PREPARATION OF GF/PVC COMPOSITES USING AQUEOUS SUSPENSION IMPREGNATION TECHNIQUE: THE INTERFACIAL ISSUES

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SUMMARY: Following our previous studies of using the aqueous suspension impregnation technique to prepare fiber reinforced polyvinyl chloride composites, the main attention of this work was given to the interfacial issues for the suspension technique. Formulas which would form different interfacial layers were designed and possible interfaces, such as fiber/coupling agent, coupling agent/binder, coupling agent/resin and binder/resin, were simulated to evaluate the formation, adhesion and interaction of the interfaces. The nature of the interfacial interactions were investigated by FTIR and electronic probe analysis. The experimental results showed that there existed not only physical interactions but also chemical reactions at the interfaces. Chemical bonding of suitable interfacial components was found to be necessary to obtain good interfacial adhesion between fibers and matrix.

KEYWORDS: GF/PVC composites, aqueous suspension impregnation technique, interfacial interaction, FTIR, electronic probe analysis

1. INTRODUCTION

It has been well recognised that the mechanical properties of polyvinyl chloride (PVC) can be modified extensively through fiber reinforcement. Glass fiber reinforced PVC (GF/PVC) composites are normally prepared using melt-blending, solution impregnation or fluid-bed processes. While property enhancement can be achieved, problems associated with those methods have imposed, including low fiber content and poor fiber dispersion due to the PVC's poor melting flowability, environmental pollution due to the use of toxic organic solvents and additives, high cost due to the requirement of expensive equipment, and *etc*.

Following our previous studies on using the aqueous suspension impregnation technique to prepare fiber (short or continuous GF and CF) reinforced poly(phenylene sulphide) and polypropylene [1-4], the suspension technique has been extended and developed to prepare rigid GF/PVC composites in our attempts to overcome the processing problems mentioned above[5-7]. These preliminary reports have shown that GF/PVC composites with satisfactory properties can be obtained using the technique, and that the addition of coupling agents, polymeric binders and other additives into the suspension system imposed significant influences on the properties of the resultant materials. It has been also found that proper use of polymeric binders gave effectively improvement on the mechanical properties of the composites[7], suggesting that there exist interactions at interface and/or interphase between fibers and matrix of the composites.

As can be expected, the interfacial issues are more complicated in the aqueous suspension systems because both the liquid-solid and solid-solid interfaces present, and the existing additives such as surfactant(s), polymeric binder and thermo-stabilizer may interact with other compositions in the suspension and function variously on the interface and interphase between the fibers and matrix. In this report particular attention has been given to reveal the nature of these interactions in the region of fiber-matrix interface.

2. EXPERIMENTAL

2.1 Materials

The PVC powder (PVC XS-5) used was a product of Guangzhou Chemical Factory. The glass fiber was a product of Zhuhai Glass Fiber Factory. Other main ingredients of the suspensions included water, polymeric binders, polymeric coatings for the fibers, thermo-stabilizer and other additives. Precipitated silica powder with high fineness was a product of Haizhong Chemical Engineering Factory of Hangu, Tianjin. Coupling agents and polymeric binders used in the experiments are listed in Table 1. All other chemicals and additives were CP grade reagents.

2.2 The Aqueous Impregnation Process

The preparation of suspension and the impregnation process were carried out according to those reported elsewhere[1-6]. Binders were resolved directly into the suspension.

2.3 The Design of Interfacial Layers

Formulas which would form different interfacial layers were designed to evaluate the interactions of glass fibers, matrix, coupling agents, binders and polymeric coatings, as listed in Table 1.

Table 1. *Formulation designed for formation of different interphase in GF/PVC composites*

Type	Polymeric coating on coupling agent[a]	Polymeric binders	Concentration range wt%, (solid content)
EVA	None	ethylene-vinyl acetate copolymer latex	1-4 (0.48)
UCAR	None	poly(methyl acrylate-butyl acrylate) latex	1-5 (0.49)
NBR	None	poly(butadiene-acrylonitrile) latex	0.5-4 (0.29)
PVCL	None	polyvinyl chloride latex	2 - 7 (0.40)
KO-2	None	acrylates copolymer latex	0.5-2 (0.40)
KO-2/LCM	LCM[b]	acrylates copolymer latex	0.5-2 (0.40)
KO-2/LCB	LCB[c]	acrylates copolymer latex	0.5-2 (0.40)

a Glass fibers were treated with coupling agent KH-550 (A-1100), KH-560 (A-187) or KH-570 (A-174) prior to use.

b LCM=vinyl chloride-vinyl acetate-maleic anhydride copolymer.

c LCB= vinyl chloride-vinyl acetate-β -hydroxypropyl acetate copolymer

As it is rather difficult to measure the interfacial region directly using ordinary means, simulative tests were introduced to investigate the interactions. Precipitated silica powder with high fineness was used as the simulator of the glass fibers as they have the same chemical composition, giving similar IR spectrogram. Additionally, the silica powder has high specific surface, which can greatly increase the proportion of the interfacial area in the samples to enhance the absorption signals attributed to the interphase. The treatment of silica powder with

coupling agents, binders and polymeric coatings were similar to that of glass fibers.

2.4 FTIR and Electron Probe Analyses

A Nicolet MS-X FTIR Spectrometer was used to measure the samples either in the film or sheets with KBr. Analyses of electron probe were carried out by a EPMA-810Q Electron Probe Instrument. The accelerate voltage used was 20KV. The samples were extracted with tetrahydrofuran for 96 hours prior to measurements.

3. RESULTS AND DISCUSSIONS

3.1 Investigation of the interaction by FTIR

As reported in the previous article[7], the addition of polymeric coatings LCB or LCM, and polymeric binders to the suspension systems can effectively improve the mechanical properties of the GF/PVC composites. This suggests that there exist interactions between glass fibers and matrix of the composites. FTIR was used to obtained rather detailed answers of the nature of interface/interphase interactions, especially to make it clear whether chemical reactions take place at the interface or interphase.

3.1.1 Interactions between silica powder (glass fiber) and coupling agents

The changes in the FTIR spectrograms of the precipitated silica powder treated with different coupling agents are given in Table 2. The absorption bands, at about 1050 cm^{-1} to 1090 cm^{-1}, of the heated samples become wider and stronger than those of the same samples without heating. This implies that certain new absorption occurs. In fact, the absorption band of SiO_2/KH-570 splits into a triplet after heating. These new absorption bands can be attributed to the motions of Si-O-Si bonds which should be the results of reaction between siloxane and SiO_2, indicating that chemical reactions take place during the heating process. This strongly supports the viewpoint that when glass fibers are treated with silicone coupling agents siloxane will be hydrolyzed to produce silanol, which then reacted with the hydroxyl groups on the fiber surfaces to form stable chemical bonds of Si-O-Si [8].

Table 2. *Changes in the FTIR spectrograms of the precipitated silica powder treated with coupling agents after heating*

Samples	Changes in the absorption bands around 1050 cm^{-1} to 1090 cm^{-1}		
	Becoming wider	Becoming stronger	Split into mullet-peaks
SiO_2/KH-550	yes	yes	no
SiO_2/KH-560	yes	yes	no
SiO_2/KH-570	yes	yes	split into a triplet

3.1.2. Interactions of silica powder (glass fibers) with coupling agents and polymeric binders

In order to study the interactions between glass fibers and polymeric binders, the precipitated silica powder pre-treated with coupling agent was mixed with polymeric binder under the conditions similar to those of composite processing, and then used as testing specimens for FTIR measurement. Table 3 showed the changes in the FTIR spectrograms of these treated silica powder samples. It can be found that apparent changes in the FTIR spectrograms can only be observed for the sample mixing with PVCL and KH-550, with the absorption band at 3400^{-1} becoming wider and weaker, and shifting to the lower wave number. These can be attributed to the formation of sec-amine (NH—) bonds, resulting from the reaction of amine groups of KH-550 with the active free radicals of allyl chloride produced due to the slight thermal decomposition of PVC under the processing conditions.

Table 3. *Changes in the FTIR spectrograms of the precipitated silica powder treated with coupling agents and polymeric binders*

Samples	Changes in the absorption band at 3400cm^{-1}		
	Peak becomes wider	Peak becomes weaker	Peak shifts to lower wave number
SiO_2/KH-550/EVA	×	×	×
SiO_2/KH-550/UCAR361	×	×	×
SiO_2/KH-550/EVA/NBR	×	×	×
SiO_2/KH-550/KO-2	×	×	×
SiO_2/KH-550/PVCL	yes	yes	yes
SiO_2/KH-570/EVA	×	×	×
SiO_2/KH-570/UCAR361	×	×	×
SiO_2/KH-570/NBR	×	×	×
SiO_2/KH-570/KO-2	×	×	×

×: no observable change

3.1.3. Interactions between coupling agents and polymeric coatings

Blends of different coupling agents and polymeric coatings, without precipitated silica powder, were made to study the possible interactions between these components. The samples again were prepared under the condition similar to those of composite processing. Table 4 gives the changes in the FTIR spectrograms of the blends of KH-550 and polymeric coatings after heating. It can be seen that the changes are similar to those of SiO_2/KH-550/PVCL as shown in Table 3, suggesting that the same chemical reaction takes place in both cases. Although there is no PVCL component in the blends of KH-550/LCB and KH-550/LCM, both LCB and LCM are copolymers containing vinyl chloride blocks to produce active free radicals of allyl chloride.

Table 4. *Changes in the FTIR spectrograms of the blends containing KH-550 and polymeric coatings*

Samples	Changes in the absorption band at 3400cm^{-1}		
	Peak becomes wider	Peak becomes weaker	Peak shifts to lower wave number
KH-550/LCB	yes	yes	yes
KH-550/LCM	yes	yes	yes

Table 5 compares the changes in the FTIR spectrograms of the blends containing KH-560 and LCB or LCM. It can be seen that the absorption peak at 913 cm^{-1}, which is the characteristics of epoxy groups in KH-560, became weaker. A new absorption peak at 1020 cm^{-1} due to the formation of ethereous bonds was also observed. These could be explained if the hydroxyl groups in the LCB have catalytic activity to promote the ring opening reaction of the epoxy cyclo-groups to produce etherification at certain temperature. In contrast, the FTIR spectrogram of the KH-560/LCM sample keep unchanged after processing, indicating that no chemical reaction takes place between KH-560 and LCM.

Table 5. *Comparison of changes in the FTIR spectrograms of the blends containing KH-560 and polymeric coatings*

	Changes in the spectrograms

Samples	Peak at 913 cm^{-1} becomes weaker	New absorption at 1020 cm^{-1} appears
KH-560/LCB	yes	yes
KH-560/LCM	no	no

It can thus be deduced from the above experimental results that chemical reactions take place not only between the fiber surface and the coupling agents, but also between coupling agents and polymeric binders as well as coupling agents and polymeric coatings in some cases.

3.2 The Electron Probe Investigation of the interactions

Electron probe measurement was used to check the type of elements, such as Cl, Si, Ca and Fe, and their quantities on the surface of the glass fiber after the impregnation processing. All the testing samples were extracted with tetrahydrofuran for 96 hours prior to measurement in order to remove the PVC resin that did not bond chemically to the fiber surfaces. The results are given in Table 6.

Table 6. *Contents of elements on the surface of fibers extracted with tetrahydrofuran*

Samples	Contents of elements (wt %)						
	Cl	Al	Si	Ca	Ti	Fe	others
$1^{\#}$ GF/KH-550/ +EVA	0	9.95	27.04	16.40	0.10	0.15	46.32
$2^{\#}$ GF/KH-550/ +UCAR-361	0	9.90	27.17	16.34	0.19	0	46.41
$3^{\#}$ GF/KH-550/ +NBR	0	9.85	27.07	16.54	0.20	0	46.34
$4^{\#}$ GF/KH-550/+KO-2	0.32	10.01	27.07	16.34	0	0	46.54
$5^{\#}$ GF/KH-550/ +PVCL	0	10.08	27.05	16.00	0.31	0.14	46.42
$6^{\#}$ GF/KH550/LCM/ +KO-2	0.32	9.64	27.57	16.02	0.02	0.02	46.40
$7^{\#}$ GF/KH-550/LCB/ +KO-2	0.44	9.45	28.17	15.32	0	0	46.62
$8^{\#}$ GF/KH-560/LCM/ +KO-2	0	10.00	27.45	15.35	0	0	46.55
$9^{\#}$ GF/KH-560/LCB/ +KO-2	0.37	9.70	27.60	15.37	0.20	0.11	46.45

It can be clearly seen that chlorine was detected on the fiber surface for samples $4^{\#}$, $6^{\#}$, $7^{\#}$ and $9^{\#}$. All of these samples contain polymeric binder KO-2, an acrylates copolymer latex. It has been reported in our previous work [7] that in the aqueous impregnation processing all the polymeric binders used could improve the melt-flowability and might be used to replace the ordinary PVC plasticizer, and that the best result was found when using KO-2 latex. This acrylates copolymer is a mutilfunctional additive unique to the aqueous suspension process not only as a processing aid agent to reduce the viscosity of PVC, but also an efficient compatibilizer to promote the wettability of melting PVC with the fiber surface. This can effectively enhance the interfacial contacts of matrix with the fibers. When the composite specimens were hot-moulded, active free radicals of allyl chloride may be produced, due to the slight thermal decomposition of PVC, and react with the amine groups of KH-550 which is coupled chemically onto the surface of glass fibers. Consequently, PVC resin would reside on the fiber surface after solvent extraction.

For samples $6^{\#}$-$9^{\#}$ with complex fiber coatings where LCB or LCM was coated on the coupling agent laryer, it can be found that the nature of interaction between coupling agent and polymeric coating will affect the adhesion and bonding of PVC resin to the fiber surface. Since there is no chemical reaction taking place between KH-560 and LCM, as discussed in section 3.1.3, no residual PVC was detected on the fiber surface (sample $8^{\#}$). In contrast, residual PVC was well detected for samples $6^{\#}$, $7^{\#}$ and $9^{\#}$ of which chemical reactions can take place either between KH-560 and LCB (sample $9^{\#}$), or KH-550 and LCM (sample $6^{\#}$) and LCB

(sample 7#). Although PVC is compatible with LCB and LCM, the non-chemically bonded nature of polymeric binder/coupling agent leads to the leaching out of PVC resin from the fiber surface during the solvent extraction.

For samples using other polymeric binders, interactions between binders and coupling agents are either non-chemical or weak, resulting removal of resin from fiber by extraction. These can be well related to the results of mechanical property studies reported previously[7], in where highest values of strength and modulus were found for the composites using formulas as samples 4#, 6#, 7# and 9#, emphasizing the important role of chemical bonding at all the possible interfaces (fiber/coupling agent, coupling agent/binder, coupling agent/resin, and binder/resin). Figure 1 shows the flexural and impact strength of GF/PVC using different polymeric binders. It is evident that using KO-2 as a binder gives the highest flexural strength but lower impact strength due likely to the strong interfacial adhesion between fibers and matrix. Direct observation of the surface morphologies on these specimens has also been carried out, and will be reported in the article elsewhere.

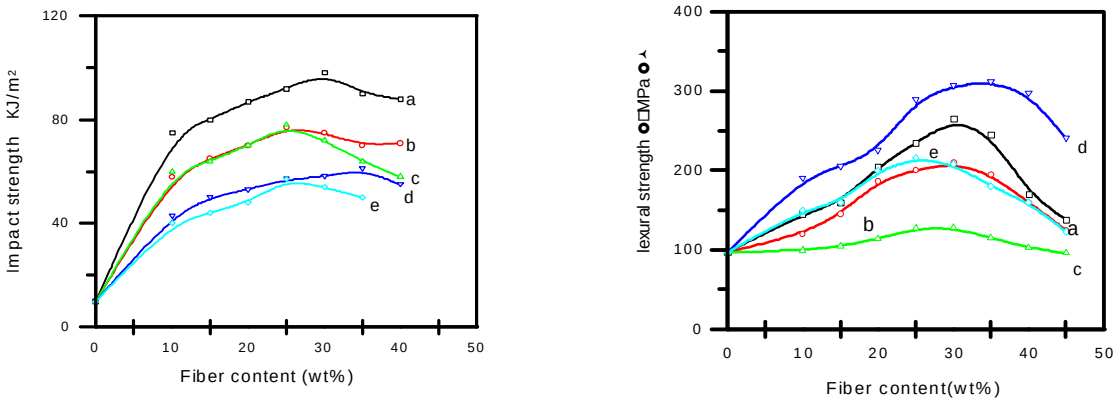

Figure 1 Flexural and impact strength of GF/PVC using different polymeric binders
a: EVA; b: UCAR; c: NBR; d: KO-2; e: PVCL

CONCLUSIONS

It can be concluded that the binding strength of the fiber/matrix interphase depends on the nature of interphase layers. The experimental results of FTIR and electron probe analysis have showed that the interfacial adhesion and interaction for the composites prepared by the formulas containing EVA, UCAR, NBR or PVCL latex were due mainly to the physical interaction between the binder and fibers. Whereas the interfacial interaction for the composite prepared by the suspension containing KO-2 latex was evidenced to involve dominantly chemical interaction and bonding between the fibers and matrix. Although polymeric binders are useful in improving the melt-flowability of PVC resin and played an important role in controlling the interfacial characteristics, chemical bonding at interfaces is necessary to obtain good interfacial adhesion between fibers and matrix. The polymeric coatings, LCB and LCM, are compatible with PVC and can bond chemically with KH-550, providing good adhesion between fibers and the resin. These are consistent very well with the results of mechanical property studies.

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