Materials Science and Engineering A 528 (2011) 3321–3325

Contents lists available at ScienceDirect

Materials Science and Engineering A

journal homepage: www.elsevier.com/locate/msea

Incorporation of nano-sized mesoporous MCM-41 material used as fillers in natural rubber composite

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ARTICLE INFO

Article history:
Received 15 October 2010
Received in revised form
15 December 2010
Accepted 21 December 2010
Available online 12 January 2011

Keywords:
Mechanical characterization
Composites

ABSTRACT

The nano-sized mesoporous MCM-41 (without template), and the modification of MCM-41 (without template) were used to prepare natural rubber (NR) composites. The effects of coupling agents γ-aminopropyltriethoxysilane (KH-550), γ-methacryloxypropyltrimethoxysilane (KH-570), bis-(γ-triethoxysilylpropyl)-tetrasulfide (Si-69), isopropyl tri-(dioctylpyrophosphate)titanate (NDZ-201) on the mechanical properties of the composites were also investigated. The results showed that the tensile properties of Natural rubber/mesoporous MCM-41 nanocomposite were improved as compared with those of NR compound. KH-570 had good effect on enhancing the overall properties of the composites. Scanning electron microscopy (SEM) observations revealed that the modified nano-sized MCM-41 material was well dispersed in the polymer matrix and the enhancement of the interface between the matrix and fillers was obtained.

1. Introduction

The incorporation of various fillers into rubbery polymers imparts many interesting and useful properties to the particle-filled composite materials. During the last years the effects of different types of fillers on rubber compounds have been studied, in search of improvements on its physical and mechanical properties. Elastomeric materials are usually reinforced with carbon black or silica, although the full effects of these fillers are diminished due to their agglomeration [1–4]. It becomes crucial to incorporate well-dispersed nano-fillers into rubber to obtain beneficial mechanical and physical properties.

Recently nano-mesoporous MCM-41 (without template) has been extensively served as an effective reinforcement filler to enhance the mechanical, thermal properties of polymer materials, due to its unusual characters, such as extended inorganic or inorganic–organic hybrid arrays with exceptional long-range ordering, highly tunable textural and large surface area properties, controlled pore size and shape [5]. It is expected that a polymer or reactive groups could either be introduced directly or produced by in situ polymerization of organic monomers inside the mesopores. The polymer or reactive groups in the nano-sized pores extending along the channels to the openings can not only enhance the miscibility through the entanglement and inter-diffusion between the matrix and the particulate, but also highly suppress the aggregation of fillers (see Scheme 1). Thus nanocomposites of polypropylene, polyethylene, epoxy resin and MCM-41 (without template) with enhanced thermal stability and mechanical strength were also reported in our previous work [6–12], while very little work has been done on incorporating the novel kind of filler in rubber.

NR is an important and widely used rubber. Thus, it is the aim of this contribution to assess the potential utilization of this novel kind of filler in rubber compounds. In this paper, the surface and the nano-channels of MCM-41 (without template) have been modified with different coupling agents. The influence of MCM-41 (without template) and modified MCM-41 (without template) on the mechanical properties and morphology of the NR composites have also been discussed.

2. Experimental

2.1. Materials

The nano-sized mesoporous MCM-41 particles were prepared by our group which was reported in the literature [8]. In this study, nano-sized mesoporous MCM-41 particles with uniform diameters in the order of 80–100 nm, spherical shape and mono-disperse were synthesized by our group in order to exclude the size and shape effects of fillers on composites. The BET surface areas and specific pore volume of MCM-41 were 732 m^2/g and 0.9 cm^3/g,

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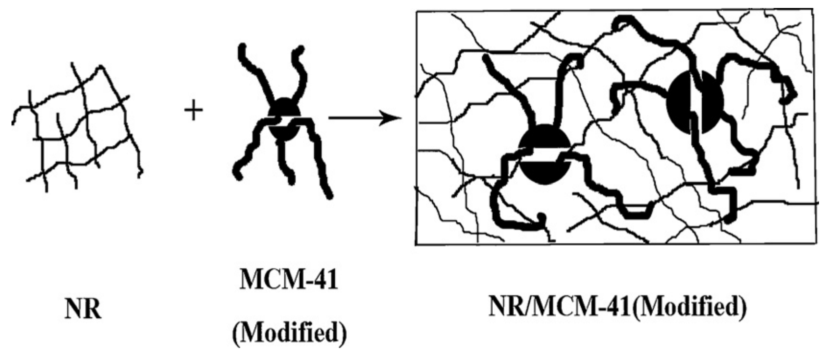
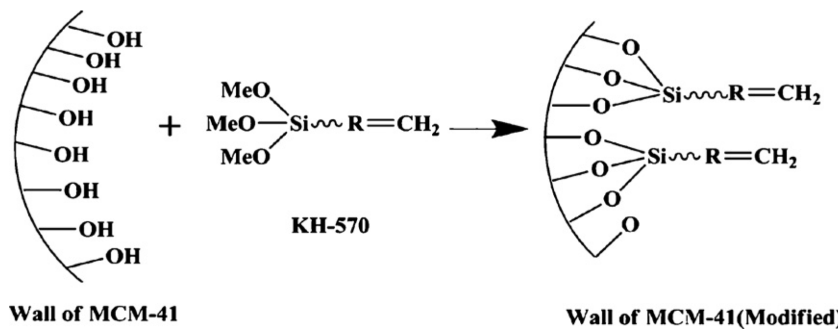
doi:10.1016/j.msea.2010.12.105



Scheme 1. Model analogy novel nanonetwork composite.



Scheme 2. The chemical reaction of KH570 with silanol groups of MCM-41.

respectively. The MCM-41 materials had a narrow pore size distribution of 3.6 nm.

All other chemicals and solvents were of analytical grade and used without further purification. NR was supplied by Petrochemical Co., Jilin. The silane coupling agents used in this study were as follows: γ-aminopropyltriethoxysilane KH-550, γ-methacryloxypropyltrimethoxysilane KH-570, bis-(γ-triethoxysilylpropyl)-tetrasulfide Si-69. The titanate coupling agent in this study was isopropyl tri-(dioctylpyrophosphate)titanate NDZ-201. They were purchased from Shuguang Chemical Co. (Nianjing, China). Zinc oxide (ZnO), stearic acid, sulfur and other chemicals used were all commercial grades.

2.2. Modification of the surface and mesopore channels of MCM-41

One gram of MCM-41 (without template), 50 ml dry hexane and 5.0 ml γ-methacryloxypropyltrimethoxysilane KH-570 were placed in a 100 ml round bottom flask. The mixture was stirred and refluxed at 343 K for 12 h under the protection of nitrogen atmosphere. The white solid was washed repeatedly with ethanol and then dried at 353 K for 12 h. The chemical reaction was illustrated in Scheme 2.

In our previous paper, we have justified that $-NH_2$ group of KH550 or the groups of KH570 indeed modified the mesopore channels or the surface of MCM-41 particle by using IR, XRD and N_2 adsorption–desorption [6].

2.3. Preparation of compounds

To obtain vulcanizates (the above) mentioned, nanocompounds were mixed with ingredients according to the recipe in Table 1 by a laboratory two-roll mill. All rubber compounds were vulcanized at 150 °C in a hot press for the optimum cure time (t_{90}) determined by a GT-M2000-A rheometer (GaoTie Limted Co., Taiwan). All specimens were then cut from the vulcanized sheets.

2.4. Characterization

A supra 35 scanning electron microscope with an accelerating voltage of 15 kV was employed to observe the morphology of the

Table 1
Recipes of NR compounds.

Ingredients (phr)	1#	2#	3#	4#	5#	6#	7#	8#	9#
NR	100	100	100	100	100	100	100	100	100
Carbon soot	30	29	27	25	22	22	22	22	22
MCM-41 (without template)	0	1	3	5	8	5	5	5	5
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	3	3	3	3	3	3	3	3	3
sulfur	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Accelerant CZ	1	1	1	1	1	1	1	1	1
Age inhibitor 4010	1	1	1	1	1	1	1	1	1
Si-69	–	–	–	–	–	1.5	–	–	–
KH-570	–	–	–	–	–	–	1.5	–	–
KH-550	–	–	–	–	–	–	–	1.5	–
NDZ-201	–	–	–	–	–	–	–	–	1.5

Note: The formulation of the compounds is expressed in phr (parts per hundred rubber).