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Thermal Properties of Nanostructured Poly(acrylonitrile)–Silica Materials

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Summary: This report describes the thermal properties of nanostructured poly(acrylonitrile)–silica materials having potential as chromatography sorbents. Thermal analysis of nanostructured materials obtained by simultaneously polymerization of acrylonitrile and hydrolytical polycondensation of tetraethoxysilane are showed the presence of two exothermic peaks in the thermogramms of the poly(acrylonitrile)–silica materials.

Keywords: poly(acrylonitrile); silicas; sol-gel reaction; thermal properties

Introduction

Acrylonitrile containing polymers such as styrene–acrylonitrile (SAN), acrylonitrile–butadiene–styrene (ABS), etc. are used as textile fibers, carbon fiber percursors, adhesives, binders, antioxidants, electrical insulations, and surface coatings among other things.[1,2]

To synthesize homogeneous polymer hybrids, organic polymers with functional groups that have specific interaction with silica gel are introduced into sol–gel reaction solution.[3,4] The example chosen here was poly(acrylonitrile) (PAN), since it contains cyano functional groups that can form hydrogen bonds with silanol groups on the ceramic phase.[5] Also, PAN may be modified, with 3-(trimethoxysilyl)propyl methacrylate for example, so that it can be covalently bonded to the silicate network in the resulting hybrid material.[6] These types of bonding can be important with regard to both the nature of the nanocomposite produced and its various other properties.[7] The ultimate goal of the material being prepared here is its possible use as novel sorbents in chromatographic separations.[5,8]

In this paper, we report the thermal properties of nanostructured PAN/silica materials syntheses using *in situ* radical polymerization of the acrylonitrile monomer during the simultaneous hydrolytic polycondensation of a starting material well-known in sol–gel technology, tetraethoxysilane (TEOS) [$Si(OC_2H_5)_4$].

Experimental

Starting Materials

Acrylonitrile (Aldrich) was washed with 5 wt % sodium hydroxide solution to remove the inhibitor and washed with distilled water to remove the basic impurities, and then dried over calcium chloride and distilled under reduced pressure. The middle fraction of the distillate was used. TEOS (Gelest) was used without further purification. Potassium persulfate ($K_2S_2O_8$) and Sodium bisulfite ($NaHSO_4$) were obtained from Baker Chemical Co. and were recrystallized by ethanol. All other reagents were used as received.

Synthesis

The silicate network was generated from the TEOS in the presence of ethanol as a co–solvent with the water required for the sol–gel reaction. The desired polymer–silica nanostructured materials were prepared as.[9]

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Results and Discussion

PAN has a transition at ~157 °C for the amorphous phase, dipole–dipole interaction for the quasicrystalline phase at about 99 °C (glass transition temperature T_g), and the secondary transition for the amorphous phase at 79 °C.[2] Thermal decomposition of PAN mainly yields hydrogen cyanide, different nitriles, and other compounds. Degradation mechanism is thought to consist of chain scission, cross–linking, hydrogenation, and cyclization. TGA–FTIR of PAN under reduced pressure and in air at 200 °C showed imine–enamine tautomerism. Simultaneous cyclization and oxidation at 160–300 °C of PAN produced black orlon.[10] At elevated temperatures, cyclization and aromatization of PAN occurs with the formation of carbon fibers. Ammonia and HCN are evolved between 250 and 350 °C, and hydrogen is evolved between 350 and 700 °C.

Fig. 1 presents the results gotten from thermogravimetric–differential thermal analysis (TGA–DTA) studies of pure PAN, acid– and base– catalyzed PAN–silica composites. The first weight loss is centered about 200 °C, which corresponds to the removal of physically adsorbed residual water. Some of the products that may have evolved above 250 °C are HCN, acetonitrile, acrylonitrile, benzonitrile, methane, acetylene, ethylene, ethane, propene, propane, 1,3-butadiene, ethyl nitrile, vinyl acetonitrile, crotonitrile, benzene, pyridine, dicyanobutene, adiponitrile, dicyanobenzene, and naphthalene.[11]

This occurrence is seen in the exothermic peaks at about 295 and 450 °C in the DTA curves presumably due to the cyclization and aromatization of PAN with the evolution of products mentioned above. At even higher temperatures, hydrogen and nitrogen are given out forming carbon fibers.

Fig. 1 shows similar thermal behavior for both pure PAN and PAN–silica samples except that the residue in the latter is more than the former. The most important point here is the fact that these calorimetric data confirm enhanced thermogravimetric

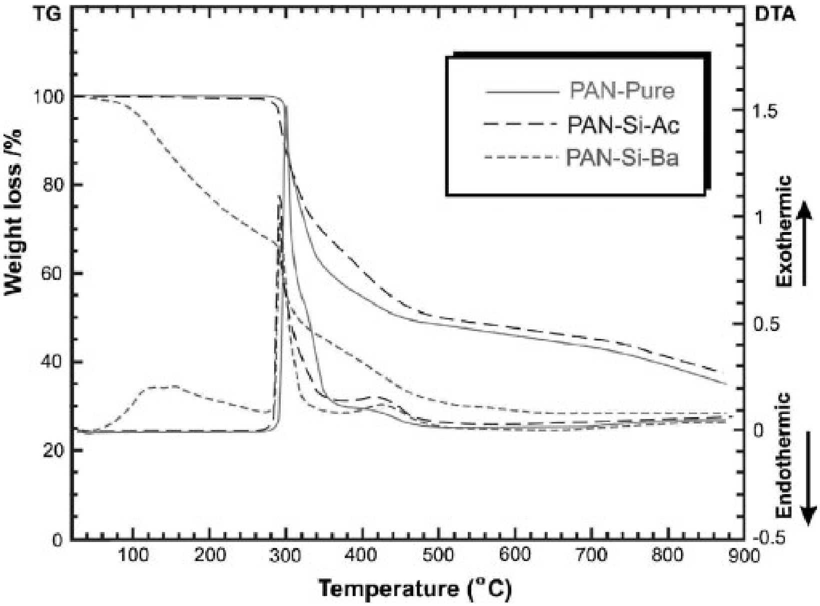

Figure 1.
TGA–DTA curves of PAN and PAN–silica materials.

stability for the nanocomposites relative to PAN itself.

Conclusion

The results of this study demonstrate the some properties of a poly(acrylonitrile)–silica nanostructured materials having improved thermal stability and a type of porous structure that could be extremely useful in the area of sorption technologies and chromatographic separations.

[1] A. L. Andrady, in: "*Polymer Data Handbook*", J. E. Mark, Ed., Oxford University Press, New York **1999**, p. 254.
[2] M. M. Wu, in: "*Encyclopedia of Polymer Science and Technology*", N. Bilakes, et al. Eds., J.Wiley & Sons, New York **2002**.
[3] H. Schmidt, *J. Non–Cryst. Solids*. **1994**, *178*, 302.
[4] Y. Wei, J.-M. Yeh, D. Jin, X. Jia, *J. Wang, Chem. Mater.* **1995**, *7*, 967.
[5] B. D. Kabulov, O. N. Ruzimuradov, G. Bekmirzaeva, D. T. Satibaldieva, S. V. Zalyalieva, S. Sh. Rashidova, *Russ. J. Phys. Chem.* **2002**, *76*, 1512.
[6] Y. Wei, D. Yang, L. Tang, *Makromol. Chem. Rapid Commun.* **1993**, *14*, 273.
[7] H. Ihara, Sh. Okazaki, K. Ohmori, Sh. Uemura, Ch. Hirayama, Sh. Nagaoka, *Anal. Sci.* **1998**, *14*, 349.
[8] G. Ranade, V. Stannett, W. J. Koros, *J. Appl. Polym. Sci.* **1980**, *25*, 2179.
[9] O. N. Ruzimuradov, B. D. Kabulov, S. Sh. Rashidova, G. S. Rajan, J. E. Mark, in proceedings of Intern.Conf. "*Sol-Gel Materials'04: Research, Technology, Applications*" Wroclaw, Poland, **2004**, 85.
[10] F. W. Billmeyer, in: "*Textbook of Polymer Science*", 3rd ed.Wiley–Interscience Publication, New York **2000**, 427.
[11] Y. Tsuchiya, K. Sumi, *J. Appl. Polym. Sci.* **1977**, *21*, 975.