ADVANCES IN NATURAL RUBBER MATERIALS RESEARCH

天然橡胶材料研究进展

Editor-in-Chief
Zheng Peng
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PREFACE

This proceedings contains 34 papers presented at the International Symposium on Natural Rubber Materials 2006 (ISNRM 2006) co-sponsored by the Chinese Academy of Tropical Agricultural Sciences (CATAS) and Chinese Agricultural Ministry Key Laboratory of Natural Rubber Processing (KLNRP), which was held in Haibin Hotel, Zhanjiang City, China on October 13-14, 2006.

The objectives of the ISNRM 2006 are to provide a forum for sharing the latest findings, experiences and exchanging the ideas on natural rubber (NR) materials, and facilitating contacts and co-operations. Scientists from research institutes, universities and companies in India, Thailand, Malaysia, Japan, Australia and China met in the symposium to exchange ideas and discuss advances on four fields of NR materials including the NR Based Composites, Modification of NR, NR Analysis and NR Designing, Processing and Manufacturing, which are also the four themes of this book. I believe that this symposium has laid a good foundation of further contacts and co-operations between respective institutions and individual scientists, and this book will be beneficial to the development of natural rubber science and technology.

With the publication of the book, special acknowledgements are due to the President of CATAS, Professor Wang Qinghuang, to the organizing committee chaired by Professor Ying Chen, the Director of KLNRP, to all chairpersons of various sessions, to all authors, and to participants of the symposium and all those who have contributed to the success of the symposium and the publication of the book.

Qiubo Chen
Honorary Chairman of ISNRM 2006
Vice-President of CATAS
Chairman of International Rubber Research and Development Board (IRRDB)

December 18, 2006

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CHAPTER 1

Advances in Natural Rubber Based Composites

Self-assembled Natural Rubber/Silica Nanocomposites: Its Preparation and Characterization

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Abstract

A novel natural rubber/silica (NR/SiO_2) nanocomposite is developed by combining self-assembly and latex-compounding techniques. The results show that the SiO_2 nanoparticles are homogenously distributed throughout NR matrix as nano-clusters with an average size ranged from 60 to 150 nm when the SiO_2 loading is less than 6.5 wt%. At low SiO_2 contents ($\leq$4.0 wt%), the NR latex (NRL) and SiO_2 particles are assembled as a core-shell structure by employing poly (diallyldimethylammonium chloride) (PDDA) as an inter-medium, and only primary aggregations of SiO_2 are observed. When more SiO_2 is loaded, secondary aggregations of SiO_2 nanoparticles are gradually generated, and the size of SiO_2 cluster dramatically increases. The thermal/thermooxidative resistance and mechanical properties of NR/SiO_2 nanocomposites are compared to the NR host. The nanocomposites, particularly when the SiO_2 nanoparticles are uniformly dispersed, possess significantly enhanced thermal resistance and mechanical properties, which are strongly depended on the morphology of nanocomposites. The NR/SiO_2 has great potential to manufacture medical protective products with high performances.

Key words: Natural rubber; latex; silica; nanocomposite; self-assembly

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INTRODUCTION

Natural rubber (NR), one of the most important biosynthesized polymers displaying excellent chemical and physical properties, finds widely application in various areas.[1],[2],[3] Particularly, as an chemical-free biomacromolecule, natural rubber latex (NRL) has been used in manufacturing medical products such as medical gloves, condoms, blood transfusion tubing, catheters, injector closures and safety bags due to its excellent elasticity, flexibility, anti-virus permeation, good formability and biodegradability.[4],[5],[6] More recently, with the worldwide spread of the epidemic diseases such as acquired immure deficiency syndrome (AIDS), hepatitis B, severe acute respiratory syndrome (SARS) and avian influenza A (H5N1), it becomes increasingly important and urgent to develop high performance NRL protective products.

However, as its macromolecular backbone incorporates unsaturated cis-1, 4-polyisoprenes, NR likes any other polymer is susceptible to oxidative or thermal degradation, particularly when formed into thin films. Once the degradation begins, NR readily becomes tacky and loses mechanical integrity. NRL products have, therefore, short shelf lives and life cycles. Though various anti-ageing agents have been successfully developed for dry NR products and limited anti-ageing agents for NRL were reported by using tris (nonylated phenyl) phosphite[7] and non-water soluble amino acids,[8] no ideal anti-ageing agents have been identified so far for medical NRL products where strict safety and hygiene are required.

Low tensile strength and poor tear resistance are the other major drawbacks encountered in NRL products, especially for medical gloves and condoms. Attempts have been made to use carbon black,[9] ultra-fine calcium carbonate,[10] modified montmorillonite,[11] silica[12] and starch[1] to reinforce dry NR or NRL. However, these traditional reinforcement materials are not so effective for NRL. Therefore, it is essential to exploit new way to enhance the ageing resistance and mechanical properties for NRL products.

Polymeric/inorganic nanocomposites (PINs) represent a radical alternative to conventional-filled polymers or polymer blends, and exhibit a controllable combination of the benefits of polymers (such as flexibility, toughness, and ease of processing) and those of inorganic phase (such as hardness, durability, and thermal stability).[13] Such

an improvement in combined characteristics is particularly significant at low loading levels of nano-fillers, which do not significantly increase the density of the compound or reduce light transmission. Therefore, introduction of inorganic nano-fillers into NR matrixes to overcome the aforementioned disadvantages of NR has recently attracted enormous interest. Most of these are using clay minerals with a unique multi-layered structure to reinforce NR via melt-intercalation,[14], [15] latex-compounding[16] and solution-mixing methods. [17] It was found that the organically modified clays with a loading up to 10 wt% have a good reinforcement on the NR matrix due to the intercalation/exfoliation of silicates and formation of a skeleton silicate network in NR matrix. [15], [16] Nair et al[18], [19], [20] also used nano crab chitin whiskers to reinforce NR. It was found that there is a three-dimensional chitin network within the NR matrix, which results in significantly improved solvent resistance and mechanical properties.

The high reinforcing efficiency of layered silicate rubber nanocompsites, even at low loading of layered silicates, is largely due to the nanoscale dispersion (the thickness of the layered silicates is 1nm) and the very high aspect ratio of the silicate platelets (length-to-thickness ratio up to 2000). However, using fillers with higher specific surface such as spherical inorganic nanoparticles to directly reinforce NR, which has the potential to further improve the material properties, has not been reported. This is probably because there is no effective process to prevent the strong self-aggregation of nanoparticles.

In our previous work, a novel self-assembly nanocomposite process was developed to prepare a bulk polyvinyl alcohol/silica (PVA/SiO_2) nanocomposites. [21], [22], [23] We found that the chemical and physical properties of nanocomposites, compared to the polymer host, were significantly enhanced. The improvement in the properties is largely due to the uniform distribution of SiO_2 nanoparticles and the strong interactions between SiO_2 and polymer matrixes. We recently extended this self-assembly process to prepare NR/SiO_2 nanocomposites and briefly reported its preparation and thermal properties. [24] In the present paper, we will systematically discuss the self-assembly mechanism of the SiO_2 and NRL particles, observe the morphology of the nanocomposite and microstructure of SiO_2 nano-clusters with SEM and TEM, and investigate the impact of SiO_2 on thermal/ thermooxidative resistance and mechanical properties.

EXPERIMENTAL

Materials

Natural rubber latex (NRL) with a total solid content of 62% was purchased from Shenli Rubber Plantation (Zhanjiang, P. R. China), and was pre-vulcanised at room temperature for 2 days with the following formula: sulfur 1.5 parts per hundred rubber (phr); accelerator PX 1.2 phr; accelerator ZDC 0.8 phr; zinc oxide 1.5 phr; and an appropriate amount of stabiliser. Silica nanoparticles (average diameter: 14 nm; surface area: 200 $m^2/g \pm 25\ m^2/g$) and poly (diallyldimethylammonium chloride) (PDDA) (mol wt ca. 100,000 – 200,000; 20 wt% in water) were brought from Sigma-Aldrich (Sigma-Aldrich, Louis, MO.). Water was Milli-Q water (18 MΩ – cm). All experimental materials were used as received.

Preparation of nanocomposite

In our previous work,[24] we briefly reported a novel process to prepare NR/SiO_2 nanocomposites by combining latex compounding and self-assembly techniques. Firstly, the negatively charged SiO_2 nanoparticles act as templates to adsorb positively charged PDDA molecular chains through electrostatic adsorption. Negatively charged NRL particles are then assembled onto the surface of SiO_2/PDDA nanoparticles. Finally, the SiO_2 nanoparticles are uniformly distributed in NR matrix. The key procedure of this process is the encapsulation of the SiO_2 nanoparticles with PDDA and NRL layers, aiming at suppressing the self-aggregation of SiO_2 nanoparticle caused by strong particle-particle interactions.

Specifically, the nanocomposites was prepared according to the following procedures. The SiO_2 nanoparticle aqueous dispersion of 1 wt % was treated with an ultrasonic vibrator for 0.5 hour, and its pH was adjusted to 10 with 0.2 M NaOH to obtain negatively charged SiO_2 dispersion. A fixed amount of positively charged PDDA solution (pH = 10) with a ratio of PDDA/SiO_2 = 5/100 w/w was then dropped into SiO_2 dispersion with mechanical stir. To remove PDDA that was not effectively absorbed on the surface of SiO_2 nanoparticles and avoid the flocculation of NRL particles cased by the redundant PDDA, the ultrasonically treated SiO_2/PDDA dispersion was

centrifuged followed by rinsing with Milli-Q water. This step was repeated for 2 times. The rinsed SiO_2 particles were then collected and ultrasonically re-dispersed to obtain SiO_2/PDDA aqueous dispersion.

A fixed amount of NRL with a total solid content of 5% was treated with an ultrasonic vibrator for 0.5 hour, and its pH was adjusted to 10 with 0.2 M NaOH to negatively charge the NRL particles. After that, the rinsed SiO_2/PDDA aqueous dispersion was then dropped into NRL with different mixture rates (NR/SiO_2 = 99.5/0.5, 99/1.0, 97.5/2.5, 96/4.0, 93.5/6.5 and 91.5/8.5 w/w) accompanying gentle mechanical stir at room temperature to obtain uniform NRL/SiO_2 dispersion, which was then dried in a vacuum oven at 50 ℃ to obtain NRL/SiO_2 nanocomposite films.

Characterizations

Scanning electron micrographs (SEM) of the nanocomposites were taken with a Philips XL 30 FEG-SEW instrument (Philips, Eindhoven, Netherlands) at an acceleration voltage of 10kV. The fracture surface was obtained by splitting bulk sample being quenched in liquid nitrogen. A sputter coater was used to pre-coat conductive gold onto the fracture surface before observation. Thin films for transmission electron microscopy (TEM) were prepared by cutting bulk samples being quenched in liquid nitrogen. TEM observation was done on a JEM-100CXII instrument (JEOL, Peabody, MA) with an accelerating voltage of 100 KV.

A Perkin Elmer TGA-7 thermogravimetric analyser (TGA) (Perkin-Elmer, Fremont, CA) was used for thermal and thermooxidative decomposition measurement. In nitrogen, the measurement of the films (ca. 10 mg) was carried out from 100 ℃ to 600 ℃ at a heating rate of 20 ℃/min. In air, the TGA analysis was carried out from 100 ℃ to 700 ℃ at the same heating rate. The flow rate of the carrying gas is 80 ml/min. Fourier transform infrared spectroscopy (FTIR) was preformed on a Perkin Elmer Spectra GX-I FTIR spectroscopy (Perkin-Elmer, Fremont, CA) with a resolution of 4 cm^{-1} in the transmission mode.

Tensile test and tear resistance experiments were conducted on an Instron Series IX Automated Materials Testing System (Instron, Acton, MA) with a cross head speed of 500 mm/min and the sample length between the jaws was 35 mm, the sample width 10

mm and the thickness 4.5 mm. The measurement was done at room temperature.

RESULTS AND DISCUSSION

Mechanism of self-assembly NR/SiO_2 nanocomposite process

When nanoparticles are dispersed with polymers, a core-shell structure tends to be formed in which nanoparticles covered with polymeric chains under certain conditions such as those used for self-assembly. By employing this approach, Caruso et al[25] developed core-shell materials with given size, topology, and composition. Han et al[26] and Rotstein et al[27] studied polypyrrole, polystyrene and silica nanocomposites, respectively, and also confirmed the formation of this core-shell structure. In the present study, SiO_2 nanoparticles act as cores or templates to assemble PDDA and then adsorb NRL particles to develop a bulk NR/SiO_2 nanocomposite. There are two electrostatic adsorption stages in this process (Figure 1).[24]

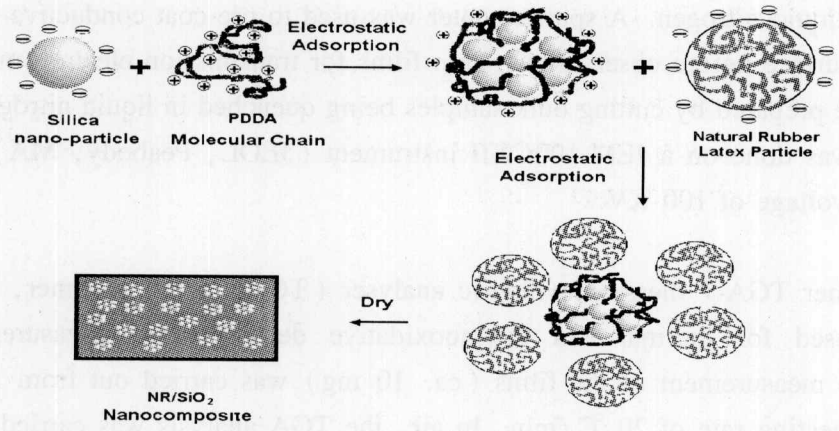


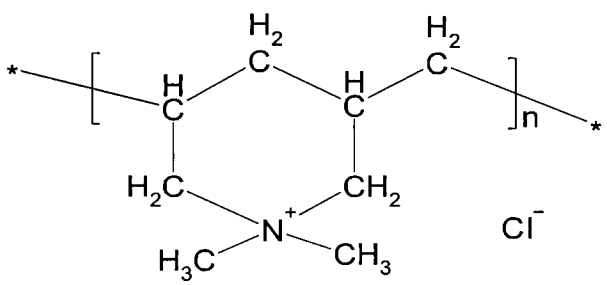
Figure 1 The schematic of the self-assembly process[24]

In the first stage, PDDA, an extensively used self-assembling material, is positively charged at the pH of 10 (Scheme 1),[28],[29],[30] and is adsorbed onto the surface of negatively charged SiO_2 nanoparticles at the same pH (Scheme 2) by using the electrostatic adsorption as driving force. However, due to a large difference in rigidity between SiO_2 and PDDA and the charge density of PDDA is significantly larger than that

on SiO_2, all of the former charges cannot form short-distance ion pairs with surface charges of rigid SiO_2 particles.[30] Therefore, the positive charge on PDDA cannot completely neutralized by the negative charge on SiO_2 particles during the assembly, and the SiO_2/PDDA core-shell particles will appear positive and be ready for next assembly with negatively charged NRL particles. To avoid the flocculation of NRL caused by the introduction of high molecular weight water-soluble cationic polyelectrolytes, PDDA that is not effectively assembled with SiO_2 is removed by the rinse presented in experimental section.

In the second assembly stage, the NRL particles are negatively charged as the protein particles adsorbed on the surface of the NRL particles contain carboxyl and amino functional groups (described as $P^{-COOH}_{-NH_2}$), which can be ionized in three different modes depending on pH value (Scheme 3). If the pH is lower than the isoelectric point of NRL (4.5 ~ 5.0), basic ionization will occur and NRL particles will be positively charged. Under isoelectric condition, NRL particles will remain neutral. As the pH used in the experiment (pH = 10) is higher than the isoelectric point, acidic ionization is generated. NRL particles are, therefore, negatively charged. Again, under the drive of electrostatic adsorption, NRL particles are adsorbed onto the surface of SiO_2.

particles that are covered with PDDA molecular chains in the previous assembly stage. Finally, the SiO_2 nanoparticles covered with PDDA and NRL layers are uniformly dispersed in NR matrix and dried (Figure 1).



Scheme 1 Structure of PDDA at pH of 10

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