Facile fabrication of mesoporous silica-based natural rubber nanocomposite with enhanced thermal stability

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Abstract: A preparation of natural rubber (NR) and hexagonal mesoporous silica (HMS) nanocomposite with enhanced thermal stability (HS-NRHMS) was facilely achieved by one-step process involving an addition of 0.5 M H_2SO_4. Decomposition temperature of NR in the resulting HR-NRHMS was 40 °C higher than that of nanocomposite obtained under neutral condition (NRHMS). Furthermore, HS-NRHMS possessed relatively well-ordered mesoporosity with wormhole motif structure and surface area (577 m^2/g) as compared to NRHMS (648 m^2/g).

Keywords: Nanocomposite material, Nanostructured, Mesoporous silica.

1. Introduction

The NRHMS nanocomposite is a functionalizable hydrophobic material with high surface area, which can be potentially used in many applications, such as catalysts, adsorbents and drug carriers. However, thermal stability of NRHMS is a great concern due to a low decomposition temperature of NR which starts from 200 ºC. A mild acidic solution can be used to enhance the rate of silica condensation to obtain mesoporous silica with higher framework stability[1]. Herein, a similar concept was applied to synthesis of the nanocomposite with enhanced thermal stability (HS-NRHMS) by using 0.5 M H_2SO_4.

2. Experimental

Pure silica HMS and NRHMS were prepared by sol-gel method as described elsewhere[2]. A small NR sheet was swollen in tetraethyl orthosilicate (TEOS) for 24 h. The swollen NR was then stirred overnight in tetrahydrofuran (THF) to attain colloidal mixture. Dodecylamine (DDA), an additional TEOS and deionized water were sequentially added to the mixture under stirring. After ageing at 40 ºC for 1 d, 0.5M H_2SO_4 was slowly dropped into the mixture under stirring, and the resulting mixture was further aged for 1 d. The weight composition of NR: THF: DDA: TEOS: H_2O: 0.5M H_2SO_4 in the synthesized mixture was 0.5: 26.67: 3.75: 10.5: 53.05: 2.55. The solid product was recovered by precipitation in ethanol, filtration and drying at 60 ºC for 18 h. The template extraction was performed in a solution of 0.05 M H_2SO_4/ethanol at 80 ºC for 4 h. The resulting solid was thoroughly washed with ethanol, and further dried at 60 ºC for 12 h.

3. Results and discussion

Table 1 Physical properties of HMS and NRHMS nanocomposites

Sample	S_{BET} (m^2/g)	S_{ext} (m^2/g)	V_T (cm^3/g)	$V_{m,H2O}$ (cm^3(STP)/g)	D_p (nm)	d_{100} (nm)	a_0 (nm)	W_T (nm)
HMS	1004	533	2.29	70.37	2.79	4.08	4.71	1.92
NRHMS	648	384	1.37	60.15	2.55	4.20	4.85	2.30
HS-NRHMS	577	401	1.50	43.32	2.56	4.66	5.38	2.82

[a] BET surface area, [b] External surface area, [c] Total pore volume, [d] Monolayer adsorption volume of water, [e] Pore diameter, [f] d-spacing of (100), [g] Lattice parameter, [h] Wall thickness

As shown in Table 1, NRHMS possessed lower surface area and pore volume than HMS. A thicker pore wall of HS-NRHMS should be attributed to an incorporation of NR and a solidification of silica wall by the addition of acidic solution that initiated the condensation enhancement[1]. Hydrophobicity of the materials was accessed by H_2O adsorption-desorption measurement, which indicated a decrease in the amount of water adsorbed for the nanocomposites. HS-NRHMS possessed the lowest affinity for water, likely due to the diminution of surface silanol groups by the enhanced condensation process.

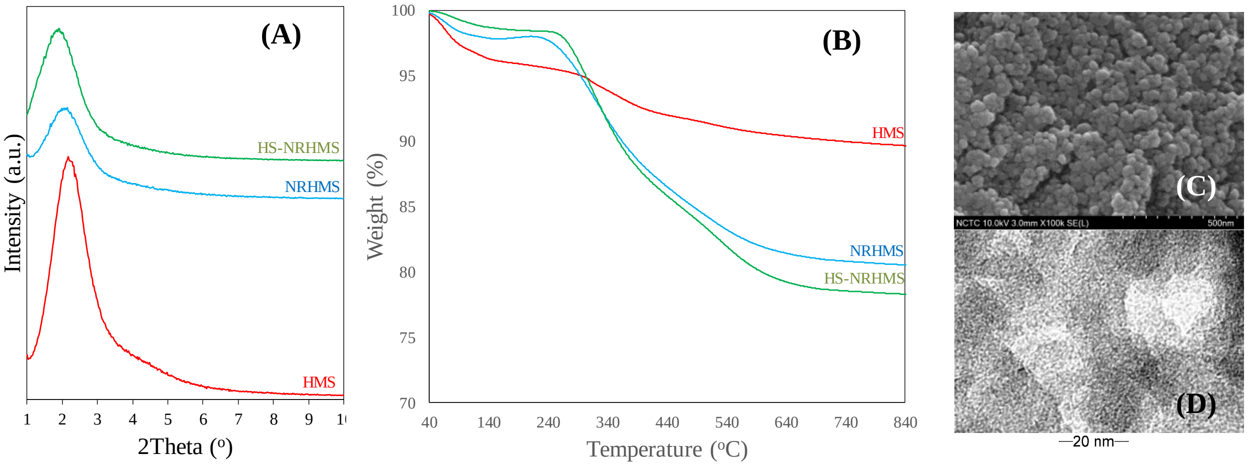

Figure 1. (A) XRD patterns and (B) TG curves of the materials, and (C) FE-SEM and (D) TEM images of HS-NRHMS.

From the results shown in Figure 1, the low-angle XRD analysis indicated that all samples possessed a characteristic diffraction peak at 2θ around 2°, which was attributed to (100) plane of hexagonal mesoporous silica with wormhole-like framework. For the NRHMS composites, the diffraction peak was shifted to lower angles, which was described by an incorporation of NR into the silicate framework, resulting in a unit cell expansion[3]. However, the presence of NR hampered the structural ordering. The addition of mild acidic solution in the synthesis mixture enhanced the condensation of silica precursor, leading to the mesoporous nanocomposite with enhanced structural order. The TG analysis indicated an initial decomposition of NRHMS at 200 °C. A weight gain around 180 °C was ascribed to the NR oxidation under air flow condition. The decomposition of NR in HS-NRHMS appeared at 240 °C, and the oxidation of NR was not observed. It was hypothesized that a majority of rubber chains was covered with silica, which mitigated their exposure to air. An increased pore wall thickness also led to thermally stable framework[4], and possibly contributed an enhanced thermal stability of this nanocomposite. The FE-SEM image revealed that HS-NRHMS exhibited nanosphere aggregates, while wormhole-like pore structure, as a prominent feature of HMS, retained as evidenced by TEM.

4. Conclusions

The HR-NRHMS nanocomposite with enhanced thermal stability was successfully synthesized in the presence of mild acidic solution. An increase in pore wall thickness and structural ordering was observed due to an enhanced condensation of silicate framework. The present work also provided a facile approach to control the distribution of rubber chains in the wormhole-like silica framework and the hydrophobicity and morphology of the resulting nanocomposite.

References

1. H.P. Lin, C.P. Tsai. Chem. Lett. 32 (2003) 1092–1093.
2. S. Nuntang, S. Poompradub, S. Butnark, T. Yokoi, T. Tatsumi, C. Ngamcharussrivichai. Mater. Chem. Phys. 143 (2014) 1199–1208.
3. S. Nuntang, S. Yousatit, S. Chaowamalee, T. Yokoi, T. Tatsumi, C. Ngamcharussrivichai. Microporous Mesoporous Mater. 259 (2018) 79–88.
4. Z.A. Alothman, A.W. Apblett. Appl. Surf. Sci. 256 (2010) 3575–3580.