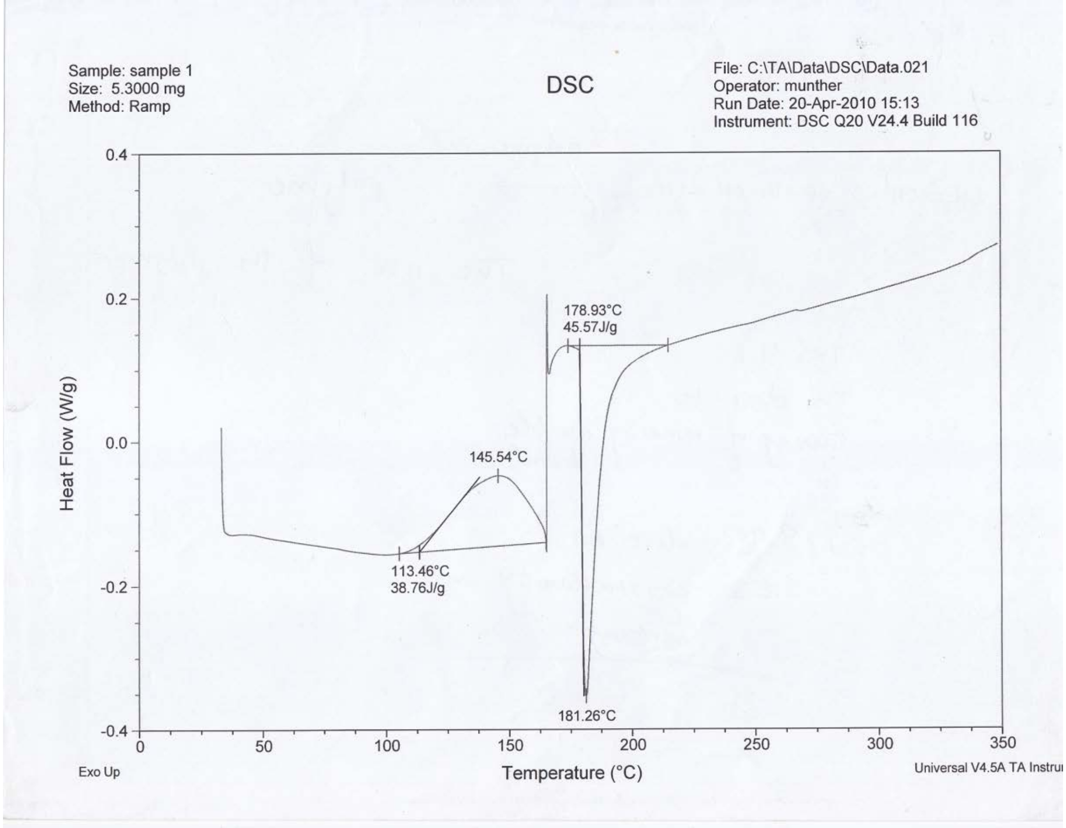
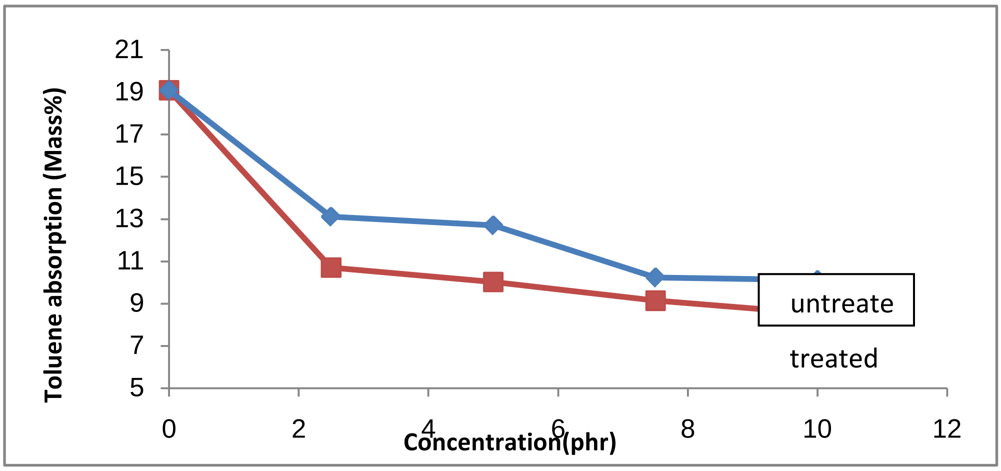


Figure (4) : DSC thermogram of polyallyloxyvinylsilane

Solvent absorption

Unsaturated poly ester composites are known for their poor resistance to aromatic solvent, due to use of styrene as reactive diluents, which is why toluene was chosen to observe the of filler addition on the solvent resistance of the composites. From Figure (5) it becomes apparent that the toluene absorption reduced with addition of untreated and treated silica due to the affinity with toluene is quite low , but the treated silica was more effect than untreated silica to reduce the absorption of toluene.



Fgure (5) : Toluene absorption of unsaturated polyester composites

In the case of water absorption the addition of untreated silica cause the increase of water absorption due to the affinity of the hydroxyl group present in the surface of silica with water, but with the treated silica with silane coupling agent (prepare in this study) the water absorption decrease with increasing percentage of treated silica due to the disapper of the hydroxyl group of silica leading to less affinity with water, Figure (6) shown this effect.

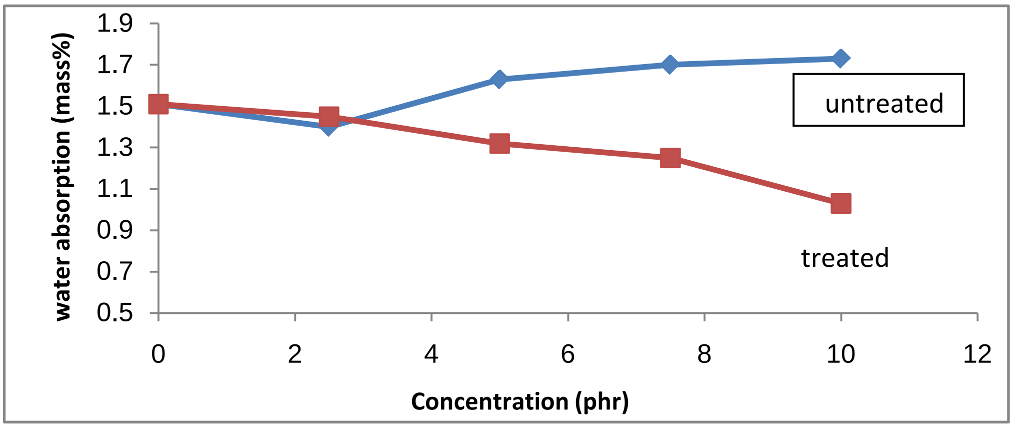


Figure (6) : Water absorption of unsaturated polyester composites

Tensile properties

The effect of untreated and treated silica on the tensile strength of unsaturated polyester are illustrated in figure 7. It is observed that the tensile strength increase with creasing filler (untreated and treated) up to (5phr) concentration of fillers, after this the tensile strength will be decrease due to more brittle structure of the composites. While the percentage of elongation of the composites showed decreasing with increasing filler content (untreated and treated), but in the case of treated silica the value of elongation of composites was rather than untreated silica especially at the concentration (7.5 &10 phr). In general the decrease in elongation due to reinforcing effect of the filler, which resulted in an creasing in the tensile strength.

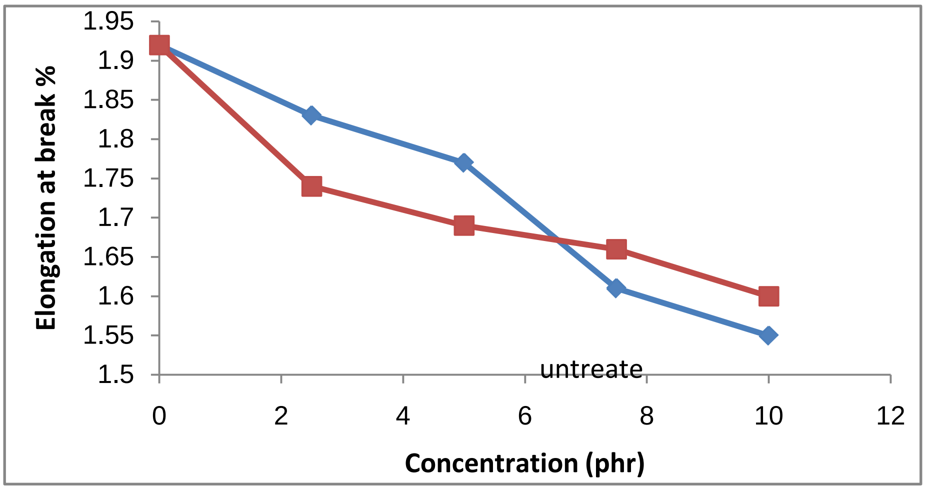


Figure (7) : Variation of tensile strength with addition of untreated and treated silica

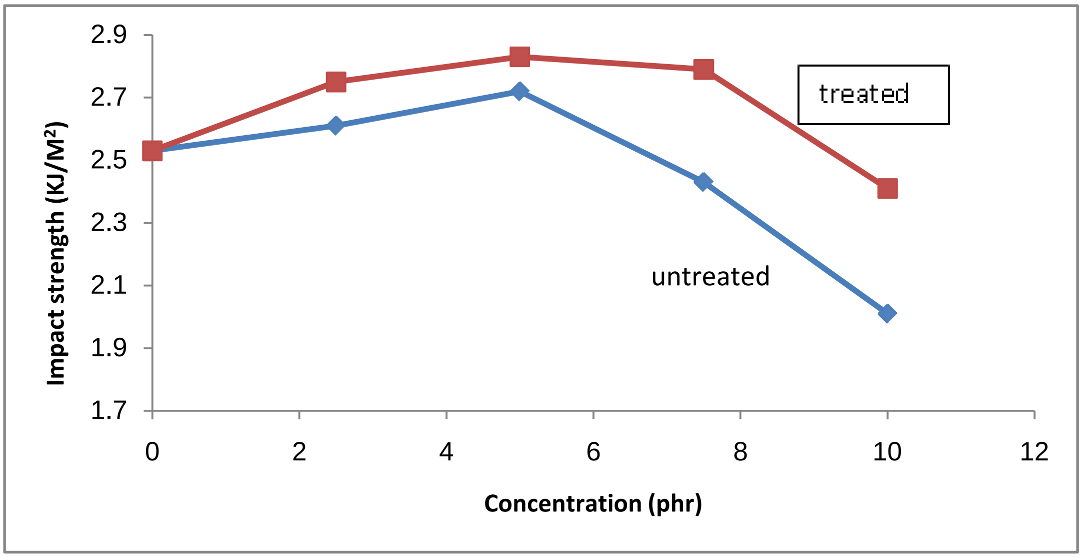


Figure (8) : Variation of elongation with addition of untreated and treated silica

Impact strength

The data on impact strength of the unsaturated polyester composites are illustrated graphically in figure (9). The figure shows that the impact strength increase with increasing untreated silica up to (5phr) concentration ,while in the case of treated silica was increase up to (7.5 phr) concentration ,after this the impact strength was decrease due to increasing the level of stress concentration in the composites . Also from the figure below the value of impact strength of the composites was improve by treated silca with silane coupling agent .

CONCLUSION

Silcaparticle untreated and treated with silane coupling agent have been utilized successfully in preparing unsaturated polyester composites. The prepared poly(vinyl triallyloxysilane) have high char residu and thermal stable polymers (decompose at temperature more thane 600 C^0). On the other hand the prepared composite by using trated silca have improved tensile strength, impact strength, water and toluene absorption. Generally silane coupling agents significantly used in producing composites due to their high matrix filler intraction.

REFERENCES

1-Hull , D., ((*An Introduction to composites Materials*)), Cambridge University press, Cambridge, 1992, 1-57 .

2-Harper , A., ((*Hand Book of Plastics Elastomers and Composites*)) 4th addition ,McGraw-Hill,New York, 2002.

3-Vale , C.P. ((*The Chemistry of Unsaturated Polyester and Allyl Resins*)) , Chapter 2 in Morgan p (Ed) , ILFFE, London 1961 , 19-36 .

4-Gue,T.; Wang,L.; Zhangaa,T.; &Cia,T.; Journal of Material Scince (2005): 97, 1154-1159.

5-Ashton , J.E., Halphine, J.C., & Petit,P.H. (1982). *On Composites Materials* ,Technomic publishing Co,Inc., Stamford Conn

6-Mohanty ,A.k., Dizal,l.T., & Miscra ,M., (2000) *Journal of Material Science* , 21, 1885-1888 .

7-Nishitani,Y.,Sekiquchi,I.; Nakamura ,K.; Nagatska,Y. &Kitano,T. (1998) ,*The journal of Japanese Society of Polymer Processing* vol.10,No.2 , 139-148.

8-Mader,E.; Jacobasch,H.J.Grundke,K.&Gietzelt,T.(1996), *Composites Part A. Applied Science and Manfacturing* Vol.27 A No. 9 , 907-912.

9- Wu,H.;Dwigth,D.; Huff,N.; *Comp. Sci.Tech* (1977) ; 57: 975-983.

10-Monticelli,F.; Toledano,M.; Osorio,R.; Ferrar,M.*; Dent. Mater* Nov (2006); 22(11): 1024-1028.

11- Martus ,P.; Kielbassa ,A.; *Am. J . Dent* Jun (2006): 19 (3) : 138-142.