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Effect of Grafted Silane on Fly Ash (Pha Lai – Vietnam) to Properties of Polymer Composite Materials Based on Bisphenol A-Type Epoxy Resin

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ABSTRACT

Recently, there has been much research on fly ash and its use as a filler in polymer composite materials. However, interfacial adhesion of fly ash with polymer matrix is weak. So, fly ash must be treated to improve interfacial adhesion. This paper reports effect of surface treatments of fly ash particles to mechanical, thermal properties and structure of polymer composites based on DER 331 epoxy resin matrix. The fly ash was treated by silane coupling agent GF 80 and GF 82. The results showed that the mechanical properties of silane GF 80 and GF 82 treated fly ash-epoxy resin composites were higher than that of untreated fly ash-epoxy resin composites. Specially at FASGF80, tensile strength, flexural strength, compressive strength and impact strength was maximum (tensile strength: 42.3 MPa increase 21.74%; compressive strength: 164 MPa increase 18.29%; flexural strength: 77.8 increase 6.4% and impact strength: 7.2 KJ/m^2 increase 20.83% compare with untreated fly ash composites).

KEYWORDS: *Bisphenol A-type epoxy resin, fly ash liquid, silane coupling agent, treatment, polymer composite*

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INTRODUCTION

Epoxy resins are one class of thermo set materials used extensively in structural and specialty composite applications. Available in a wide variety of physical forms from low-viscosity liquid to high-melting solids, they are amenable to a wide range of process and applications. Epoxy resins are cured using a wide variety of curing agents via curing reaction. Their properties depend on the specific combination of the type of epoxy resins and curing agents used. Because of their excellent mechanical properties, high adhesiveness to many substrates, and good heat and chemical resistances, currently epoxy resins are intensively used across a wide range of fields such as in composites, coatings, adhesives and in encapsulating materials [1-3].

Fly ash (FA) is a fine, glass-like powder recovered from gases created by coal-fined electric power generation. Vietnam power plants produce millions of tons of fly ash annually, which is usually dumped in landfills. This material causes significant economic and environmental problems. However currently, fly ash has been used widely as an excellent mineral additive in the construction industry. The use of fly ash prevents environmental pollution, and it contributes to a reduced need for natural resources. There are many studies investigating fly ash and its use as a filler in cement mortars, recovery of metals and agriculture. With small size, good dispersion and fluidity of globular, fly ash can be used as filler in the production of polymer composite materials [4-7].

However, untreated fly ash (UFA) has smooth surface, its adhesion with polymer matrix at the interface is not good. The role of the polymer matrix is to transfer the load to the filler, the interface between the filler and the polymer matrix influences to a significant extent the properties of the composites. So fly ash should be modified to improve its dispersion in the polymer matrix [8-11].

Silane coupling agents are considered useful as promoters of adhesion between mineral fillers and organic matrix. They provide improved mechanical strength as well as chemical resistance to composites [12-14].

This study presents the silane coupling agents as GENIOSIL GF 80 and GENIOSIL GF 82 with the appropriate functionality provide bonded coupling between the fly ash particles and the epoxy resin. The modified fly ash can be improved the properties of the material in which it is dispersed.

Experimental

Materials

Bisphenol A-type epoxy resin (DER 331) was supplied from Dow Chemical Company in American: Mw: 5260-5420 mmol/kg; d: 1.16 g/cm^3; Epoxide group content: 22.6%; Viscosity (25^{0}C): 11-14 Pa.s; Epoxide equivalent weight (EEW): 186-192.

Curing agent: Diethylenetriamine (DETA) was purchased from Dow chemical Company in American: Mw: 103 mmol/kg; d: 0.95 g/cm^3; Melting point: -35^{0}C; Boiling point: 206-209^{0}C.

Fly ash was collected from Pha Lai thermal power plant. It consists of a mixture of solid and hollow spherical particles of varying size (from 1 µm to 100 µm, medium size: 28 µm). The chemical composition of the fly ash particles with total content: $SiO_2 + Al_2O_3 + Fe_2O_3 > 70\%$; d: 0.868 g/cm^3; LOI (Loss on ignition): 3.33%.

The silane coupling agents: GENIOSIL GF 80 and GENIOSIL GF 82 were supplied by Wacker (Germany). GENIOSIL GF 80: Mw: 236 mmol/kg; d: 1.07 g/cm^3; Flash point: 122^{0}C; Boiling point: 248^{0}C. GENIOSIL GF 80 (3-Glycidoxypropyl trimethoxysilane) $C_9H_{20}O_5Si$; Epoxide group content: 17.5 %. GENIOSIL GF 82: Mw: 278 mmol/kg; d: 1.01 g/cm^3; Flash point: 101^{0}C; Boiling point: 143^{0}C. GENIOSIL GF 82 (3-Glycidoxypropyl triethoxysilane) $C_{12}H_{26}O_5Si$; Epoxide group content: 15 %.

Methods

Surface treatment of fly ash with silane coupling agents

The weight of silane coupling agent (GF 80 or GF 82) was mixed with 100 ml of the ethanol solution and stirred for 30 minutes at 40^{0}C. 100 g of the untreated fly ash (UFA) were added into the solution and stirred in 4h at 40^{0}C.The treated fly ash was then filtered, washed and dried at 100^{0}C in oven for about 12h to remove the solvents. The silane treated fly ash was noted as FASGF80 and FASGF82.

Preparation of DER 331 epoxy resin/silane treated and untreated FA composites

To prepare polymer composite materials, silane treated and untreated fly ash particles were mixed into the DER 331 epoxy resin with content of 40 percent by weight (% wt) of the mixture (consist of fly ash and epoxy resin). After the mixture were homogenously mixed, the curing agent DETA (amount of curing agent was calculated by epoxide group content of epoxy resin) was added into them and were molded for curing. The samples were cured at room temperature for about 24h and further cured at 80^{0}C in the laboratory oven for 3h. then, the samples were removed from the mold and were kept steady for about one week and were tested for the mechanical-thermal properties.

Mechanical-Thermal properties of polymer composite materials

The tensile strength was measured on Instron-5582 KN machine (USA) according to ISO 527-1993 of 5mm/min of cross-head speed. The flexural strength was measured on Instron-5582 KN machine (USA) according to ISO 178-1993 of 5mm/min of cross-head speed. The compressive strength was measured on Instron-5582 KN machine (USA) according to ISO 604-1993 of 5mm/min of cross-head speed. The impact strength was measured on Ramana ITR-2000 machine (Australia) according to ISO 179-1993 of 3.5mm/min of cross-head speed. A minimum of five replicate samples were tested for each composition and the data reported were average of five specimens.

IR analysis of fly ash samples were carried out by mixing fly ash samples with KBr in 1:20 weight ratio and mixed gently with the help of mortar and pestle, being careful about atmosphere moisture absorption. In this study, IR spectra of the materials were recorded in the range 400-4000 cm^{-1} with a resolution of 4 cm^{-1}, using IR Tensor 27 Brucker with DR accessory.

The thermal stability of materials was examined by Thermo gravimetric Analysis (TGA).Samples of ~ 10 mg were loaded into alumina pans and heated from room temperature to 800^{0}C at a ramp rate of 10^{0}C/min in nitrogen atmosphere (60 mm/min).

The structure of polymer composite materials based on fly ash and DER epoxy resin were analyzed by Scanning Electron Microscopy (SEM) technique model JSM-6490 (JEOL-Japan). The SEM was operated at the accelerating voltage of 10 keV for mineral analysis of representative samples. The fractured surfaces of the tested specimens were vacuum coated with a thin layer of gold to make them electrically conductive.

Contact angle measurement by using force tensiometer

Dynamic contact angles are measured by using Sigma force tensiometer. Force tensiometer measures the mass affecting to a balance when a sample of solid is brought in contact with a test liquid. The contact angle (θ) is calculated by using the equation (1) when surface tension of the liquid (γ_l) and the perimeter of the sample (P) are known.

$$Wetting\ force = \gamma_l P \cos\theta \qquad (1)$$

Results and discussion

Characterization of fly ash after grafting siane coupling agents

In order to increase the activity of the particle surface or increase the wet ability of the particles of fly ash carried out grafted silane GF 80 and GF 82 which contain epoxide group in its molecule on fly ash. The content of silane GF 80 and GF 82 is 2%wt comparing to UFA. The differences on the surfaces of untreated and treated fly ash were analyzed using IR spectroscopy. The analysis results are shown in Figure 1.

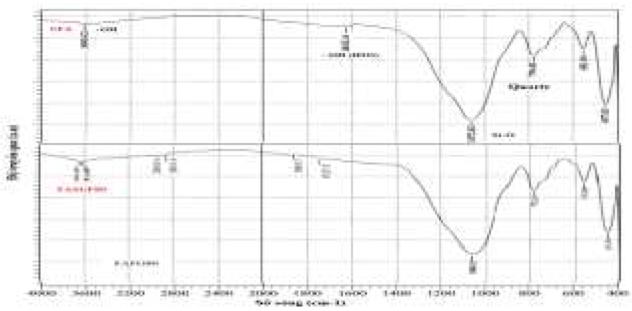


Fig.1: IR spectra of UFA and FASGF80

The results in Figure 1 show that the IR of modified fly ash (FASGF80) display new peak at 1,727 cm^{-1}, which is the wave number specific to silane functional groups. This demonstrates the presence of these functional groups on the surface of FASGF80. The contact angle of the fly ash samples treated with silane GF 80 and GF 82 in different liquid environments with same operating conditions was measured. In this study, polar liquids were used for the contact angle measurements: double deionized water and ethylene glycol with surface tension is 72±0.05 mNm^{-1} and 47.3 mNm^{-1} at 25^0C, respectively. The results are shown in Table 1.

As can be seen in Table 1, the contact angle of the samples FASGF80 and FASGF82 are higher in both polarized environments compared to untreated fly ash.

Table 1: Contact angle of test liquids on silane treated and untreated fly ash

Sample	Test liquid	Contact angle
UFA	Water	77.62^0
	Ethylene Glycol	61.66^0
FASGF80	Water	109.95^0
	Ethylene Glycol	100.64^0
FASGF82	Water	108.60^0
	Ethylene Glycol	96.77^0

Effect of silane treated fly ash on mechanical properties of polymer composites based on DER 331 epoxy resin

The silane GF 80 and GF 82 were used to improve the reinforcing capability of fly ash with silanol group on their surface and also as an integral part of curing systems to improve cross linking network properties. A comparative account with neat DER 331 epoxy resin, untreated fly ash and GF 80 and GF 82 treated fly ash composites at 40% fly ash was studied. The results of testing for the tensile strength, flexural strength, compressive strength and impact strength were represented in Table 2.

Table 2: Mechanical properties of epoxy DER 331/treated and untreated fly ash composites

Sample	Tensile strength, MPa	Compressive strength, MPa	Flexural strength, MPa	Impact strength, KJ/m^2
UFA	33.1	134	62.8	5.7
FASGF80	42.3	164	77.8	7.2
FASGF82	40.2	152	73.4	6.8

The results showed that the mechanical properties of silane GF 80 and GF 82 treated fly ash-epoxy resin composites were higher than that of untreated fly ash-epoxy resin composites. Specially at FASGF80, tensile strength, flexural strength, compressive strength and impact strength was maximum (tensile strength: 42.3 MPa increase 21.74%; compressive strength: 164 MPa increase 18.29%; flexural strength: 77.8 increase 6.4% and impact strength: 7.2 KJ/m^2 increase 20.83% compare with untreated fly ash composites). So, the treatment of fly ash with silane GF 80 and GF 82 has improved the quality of polymer composite materials based on DER 331 epoxy resin matrix.

Effect of silane treated fly ash on thermal properties of polymer composites based on DER 331 epoxy resin

Table 3: TGA characteristic of polymer composites based on DER 331 epoxy resin with UFA and grafted silane GF 80, GF 82 fly ash

PC with	TGA characteristic			
	Tmax, °C	T-50%, °C	Weight loss in range 300°C ÷ 500°C, %	Weight loss in range 500°C ÷ 800°C, %
/UFA	370	440	46,18	11,42
FASGF80	372	452	44,64	12,67
FASGF82	373	450	44,82	12,04

The results from Table 3 showed that the polymer composites based on DER 331 epoxy resin with UFA and with both FASGF80 and FASGF82 were thermal stability. From 300^0C to 500^0C, the weight of all samples was about 45% and from 500^0C to 800^0C, the weight loss of samples was about 12%. The sample PC with FASGF80 has highest temperature value when the mass loss reaches 50%.

Effect of content of silane coupling agent on the properties of PC based on DER 331 epoxy resin matrix with UFA and silane treated fly ash

Silane coupling agent GF 80 was selected to investigate the effect of denatured silane content on the properties of DER 331 epoxy resin/fly ash composites. The content of silane is 1, 2, 3, and 4%. The amount of silane is calculated by the amount of fly ash to be turned. The solvent used to hydrolyze silane is pure ethanol. After treatment, fly ash particles with corresponding symbols of FAS1%, FAS2%, FAS3% and FAS4% were analyzed by IR infrared spectrum. Comparison of spectral lines is shown in Figure 2.

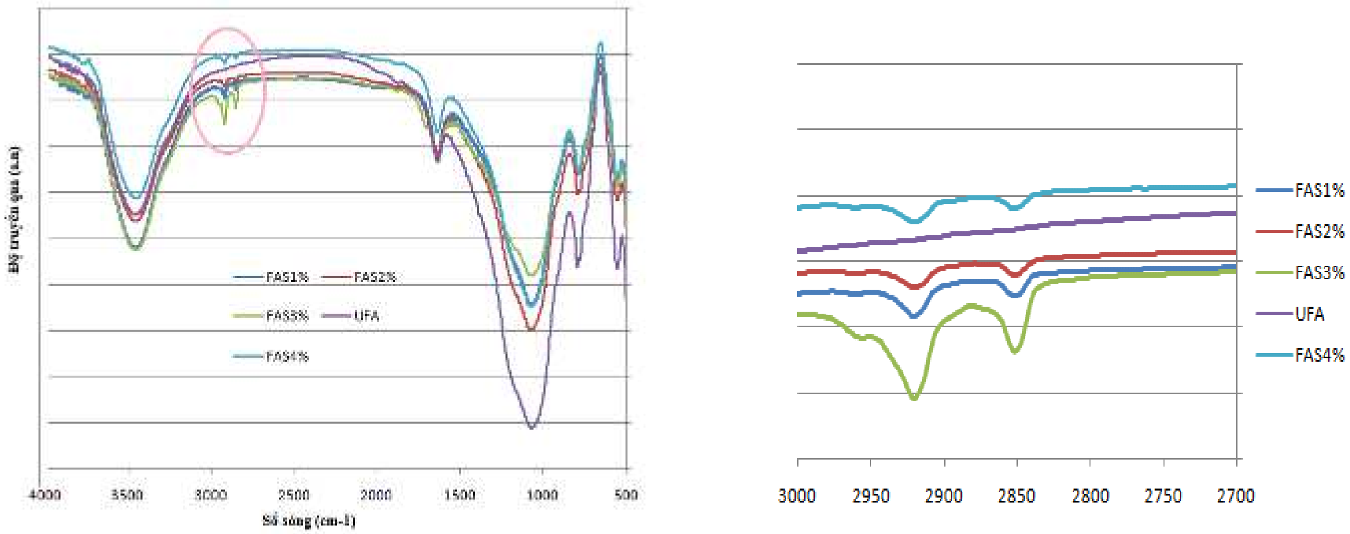


Figure 2: IR spectra of PC with different content of silane treated fly ash

From figure 2, the intensity of the spectral line specific to the silane molecule increased in denatured fly ash samples in a solution containing 2% silane and 3% silane compared to samples treated in a 1% and 4% solution. This proves that the adsorbed silan content on the surface increases with increasing silan concentration. However, when this content is high, it is easy to create multi-layer silane on the surface of fly ash making their durability decrease. Thus, with the content of 2% and 3% silane by mass is appropriated and ensure the durability of the silane layer on the surface of fly ash.

The properties of PC based on DER 331 epoxy resin matrix with UFA and silane treated fly ash with different content of silane GF 80 was represented in Table 4 and Table 5.

Table 4: Tensile strength and flexural strength of PC based on DER 331 epoxy resin with different content of silane GF 80 treated fly ash

Content of silane, %	Tensile strength, MPa	Tensile modulus, GPa	Flexural strength, MPa	Flexural modulus, GPa
0	33.1	2.41	62.8	4.83
1	34.9	2.57	67.8	5.05
2	42.3	2.85	77.6	5.29
3	44.2	2.78	66.3	4.82
4	39.7	2.55	64.5	4.44

Table 5: Compressive strength and impact strength of PC based on DER 331 epoxy resin with different content of silane GF 80 treated fly ash

Content of silane, %	Compresive strength, MPa	Impact strength, KJ/m²
0	134	5.7
1	156	6.1
2	164	7.2
3	170	6.6
4	136	5.9

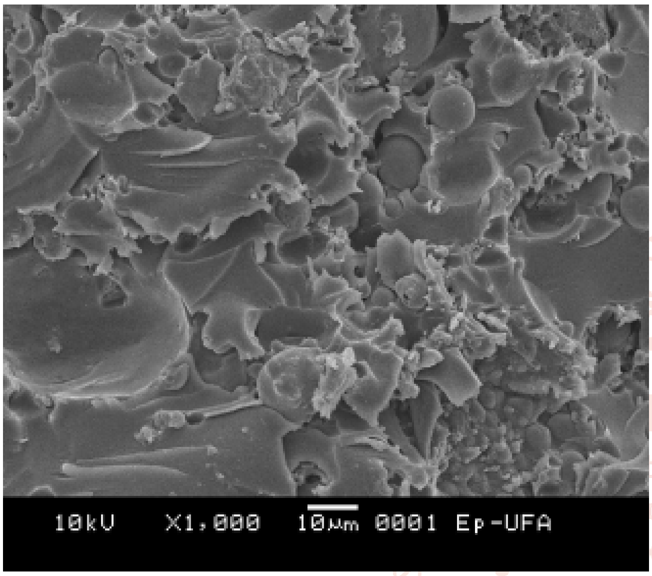
The results in Table 4 showed that all fly ash composite samples treated with silan showed higher tensile strength original composite fly ash samples. Especially when increasing the content of silane, the tensile strength and tensile modulus both increase. Maximum tensile strength value achieved at silan content than the is 3%. Maximum tensile strength is 44.2MPa, maximum tensile modulus recorded at 2% silan content is 2.85 GPa. But as the amount of silane continues to increase, both the tensile strength and the tensile modulus decreased particularly at silane content of 4%.

This variation is similar to the graph showing the effect of the GF80 silan content on flexural strength and bending module. The EP/FAS2% samples had the maximum flexural strength of 77.6 MPa, increased by 23.88% and the bending modules increased by 9.52% compared to the EP / FAS0% samples. The value of tensile strength and flexural strength of composite materials obtained at a content of 2% GF 80 is not only higher than that of the untreated fly ash samples, but also higher than those of composites with other modifier fly ash.

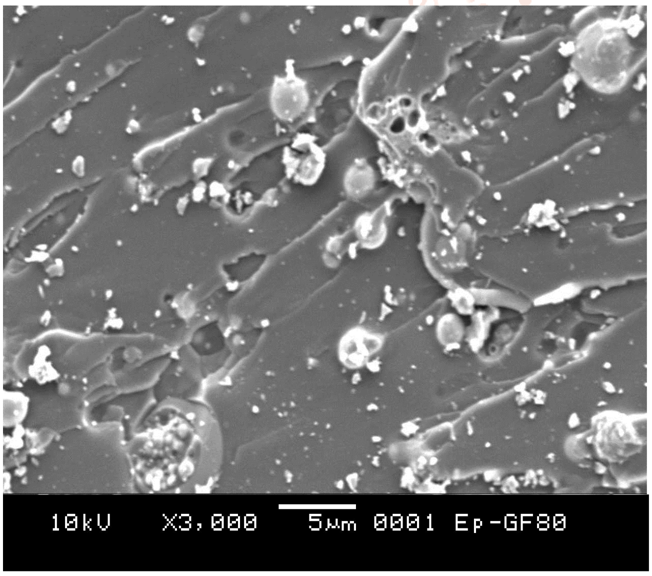
Comparing the change of compressive strength and impact strength of composite samples with different silan content in Table 5, it can be clearly seen that the compressive strength increases with increasing silan content from 1% to 3%, then decreases. at 4% silan content. Impact resistance also achieved a maximum value of 6.62 (KJ/m2) of EP / FAS3% samples, an increase of 16.14% compared to EP / FAS0%

samples. This once again confirms the method of denaturing fly ash before making DER 331 based epoxy composites. Initially, the modification of fly ash by silan coupling agent has improved the mechanical properties of the material. And the most suitable silan content is 2%. As such, the formation of physical interactions and silane bonds with OH group on fly ash particle surface has also contributed to improving the mechanical strength of the material. Especially, the flexural strength increases by more than 20% compared to composite samples, which have not been modified by fly ash. Denaturing fly ash by this method has overcome the brittle properties of epoxy substrate.

The structure of PC based on DER 331 epoxy resin with UFA and silane GF 80 (2 wt%) fly ash is shown in Figure 3.



(a)



(b)

Figure 3: SEM image of PC with UFA (a) and with silane GF 80 (2% wt) fly ash (b)

Observing the SEM image in Figure 3, the fly ash has a spherical structure even when its size is very small, with untreated fly ash they exist relatively independently, not associated with epoxy resin. But with fly ash treated by silane coupling agent, the fly ash is covered with plastic and distributed in the base resin more regularly, there is no discrete particles as much as the sample with untreated fly ash. The phase interaction between fly ash and epoxy resin is better thanks to the active groups of coupling agents on the fly ash surface, which reduces the surface tension between the two phases. This morphological structure explained the increase in mechanical properties of the material when fly ash is denatured.

The phase interaction of composite materials has been improved, but some fly ash particles still exist independently. The surface of fly ash is denatured by silane coupling agent with epoxy group in its molecule which has the effect of increasing the phase interaction between resin base and inorganic fly ash fillers.

Conclusion

The treatment of fly ash with silane coupling agent GF 80 and GF 82 improved the mechanical and thermal properties of PC based on DER 331 epoxy resin matrix. The PC based on DER 331 epoxy resin matrix reinforced with fly ash exhibited the best mechanical properties when fly ash was treated with silane coupling agent GF 80 and GF 82 at 2% wt. The treatment of fly ash by silane coupling agent also overcome the brittleness of epoxy resin in polymer composites reinforced with fly ash.

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