

Effect of the clay on the thermal stability and mechanical properties of Nitrile-Butadiene Rubber (NBR)/clay nanocomposites

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The role of the aspect ratio of the clay, OMMT and MMT on the thermal stability, mechanical properties and flame retardancy of NBR/clay composites was investigated. NBR was mechanically mixed with clay via melt blending method. The dispersion of clay in the NBR matrix was also studied by XRD. The results of XRD indicated that the composites belonged to the exfoliated and interlayer structure respectively. The OMMT has better dispersity in the NBR matrix than the MMT. The torque of NBR/OMMT composite was higher than that of NBR/MMT composite and pure NBR composite. NBR/OMMT nanocomposites and NBR/MMT composites exhibited excellent mechanical properties, thermal stability and flame retardancy. It's obvious that the OMMT filled nanocomposites has far better properties than that of MMT filled NBR and unfilled NBR.

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1. Introduction

Polymer/Layered Silicate (PLS) nanocomposites have attracted great interest both for industrial and scientific applications [1-6]. This kind of novel nanocomposites displayed increasing in the mechanical properties [7-12], thermal stability [13,14], gas permeability resistance [10,15] and fire retardancy [16-18].

Several developments and investigations were performed for rubber/clay systems [19-25], which have been proved to be an extremely effective and necessary way in rubber application. The clay dispersion in the rubber compounds can control the properties of the rubber/clay nanocomposites [1,7,10,19-26]. Commercial clay has also been used as a cheap and reinforcing filler in the rubber industry for many years. The most commonly used clay material was modified montmorillonite (MMT), where the interlayer cations were replaced by quaternary ammonium cations [27]. Organic particles with nano-scale dimension dispersed in the polymer matrix and special phase structure involved compared to their micron- or macro- composites that already exhibit new and improved properties [28-31].

Acrylonitrile butadiene rubbers (NBR) was widely used in the automotive industry, especially for lip seals of ball-bearings for their moderate cost, excellent resistance to oils, fuels and greases, processability and very good resistance to swelling by aliphatic hydrocarbons [32,33]. For the good performance of NBR/clay nanocomposites,

the microstructure of materials, rheological properties, mechanical properties and the blocking performance were studied [20-22]. And for similar layered silicates disperse in the rubber matrix the silicate modification is of great importance as it affects the final properties of the composites [25, 28]. However, these studies have not addressed the issue of how the morphology resulting structure affects the interphase quality and the final properties of the composites.

The main object of this work was to investigate the influence of the aspect ratio of the clay on the mechanical properties, thermal stability and flame retardancy of the Nitrile-butadiene rubber (NBR) composites. Commonly, the clay used for preparation of polymer matrix composites is OMMT and MMT. The explanation of the structure-properties-relationships based on the underlying morphology and the filler structure is the major aspect of this work.

2. Experiments

2.1 Materials

Fully Nitrile-Butadiene Rubber (NBR) (NBR-40) was provided by Bayer AG. This rubber exhibits a Mooney viscosity $ML_{1+4} 100^{\circ}C=60$. The clay of OMMT and Na^{+} -montmorillonite (MMT) was provided by Zhejiang Fenghong Clay Chemicals Co., Ltd.

2.2 Preparation of NBR/OMMT nanocomposites

The NBR/OMMT nanocomposites and NBR/MMT composites were prepared by the melt intercalation methods [34]. For compounding and curing, the additives listed in Table 1 were purchased in the vicinal Market.

The additives were gradually added in the kneader. Incorporation of the curatives ZnO, SA and DM, TMTD

and sulfur took place at room temperature on a two roll mixing mill, model SK-160B (Shanghai Liuling instrument factory) with a nip clearance of 1 mm and friction ratio 1.3 (22/17 rpm). Mixing was performed for about 15-20 min. The cure time was sufficient to well crosslink NBR compounds as verified by means of M-2000 Moving die Rheometer at 150 °C.

Table 1. The formation of NBR mixtures.

Material	NBR	NBR/ MMT	NBR/ OMMT	ZnO	SA	DM	TMTD	S
Parts (phr)	100	100/5	100/5	5.0	1.0	1.0	0.1	1.5

2.3 Characterization of NBR/OMMT Nanocomposites

The tensile performance was tested with universal tensile tester (Model DCS-5000, Shimadzu Co.) at 25 °C, the head speed was 500 mm/min, according to ASTM D412 specifications. Hardness was measured by a Shore-A hardness instrument (LX-A, Shanghai Liuling instrument factory, China). All measurements were made several times and the result values were averaged.

Rheological properties of NBR and NBR/clay composites were measured using a RM-200 type torque rheometer (Harbin University of Science and Technology) at 75 °C. The rotate speed is 60 rpm and the recording time is 900 s. The torque rating of mixing was used to analyze rheology behavior of composites.

The basal spacing and the dispersion of OMMT after mixing with NBR matrix was studied by X-ray diffraction (XRD) (Phillips X'Pert X-ray generator). The diffractograms were scanned in 2θ range from 1° to 10° at a rate of 2.4°/min with CuKα radiation at 40 KV and 40 mA.

TG-DSC was performed on STA-499 instrument (Netzsch Co.). The experiments were carried out from 30 °C to 600 °C at a heating rate of 10 °C/min and the experiments were performed under Ar gas.

The flame retardancy analyses were carried out in an instrument with samples following the procedure described in the GJB 323A-96 standard.

3. Results and discussion

3.1 XRD analysis

XRD offers a convenient method to determine the interlayer spacing [7, 10, 24]. It is interesting that XRD (Fig. 1) shows no characteristic diffraction peaks for the OMMT in the rubber matrix. Thus, it is concluded that OMMT has been fully dispersed in NBR matrix. The OMMT belongs to exfoliation structure in the NBR matrix. The OMMT were prepared by using organic modifiers.

The organic modifiers have the positive effect on the compatible of rubber chains and the silicate layers [7, 10, 24]. The OMMT become more the compatible with NBR Matrix, but also together with the interlayer spaces expand and facilitate the intercalation of polymer chains.

In addition, NBR has cyanogroup and unsaturation double bond, which is a kind of polyolefin type rubber and has relative stronger polarities. The polarity become smaller between OMMT and NBR, Therefore NBR chain can easily enter into the clay layers when preparing the NBR and OMMT nanocomposites by melt intercalation.

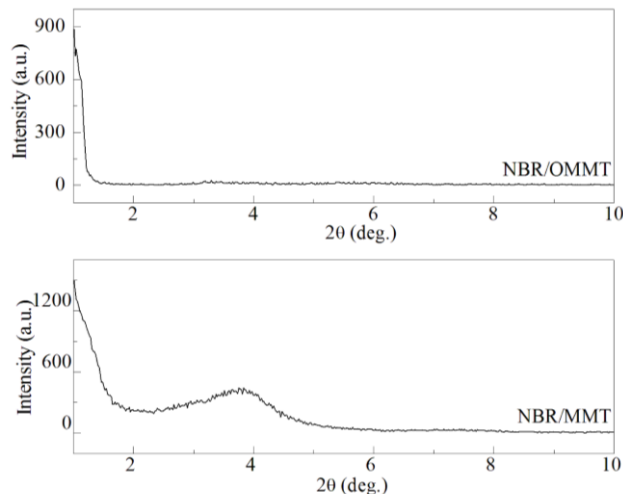


Fig. 1. XRD patterns of composites.

3.2 The rheology analysis

The torque rheometer RM-200 was used to record rheological data of different compound mixing process (Fig. 2). The rheological properties was relatively stabilization and suitable for analysis at the temperature between 124 °C~127 °C. The smooth process was done to the torque-temperature curve for eliminating the interferential factors. The torque of NBR/OMMT composites is bigger than the NBR/MMT composites. The torque of composites was far higher than the torque of pure NBR in the mixing process, which was for the tangles

and coupling effect between clay layer and rubber matrix. The tangling and coupling effect result in increasing internal interface shear force, and rheological torque increasing in the macroeconomic performance.

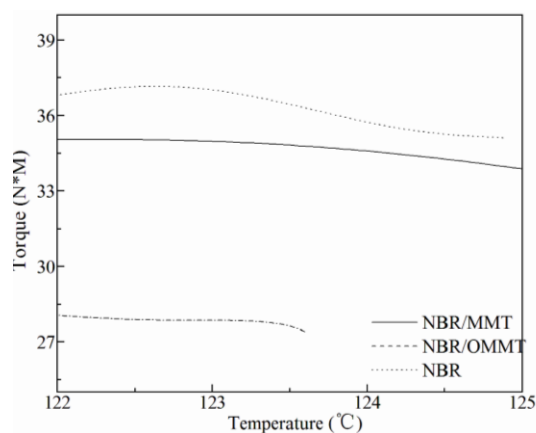


Fig. 2. The torque-temperature pattern of composites.

3.3 TG-DSC analysis

In the Fig. 3, the TG patterns of NBR/OMMT nanocomposites and NBR/MMT composites were almost the same, the remarkable weightlessness occurs in the area of temperature range from 400 °C to 500 °C. Fig. 4 was the DSC pattern of composites. In the Fig. 4, the NBR/OMMT nanocomposites heat change was smaller than ordinary NBR/MMT composites, especially when it starts significantly weightlessness in 400 °C. The heat of NBR/MMT composites exhibits a big change from the trend and the peak area of DSC curve. So micron composites was more unstable than nanocomposites when temperature changes.

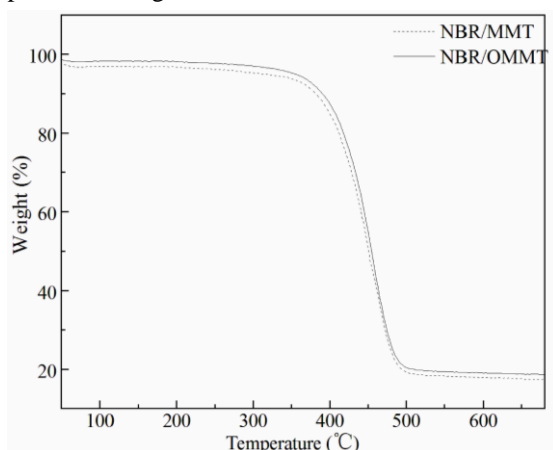


Fig. 3. The TG pattern of the composites.

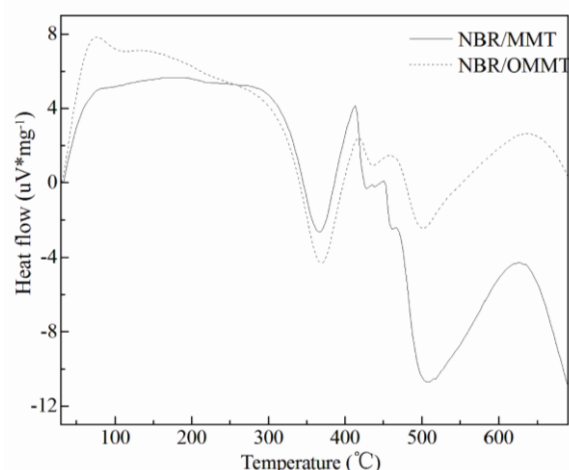


Fig. 4. The DSC pattern of the composites.

Thermo-gravimetric rate was measured for further analysis, as shown in the Fig. 5. NBR/MMT composites in 383 °C begin with obvious weightlessness rate. When the temperature reaches 450 °C, weightlessness rate reaches maximum. NBR/OMMT nanocomposites was about to accelerate decompose in 383 °C, and maximum weightlessness speed temperature is 456 °C, which was a bit higher than NBR/MMT composites. The nanocomposites thermolysis temperature and maximum weightlessness speed temperature were both higher than NBR/MMT composites.

In the nanocomposites, clay layer could slow and block small molecules of polymer molecular chain decomposition move into the nanocomposites interior, which served as a protective effect and effectively reduced the decomposition rate. OMMT can evenly disperse in NBR matrix in the shape of nanometer scale, which has been confirmed by the XRD. And OMMT has stronger interfacial interaction with rubber, which can eliminate incompatible of MMT and NBR matrix.

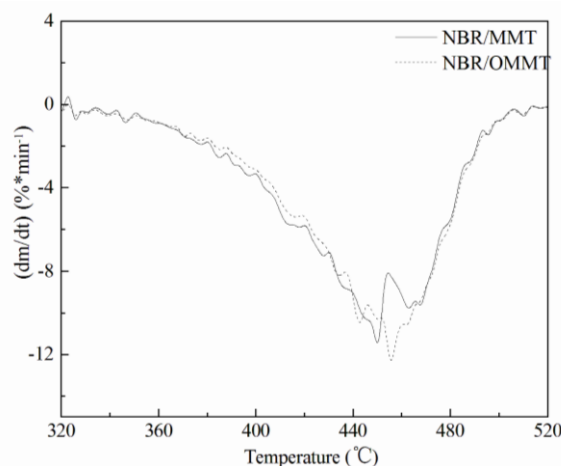


Fig. 5. Differential thermo-gravimetric curve of the composites.

3.4 Mechanical properties

From the Table 2, the tensile strength, elongation at break and harness of NBR/OMMT nanocomposites were higher than that of NBR/MMT composites. It is well known that the mechanical properties of composites are strongly related to the filler aspect ratio^[10,28,35].

During exfoliation, the OMMT not only become much smaller but change their shape from cubical blocks to flat platelets. Dispersion of OMMT has resulted in reproducible enhancement of mechanical properties of the nanocomposites. MMT has the poor dispersion in the NBR matrix. The clay was present in larger coacervate form, has low degree of interfacial interaction with rubber, so its performance was lower.

Table 2. The mechanical properties of the composites.

Type\Properties	Tensile strength (MPa)	Elongation at break (%)	Harness
NBR	4.57	409	43
NBR/MMT	8.39	433	50
NBR/OMMT	11.93	492	54

3.5 Flame retardant

The flame-retardant of composites was also tested, as shown in Fig. 6. NRB/OMMT nanocomposites and NRB/MMT composites showed excellent flame-retardant.

The flame retardant character is traced to the response of a carbonaceous-char layer, which depends on the outer surface. The surface of nanocomposites has a high concentration of clay layers and becomes an excellent insulator and a mass transport barrier. In addition, clay in polymer matrix with nanometer size had prominent effect on limiting polymer molecular chain activity, thus when polymer molecular chain in the heat decomposition process, it has higher decomposition temperature than completely free molecular chain.

The different basal spacing (MMT and OMMT) influence consists in a decrease of the concentration of exfoliated and intercalated particles in the rubber matrix, this interfere with the reinforcing effect of nano-layer formed in the nanocomposites, which is important and crucial effect on the flame retardant properties. The OMMT has better dispersity in the NBR matrix than that of the MMT, thus, NRB/OMMT nanocomposites showed excellent flame-retardant than NRB/MMT substantially.

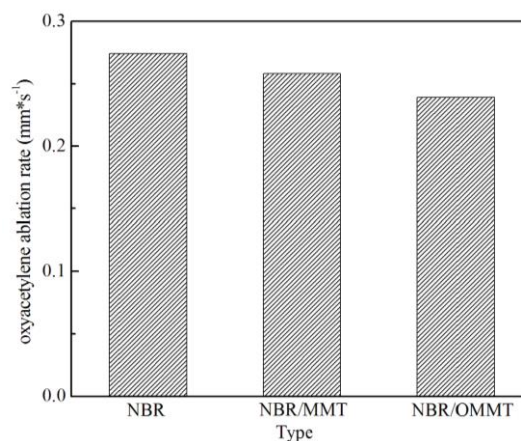


Fig. 6. The flame-retardant of the composites.

4. Conclusions

NBR/OMMT nanocomposites and NBR/MMT composites were prepared by the melt blending method, based on the characterization and performance of material, the following can be deduced:

(1) The OMMT has better dispersity in the NBR matrix than that of the MMT.

(2) The torque of NBR/OMMT composite was far higher than the torque of NBR/MMT composite pure and NBR composite.

(3) The TG patterns of NBR/OMMT nanocomposites and NBR/MMT composites were almost the same, and the remarkable weightlessness occurs in the area of temperature range from 400 °C to 500 °C. The NBR/OMMT nanocomposites heat changes was smaller than ordinary NBR/MMT composite, especially when it starts significantly weightlessness in 400 °C. Micron composites was more unstable than nanocomposites when temperature changes.

(4) The tensile strength, elongation at break and harness of NBR/OMMT nanocomposites were higher than that of NBR/MMT composites and NBR composites.

(5) NRB/OMMT nanocomposites and NRB/MMT composites showed excellent flame retardancy. NBR/OMMT nanocomposites have better flame retardancy than that of NBR/MMT composites and NBR composites.

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