Journal of Applied Polymer Science

New Damping Materials by Fabrication of ACM/PVC Alloy into Hollow Fibers

Mingjun Li, Yan Cheng, Yongwen Xu, Yuancheng Qin

Department of Environmental and Chemical Engineering, Nanchang Hangkong University, Nanchang, 330063, People's Republic of China

Correspondence to: M. Li (E-mail: limingjun1958@gmail.com)

ABSTRACT: New acrylic rubber hollow fiber damping materials were successfully produced by dry–wet spinning technique. The effect of polymer concentration and blending ratio on ACM/PVC hollow fiber were investigated. The results showed that the tensile strength increased with the increase of polymer content and decreased with the decrease of blending ratio. DMA revealed that varying the size of inner diameter, the loss tangent (tan δ) would change. FTIR proved certain interactions among them. In addition, the position of peak of the glass transition temperature not only shifted to a higher temperature with the increase of PVC content, but also its temperature range of tan $\delta > 0.3$ was 40–65°C, inferring that ACM/PVC mixture is a promising damping-material. The outer skin and inner skin structure of ACM/PVC hollow fiber by SEM were different from that used in water treatment due to the differences between materials. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 1334–1339, 2013

KEYWORDS: blends; fibers; glass transition

Received 16 June 2012; accepted 13 November 2012; published online 5 December 2012

DOI: 10.1002/app.38821

INTRODUCTION

Hollow fiber is a kind of tubular chemical fiber with their intrinsic characteristics of low energy consumption, high surface area per unit volume, easy operation, high efficiency, and no secondary pollution. It is found widely applications in resource, energy, and environment, especially in water treatment, energy conservation, and emisstion reduction fields.[1–4] In the recent preliminary studies, we had prepared the nondamping material of polysulfone (PS) hollow fiber to be the honeycomb composite structure, which the value of tan δ could reach 0.59.[5] Comparing hollow structure with plate structure, it was found that the damping property of the hollow fiber structure was superior to that of the plate membrane with the same material under the same conditions, which suggested that the cavity structure of hollow fiber with a buffer working on energy could consume part of the vibrational energy. The hollow fiber structure damping materials could be apt to damping applications and have the great advantages in vibration reductions. In addition, the temperature range of tan $\delta > 0.3$ of nitrile rubber(NBR) hollow fiber damping material was 35–55°C, higher than that of the average of the homopolymer (20–30°C), resulting in improving the damping temperature of the rubber and broadening the damping temperature region and widening hollow fiber membrane applications.

Acrylic rubber(ACM), the same synthetic rubber as NBR, is known to be an excellent viscosity and elasticity with heat-, oil-, ozone-, anti-cracking, and weather resistance, furthermore the heat-resistance is superior to NBR. Meanwhile, it has broad application prospects in the aerospace, civil aviation and maritime fields. However, the damping properties of ACM are dominated by the glass transition, and the useful damping temperature range of the pure ACM is narrow. Therefore, it is difficult to meet the damping performance requirement above the room temperature.[6,7] To obtain a broader damping property, researchers blend ACM with rubbers or thermoplastics such as nylon,[8–11] polyvinyl chloride(PVC),[12,13] poly(vinylidene fluoride) (PVDF),[14] poly (ethylene terephthalate) (PET),[15] and chlorinated polypropylene.[16] In all these blends, the thermoplastic component is polar, and presents some affinity with the ACM rubber, and most of their blends were vulcanizated to use in dynamic vulcanization field. While the hollow fiber of ACM blended with all these thermoplastics were prepared to use in damping materials are rarely reported.

As part of our ongoing investigations aimed at the development of hollow fiber damping materials, we wish to report here that new acrylic rubber hollow fiber damping materials were successfully produced by dry–wet spinning technique. The structures and properties of the products were characterized by FTIR, SEM, and DMA.

© 2012 Wiley Periodicals, Inc.

Table I. The Different Polymer Concentration and Blend Ratios of ACM/PVC

15 wt %	18 wt %	20 wt %	22 wt %
50:50	50:50	50:50	50:50
60:40	60:40	60:40	60:40
70:30	70:30	70:30	70:30

EXPERIMENTAL

Materials

ACM (commercial grade Ar-81) was supplied by Changzhou Haiba Rubber (China). PVC was purchased from Sanmenxia Jie Ma Electrochemical (Henan, China). *N, N*-Dimethyl Acetamide (DMAc) was purchased from Sumsung, South Korea. All other solvents were obtained from commercial sources and were used as received.

Sample Preparation

The PVC and ACM were dissolved in DMAc to form the casting solution according to the Table I. The mixture was stirred at 40°C for 48 h, then standing until no bubbles. The casting solution was extruded through a hollow fiber spinneret above the coagulation bath under certain pressure. The core liquid pumped with a metering pump was injected through the center tube to cause the shape of hollow fiber. The ACM/PVC blend solution entered the external coagulation bath through the air gap between the nozzle and external coagulation bath. After fully solidified and completely phase transformation, these hollow fibers were washed with water to remove residual DMAc.

After rinsing, the ACM/PVC blend hollow fibers were post-treated by which they were soaked in a 30 wt % glycerol aqueous solution for two days and dried in air at room temperature in order to minimize the shrinkage effect for studying the mechanical properties and dynamic mechanical properties.

Characterization

Tensile properties were studied on computer-controlled electronic universal testing machine (*WDW*-50, Jinan Testing Machine Factory, Jinan Test Group), according to GB/T1447-2005 under ambient condition.[17] The one end of 10 cm long dried hollow fiber intercepted was fixed with a clip and the other end was fixed on another clip with a plastic beaker. The sand was added slowly into the beaker until the fiber rupturing, recorded the weight of the sand. The strength of fiber was characterized by the minimum value of the ratio of the cross-section area to the weight of the sand. Each test repeated three times. The maximum elongation was obtained by which fixing the both ends of the 10 cm long fiber was stretched slowly and evenly until fractured, and measured the maximum extension length of the fiber with the ruler. Dynamic mechanical thermal analysis (DMA) (DMA Q800, TA Corp. USA) was carried out using Rheometric dynamical analyzer in a tensile mode. The dynamic Storage Moduli (E') and Loss Moduli (E'') were determined at a frequency of 1 Hz and a heating rate of 5 °C/min as a function of temperature from −20 to 120 °C. The tan δ is often used to characterized the damping properties of materials for tan $\delta = E''/E'$.[18] Usually, the temperature range with tan $\delta > 0.3$ is taken as a standard to evaluate damping materials.[19] The morphology of ACM/PVC hollow fibers were observed directly using scanning electron microscopy (SEM) (Hitachi Japan). Fourier transform infrared (FTIR) spectra of the products in KBr pellets were recorded on a Nicolet 320 FTIR spectrometer (USA). Inner and outer diameter were determined by the photography production prompts microscope (XTS3022, Beijing). The average values were obtained.

Table II. Effect of Different Polymer Concentrations and Blending Ratios on Elongation Strength

Blending ratios	15 wt %/MPa	18 wt %/MPa	20 wt %/MPa	22 wt %/MPa
50:50	4.257	6.119	8.184	8.503
60:40	3.198	5.611	6.537	8.312
70:30	2.539	4.830	6.277	6.889

RESULTS AND DISCUSSION

Polymer Content and Blending Ratio Effect on the Tensile Properties of ACM/PVC Hollow Fibers

Tables II and III show the tensile strength and the elongation at break of ACM/PVC hollow fibers respectively. As shown in the tables, within experiment range, by increasing the PVC content in the blend, the tensile strength increases while the elongation at break decreases. These results suggest that when the PVC content increases in ACM/PVC blends, the intermolecular interaction between PVC molecules increases. PVC shows the nature of the glass state. And the ability to resist external damage is stronger than the rubber. So, they play a role in constraining deformation in ACM/PVC blends. For the same blending ratio, with increasing of polymer concentration, the tensile strength of ACM/PVC hollow fiber increases. This is probable because increased polymer content, the macromolecules close to each other lead to improve the force of polymer and increase the entanglement point density. Consequently, the tensile strength is enhanced. By the contrast, the lower tensile strength is caused by the low polymer content because of macromolecules contacts less with each other resulting in establishing few of physical crosslinking points and no gel formed.

As shown in Table III, when the blending ratio was 50:50, the elongation at break of ACM/PVC hollow fibers were increased with the increasing polymer content. But when the blend ratio were 60:40 and 70:30, the elongation at break of ACM/PVC hollow fibers did not appear obvious regularity. This may be due

Table III. The Effect of Different Polymer Concentrations and Blending Ratios on Elongation at Break

Blending ratios	15 wt %	18 wt %	20 wt %	22 wt %
50:50	0.670%	1.100%	1.421%	1.586%
60:40	2.790%	2.448%	2.564%	3.152%
70:30	3.735%	3.684%	3.325%	3.645%

Journal of Applied Polymer Science

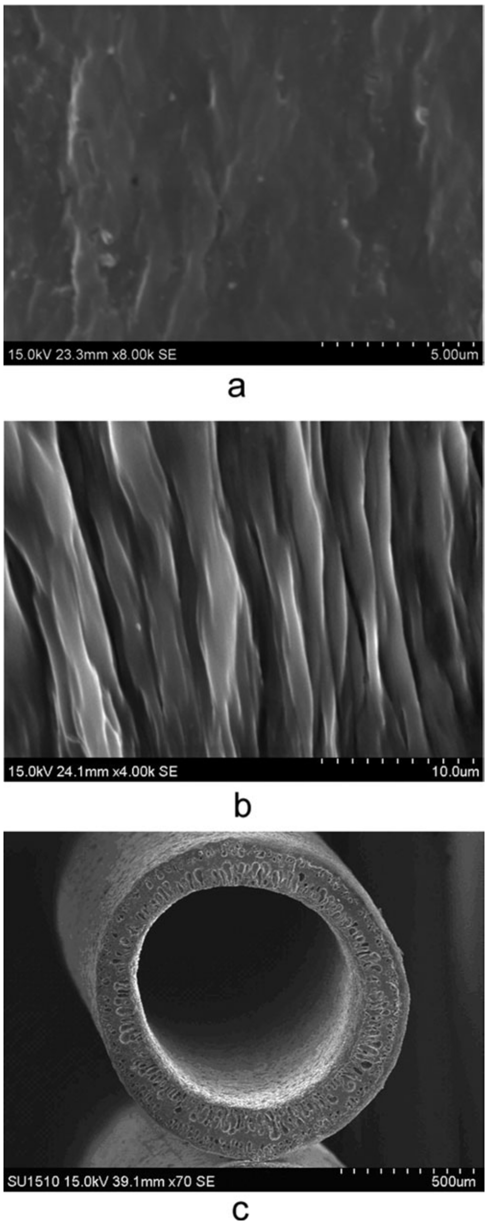

Figure 1. SEM photographs of ACM/PVC composite hollow fiber damping materials: (a) outer surface (8k), (b) inner surface (4k×) and (c) cross section.

to polymer content is relatively low, the viscosity of polymer blends is small, so that the PVC powder dispersed in ACM phase more evenly. Therefore the elongation at break in low polymer content is higher than that of the high polymer content at the blending ratio 70:30. Another reason is probable related to outer skin and inner skin of hollow fibers as shown in Figure 1. Some defect pores are in the inner layer. In drawing process, the drawing stress would be concentrated at these regions, resulting in the defect pores to extend and evolve into voids until rupture.

The Damping Properties of ACM/PVC Hollow Fibers

The damping of material is usually characterized by the tan δ value, and the larger tan δ represents the better damping. The dynamic mechanical properties of ACM/PVC hollow fiber damping materials were examined by DMA. The temperature dependence of the loss langent (tan δ) for ACM/PVC blends with different polymer content is plotted in Figure 2. As shown in Figure 2, we observe that all the hollow fibers damping materials exhibit single tan δ peaks, so only one glass transition temperature is exhibited. This is probable because in ACM/PVC blends system, ACM matrix provides the flexibility for

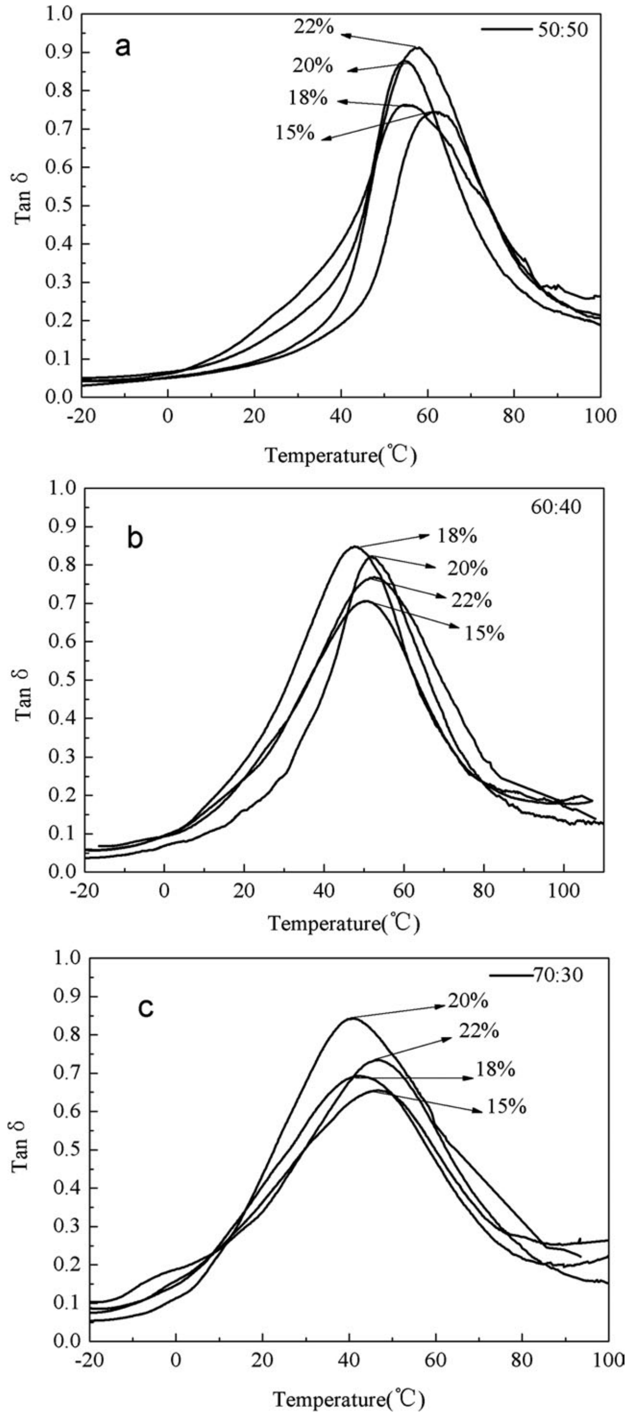

Figure 2. The influence of damping factor arouses by changing polymer concentration: (a) ACM/PVC blend ratio 50:50, (b) 60:40 and (c) 70:30.

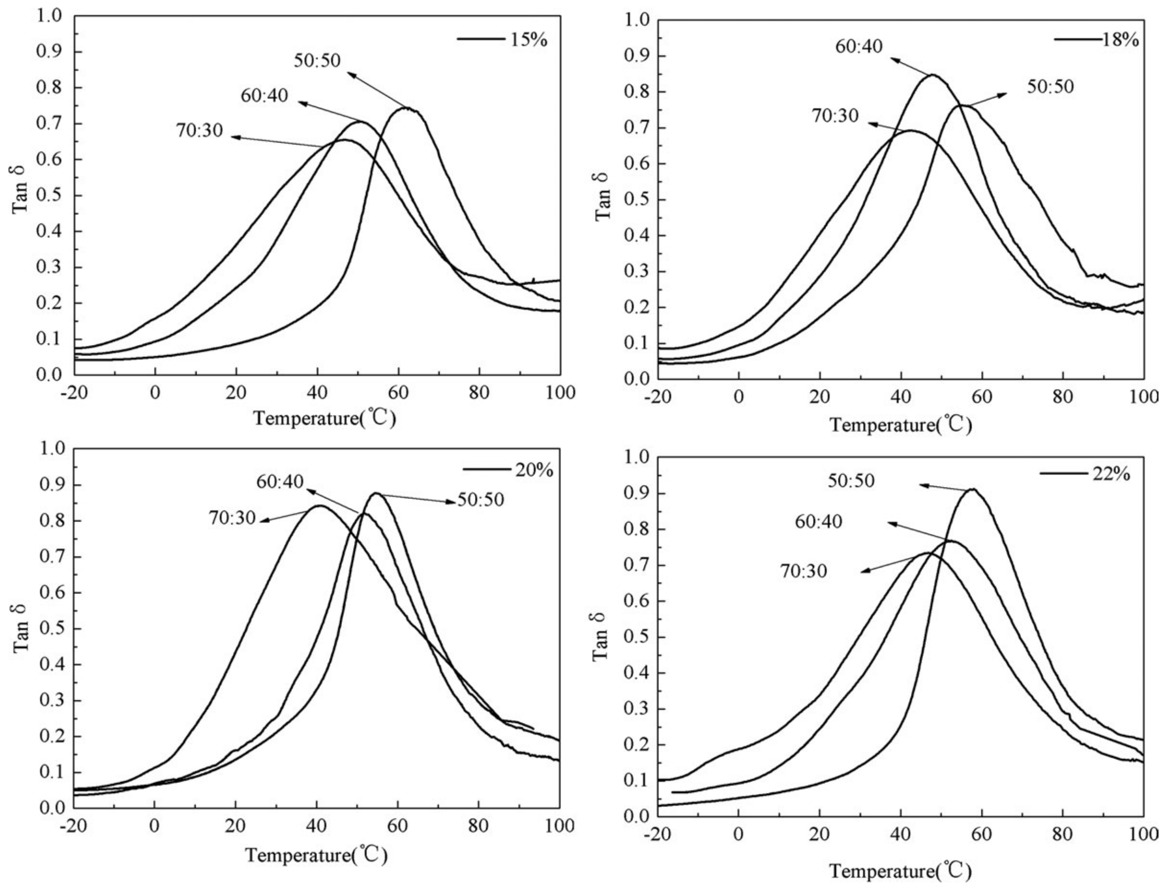

Figure 3. The influence of damping factor arouses by changing polymer blend ratio.

materials, while the dispersed phase of PVC is mainly to offer the rigidity, leading to PVC macromolecular effectively limit the movement of the ACM macromolecular chain so that the coordinated movement both the ACM and PVC make the glass transition temperature of the damping material close to each other to form one transition region. On the other hand, it may be caused by the compatibility both ACM and PVC. Moreover, we note that the peak location shifts to higher temperature with increasing the PVC content which is shown in Figure 3. The peak shifts in the ACM/PVC blends also implying that ACM has a good compatibility with PVC caused by the interaction between macromolecules of ACM and PVC.

To further prove the results of DMA due to the interaction between macromolecules of ACM and PVC, infrared spectroscopy as a powerful tool is used to investigate specific interaction between polymers. The molecular interaction between polymers is main the dipole and hydrogen bonding which result in the specific functional groups of the polymer in the frequency shifting. For the compatible blends, it is found in FTIR that the obsorption peaks of some groups with frequence shift, especially hydrogen bond of carbonyl.

Figure 4 shows infrared spectra of carbonyl stretching measured at ranging from 500 to 4000 cm^{-1} for pure ACM and ACM/PVC. The infrared carbonyl stretching for pure ACM only gives a single band centered at 1733 cm^{-1}, corresponding to the free carbonyl groups, as shown in Figure 4(a). Furthermore, the characteristic peak of carbonyl stretching shifts to lower frequency for 1 cm^{-1} after blending ACM to PVC which is showed in Figure 4(b). This is probable that there is a kind of the similar special interaction to the hydrogen bond between the molecular of ACM and PVC polymer, which plays an important role in further proving the miscibility for the ACM/PVC blends. Another characteristic absorption peak appears at 1427 cm^{-1} in Figure 4(b), which is a significant of PVC phase, and at 1500–800 cm^{-1} there is obvious characteristic absorption peaks which are unique absorption vibration of PVC. It indicated that blending ACM to PVC, the structure of PVC has not changed. The results obtained from infrared spectra demonstrate that ACM/PVC blends system was just a simple blend, but a stronger special interaction benefits for the miscibility further proved. Hence, these results are consistent with the dynamic mechanical properties discussed above.

From the Figure 3, we also note that 22 wt % ACM/PVC blends at blending ratio 50:50 has the highest tan δ peak with a maximum approaching to 0.9. The glass temperature of all samples is above the room temperature and the effective damping range with tan δ above 0.3 is 40–65 °C. This suggests that the modification of ACM with PVC broaden the temperature range of damping materials. Besides, the tan δ value at blending 50:50 increases with the increase of polymer content,

Applied Polymer

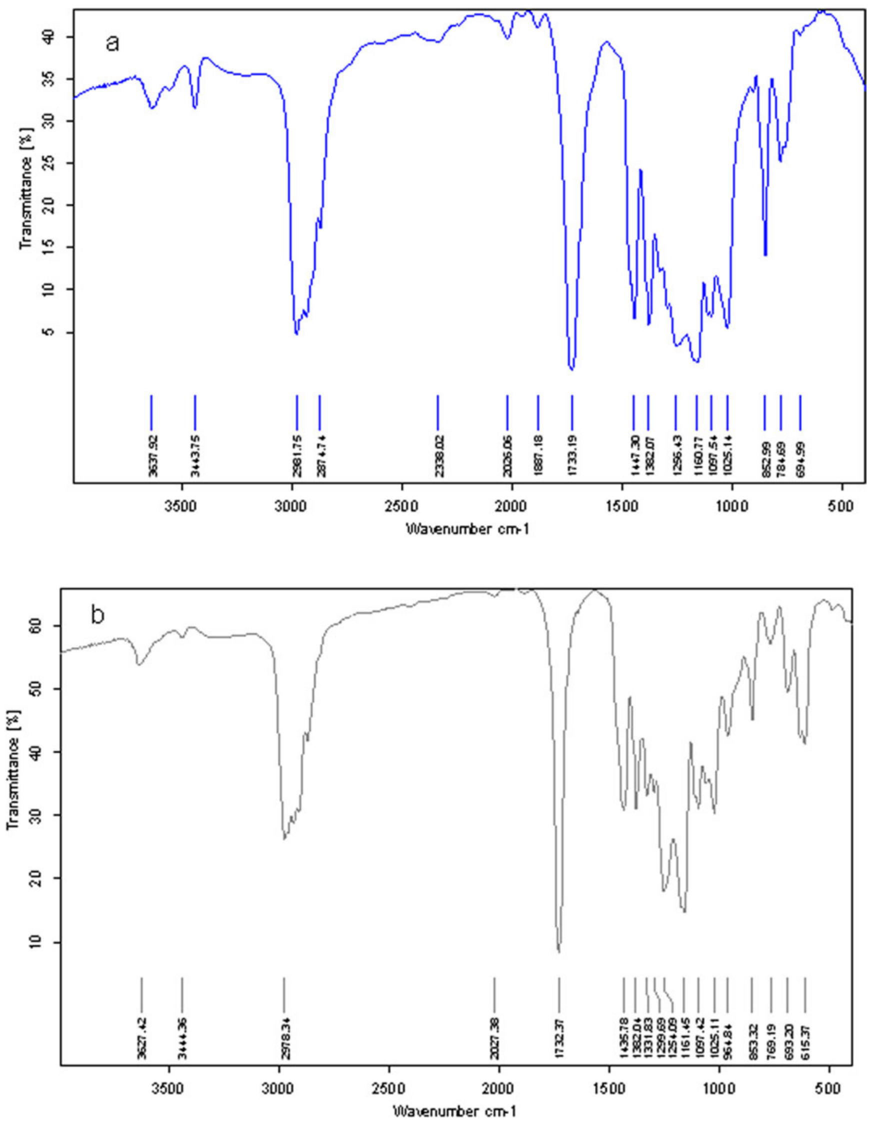

Figure 4. FTIR curve of ACM and ACM/PVC materials: (a) ACM and (b) ACM/PVC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

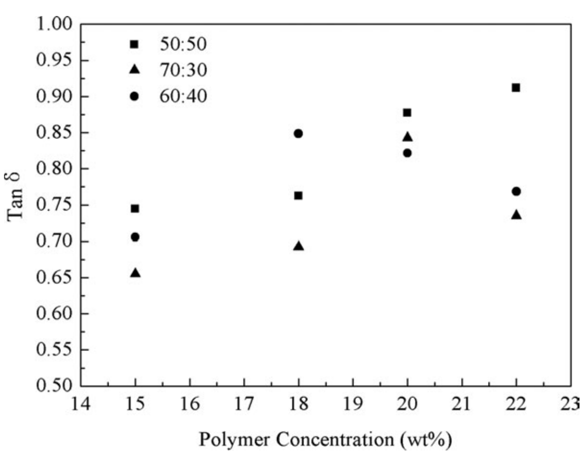

Figure 5. The curve of damping peak in different polymer concentrations.

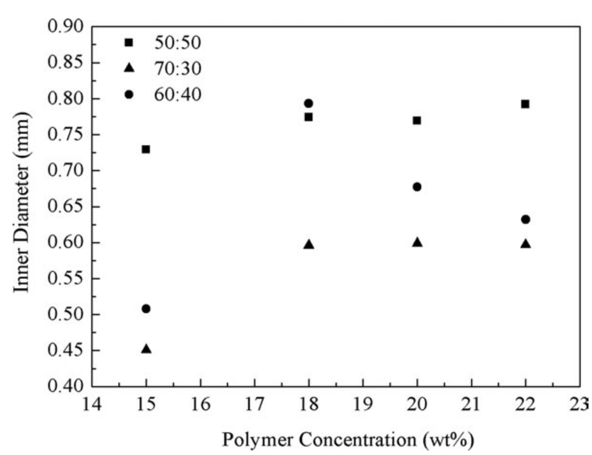

Figure 6. The curve between inner diameter and different polymer concentrations.

this trend is similar to that the tan δ value of nitrile rubber hollow fiber damping materials dependence of the temperature in our previous study.[20] However, it doesn't present at blending ratios 60:40 and 70:30. Meanwhile, we could see that the variations of the tan δ value have no regular in Figure 3. This is likely to be related to the inner diameter. Figure 5 presents information related to the value of the tan δ peaks, and the inner diameter dependence of the polymer contents with different blending ratios is listed in Figure 6. As shown in Figures 5 and 6, the tan δ value and the inner diameter dependence of the polymer contents with different blending ratios have the same trend. It indicates that the size of the hollow fiber cavity has a great impact on the tan δ value. The hollow fiber cavity has a shrink in dry process due to the increase of the ACM content. The bigger inner diameter is the greater volume of air contained in hollow fiber. The greater friction produced under the stress and the more energy are dissipated via the friction producing the heat. So the value of the tan δ peak dependence on polymer content and the blending ratios is affected by the inner diameter.

CONCLUSIONS

The ACM damping materials of hollow fiber modified with PVC were first prepared by dry–wet spinning technique to improve their damping performance, based on the hollow structure had a good cushion performance. Adding PVC to ACM not only decreases the viscous and rises the speed of phase inversion, but also improves the mechanical strength of ACM damping materials, above all, enhances the glass transition temperature and damping temperature range.

PVC was compatible with ACM at blending ratio 50:50∼70:30. DMA and FTIR studies also provided positive evidence for the intermolecular interaction between the ACM carbonyl groups and PVC, which had an effect on damping performance. The tan δ peak the ACM/PVC hollow fibers shifted to the higher temperature with the increase of the content of PVC, but the value of tan δ peak was mainly related to the inner diameter of hollow fiber and increased with the increase of inner diameter, indicated that it was convenient to adjust the value of tan δ peak and the temperature range just by varying the inner diameter and the blending ratio of ACM/PVC blends in costing membrane liquid to meet the practical demands. In addition, SEM observed the morphology structure of ACM/PVC hollow fiber. It is found that the inner skin or outer skin is different from that used in water treatment due to the differences between materials.

ACKNOWLEDGMENTS

The work was financially supported by the Natural Science Foundation of Jiangxi Province and the National Natural Science Foundation of China (10962006).

REFERENCES

1. Qin, J. J.; Cao, Y. M.; Oo, M. H. *J. Appl. Polym. Sci.* **2006**, *99*, 430.
2. Dahe, G. J.; Teotia, R. S.; Bellare, J. R. *J. Appl. Polym. Sci.* **2012**, *124*, E134–E146.
3. Chou, W.; Yu, D.; Yang, M. *J. Polym. Res.* **2005**, *12*, 219.
4. Kola, A.; Ye, Y.; Ho, A.; Le-Clech, P.; Chen, V. *J. Membrane Sci.* **2012**, *409-410*, 54.
5. Li, M.; Li, R.; Xu, Y.; Wu, H. *J. Nanchang Hangkong Univ.* **2009**, *23*, 10.
6. Wu, C.; Akiyama, S. *Polym. J.* **2001**, *33*, 955.
7. Wu, C. *Chinese J. Polym. Sci.* **2003**, *21*, 483.
8. Jha, A.; Dutta, B.; Bhowmick, A. K. *J. Appl. Polym. Sci.* **1999**, *74*, 1490.
9. Jha, A.; Bhowmick, A. K. *Polym. Degrad. Stab.* **1998**, *62*, 575.
10. Ding, X.; Xu, R.; Yu, D.; Chen, H.; Fan, R. *J. Appl. Polym. Sci.* **2003**, *90*, 3503.
11. Jha, A.; Bhowmick, A. K. *J. Appl. Polym. Sci.* **1998**, *69*, 2331.
12. Wong-On, J.; Wootthikanokkhan, J. *J. Appl. Polym. Sci.* **2003**, *88*, 2657.
13. Wimolmala, E.; Wootthikanokkhan, J.; Sombatsompop, N. *J. Appl. Polym. Sci.* **2001**, *80*, 2523.
14. Li, Y.; Yuko, O.; Kadowaki, Y.; Inoue, T.; Nakayama, K.; Shimizu, H. *Macromolecules* **2006**, *39*, 4195.
15. Shivakumar, E.; Srivastava, R. B.; Pandey, K. N.; Das, C. K. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2005**, *42*, 1181.
16. Wu, C.; Otani, Y.; Namiki, N.; Emi, H.; Nitta, K. H. *Polym. J.* **2001**, *33*, 322–329.
17. Guo, M.; Sun, Z.; Li, J. Luan, G.; Chen, X. *Mater. Mech. Eng.* **2012**, *36*, 38.
18. Guo, M. Dynamic Mechanical Thermal Analysis of Polymer Composites. Beijing: Chemical Industry Press; **2002**. p 18.
19. Hu, R.; Dimonie, V. L.; ElAasser, M. S.; Pearson, R.A.; Hiltner, A.; Mylonakis, S. G.; Sperling, L. H. *J. Polym. Sci. Part B: Polym. Phys.* **1997**, *35*, 1501.
20. Li, M.; Liu, M.; Xu, Y.; Wu, H.; Cao, Y. *Acta Materiae Compositae Sinica* **2011**, *28*, 45.