Effect of solvents on adsorption of phenolic resin onto γ-aminopropyl-triethoxysilane treated silica fiber during resin transfer molding

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Phenolic resin-based composites obtained by resin transfer molding (RTM) process have been extensively used in aerospace industry and commercial applications for their outstanding fire resistance and cost effectiveness [1, 2]. A typical RTM process involves injecting a liquid resin into a mold cavity containing a dry fibrous assembly and then curing the resin-infused preform at varying levels of heat, both external and chemical-reaction derived. An important requirement for a resin amenable to RTM is that the viscosity of the resin is low enough to facilitate mold filling. The high viscosity of phenolic resin necessitates the use of organic solvents to provide a low-viscosity medium so as to easily wet-out the reinforcements. Components of resulting resin solution are adsorbed onto the reinforcements and subsequently, an interface between resin and reinforcement develops which determines, to a large extent, the overall performances of the ultimate product. It is manifested that solvent plays a crucial role in many physical and chemical processes [3–5], however, much less attention has been paid to the effects of solvent on adsorption of resin onto reinforcement. Silane coupling agents have been used to effectively improve the overall properties of composites by facilitating adhesion of inorganic reinforcement to the polymer matrix. It can be expected that the adsorption of phenolic resin onto fiber surface is complicated due to the presences of silane and solvent in a RTM process. The intention of the present study was to explore solvent effect on the adsorption of phenolic resin onto silane modified silica fiber in an attempt to elucidate the role of solvent in a RTM solution impregnation route.

The commercial silica fiber (diameter=8 μm) used in this study was silanized with an aliphatic silane coupling agent, γ-aminopropyl-triethoxysilane (γ-APS) according to the method described in the literature [6]. A resol-type of phenolic resin was obtained from the Beijing Research Institute of Materials and Technology, China. Three types of solvents (AR grade), ethanol, acetone, and tetrahydrofuran (THF), were dried over molecular sieves and distilled under nitrogen prior to use.

The phenolic resin solution (55 wt%) was injected into a RTM apparatus (Φ10 mm$\times$250 mm) at a pressure of 20 kPa, where certain silica fiber bundles had been placed ensuring that fiber volume fraction of bulk specimens was about 50%. Then several fiber bundles with adsorbed phenolic resin were pulled out and dried in vacuum at 50 °C. XPS measurements were performed using a VG ESCALAB MKII photoelectron spectrometer. The electron paramagnetic resonance (EPR) spectra were recorded on a JEOL JES-FE3AX spectrometer. The value of the rotational correlation time, τ, in EPR measurement was calculated according to the reported method [7]. The adsorption amount of phenolic resin at different region of the RTM apparatus was measured on a Netzsch STA449C thermogravimetric analyzer. The interlaminar shear strength (ILSS) of silica fiber/phenolics composites was tested on a universal testing machine (WD-1, Changchun, China) using a three-point short beam bending test method accord to ASTM D-2344-76. The distribution coefficient (D) was calculated by the following equation from the TGA and ILSS results:

$$D = \frac{F_{\text{outlet}}}{F_{\text{inlet}}}$$

where F_{outlet} and F_{inlet} are weight losses or ILSS of the specimens taken at the outlet and inlet region of the RTM apparatus, respectively.

Fig. 1a–c give the C1s spectra of the silica fiber with adsorbed phenolic resin from different solvents, which comprise four components at 284.2, 285.0, 286.1, and 287.9 eV representing aromatic ring, aliphatic, C–O and C=O carbon species, respectively [8]. The band at 287.9 eV results from the residue formaldehyde inherently present in resol-type phenolic resin, whereas aliphatic and C–O carbon species are attributed to resin,

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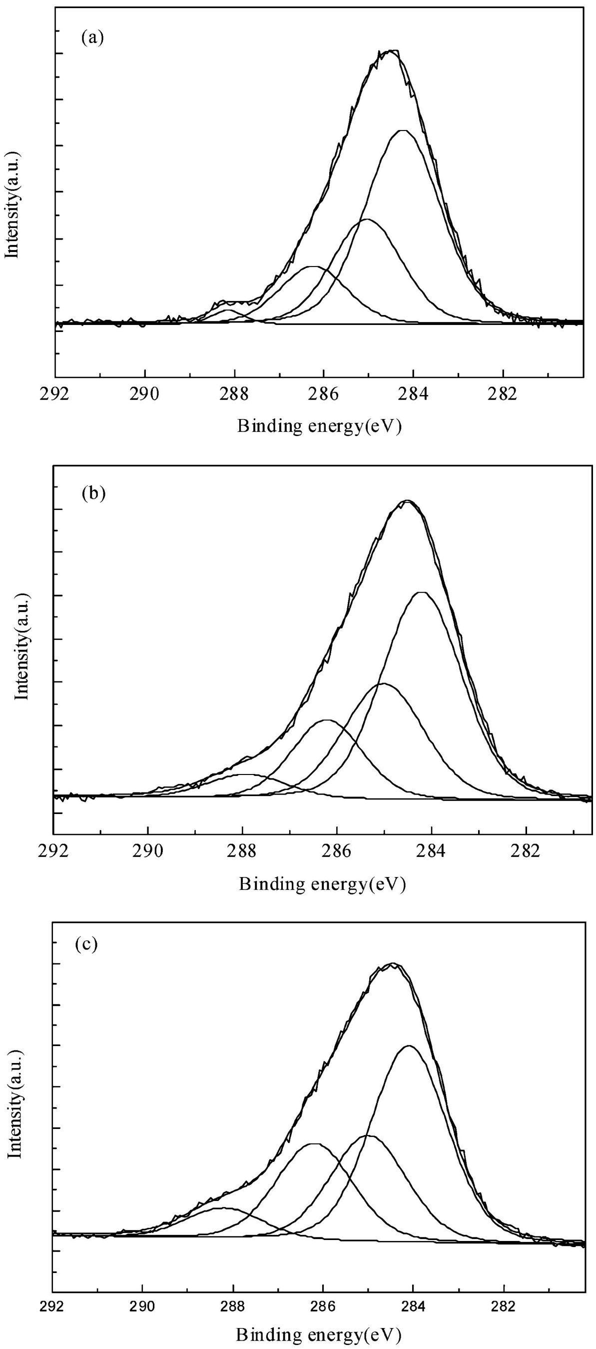

Figure 1 The C1s spectra obtained from γ-APS-treated silica fiber with adsorbed phenolic resin from: (a) THF, (b) ethanol, (c) acetone.

TABLE I XPS C1s and N1s Spectra Curve fit results of APS treated silica fiber with adsorbed phenolic resin from different solvents

	C1s (%)				N1s (%)	
Solvent	$C_{aromatic}$	$C_{aliphatic}$	C–O	C=O	NH_2	$NH_3{}^+$
THF	59.98	19.58	16.89	3.55	64.65	35.35
Acetone	53.70	26.22	12.48	7.60	69.69	30.31
Ethanol	49.58	28.32	17.26	4.84	60.78	39.22

solvent and silane, whose major contributions originate from the solvents and not the phenolic resin. What is of interest here is the aromatic carbon region centered at 284.2 eV, which is only present in phenolic resin. Table I shows that the aromatic carbon content decreases in the following order: ethanol < acetone < THF, indicating that solvent species have significant influence on the adsorption of phenolic resin onto γ-APS treated silica fiber. The C=O content on the sample surface greatly increased when acetone was used as solvent. With regard to ethanol, there is 28.32% of the total carbon species present as aliphatic carbon and 17.26% present as C–O detected and these values are higher than those obtained from other solvents. Data in Table I clearly reflect the co-adsorption of acetone and ethanol as solvents onto the γ-APS treated silica fiber.

Important information on the interactions occurring on the surface of the samples is obtained by analyzing the XPS N1s spectra (Fig. 2a–c). The peaks with higher and lower binding energies are characteristic of protonated and aliphatic amine groups. The hydrogen bonding interactions between γ-APS and the hydroxyls of the components in solution are responsible for the protonated amino groups observed, which are consistent with the reported results [6]. Table I demonstrates that the greatest protonated amino groups are detected for the ethanol system, followed by those of the specimens adsorbed from THF and acetone, respectively.

Another interesting phenomenon is observed from the binding energy shifts of the protonated N1s species. From the specimen adsorbed from THF, the binding energy of the protonated N 1s species is 2.0 eV higher than that of N1s from the unprotonated amino groups. But a binding energy shift of 2.4 eV is observed when using acetone as solvent. Additionally, a binding shift of 1.5 eV is observed from the specimen adsorbed from ethanol. It is possible that different interactions occurred between the amino groups and the constituents of phenolic resin solution.

Protonated amino groups possessing unpaired electron offer the potential for employing EPR spectroscopy to detect its microenvironment around. Rotational correlation time, τ, calculated from the spectra characteristic of ^{14}N species in a motionally hindered environment is connected with the microviscosity of EPR probe surrounding and gives information on significant changes in the microenvironment of the probe [9]. The XPS protonated amino group percentage detected and the probe mobility changes as a function of aromatic carbon species content are shown in Fig. 3. It is noteworthy that the mobility of the protonated amino groups for specimens adsorbed from different solvents changes linearly with the XPS aromatic carbon species percentage, however, the least adsorption of phenolic resin corresponds to the greatest protonated amino groups. In acetone and THF where the probe exhibits low mobility, protonated amino groups orienting away from the fiber surface are more motionally restricted. In the case of ethanol, amino groups are protonated both by phenolic resin and ethanol due to their proton donor nature [10],

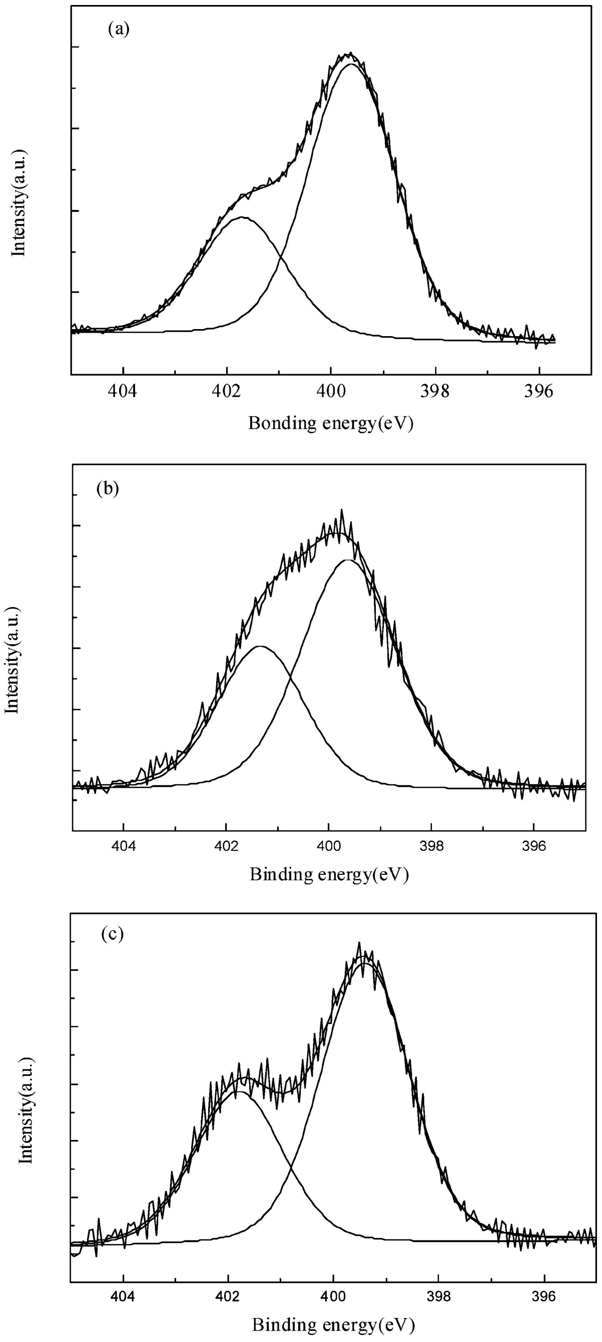

Figure 2 The N1s spectra obtained from γ-APS treated silica fiber with adsorbed phenolic resin from: (a) THF, (b) ethanol, (c) acetone.

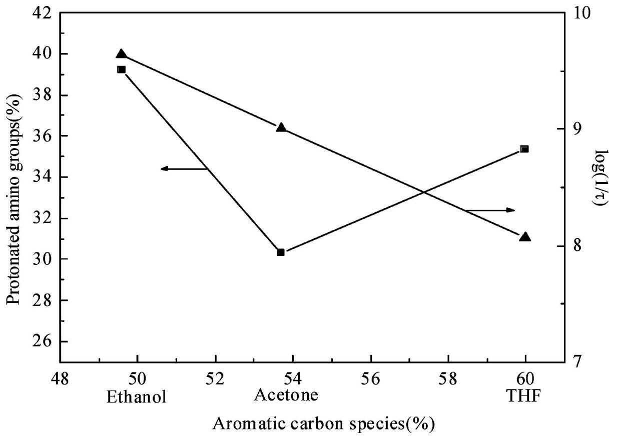

Figure 3 XPS protonated amino groups content and its mobility versus aromatic carbon species percentage for specimens adsorbed from different solvents.

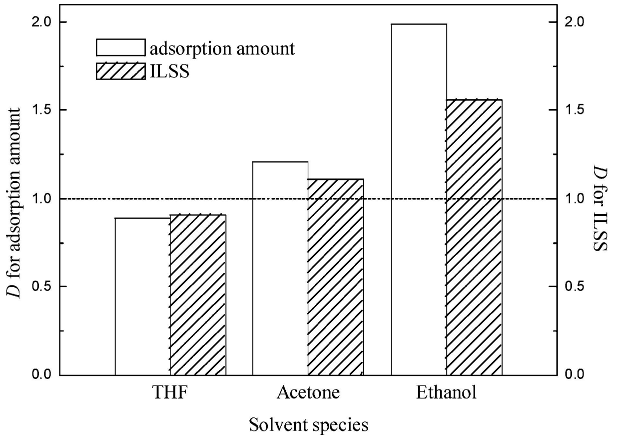

Figure 4 Distribution coefficients for phenolic resin using different solvents throughout the RTM apparatus.

leading to less adsorption of phenolic resin and a small rotational correlation time value. Whereas in acetone and THF, the protonation of amino groups is only caused by phenolic resin molecules. EPR results indicate that phenolic resin with high viscosity was adsorbed, differing in amount, from solvents onto the γ-APS treated silica fiber resulting in the entrapment of the bound protonated amino groups, to varying extent, in the adsorbed resin layer.

The effect of solvent in a RTM process was examined by evaluating the distribution coefficient *D*. A distribution coefficient *D* of unity can imply the uniformity of resin adsorbed throughout the RTM apparatus and that of the interfacial bonding strength measured at different locations of a specimen. It can be found in Fig. 4 that both *D* values deviate most from unity for ethanol system and least for THF system indicating that ethanol as solvent is preferentially adsorbed onto fiber surface at the inlet region of the RTM apparatus and even partly displace the phenolic resin already adsorbed. The opposite is true for THF. The inhomogeneity of resin distribution in the presence of solvent induces difference in performance at different positions in RTM parts [3]. It can also be seen in Fig. 4 that solvent species affect, to a less degree, ILSS than do resin distribution.

Phenolic resin is known to be surface active via hydrogen bonding interactions between its hydroxyls/hydroxymethyls and the amino groups on the fiber surface, which is a prerequisite to the effective interfacial bonding. The competition between phenlic resin and solvent for amino groups on silica fiber surface occurs due to the hydrogen bonding tendency of solvents used here. The adsorption discrepancies of resin in a RTM process are mainly due to differences in hydrogen bonding ability of solvents, as resin and fiber are common in three solvents. The competitive adsorption of solvent molecule can be explained by the results obtained in XPS and EPR measurements.

In conclusion, the adsorption of phenolic resin onto γ-APS treated silica fiber is highly solvent-dependent. THF seems to be a promising candidate for RTM applications. Microscopic interactions occurring among phenolic resin, solvent and amino groups are responsible for the difference in the resin distribution and the ILSS inhomogeneity. The competitive adsorption of solvent onto γ-APS-treated fiber suppresses the adsorption of phenolic resin and this suppression is unfavorable in solution impregnation route. Future efforts will be devoted to solvent effect on the mechanic properties of a three-dimensional RTM product.

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