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Preparation of novel flame-retardant organoclay and its application to natural rubber composites

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ABSTRACT

In this study, a novel type of flame-retardant montmorillonite (MMT) was prepared using a new approach to obtain highly branched polymer chains. First, MMT was modified using a small liquid crystal molecule comprising N,N,N tris(2-hydroxyethyl)—N-dodecylammonium bromide and organic MMT (OMMT) was obtained. Next, three generations of dendrimer-modified organoclay comprising DOMMT-1, DOMMT-2, and DOMMT-3 were successfully prepared using OMMT and branching units of ethylenediamine and methyl acrylate. Their chemical structures were characterized and confirmed by different methods. The DOMMT organoclay was used in the preparation of natural rubber (NR) composites. The tensile strength and elongation at breakage for NR/DOMMT-10 were 17.3 MPa and 697%, respectively, which were about 13.8% and 10.8% higher, respectively, compared with that for the pure NR. After the addition of DOMMT, the horizontal burning time increased by about 69% and the thermal stability was also improved. We also propose a possible flame-retardant and reinforcing mechanism for this novel organoclay in an NR matrix.

1. Introduction

Natural rubber (NR) mainly comprises polymerized *cis*-1,4-polyisoprene. This type of rubber can be obtained as an aqueous dispersion from the rubber tree and as a dried solid phase [1]. Due to its unique combination of physicomechanical properties, NR is characterized as both a "commodity polymer" and an "engineering elastomer." However, NR has disadvantages because of its high flammability in a similar manner to most synthetic rubbers [2].

The fire properties of polymers can be optimized by using flame-retardant additives [3,4]. Better flame-retardant effects can be obtained with the traditional halogen flame-retardant additives, but they may be harmful to the human body and environment due to the release of poisonous hydrogen halogens into the air [5]. Inorganic flame-retardant fillers such as aluminum hydroxide are typical green additives with flame-retardant effects. However, high quantities of these green additives are needed and this may influence the mechanical properties of polymeric materials. Therefore, a new class of effective and environmentally friendly flame-retardant additives has now attracted more attention.

Due to its simple modification, good swelling ability, and high cation exchange capacity, montmorillonite (MMT) is now used frequently in the preparation of polymer nanocomposites [6–8]. MMT is a type of hydrated alumina-silicate clay where its unit comprises two silicate tetrahedral sheets and an alumina octahedral sheet [9]. Different surfactants have been used to prepare organic MMT (OMMT) [10,11]. Prior to its use in the preparation of clay polymer nanocomposites, cationic surfactants are often employed to modify the surface of the clay mineral [12].

Rubber/OMMT nanocomposites are new materials and they have been studied widely in recent years [13–16]. These nanocomposites contain a small amount of organoclay and they exhibit excellent performance compared with general materials because of their improved mechanical properties, better thermal stability, and decreased gas permeability due to the addition of fillers.

However, in practice, the properties of clay polymer nanocomposites are limited by the characteristics of the clay employed. Many studies have tried to synthesize novel flame-retardant organoclays based on OMMT [17]. Ionic liquid crystals are a class of liquid-crystalline compounds that contain anions and cations, and some of the properties of ionic liquid crystals differ significantly from those of conventional liquid crystals. The typical characteristics of ionic liquid crystals are their ion conductivity and ionic interactions, which can stabilize lamellar mesophases [18]. Studies of these crystals have been conducted throughout the world [19]. Ionic liquid crystals that act as quaternary ammonium

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surfactants can be used to modify MMT and this type of OMMT is expected to exhibit good thermal stability.

Dendrimers are defined as novel types of polymers with a central core shell and repeating branched units [20]. They have attracted much attention due to their special structural characteristics, such as porous networks, abundant functional end groups, difficult crystallization, and high compatibility with other polymers [21]. The characteristic features of dendrimers are of interest in terms of both their molecular chemistry and polymer chemistry. In molecular chemistry, their properties are ascribed to their step-by-step controlled synthesis, whereas their polymer chemistry properties are related to their synthesis from monomers [22]. Poly(amidoamine) (PAMAM) is a well known class of commercial dendrimer, which was first synthesized by Tomalia in 1985 [23]. PAMAM has a radially symmetrical and hyperbranched structure, and it comprises a large amount of amine groups (—NH_2) on dendrimer branches. PAMAM possesses active sites for chemical attachment [24,25], and thus it may create a less compact structure for organoclays. Liyanage et al. [26] used lower generations (G0.0–2.0) of PAMAM dendrimers to modify sodium MMT (Na-MMT) in a solution-phase exfoliation adsorption reaction, where a novel type of organoclay was synthesized. This was the first report of a PAMAM-modified clay where its structure was determined by the generation of PAMAM dendrimers as well as its composition.

In the present study, we prepared and characterized liquid crystal and dendrimer-modified OMMT (DOMMT) as well as investigating its application in NR composites. Novel types of enhanced clay polymer nanocomposites were fabricated to exploit the flame-retardant effects of nitrogen and silicon elements in OMMT and dendrimers. We analyzed the properties of NR/DOMMT composites in terms of their cure characteristics, tensile properties, thermal stability, and flame-retardant effects.

2. Experimental

2.1. Materials

Sodium-MMT (cation exchange capacity = 0.9 mmol/g, denoted as MMT; industrial grade) was obtained from Zhejiang Fenghong Clay Company (Zhejiang, China). Its structural formula can be expressed as $Na_{0.02}K_{0.02}Ca_{0.32}[Fe_{0.41}Mg_{1.18}Al_{2.50}][Si_{6.87}Al_{0.08}]O_{20}$ $(OH)_4{\cdot}nH_2O$ when calculated based on the chemical composition. 1-Bromododecane, diethanolamine, and 2-bromoethanol (analytical reagents) were obtained from Aladdin Industrial Corporation (Shanghai, China). Ethylenediamine and methyl acrylate (analytical reagents) were supplied by Shanghai Guoyao Chemical Company (Shanghai, China).

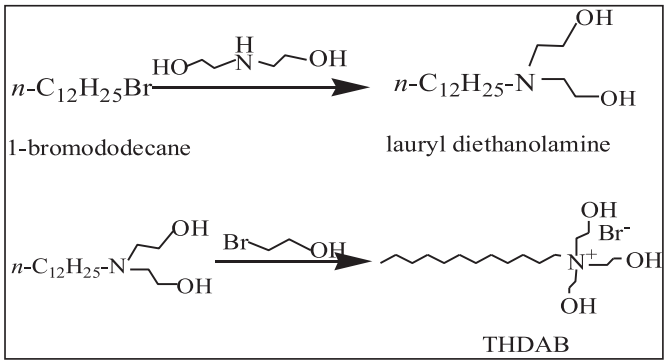
The formulation shown in Table 1 was used to apply the novel DOMMT in rubber vulcanizates. The components of this formulation were purchased from Dongying Wantong Additives Company (Shandong, China).

2.2. Synthesis of N,N,N tris(2-hydroxyethyl)—N-dodecylammonium bromide (THDAB)

First, 0.2 mol of 1-bromododecane, 0.8 mol of diethanolamine, and 100 mL of absolute ethanol were placed in a three-necked flask with a stirrer. The mixture was heated at 60 °C for about 48 h. After cooling, 0.25 mol of NaOH was added to the flask and it was stirred for 1 h. Distilled water and petroleum ether were added after removing the ethanol by rotary evaporation. The intermediate product comprising lauryl diethanolamine was obtained as a colorless viscous liquid.

Table 1
Formulation of rubber vulcanizates.

Component	Phr
NR	100
sulfur	2.5
zinc oxide	5.0
stearic acid	1.0
accelerator M	1.2
accelerator tetramethylthiuram disulfide (TMTD)	0.2
accelerator diphenyl guanidine	0.3
antioxidant N-phenyl-2-naphthylamine	1.0
DOMMT-3	0, 5, 10, 15, 20



Scheme 1. Chemical synthesis of THDAB.

Next, 0.028 mol of lauryl diethanolamine, 0.57 mol of 2-bromoethanol, and 100 mL of a mixed solvent comprising acetone/diethyl ether (volumetric ratio = 1:1) were added to a single-necked flask equipped with a reflux condenser. The mixture was heated at 80 °C for about 48 h. The product was separated by rotary evaporation and washed until no impurities remained. The quaternary ammonium salt THDAB was obtained as a white solid. The chemical synthesis of THDAB is shown in Scheme 1.

2.3. Preparation of OMMT

A 500-mL round-bottomed three-necked flask with a mechanical stirrer, thermometer, and a condenser with a drying tube comprised the reactor system. First, 8 g of MMT was gradually added to a previously prepared solution of THDAB (3.2 g), which was dissolved in 100 mL of a mixture of ethanol and water (weight ratio = 1:1). The resultant suspension was stirred vigorously at 65 °C for 5 h. The treated MMT was washed repeatedly with deionized water. The filter cake was then placed in a vacuum oven at 80 °C to dry for 12 h. The dried cake was ground to obtain the OMMT. A schematic showing the intercalation process between the inorganic MMT and the intercalation agent is shown in Scheme 2.

2.4. Preparation of DOMMT

A 250-mL three-necked flask with a mechanical stirrer and a thermometer was used as the reactor system. First, 12 g of OMMT and 5 mL of acrylonitrile were added to 100 mL of a previously prepared solution of KOH at a concentration of 100 g/mL. The suspension was stirred for 10 h. Next, 10 mL of hydrochloric acid and 10 mL of methanol were added to the flask. The mixture was stirred for 10 h, before 10 mL of ethylenediamine was slowly added to the flask under ice-salt bath conditions. The resultant suspension was stirred for 48 h. Methanol and excess ethylenediamine were removed by rotary evaporation. The product comprising DOMMT-1 was obtained.

Next, 15 g of DOMMT-1 and 15 mL of methyl acrylate were added to 120 mL of a previously prepared solution of methanol. The suspension was stirred for 48 h. Methanol and excess methyl acrylate were removed by rotary evaporation. The product comprising DOMMT-1.5 was obtained. Subsequently, 18 g of DOMMT-1.5 and 20 mL of ethylenediamine were added to 140 mL of a previously prepared solution of methanol. The suspension was stirred for 48 h. Methanol and excess ethylenediamine were removed by rotary evaporation. The product comprising DOMMT-2 was obtained. DOMMT-2.5 and DOMMT-3 were obtained by repeatedly adding excess methyl acrylate and