

Preparation and Characterization of Poly(styrene-*co*-divinylbenzene)/Fiberglass Cation-Exchange Composites

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ABSTRACT: Cation-exchange composite materials were prepared by the sulfonation of the copolymer of styrene (St) and divinylbenzene (DVB) coated on glass fibers previously surface-treated by a silane coupling agent. The results show that the surface treatment of the glass fibers by the coupling agent γ -(methacryloyloxyethyl) trimethoxysilane led to a vinyl functionalized fiberglass surface, which served to covalently bond the copolymer to the fiberglass. Increasing the amount of the coupling agent increased the degree of coating of the copolymer on the

fiberglass. A cation-exchange composite with an exchange capacity of 4.08 mmol/g of resin was prepared by the copolymerization of St and DVB at a weight ratio of 95 : 5 for 30 min; this was followed by sulfonation of the copolymer at 100°C for 12 h. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 944–949, 2011

Key words: composites; copolymerization; fibers; functionalization of polymers, ion exchangers

INTRODUCTION

Ion-exchange materials have been used extensively in water treatment and the pharmaceutical, food processing, and other industries.¹ In practice, ion-exchange materials are often used in the form of polymeric membranes. However, polymeric membranes usually have some inherent limits in their thermal and chemical stabilities.^{1–3} Therefore, ion-exchange membranes based on inorganic or organic–inorganic hybrid materials can be promising for overcoming these problems associated with polymeric membranes.

Wu et al.^{4–6} prepared organic–inorganic hybrid ion-exchange membranes via a sol–gel process; these membranes showed improved thermal and chemical stabilities. To prepare positively charged membranes, Wu et al. coated trimethoxysilyl-functionalized poly(ethylene oxide) precursors with amide groups [obtained by the endcapping of Poly(ethylene oxide)-400 with tolylene 2,4-diisocyanate and then coupling with *N*-[3-(trimethoxysilyl)propyl] ethylenediamine] on a microporous alumina plate to form a thin film by dehydration condensation and used C₂H₅Br for a further quarteramination reaction.⁴ Alkoxysilane-containing sol–gel precursors, obtained from the same end-capping procedure but coupled with phenylaminomethyl triethoxysilane, were coated

on a Teflon plate and further sulfonated to form negatively charged membranes.⁶ They also tried the sol–gel and oxidation processes with 3-(mercaptopropyl) trimethoxysilane on a microporous alumina plate to obtain cation-exchange membranes.⁵

Ion-exchange materials have been previously made by the sulfonation of poly(styrene-*co*-divinylbenzene) [poly(St-*co*-DVB)].⁷ In this study, we aimed to further improve the mechanical and thermal properties of such ion-exchange materials by using them in combination with a fiberglass substrate. In particular, we used γ -(methacryloyloxyethyl) trimethoxysilane (KH570) to treat fiberglass to introduce unsaturated functional groups onto the fiberglass surface. We then coated partially copolymerized styrene (St) and divinylbenzene (DVB) on such surface-modified fiberglass, allowed the coated fiberglass to cure for an extended period of time, and then sulfonated the copolymer coating. We investigated various parameters in the preparation of the ion-exchange composite, discovered the optimal conditions and parameters for the procedure, and obtained cation-exchange fiberglass composites with excellent thermal stability.

EXPERIMENTAL

Materials

Fiberglass mats (4 mm in thickness, 14 μ m in diameter) were provided by Beijing Jinghua Fiberglass Product Industries, Co. (Beijing, China); benzoyl peroxide (BPO), St, DVB, sulfuric acid (98%), and 1,2-

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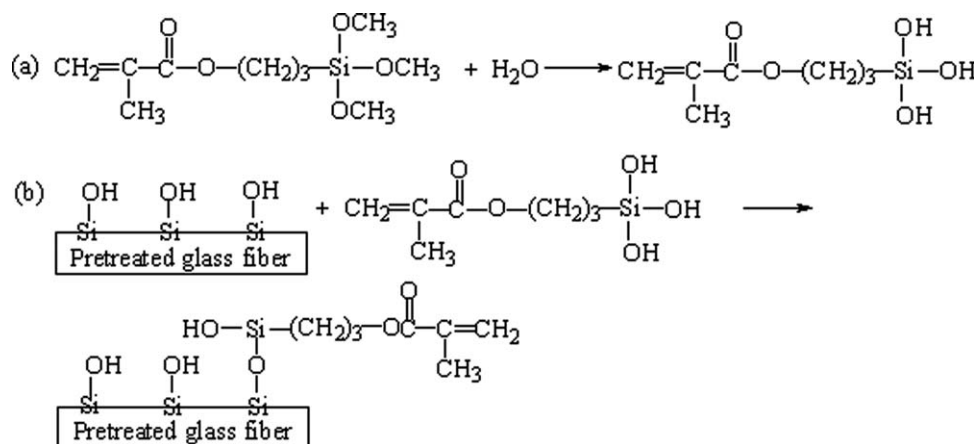


Figure 1 Chemical reactions of the fiberglass and silane coupling agent.

dichloroethane were provided by Beijing Yili Chemical Reagent Co. (Beijing, China); KH570 [molecular formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$] was provided by Nanjing Yude Chemical Reagent Co., Ltd., (Nanjing, China)

Surface treatment of the fiberglass

A fiberglass mat was heated at 550°C in a furnace for 2 h to remove any organic coating agent, cooled to room temperature, and then dipped in a solution of KH570 (the solvent was 95 : 5 methanol/water) for 30 min. The fiberglass mat was then removed from the solution, heated at 120°C for 4 h, washed with methanol to remove any unreacted KH570, and then dried. In this procedure, the silane group in KH570 could undergo hydrolysis to produce $-\text{SiOH}$ groups, which could react with the $-\text{SiOH}$ on the surface of the fiberglass substrate. The vinyl group in KH570 could then react with St or DVB and, thereby, provide covalent linking (hence, excellent interfacial adhesion) between poly(St-co-DVB) and the fiberglass. These chemical reactions are illustrated in Figure 1.

Preparation of the poly(St-co-DVB)/fiberglass composite

St, DVB, and BPO were added to a flask equipped with ports accommodating a reflux condenser, a thermometer, a stirrer, and a nitrogen inlet and outlet, respectively. After BPO was completely dissolved at room temperature, the reaction was carried out at 85°C for 10–35 min and then stopped before gelation was observed. The reaction system thus obtained (containing the copolymer product and unreacted monomers) was cooled in an ice bath; meanwhile, a fiberglass mat was immersed in the reaction solution to adequately soak. The soaked fiberglass mat was then placed in an oven at 100°C for the polymerization to continue for 4 h. There-

after, the fiberglass mat was treated by a Soxhlet extractor with ethyl acetate for 24 h to remove the polystyrene homopolymer. Such a treated fiberglass mat is referred to as a poly(St-co-DVB)/fiberglass composite (or simply a fiberglass composite).

Sulfonation of the poly(St-co-DVB)/fiberglass composite

The poly(St-co-DVB)/fiberglass composite obtained by the previous procedure was subjected to 1,2-dichloroethane swelling and then treated with concentrated sulfuric acid to introduce $-\text{SO}_3\text{H}$ groups onto its surface. The sulfonated fiberglass composite was then washed with deionized water and dried. The chemical reactions occurring in the previous step and this step are illustrated in Figure 2.

Characterization and testing

Degree of poly(St-co-DVB) coating on the fiberglass

The fiberglass composite was dried in a vacuum oven to a constant weight. The degree of coating (C) of poly(St-co-DVB) was calculated with eq. (1):

$$C = \frac{W_c - W_i}{W_i} \times 100\% \quad (1)$$

where W_c is the weight of the fiber composite and W_i is the weight of the substrate fiberglass.

Determination of the cation-exchange capacity (CEC)

CEC of the sulfonated fiberglass composite was measured by acid titration. The sulfonated composite (1 g) was soaked in 100 mL of an NaCl solution (1 mol/L) for 2 h and was then titrated with a standard NaOH solution to the endpoint with phenolphthalein as the indicator. CEC (mequiv/g) was calculated according to eq. (2):

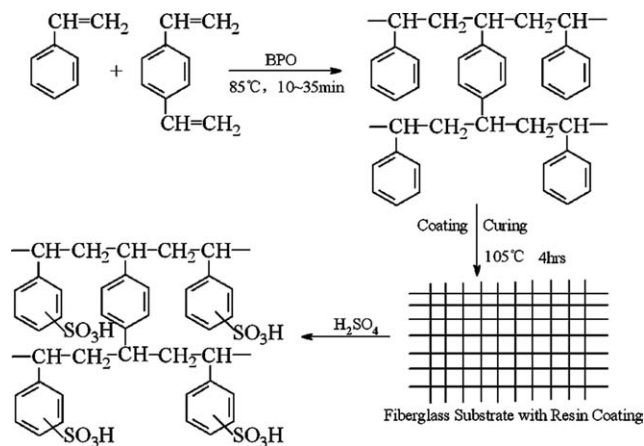


Figure 2 Chemical reactions involved in the preparation of the cation-exchange poly(St-co-DVB)/fiberglass composite

$$\text{CEC} = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}}}{W} \quad (2)$$

where V_{NaOH} is the volume of the NaOH solution consumed in the titration, N_{NaOH} is the concentration of NaOH (mmol/L), and W is the weight of the fiberglass composite (g).

Infrared analysis of the fiberglass substrate, fiberglass composite, and sulfonated fiberglass composite was performed on a TENSOR 37 FT-IR spectrometer (Bruker Corporation, Karlsruhe, Germany).

Thermogravimetric analysis (TGA) of the fiberglass composite was performed on a thermogravimetric analyzer TG 209 (Netzsch Group, Bavarian, Germany) with a heating rate of 10°C/min from 50 to 600°C in N_2 . The fiberglass surface was observed by means of a polarizing microscope DMLP (Leica Microsystems GmbH, Wetzlar, Germany) and a metallographic microscope (GRME-LUX2-3L, Kyowa Electronic instruments Co., Ltd, Tokyo, Japan).

RESULTS AND DISCUSSION

Poly(St-co-DVB) content in the fiberglass composite

The sulfonated poly(St-co-DVB) imparted the fiberglass composite with CEC. It follows that the CEC of the fiberglass composite was positively correlated with the copolymer content (or its degree of coating) in the fiberglass composite. The degree of coating of the copolymer was influenced by the surface properties of the fiberglass, the ratio between the added monomers (St/DVB), and the polymerization reaction time.

Effects of the fiberglass surface treatment on the coating degree of the copolymer

Commercial fiberglass usually contains coated epoxy adhesives and is poor in compatibility with St. Therefore, it was important to first treat the fiberglass surface

to improve the adhesion between the fiberglass and polystyrene resin. In this study, the KH570 silane coupling agent was used to treat fiberglass to introduce to the fiberglass surface vinyl moieties, which could react with the monomers (St or DVB) during their polymerization and, thereby, bind the polymer covalently with the fiberglass substrate. Figure 3 shows the IR spectra before and after the surface treatment of the fiberglass. Figure 3(b) indicates an increase in four peaks centered at 2943, 2887, 1723, 1640, which corresponded to the $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{OCO}-$, and $-\text{C}=\text{C}-$ groups, respectively, of the incorporated copolymer. In particular, the broadened band centered at 1006 cm^{-1} was attributed to Si—O—Si stretching vibrations; this indicated that the KH570 coupling agent reacted with the fiberglass to form covalent Si—O—Si bonds.

After the first stage polymerization (30 min) of St/DVB (95 : 5 wt %) with BPO (1% of the total weight of St and DVB) as the initiator, the reaction system containing the formed copolymer and unreacted monomers was coated on fiberglass substrates pretreated with different concentrations of the KH570 coupling agent. Figure 4 depicts the degrees of coating of the poly(St-co-DVB) obtained with different concentrations of the KH570 coupling agent. In general, a higher concentration of KH570 led to a higher degree of coating. At 3% KH570, the degree of coating reached 59%. However, the increase in the degree of coating started to level off after the concentration of KH570 exceeded 1.5%. Therefore, in the follow-up study, a 1.5% KH570 solution was used for the fiberglass surface treatment.

Influence of the polymerization time before the coating of the fiberglass substrate on the degree of the poly(St-co-DVB) coating

During the copolymerization of St and DVB, the viscosity of the reaction system quickly rose as the

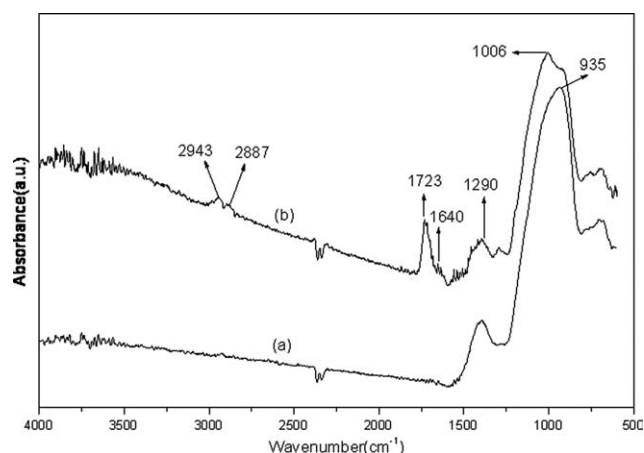


Figure 3 FTIR spectra of the (a) fiberglass and (b) KH570-modified fiberglass.

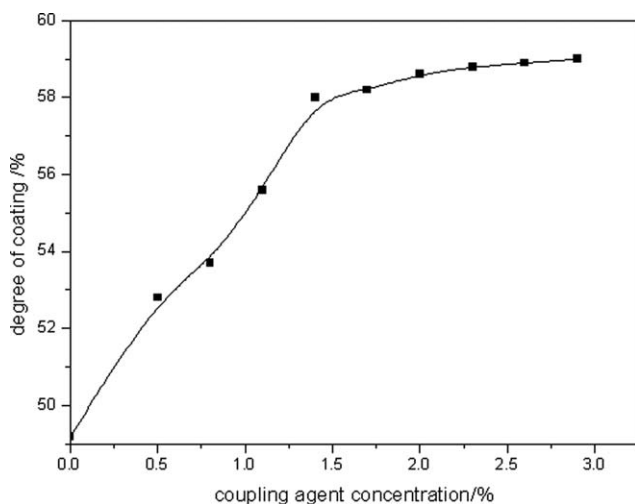


Figure 4 Effects of the KH570 concentration on the degree of poly(St-co-DVB) coating.

monomer conversion increased. To ensure adequate wetting of fiberglass substrate, the monomer conversion rate and viscosity should be controlled below certain thresholds. Thus, the duration of the polymerization time was investigated to determine its effect on the degree of coating of poly(St-co-DVB) with a reaction system starting with St/DVB at 95 : 5% and 1% BPO, where the polymerization was quenched at different times. The results of the investigation are shown in Figure 5. Initially, the degree of coating increased linearly with the polymerization time. When the polymerization time was 30 min, the degree of coating reached 58.1%. However, when the polymerization time was 35 min or longer, gelation started to appear in the reaction system, and it became practically difficult to coat such a reaction

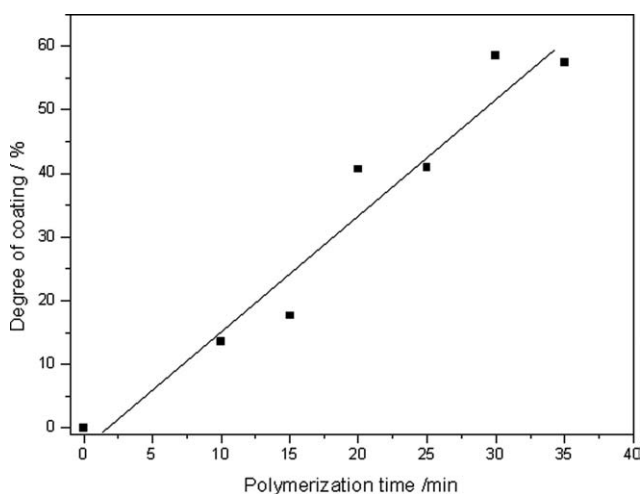


Figure 5 Influence of the polymerization time of the soaking solution on the degree of the poly(St-co-DVB) coating.

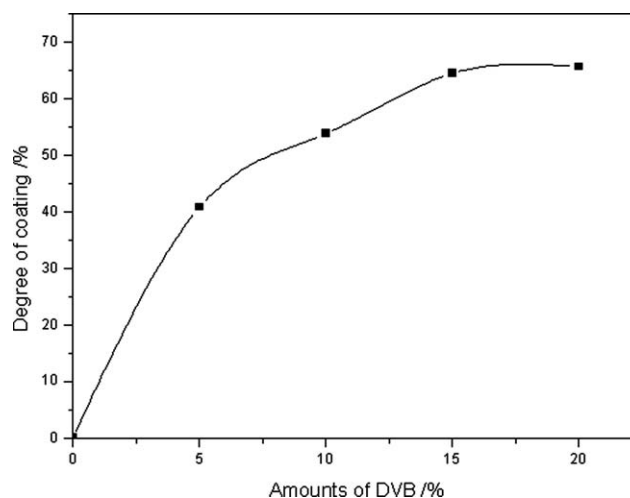


Figure 6 Degree of poly(St-co-DVB) coating in the fiberglass composite.

system onto the fiberglass mat substrate. Therefore, to maintain good wettability of the polymerization system, the reaction time was controlled at 20–30 min.

Influence of the amount of DVB versus St on the poly(St-co-DVB) content in the fiberglass composite

Because of the presence of two reactive vinyl groups in each DVB monomer, DVB also acted a crosslinking agent. Accordingly, an increase in the amount of DVB relative to St increased the crosslinking density of poly(St-co-DVB). DVB/St at different ratios (5 : 95, 10 : 90, 15 : 85, and 20 : 80) were polymerized for 20 min to study the effect of the DVB amount on the degree of coating of poly(St-co-DVB) on the fiberglass substrate. As shown in Figure 6, with increasing relative amount of DVB in the monomers, the degree of coating of poly(St-co-DVB) tended to increase: for example, when the DVB content was 5%, the degree of coating was 40.8%, and when the DVB content was 15%, the degree of coating was 64.5%. More DVB content did not significantly increase the degree of coating, but would cause resin gel faster.

Effect of the sulfonation conditions on the CEC

CEC depended on the concentration of the $-\text{SO}_3\text{H}$ groups in the cation-exchange resin: the higher the concentration was, the higher CEC was. In turn, the concentration of $-\text{SO}_3\text{H}$ was influenced by the crosslinking degree of poly(St-co-DVB), the sulfonation reaction time, the temperature, and so on.

When the crosslinking degree of poly(St-co-DVB) was high, it was difficult for the sulfonation reaction to proceed because the diffusion of sulfuric acid was hindered. When the fiberglass composite was first

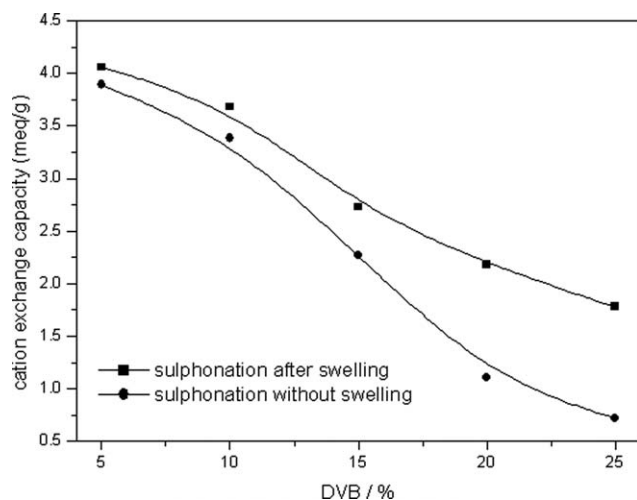


Figure 7 Influence of the relative DVB content and swelling of poly(St-co-DVB) before sulfonation on CEC.

treated by 1,2-dichloroethane to swell the cross-linked poly(St-co-DVB), the degree of sulfonation was improved. Figure 7 illustrates the degree of coating of the copolymer made with different DVB amounts (5, 10, 15, 20, and 25%, with the remaining being St) with and without 1,2-dichloroethane treatment (bottom curve and top curve, respectively). As the amounts of DVB increased, the degree of sulfonation decreased. The treatment by 1,2-dichloroethane helped to improve the degree of sulfonation, hence the higher degree of coating of poly(St-co-DVB).

As the sulfonation reaction primarily occurred on the benzene ring of St, when a copolymer with a low DVB content was made, a large amount of polystyrene homopolymer also formed. However, as the polystyrene was not covalently bound to the surface of the fiberglass substrate, it was extracted out by the Soxhlet extractor. As a result of the extraction,

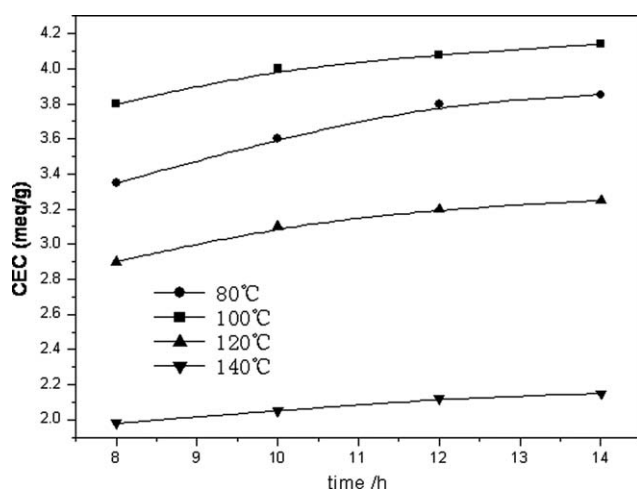


Figure 8 Influence of different reaction temperatures and reaction times on CEC.

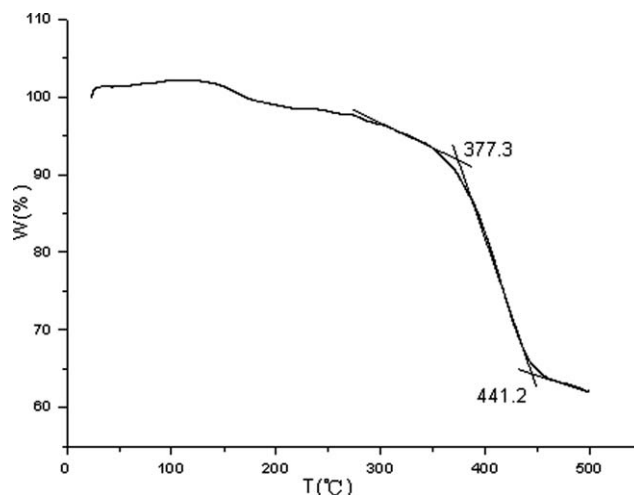


Figure 9 TGA curve of the sulfonated fiberglass composite.

many pores formed within poly(St-co-DVB), which facilitated the diffusion of sulfuric acid and the sulfonation reaction. This porous structure also facilitated the ion exchange when the fiberglass composite was put to use for such applications. As shown in Figure 7, when the DVB content was increased to 25% (i.e., the St content was 75%), CEC of the fiberglass composite dropped dramatically.

The sulfonation temperature and time were important factors for the ion-exchange capacity of the sulfonated fiberglass composite. Figure 8 shows the CEC of fiberglass composites with 5% DVB content sulfonated at 80, 100, 120, and 140°C for 8–14 h. At different reaction temperatures, extending the sulfonation reaction time tended to improve CEC, but CEC improvement after 12 h of sulfonation was no longer significant. In addition, the sulfonation temperature had great impact on the CEC of the fiberglass composite. A sulfonation around 100°C appeared to be optimal for achieving maximum CEC. A further increase in the sulfonation temperature caused CEC to drop sharply. For example, for the same sulfonation time of 14 h, at a sulfonation temperature of 120°C, CEC decreased to 3.2 mequiv/g, and at 140°C, CEC decreased to 2.12 mequiv/g. At a higher temperature, the oxidation of the copolymer caused by the sulfuric acid became more pronounced, and because of the reversible nature of the sulfonation process, a higher temperature also caused the reverse sulfonation to be more remarkable. Therefore, a sulfonation temperature around 100°C was shown to be the optimal temperature for the fiberglass composite in this study.

Thermal stability of the fiberglass composite

We performed TGA on a fiberglass composite prepared by polymerizing a mixture of 95 : 5% St/DVB for 30 min, soaking a fiberglass mat pretreated with

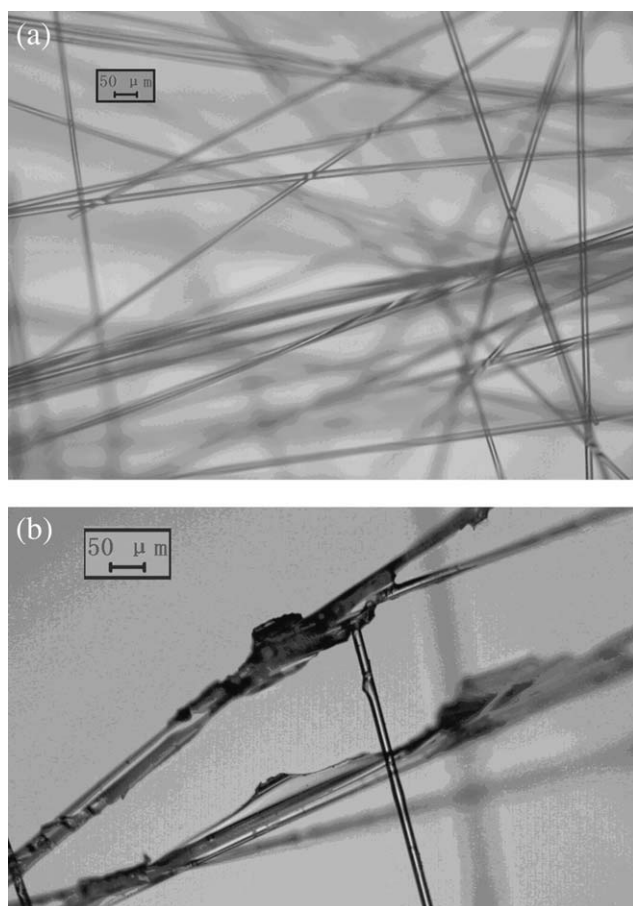


Figure 10 Polarizing micrographs of the (a) original fiberglass and (b) composite.

KH570 with the reaction mixture, and sulfonating the copolymer at 100°C for 12 h. As shown in Figure 9, the fiberglass composite exhibited excellent heat resistance; from room temperature to up to 140°C, the weight of the sample increased slightly because of absorbed moisture from the air because the sulfonic group had a strong affinity with water. From 140 to 280°C a small amount of volatile matter was removed, but the weight loss was less than 2%. When the sample was heated over 280°C, the poly(St-co-DVB) started to decompose and reached its maximum decomposition rate at 377.3°C. At 441.2°C the copolymer decomposed completely, leaving behind the fiberglass substrate and carbon residue.

Figure 10 shows the surface morphologies of the fiberglass and composite. The original fiberglass surfaces were smooth and homogeneous [Fig. 10(a)]. After it was coated and sulfonated with poly(St-co-DVB), the fiberglass's diameter increased because resins adhered on the fiberglass surface [Fig. 10(b)].

Fiberglass, a major component in the composite, provided good mechanical properties and heat resistance.

These results indicate that the poly(St-co-DVB)/fiberglass composite had excellent thermal stability, can be used for high temperature ion exchange materials.

CONCLUSIONS

Cation-exchange composite materials with excellent CECs and thermal stability were prepared by the sulfonation of the copolymer of St and DVB grafted on fiberglass and pretreated by the coupling agent KH570. The treatment of the fiberglass with the coupling agent introduced vinyl functional groups on the fiberglass surface, which reacted with St, DVB, or the copolymer to covalently bind the copolymer to the fiberglass. Increasing the amount of coupling agent led to a higher degree of coating of the copolymer on the fiberglass, but this effect leveled off after the concentration of the coupling agent was greater than 1.5%. The degree of coating of the copolymer increased linearly with polymerization time at low degrees of monomer conversion; however, a prolonged polymerization time (>30 min) led to gelation in the reaction system and made the next step of soaking the fiberglass mat difficult. The degree of coating of the copolymer on the fiberglass also increased with increasing amount of DVB monomer, but CEC suffered from the increased DVB amount. The optimal ratio of DVB/St was found to be about 5 : 95. The sulfonation of the copolymer needed to be performed at an appropriate temperature, for example, around 100°C, because too high a temperature led to the undesired oxidation of the copolymer and a more pronounced reverse sulfonation reaction. The prepared poly(St-co-DVB)/fiberglass composite showed excellent thermal stability, which was evidenced by its less than 2% weight loss when it was heated up to 280°C.

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