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Sizing of carbon fibres with aqueous solutions of poly(vinyl pyrollidone)

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A sizing apparatus to coat carbon fibres with aqueous water-dispersible polymeric interphases was developed. The apparatus utilizes a high level of fibre spreading achieved through control of fibre tension and the application of rollers. A statistical process model was developed to relate the mean sizing level to the process independent variables. Pyrolysis in a nitrogen atmosphere was developed as a quantitative sizing level determination technique for the polymer poly(vinyl pyrollidone) (PVP). Scanning electron microscopy demonstrated that the PVP was deposited on to the fibres in a highly uniform manner. The sizing process along with the statistical process model and the characterization techniques allow for the precise development of interphase materials which are tailored for optimal composite performance. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: interphase; sizings; coupling agents)

INTRODUCTION

Fibre reinforced polymer composites consist of a reinforcing fibre embedded in a polymeric matrix material. The resulting composite material has a high strength/weight ratio when compared with traditional metallic materials[1]. The matrix protects the brittle reinforcing fibre and transfers the load to the fibre. Polymer matrix materials include thermosets such as epoxies, unsaturated polyesters, and phenolics and also thermoplastics such as poly(ether ether ketone) (PEEK), LaRC TPI, and poly(phenylene sulfide) (PPS). Carbon fibres possessing high modulus and strength are typically used. In many aerospace and civil applications, other fibre types include ceramics, E-glass, Kevlar and Spectra. A third constituent, the 'interphase', is now known to affect composite performance drastically[2]. The interphase is a region of finite mass located at the fibre/matrix interface. This region has gradients in physical properties that greatly influence the performance of the final composite. One way to modify the physical properties of this interphase region is through the application of a sizing material to the surface of the carbon fibre prior to impregnation with the matrix material. The process of applying a sizing to a carbon fibre surface is referred to as sizing.

Recent research has demonstrated that the application of thermoplastic sizings to carbon fibres can improve composite performance, especially durability and lifetime. Lesko *et al.* compared mechanical properties of composites constructed from an epoxy matrix and carbon fibre sized with two different agents[3]: Bisphenol-A, an epoxy, and K-17 poly(vinyl pyrollidone) (PVP), a thermoplastic sizing. The K-17 PVP sized fibre showed an increase in fatigue life by a factor of 100 over the Bisphenol-A sized fibre. The static compressive strength of the K-17 PVP sized composites was 51% greater than the Bisphenol-A case. The K-17 PVP sized fibres showed a 62% greater strain to failure. The results show that it should be possible to engineer an optimal sizing material to tailor selected composite properties.

Before optimal sizing materials can be developed, a process for effectively applying the interphase material to the fibre surface needs to be developed. Since any engineering sizing material must eventually find acceptance in industry, the sizing process must meet current and anticipated environmental safety standards. Given the range of chemistries available for polymeric matrices and interphase materials, this requires utilizing aqueous solutions or suspensions to accomplish the coating.

Much of the previous work with sizing processes has focused on organic solvent systems. Jenkins and co-workers[4] developed a solvent-based sizing apparatus for 12K carbon fibre tows. The sizing system consisted of an unwind spool, a dip bath, a drying unit and a wind-up device. The system utilized rollers but no information about number or size was given. The typical line speeds utilized

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by this system were 2.7 cm s^{-1}. This resulted in a residence time of approximately 30 s in the drying unit which utilized forced convection for the heat source and reached temperatures in excess of 200°C. These high temperatures were needed, since NMP was used as the solvent (boiling point $\cong$ 202°C). The three sizing systems tested were polyisoimide, polyarylsulphone and an imidized polyarylsulphone. Very dilute sizing bath concentrations (0.063–0.13% w/v) were used which corresponded to a very low final sizing level ($<$ 0.1 wt%) although precise values of the final sizing levels were not reported. Thomas and coworkers[5] also developed a sizing apparatus for coating carbon fibres from solvents that were similar to that of Jenkins *et al.* The system typically operated using methylene dichloride as the solvent, and the sizing bath concentration of numerous coupling agents was typically 0.75 wt%. The drying temperature was 50°C.

Tryson and Kardos developed an aqueous sizing apparatus to coat fibre glass with ductile, unreacted epoxies[6]. These researchers utilized both 5-mil monofilaments and one-mil 22-filament fibre glass fibres in their system. Their system employed active control of the fibre tension and a preheater section to dry the fibres. After going through the sizing bath, the wet fibres were pulled through drying sections that were heated by forced convection. The typical temperatures ranged from 150 to 264°C. Finally, the fibre were wound up on a spool utilizing a motorized roller with a roving arm. This motorized roller controlled line speed typically at 16 cm s^{-1}. This system was used successfully to control coating thickness from 1 to 2 microns with a standard error of ± 5%.

In the present work, an apparatus was constructed to coat carbon fibre tow uniformly with water-soluble and dispersible polymers. Due to the high surface tensions of the aqueous solutions, fibre clumping and heterogeneous sizing deposition were major bottlenecks. The process described herein utilizes high tensions, high fibre spreading and low line speeds to accomplish the sizing step. As a test case, K17 and K-30 PVP were used to verify that the sizing process satisfied three performance criteria:

1. The average sizing level or weight per cent on the final fibre can be readily controlled to achieve typical target values in the range 0.4–2 wt%.
2. Filament clumping as a result of cohesion between correspnding filaments is kept to a minimum.
3. The sizing process produces fibre with a consistent level of polymer sizing, i.e. no significant variations in sizing level during and between sizing runs.

Criterion 1 was established by correlating the mean sizing level to the process independent variables. Criterion 2 was assessed with scanning electron microscopy (SEM). Finally, criterion 3 was met by determining the effect of the duration of the sizing run on the mean sizing level. The PVP sized fibre produced by the apparatus was shown to be of similar quality to commercially available fibre sized with PVP.

EXPERIMENTAL

Materials

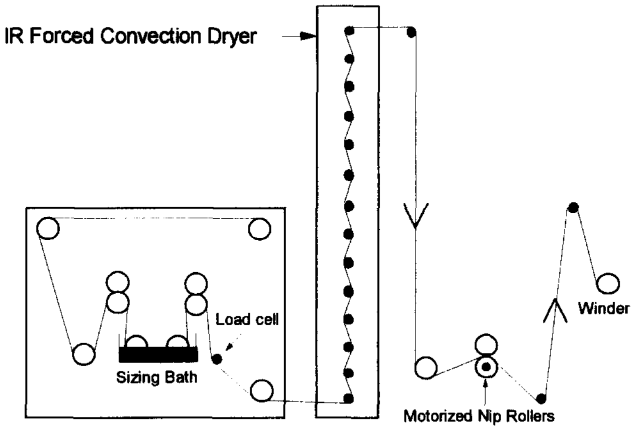
The unsized carbon fibres used in this work were Hercules AS-4 12 K (lot # 1187-4E) and Zoltek PANEX 48 K. The sizing material used was LUVISKOL K-17 PVP (BASF lot # 58-0978) and LUVISKOL K-30 PVP (lot # G501861D0) supplied by BASF. Commercially available PVP sized fibres used as controls were Zoltek PANEX 48 K with a nominal 0.7 wt% K-30 PVP sizing level and Courtaulds 12 K with a nominal 0.7 wt% K-17 PVP sizing level.

Apparatus design

The sizing apparatus was designed to achieve a high degree of fibre spreading and to dry the fibre in a spread configuration as shown in *Figure 1*. The carbon fibre is fed from a spool and directed into the process via a guide bar. The fibre tension is controlled by a nip roller that is attached to a magnetic brake. The magnetic brake is in a control loop with the tension-sensing load cell such that tension is continuously monitored and controlled between 0 and 130 N. The fibres are dipped in the aqueous bath containing the sizing solution and then spread on the series of rollers following the bath. The wet fibres enter the drying tower, where the fibres are dried in a spread configuration. The dryer utilizes a combination of I.R. radiation heaters and forced convection. The I.R. heaters take advantage of the high radiative emissivity of carbon fibres[7]. The surface temperature of the i.r. panels can be controlled from 100 to 500°C. A series of 12 stainless steel rollers keep the fibres spread while drying occurs. The fibres are then pulled by a motorized nip roller where the line speed is controlled between 0.05 and 6.08 cm s^{-1}. This corresponds to dryer residence times between 30 and 720 s. The fibres are finally wound up on a spool by a rewinder at constant tension.

Measurement of sizing level and uniformity

The quantitative level of sizing on the carbon fibres was determined by pyrolysis in a nitrogen atmosphere. The method used was a modified version of test method # SRM 14 specified by SACMA[8]. The fibre was dried at 105°C in air for approximately 12 h prior to the pyrolysis step due



Process Variables

- Line tension controllable from 0- 130 Newtons
- Spreading controllable up to 15 cm
- Line speed controllable from 3.0-365 cm/min

Figure 1 Schematic of the sizing process to the hygroscopic nature of the PVP. The fibre was then weighed and placed in a high temperature furnace with a nitrogen purge at a flow rate of approximately 40 cm^3 s^{-1}. The purge gas residence time was 30 s. Typically 15 min were required for heating the chamber from room temperature to the pyrolysis temperature of 500°C. Thus, the pyrolysis chamber typically was purged with gas for about 30 residence times prior to reaching the pyrolysis temperature. This ensured that there was no unwanted oxidation of the carbon fibres. Pyrolysis then proceeded for 30 min at 500°C. The sizing level was then determined from the weight of the pyrolized fibre. The pyrolysis technique was verified with fibre samples containing a known amount of PVP determined independently by a gravimetric technique and was shown to have a standard deviation of ± 0.03 wt%[9].

Preparation of sizing solutions

The K-17 and K-30 PVP were dried in a convection oven at 105°C for approximately 12 h before solutions were prepared. This dried PVP was then weighed in the appropriate amounts and added directly to deionized water. The deionized water came from a NanoPure II™ unit equipped with a 0.2 μm filter and had a resistivity typically of 15 MΩcm or higher. The solutions were then allowed to stir at room temperature for at least 30 min.

Scanning electron microscopy

Fibres to be analysed via SEM were first secured in a standard ESCA mount. The fibres were sputter coated with gold for approximately 2 min. Analaysis was conducted in a International Scientific Instruments Model SX-40 SEM.

MODEL DEVELOPMENT

Sizing level prediction

It was assumed that the amount of void volume in the carbon fibre tow controlled the amount of aqueous sizing solutions absorbed by the tow. In turn, the amount of sizing solution absorbed by the tow determined the amount of sizing material deposited onto the tow surface. These assumptions were tested with the model described in this section.

The theoretical sizing level, in wt%, W_{sizing}, can be expressed as a function of the tow void volume fraction V_{void} and the sizing bath concentration C_{sizing} expressed as wt% polymer in solution so that:

$$W_{\text{sizing}} = 100/\{1 + 100(1 - V_{\text{void}})\rho_{\text{fibre}}/(V_{\text{void}}\rho_{\text{solution}}C_{\text{sizing}})\} \tag{1}$$

where ρ_{solution}, the density of the solution, is for small C_{sizing}:

$$\rho_{\text{solution}} \approx \rho_{\text{water}}/\{1 - C_{\text{sizing}}/100\} \tag{2}$$

For $C_{\text{sizing}} = 2.0\%$, equation (2) gives a value of ρ_{solution} that is approximately 2% in error. This results in a final error in calculating W_{sizing} of 2% and so is negligible. For all of the calculations in this work, the following values were used: fibre density[10] $\rho_{\text{fibre}} = 1.78$ g ml^{-1} and $\rho_{\text{water}} = 1.0$ g ml^{-1}. In deriving equation (1), it is assumed that the internal voids in the tow are filled with sizing solution, i.e. $V_{\text{void}} = V_{\text{sizing}}$ (the volume fraction in the tow occupied by the sizing solution) when the tow exits the sizing bath. This assumption will be proven later. The derivation of equation (1) does not make any assumptions about the effect of line speed, fibre spreading etc., since these effects are contained in the V_{void} term. Any film of sizing solution on the exterior of the tow was neglected in this analysis. This assumption is valid in the present case given the extensive use of rollers which removes most of the exterior liquid film. The fibre moisture mass fraction X_{moisture}, defined as

$$X_{\text{moisture}} = (\text{mass of solution})/(\text{mass of fibre} + \text{mass of solution}) \tag{3}$$

is related to V_{sizing} for $C_{\text{sizing}} < 2.0$ wt% by

$$V_{\text{sizing}} = 1/\{1 + (\rho_{\text{water}}/\rho_{\text{fibre}})(1/X_{\text{moisture}} - 1)/(1 - C_{\text{sizing}})\} \tag{4}$$

Substituting equation (4) into equation (1) leads to

$$W_{\text{sizing}} = C_{\text{sizing}}\{(1/X_{\text{moisture}} - 1) + C_{\text{sizing}}/100\} \tag{5}$$

For small values of C_{sizing}, equation (5) reduces to

$$W_{\text{sizing}} = C_{\text{sizing}}/(1/X_{\text{moisture}} - 1) \tag{6}$$

For $X_{\text{moisture}} = 0.4$ and $C_{\text{sizing}} = 1.75\%$, $W_{\text{sizing}} = 1.15$ wt% from equation (5) whereas $W_{\text{sizing}} = 1.17$ wt% from equation (6), an error of only 1.7%. From equation (6), it is apparent that the sizing level is linear with respect to bath concentration C_{sizing} for low sizing bath concentrations and for a constant moisture content X_{moisture}. X_{moisture} will be constant if $V_{\text{sizing}} = V_{\text{void}}$ are constant.

Tow wetting calculations

In the derivation of equations (1)–(6), it was assumed that the voids in the tow were completely filled with the sizing solution by the time the tow exited the sizing bath. The internal voids of the tow are linked via micro-capillaries. These micro-capillaries control the capillary pressure drop, ΔP_{c}, which is the driving force for internal tow wetting. The internal micro-capillary radius can be approximated by assuming the fibres are arranged in a hexagonal packing array and determining the fibre–fibre separation. The fibre–fibre separation R can be determined from the fibre void fraction as follows.

$$R = 0.5\{\pi r^2/(\{1 - V_{\text{void}}\}\sin(\pi/3))\}^{0.5} - r \tag{7}$$

where the fibre radius, r, was taken to be 3.5 microns.

The Kelvin equation relates ΔP_{c} to the wetting of the sizing solution in the micro-capillaries by[11]

$$\Delta P_{\text{c}} = \{2/R\}\cdot\gamma_{\text{sizing}}\cdot\cos\theta \tag{8}$$

where θ is the contact angle, and γ_{sizing} is the surface tension of the aqueous sizing solutions.

The time required to fill the tow voids, t_{f}, can be approximated with Darcy's Law for flow in porous media integrated for constant pressure injection[12]

$$t_{\text{f}} = l^2\mu V_{\text{void}}/(2S_{\text{b}}\Delta P_{\text{c}}) \tag{9}$$

where μ is the solution viscosity, t_{f} is the tow wetting time, l is the tow depth or thickness which is approximately 1.6 cm for the present apparatus, and S_{b} is the permeability of tow perpendicular to the fibre direction. This last term can be estimated from[12]

$$S_{\text{b}} = 16/(9\pi\sqrt{6})\{[\pi/(2(1 - V_{\text{void}})\sqrt{3})]^{0.5} - 1\}^{5/2}r^2 \tag{10}$$

Substituting equation (7) into equation (8) leads to

$$t_{\text{f}} = l^2\mu V_{\text{void}}/\{2S_{\text{b}}(2/R)\gamma_{\text{sizing}}\cos\theta\} \tag{11}$$

Reported values for the contact angle of water with unsized

Table 1 Analysis of factorial design showing main effects and interaction effects for a 1.75 wt% K17 PVP sizing bath concentration

Variable	Units	Low level	High level
Line tension	Newtons	0.0	27.0
Line speed	cm s^{-1}	0.51	2.54
Emitter surface temperature	°C	200.0	300.0

Variable effects	
Average tension main effect	0.026
Average speed main effect	0.014
Average emitter surface temperature main effect	−0.019
Average tension by speed interaction effect	0.041
Average tension by temperature interaction effect	−0.023
Average speed by temperature interaction effect	−0.008
Average tension by temperature by speed interaction effect	−0.015

Average sizing level = 1.200 wt% (averaged over 24 tests)
Average error in the effects = 0.024 wt%

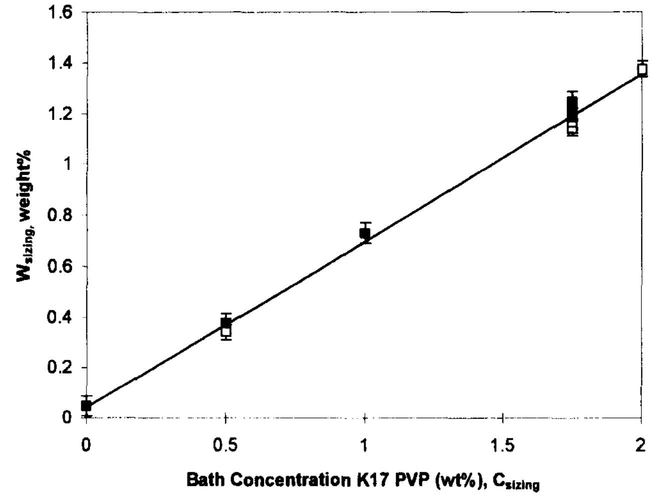


Figure 2 Sizing level W_{sizing} (wt%) *versus* bath concentration C_{sizing} (wt%) for K-17 PVP at various line speeds: (■) 2.54 cm s^{-1}; (□) 0.51 cm s^{-1}

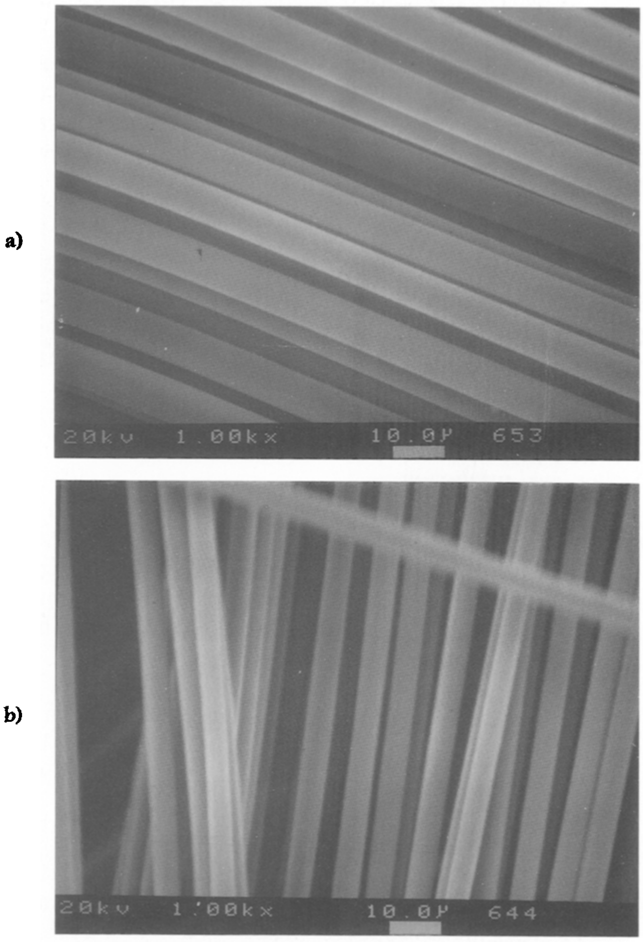


Figure 3 SEM at 1000 × magnification of (a) Hercules AS-4 12 K material sized with 0.5 wt% K-17 PVP by sizing apparatus, and (b) commercially available Courtaulds material sized with 0.5 wt% K-17 PVP

Hercules AS-4 have ranged from 30°[13] to 89°[14]. Since wetting was observed for the carbon fibres used in the present study, it was concluded that the contact angle was less than 90°.

Darcy's Law is rigorously accurate for flow situations involving steady flows of Newtonian fluids where inertial effects can be ignored. While this is not the case for tow wetting, Darcy's Law should be sufficient for order-of-magnitude estimates of t_f. Equations (10) and (11) will be used in the next section to estimate t_f. This will be compared with the fibre residence time in the sizing bath to draw a conclusion about the relation between V_{void} and V_{sizing}.

RESULTS AND DISCUSSION

Statistical process model

The mean sizing level W_{sizing} on the fibre was correlated with the process independent variables: sizing bath concentration C_{sizing}, fibre line speed, fibre tension and I.R. dryer emitter surface temperature. Since C_{sizing} was the only variable that was expected to affect sizing level, a 2^3 factorial design approach was used to confirm that fibre line speed, line tension and dryer emitter surface temperature did not affect sizing level[15]. In all these experiments $C_{sizing} = 1.75$ wt% K-17 PVP. Each of the eight independent tests was repeated three times. The main effects and interaction effects for the various process independent variables along the error in the calculated effects are presented in *Table 1*. Since all the main effects and interaction effects (−0.019 to 0.041 wt%) were similar in magnitude to the error calculated from the replicate runs (0.024 wt%), it was concluded that the effect of these variables on the sizing level was negligible at a sizing bath concentration of 1.75 wt% K-17 PVP.

The factorial design results are consistent with the assumptions that $X_{moisture}$ and V_{sizing} were constant for fixed

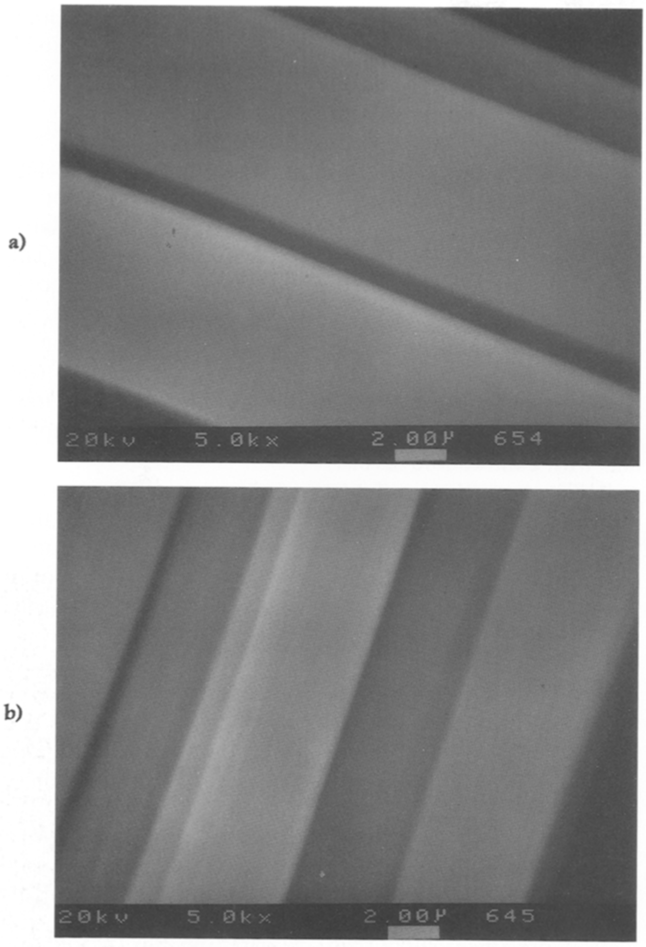


Figure 4 SEM at 5000 × magnification of (a) Hercules AS-4 12 K material sized with 0.5 wt% K-17 PVP by sizing apparatus, and (b) commercially available Courtaulds material sized with 0.5 wt% K-17 PVP

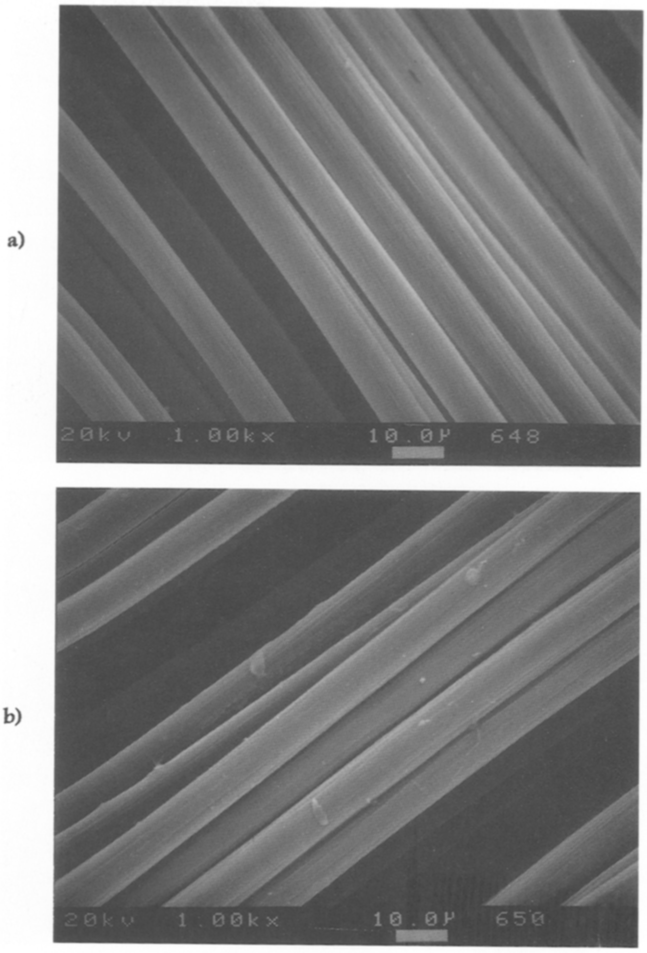


Figure 5 SEM at 1000 × magnification of (a) Zoltek Panex 48 K material sized with 0.4 wt% K30 PVP by sizing apparatus, and (b) commercially available Zoltek Panex 48 K material sized with 0.4 wt% K30 PVP

C_{sizing} and that $V_{\text{void}} = V_{\text{sizing}}$. This can be seen by substituting $C_{\text{sizing}}(= 1.75\%)$ and the mean sizing level, 1.20%, from the factorial design experiments into equation (6) and solving for an average X_{moisture}. This value, $X_{\text{moisture}} = 0.4$ when substituted into equation (4) yields $V_{\text{sizing}} = 0.54$. Setting this equal to V_{void} and substituting into equation (7) yields a value for the micro-capillary radius $R = 1.4\ \mu\text{m}$. Substituting this value into equations (8)–(11) gives tow wetting times t_f ranging from 0.6 to 28 ms as the contact angle is varied from the high (89°) and low (30°) literature values reported earlier. The tow residence times in the sizing bath varied typically from 8 to 180 s. Therefore, the voids in the tow should be completely saturated, substantiating the assumption that $V_{\text{void}} = V_{\text{sizing}}$. This was confirmed at the 1.75 wt% K-17 PVP bath concentration where line speed was shown not to affect sizing level W_{sizing} or fibre moisture content X_{moisture}. X_{moisture} had an average value of 0.4 with a standard deviation of 0.015 for the variations in line speed, line tension and dryer emitter surface temperature utilized in the factorial design. The same is expected for solution concentrations less than 1.75 wt%, since the viscosity decreases with decreasing PVP concentration.

Since X_{moisture} was shown to be constant, i.e. constant V_{void} and voids were saturated in all cases in the factorial design experiment, the fibre sizing level W_{sizing} can be calculated from equation (6) for $X_{\text{moisture}} = 0.4$. The resulting theoretical relation is linear with respect to sizing bath concentration

$$W_{\text{sizing}} = (2/3)C_{\text{sizing bath}} \tag{12}$$

This was confirmed experimentally. Sizing bath concentration was varied from 0 to 2 wt% K-17 PVP and the resulting sizing level on the fibres was determined, as shown in *Figure 2*. The line speed was varied from 0.51 to 2.54 cm s^{-1} to confirm that line speed was indeed negligible for all cases. Linear least squares analysis gave the following relation

$$W_{\text{sizing}} = -0.015 + 0.669 \cdot C_{\text{sizing}} + 0.013 \cdot (\text{line speed}) \tag{13}$$

Since the contribution of the line speed term is negligible, it can be neglected in rest of the analysis.

Fitting the same data to sizing bath concentration only and neglecting any line speed effect gave

$$W_{\text{sizing}} = 0.041 + 0.656 \cdot C_{\text{sizing}} \tag{14}$$

where $\sigma_{y\text{-int}} = 0.024$ and $\sigma_{\text{slope}} = 0.016$. The relative standard deviation of the slope was 2.4%, and so the experimental results expressed by equation (14) confirm quite well the theoretical prediction from equation (12). Therefore, to a very good approximation, the moisture uptake on Hercules AS-4 12 K carbon fibre is not a function of PVP sizing bath concentration, line speed, line tension and dryer emitter surface temperature. The same moisture uptake should

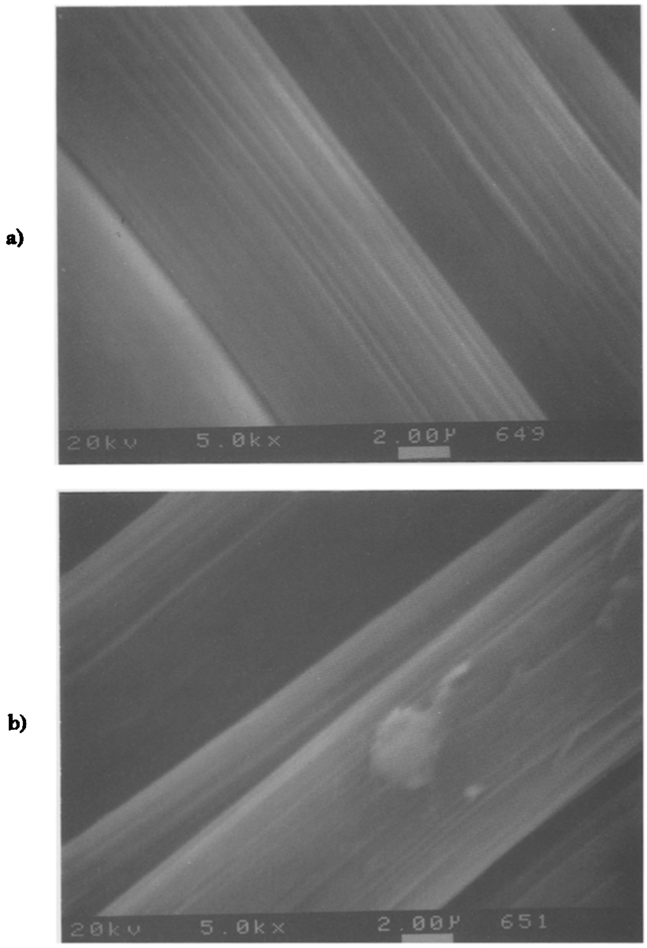


Figure 6 SEM at 5000 × magnification of (a) Zoltek Panex 48 K material sized with 0.4 wt% K30 PVP by sizing apparatus, and (b) commercially available Zoltek Panex 48 K material sized with 0.4 wt% K30 PVP

also be observed for any sizing system in which the carbon fibres are wetted by the aqueous solutions.

Sized fibre uniformity and process consistency

Filament clumping or filament/filament cohesion must be kept to a minimum for the fibre to be useful for composite processing. This was established by comparing the filament/filament cohesion observed in fibres sized by the apparatus and similar sized fibres from industrial sources. Hercules AS-4 12 K material sized by the apparatus with 0.4 wt% K-17 PVP was compared with Courtaulds 12 K material sized with 0.4 wt% K-17 PVP in *Figures 3 and 4*. The SEM micrographs show that filament clumping was not observed in either case. No sizing material can be seen on either fibre which is understandable given the small sizing layer thickness expected from such a small amount of sizing material. The theoretical thickness is 12 nm when using the density of PVP = $1.1\ \mathrm{g\ cm^{-3}}$. Zoltek Panex 48 K material sized by the apparatus with 0.4 wt% K-30 PVP was compared with Zoltek Panex 48 K material sized with 0.4 wt% K-30 PVP in *Figures 5 and 6*. The SEM micrographs again show no filament clumping in either case. However, for the case of the higher molecular weight K-30 PVP, some sizing material can be seen on the fibre surface.

Finally, the consistency of the process during a sizing run was studied. Repeated tests for periods as long as 45 min have shown that the process produces sized fibre with no variation in sizing level within experimental error as long as the sizing bath is replenished with fresh sizing solutions.

CONCLUSIONS

An apparatus to coat carbon fibres with aqueous water-dispersible polymeric interphase or sizings was developed. The apparatus was able to produce fibre with a controllable amount of deposited polymer in the range 0.1–1.4 wt%. The sizing level was shown to be independent of all process variables except for sizing bath concentration. The sizing bath concentration was shown to be a linear function of K-17 PVP bath concentration with a slope of 2/3. This was shown to be consistent with complete wetting of the tow. The apparatus produced fibre with minimal fibre clumping and with controllable levels.

In future work, sized fibre produced by the apparatus will be processed into unidirectional fabric which will then be prepregged to form composites. Sizing systems other than PVP will be tested and correlated to composite performance. This will enable the optimization of the sizing material for the needed composite performance.

In addition, a dryer simulation program is being tested. The simulation predicts fibre moisture content, fibre temperature, air moisture content, air temperature and extent of sizing cure as a function of dryer position. This simulation program will enable the precise determination of the extent of cure for reactive sizings.

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