Preparation, structure, performance, industrialization and application of advanced rubber/clay nanocomposites

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Clay/polymer nanocomposites have attracted great interests in the field of materials science and engineering for some superior properties. However, further development is limited by reasons like high price/performance ratio and deficiency in some properties. To break through the bottleneck we have to (1) develop preparation techniques with low cost; (2) exploit the acquired excellent properties and find optimum application fields. In this report, the compositing method using pristine clay and commercialized rubber latex to produce layered silicate/rubber nanocomposites, namely latex compounding method, is introduced. The unique compositing mechanism and structure of the obtained nanocomposites are discussed, and properties of series of clay/rubber nanocomposites prepared by this method are systematically presented. Latex compounding method is a low-cost and easily controlled process, and quite promising to be industrialized. The structure of the nanocomposites is either "Separated Structure" or "Intercalated Structure". The nanocomposites show desirable properties, such as excellent tensile strength, superior gas barrier property, improved flame retardant property, outstanding anti-fatigue properties, etc. As a result, the first production line of kiloton clay/rubber nanocomposites materials in China was established and ten thousands tons scaled production line is being constructed. The applications of the nanocomposites in tyre inner tube, tyre inner liner, OTR tyre tread and conveyor belts are presented.

Keywords: clay, rubber, nanocomposites

Introduction

Reinforcement, especially reinforcement of nano-fillers, is very important for rubber applications, which can be confirmed by the developing history of the rubber industry. Carbon black (nanometer particles, spherical) was first taken as reinforcing filler in 1904, and from then on carbon black reinforced rubber nanocomposites have been widely used in various rubber products such as tires, tubes, etc. It is the excellent nano-reinforcing effect of carbon black that greatly upgrades the mechanical properties of rubber, and makes many rubber applications possible. Recently, rubber-clay nanocomposites have attracted great interests. It can be expected that, exfoliated clay, as a novel class of nanofiller independent on oil resources, will play big roles in the rubber industry. The approach of preparing rubber-clay nanocomposites - co-coagulating rubber latex and clay aqueous suspension developed by our lab[1], where pristine clay (non-organoclay) is employed, is promising for industrialization due to the low cost of pristine clay, simplicity of preparation process and superior cost/performance ratio. In this paper, the structure and properties of a series of rubber-nanocomposites prepared by co-coagulating were demonstrated [2-10]. The advantages and disadvantages of these nanocomposites are illustrated. Potential industrial applications, such as inner tubes, the inner layer of tires, hose, rubber rollers, belting, and etc., are suggested. The industrialization of these composites in China is also reported.

Experimental

Materials: The clay (Na^+-montmorilonite, Na^+-MMT) with a cationic exchange capacity (CEC) of 93 mequiv/100g, was from Liufangzi Clay Factory, Jilin, China. SBR latex (St 23%, solid content 20%) was provided by Qilu Petrochemical Company (China); NR latex (solid content 60%) was from Beijing Latex Products Factory (China); NBR latex (AN 24-26%, solid content 45%) was supplied by Lanzhou Petrochemical Company (China); CNBR latex (AN 31-35%, solid content 40%) was purchased from Taiwan Nancar Corp..

RNH_3^+-MMT and Ca^{2+}-MMT were prepared by a cation exchange reaction between Na^+-MMT and excess ammonium cations from triethylenetetrammonium chloride and calcium cations from calcium chloride, respectively.

Preparation of rubber-Clay Nanocomposites: About 3% clay aqueous suspension and the rubber latex were mixed and vigorously stirred for a given period of time.   After that, the mixture was co-coagulated in the electrolyte solution (2% dilute triethylenetetrammonium chloride solution for the NR and SBR systems and 1% calcium chloride aqueous solution for the NBR and CNBR systems), washed with water and dried in an oven at 80 ^{o}C for 18 h, and then the rubber-clay nanocompound (uncured nanocomposite) was obtained. The vulcanizing ingredients and other additives were mixed into the nanocompound with a 6-in. two-roll mill; then, the compound was vulcanized in a standard mold. The vulcanizates are referred to as rubber-clay nanocomposites. Vulcanizates filled with silica or clay were prepared using the same processing procedure as references.

Characterization: Transmission electron microscopy (TEM) micrographs were taken from ultrathin sections of nanocomposites with an H-800 TEM, using an acceleration voltage of 200 kV.   XRD analyses were carried out on Rigaku RINT using a Cu target, a 0.02 ^{o}C step size, and 5.00 ^{o}/min.   A cone calorimeter was used to evaluate the flammability of these composites under a heat flux of 50kW/m^2 according to ASTM-1356-90. The permeation experiment of nitrogen was carried out with a gas permeability-measuring apparatus. The pressure on one face of the sheet (about 1 mm thickness and 8 cm diameter) was maintained at 0.57MPa with the other face at zero pressure initially, and the nitrogen permeated through the sheet. The rate of transmission of nitrogen at 40℃ was obtained by gas chromatography and with which the nitrogen permeability was calculated.

Abrasion loss was carried out on Akron abrader; Demattia flex-cracking tester was used to measure fatigue life at ambient temperature.

Results and Discussion

Fig.1 shows TEM micrographs of four rubber-clay nanocomposites containing 20 phr clay. In Fig.1, the dark lines are the intersections of the silicate layers.   From Fig. 1(a)-(d), there are both individual layers and stacking silicate layers with the thickness of about 10-30 nm.
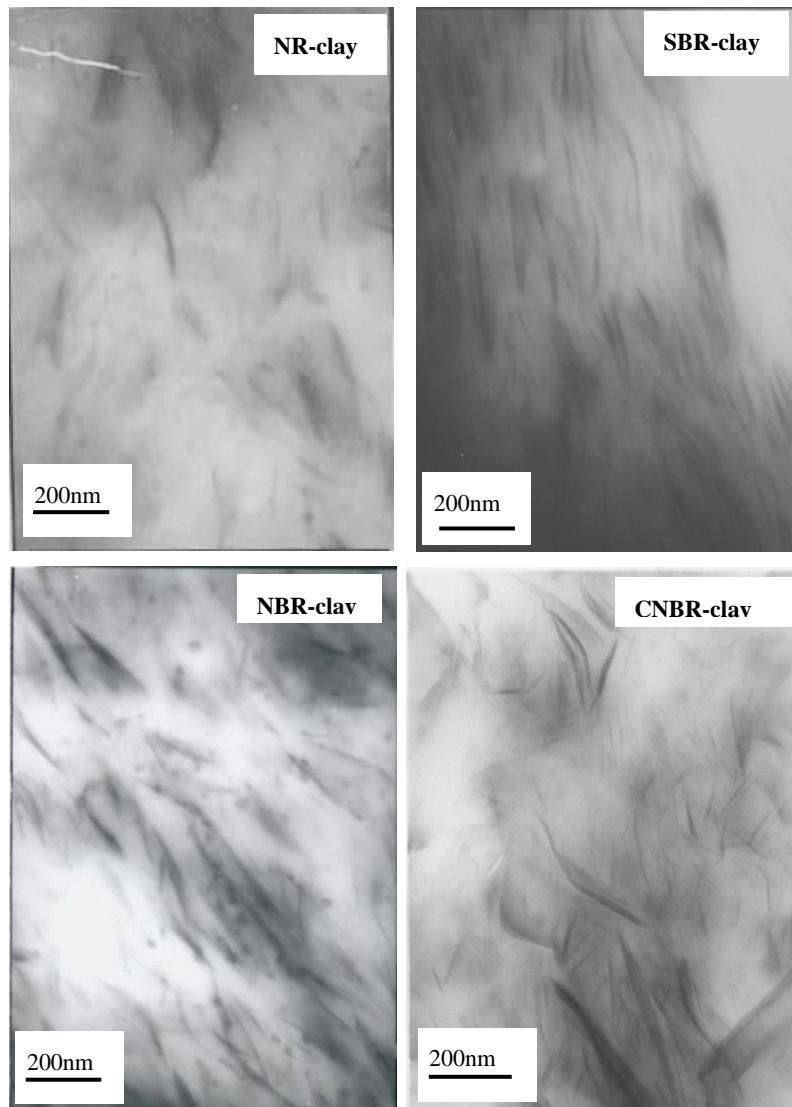
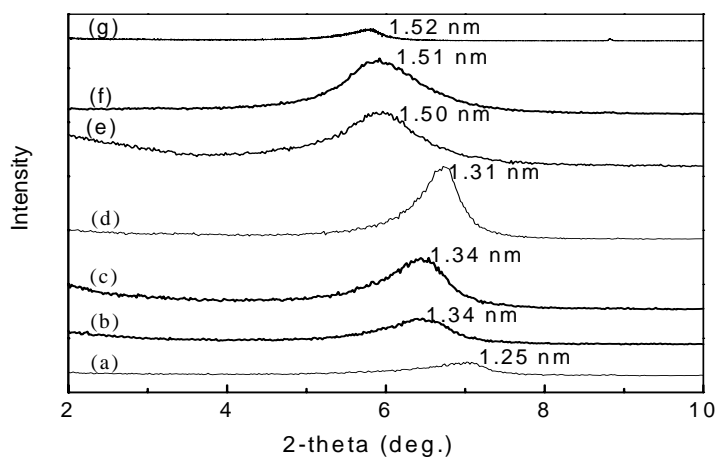Figure 1. TEM micrographs of four rubber-clay nanocomposites

Figure 2. XRD patterns of four rubber-clay nanocomposites: (a) Na$^+$-MMT; (b) SBR-clay; (c) NR-clay;

(d) RNH$_3^+$-MMT; (e) NBR-clay; (f) CNBR-clay; (g) Ca^{2+}-MMT.

The XRD patterns of Na$^+$-MMT and the above four nanocomposites are presented in Fig. 2. The peaks correspond to the (001) plane reflections of the silicate layer aggregates.   From Fig. 2, the peaks of the NR-clay and SBR-clay nanocomposites are both at 1.37 nm, and the NBR-clay and CNBR-clay nanocomposites show the peak at 1.50 nm and 1.51 nm, respectively.   All of these intergallery distances are larger than the initial value of Na$^+$-MMT (1.25 nm), which seems to indicate that rubber molecules are intercalated into the clay interlayer.   However, the basal spacing of the four nanocomposites (1.37-1.51 nm) is smaller than that of organoclay in the literature (larger than 1.7 nm) , and thus it is unreasonable to conclude that the intercalation of rubber macromolecules into the interlayer occurred.   Moreover, in Fig. 2, the basal spacing 1.37 nm of NR-clay and SBR-clay nanocomposites using triethylenetetrammonium chloride as the flocculant is close to 1.31 nm of RNH$_3^+$-MMT, and in the cases of NBR-clay and CNBR-clay nanocomposites using calcium chloride as the flocculant, it is 1.50 and 1.51 nm, respectively, almost the same as 1.52 nm of Ca^{2+}-MMT. Here, the differences between 1.37 and 1.31 nm, and 1.50 or 1.51 and 1.52 nm may be due to the undulation of the experimental value. Accordingly, the diffraction peaks of rubber-clay nanocomposites by co-coagulation should originate from the cations of flocculant in the intergallery, and no rubber molecules intercalate into clay galleries.

On the basis of these results, we assumed that a cation exchange reaction occured during the process of co-coagulating. According to the above results, the rubber-clay nanocomposites prepared by co-coagulation are a kind of partly exfoliated structure, in which the rubber molecules "separate" the clay into either individual layers or just silicate layer aggregates of nanometer thickness without the intercalation of rubber molecules into clay galleries. The schematic illustration of the mixing and co-coagulating process is presented in Fig. 3.
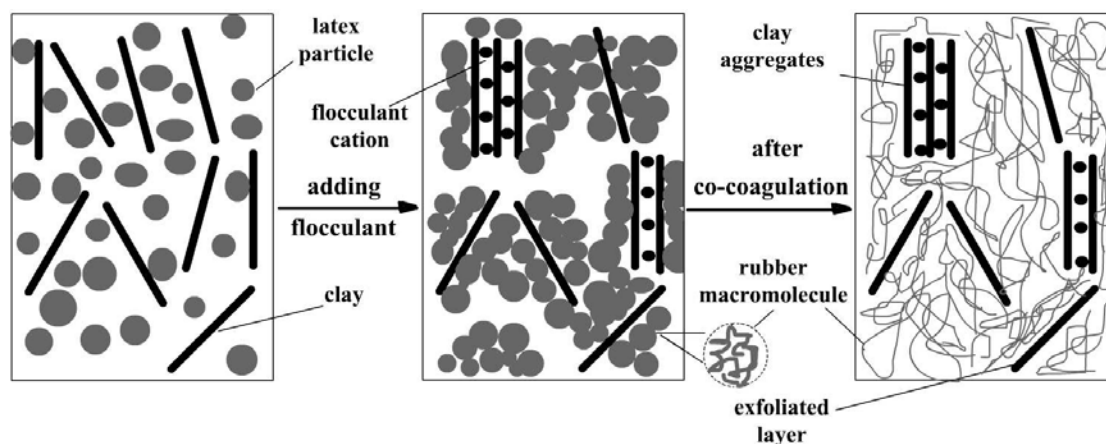

Figure 3. Schematic illustration of the mixing and co-coagulating process.

At the stage of mixing, the rubber latex particles were mixed with the clay aqueous suspension, in which clay was dispersed into individual silicate layers. After adding a flocculant, the flocculant coagulated the rubber latex and the silicate layers simultaneously, but the rubber macromolecules did not exactly intercalate into the galleries of clay. This mainly resulted from the competition between separation of rubber latex particles and re-aggregation of single silicate layers upon addition of flocculant. Since rubber latex particles are composed of several molecules, the existence of latex particles between the galleries of silicate layers in the water medium should result in a completely separated (exfoliated) silicate layers. However, cations of flocculant cause separated silicate layers to re-aggregate so that the rubber latex particles between the silicate layers may be expelled. As a result, there are some non-exfoliated layers in the nanocomposites. In the meantime, due to the fact that the amount of latex is more than that of silicate layers and the latex particles agglomerate rapidly, the re-aggregation of silicate layers is evidently obstructed to some extent by the agglomerated latex particles around the silicate layers. Consequently, the size of aggregates of silicate layers is at the nano-meter level, and the thus obtained nanocomposites contain both the exfoliated silicate layers and non-exfoliated (not intercalated) aggregates of nanometer thickness in the rubber matrix.

According to the above nanocompounding mechanism, the factors affecting the final dispersion level of nanocomposites mainly include the size of rubber latex particles, the ratio of rubber latex to clay suspension, and the speed of co-coagulating. It can be expected that, based on the present investigations, the smaller latex particles, the more latex content, and the faster speed of co-coagulating rubber latex and clay layers will provide nanocomposites with fewer non-exfoliated layer aggregates, and even completely exfoliated nanocomposites.

The mechanical properties of three rubber-clay nanocomposites: SBR-clay, NR-clay and CNBR-clay, are listed in Table 1. Compared to the corresponding conventional rubber-clay composites containing the equivalent amount of clay (20 phr), all of the three nanocomposites exhibit substantially higher 300% stress, shore A hardness, tensile strength and tear strength.   Of particular notice is that the tensile strength of SBR-clay nanocomposite exhibited 6.0 times higher value than that of conventional SBR-clay composite.   The largely increased reinforcement and the tear resistance of the nanocomposites should be ascribed to the dispersed structure of clay at the nano level, the high aspect ratio and the planar orientation of the silicate layers

Table 1 Mechanical properties of rubber-clay nanocomposites (NC samples) and conventional

rubber-clay composites (MC samples) with 20 phr clay

Sample	SBR-Clay		NR-Clay		NBR-Clay	
	MC	NC	MC	NC	MC	NC
Stress at 300％ strain /MPa	1.9	8.1	2.8	11.6	-	-
Tensile strength /MPa	2.5	14.5	20.7	23.3	3.8	14.1
Elongation at break /%	400	548	581	400	595	268
Shore A hardness	51	60	49	54	62	84
Tear strength/(KN/m)	15.3	47.4	26.7	45.2	15.3	40.5

The gas permeabilities of SBR-clay, NR-clay, and NBR-clay nanocomposites with 20 phr clay are presented in Table 2. Compared to the corresponding gum vulcanizates, the nitrogen permeability of SBR-clay, NR-clay, and NBR-clay nanocomposites reduced by 54.1%, 46.7% and 47.8%, respectively, and the decrease amplitude is about 50% for all of the three nanocomposites. The gas permeabilities of gum SBR vulcanizate, SBR-clay nanocomposites (SBR-clay NC), conventional SBR-clay composites (SBR-clay MC) and SBR filled with carbon black (SBR-N330) are presented in Figure 4. In Figure 4, the nitrogen permeabilities reduce with the increase of the amount of filler, and SBR-clay nanocomposites have the best gas barrier property among the three classes of composites. Compared with the gum SBR vulcanizate, the nitrogen permeability of SBR-clay nanocomposites with 1.96, 7.40 and 13.8 vol-% clay reduces by 27.3%, 54.1%, and 61%, respectively. It can be concluded that the silicate layers having the large aspect ratio and the planar orientation lead to the great increase of the diffusion distance by creating a much more tortuous path for the diffusing gas.

Table 2 Nitrogen permeabilities of clay/rubber nanocomposites with 20 phr clay ($10^{-17}m^2 \cdot Pa^{-1} \cdot s^{-1}$)

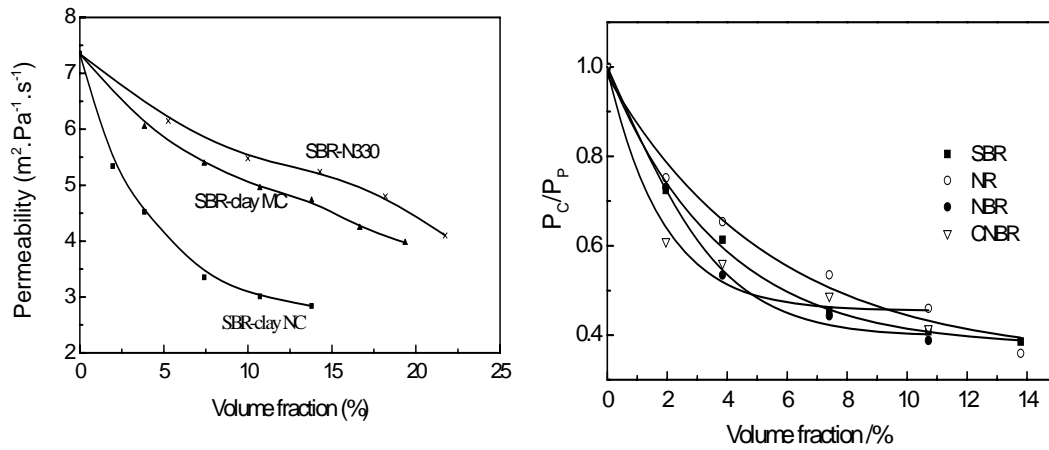| Materials	Pure SBR	SBR - Clay	Pure NR	NR - Clay	Pure NBR	NBR- Clay
Permeability	7.4	3.4	13.7	7.3	2.3	1.2

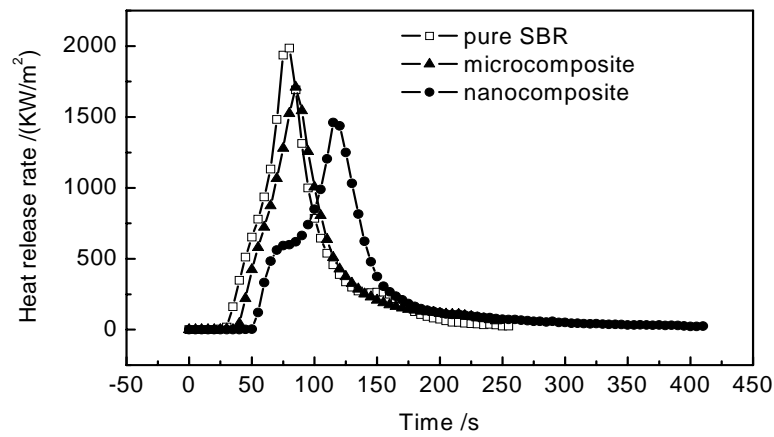Figure 4. Effect of filler volume fraction on gas permeability.

Figure 5. Comparison of the Heat Release Rate (HRR) plot for pure SBR and its composites

(SBR/clay:100/20) at 50 kW/m^2 heat flux

Table 3　Cone calorimeter data for pure SBR and its composites

Sample	$t_{ignition}$ (s)	PHRR (kw/m^2)(%diff)[a]	t_{PHRR} (s)	Mean HRR (kw/m^2)	
Pure SBR	18	1987	76	393	
Nanocomposite	44	1442(27%)	117	234	
Microcomposite	31	1693(13%)	85	371	

The heat release rate plots for pure SBR, SBR-clay nanocomposite and SBR-clay micro composite at 50kW/m^2 heat flux are shown in Figure 5, and the cone calorimetry data is found in Table 3. The cone calorimetry data shows that the peak HRR of SBR-clay nanocomposite decreases 27 %

comparing with that of pure SBR. However, the peak HRR of a microcomposite, which contains the same amount of clay as that of the nanocomposite, is very similar to that of pure SBR and slightly lower because of the dilution effect. The heat release and the peak of HRR for the nanocomposite begin later than that for virgin SBR and conventional composite, which means a significant reduction of the flammability of the SBR-clay nanocomposite. As shown in Table 3, the time to ignite the nanocomposite occurs at 44 s and, for the pure SBR, at 18 s. The nanocomposite exhibits the longest time to ignite and time to burn out among others. The effect of the clay amount on the HRR is illustrated in Figure 6. The HRR drops with the increasing amount of the clay.
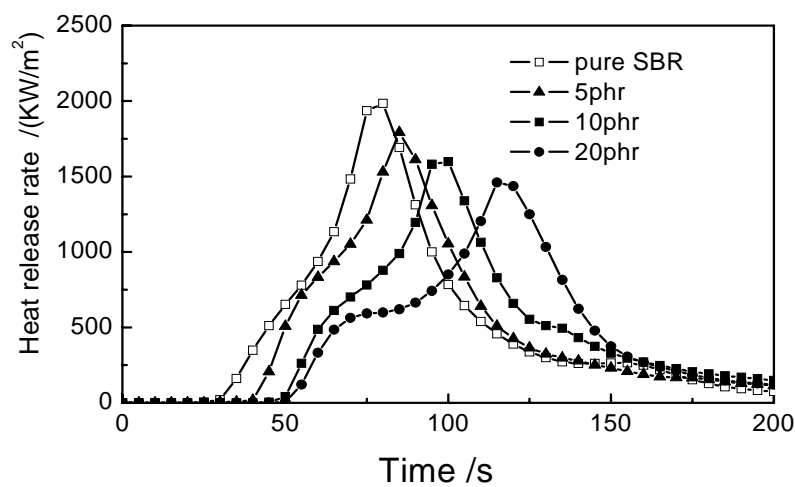

Figure 6. Comparison of the Heat Release Rate (HRR) plot for MMT/SBR nanocomposites with different loading amount at 50kW/m^2 heat flux.

In order to promote the application of rubber-clay nanocomposites, carbon black (N330 or N234) was partly replaced by nano-clay, and properties of the corresponding composites were shown in Table 4 and 5. From Table 4, when the amount of filler is 30 phr, addition of nanoclay enhances 300% stress, tensile strength, enlongation at break, tear strength, hardness and fatigue life. It was worthy to note that the fatigue life of the composite replacing 5 phr N330 with 5 phr nanoclay was increased by more than 20 times compared with that of the corresponding carbon black composite. Figure 7, SEMs of composites with clay and without clay after fatigue demonstrated that the high fatigue life was partly corresponding to the resistance of clay layers to the micro-crack propagation.

From Table 5, by replacing 5 phr N234 carbon black with 2 phr or 1 phr nanoclay, 300% stress, tensile strength and tear strength almost remained the same as that of N234/SBR composite, whereas

the fatigue life was enhanced evidently. By replacing 10 phr N234 carbon black with 4 phr or 2 phr nanoclay, tensile strength and tear strength did not alter, and however, fatigue life was improved greatly. It is clear that low levels of nanoclay, together with utilization of lower carbon black can improve flex fatigue properties.

Table 4   Properties of N330/SBR-clay nanocomposites

N330/clay	30/0	29/1	28/2	27/3	26/4	25/5
300% stress, MPa	7.8	8.7	10.5	9.6	9.1	10.0
Tensile strength, MPa	20.8	26.1	26.9	28.5	28.4	28.1
Elongation at break, %	523	573	531	586	643	613
Tear strength, kN/m	36.5	42.2	42.7	43.2	49.8	49.9
Shore A Hardness	62	64	65	66	67	68
Flex fatigue life, 10^4 cycles	8	20	22	45	80	>200

Table 5   Properties of N234/SBR-clay nanocomposites

N234/clay	60/0	55/2	55/1	50/4	50/2
300% stress, MPa	14.7	13.5	14.2	11.8	11.9
Tensile strength, MPa	23.4	24.8	23.7	24.9	24.8
Elongation at break, %	440	522	470	567	540
Tear strength, kN/m	53.4	55.3	54.4	58.4	54.9
Shore A Hardness	80	80	78	78	75
Akron abrasion, cm^3/1.61 km	0.032	0.037	0.040	0.058	0.049
Flex fatigue life, 10^4 cycles	2	11	5	47	20

From that above talked, rubber-clay nanocomposites exhibit excellent gas barrier properties, flex fatigue properties, etc. They are expected to apply to inner tubes, the inner layer of tires, hose, rubber rollers, belting, etc. Now, after over 10 years research, two plants of preparing rubber-layered silicates nanocomposite by co-coagulating rubber latex and layered silicates aqueous suspension have been built in Hubei Celebrities Rectorite Technology Co., Ltd (Rectorite typed, Hubei Province, China) and

Jilin SiPing Liufangzi Mine Co.,Ltd (clay typed, Jilin Province, China). Authors hope these factories will greatly push the application of rubber/clay nanocomposites.
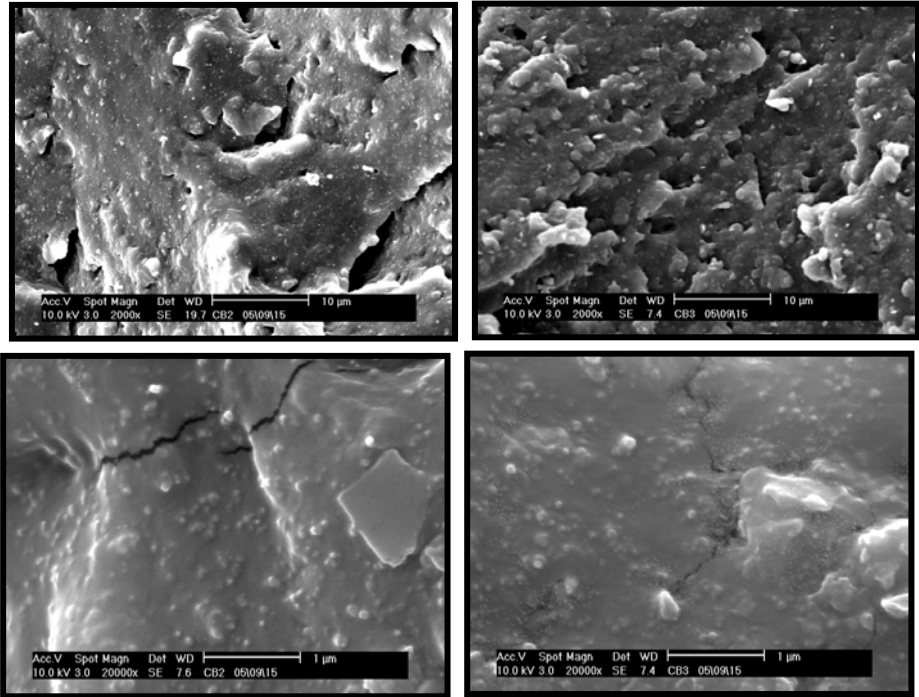
carbon black/clay 30/0   **carbon black/clay 25/5**

Figure 7   SEM of composites with clay and without clay after fatigue

Figure 8 The industrialization of rubber/clay nanocomposites based on Latex Compounding Method

Table 6 compared the performance of layered silicate/SBR NC experimental inner tube and NR

and IIR commercial inner tubes. It can be seen that the hardness of nanocomposites tube is higher than that of two commercial inner tubes, and the gas barrier property of nanocomposites tube is higher than that of commercial NR inner tube and lower than that of commercial IIR inner tube. However, the calculated cost of nanocomposites tube is much lower than that of commercial IIR inner tube and almost same as that of NR inner tube. Figure 9 displays the preparation of layered silicate/SBR NC experimental inner tube in factory.

Table 6 Comparison of l experimental inner tube materials and commercial inner tubes materials

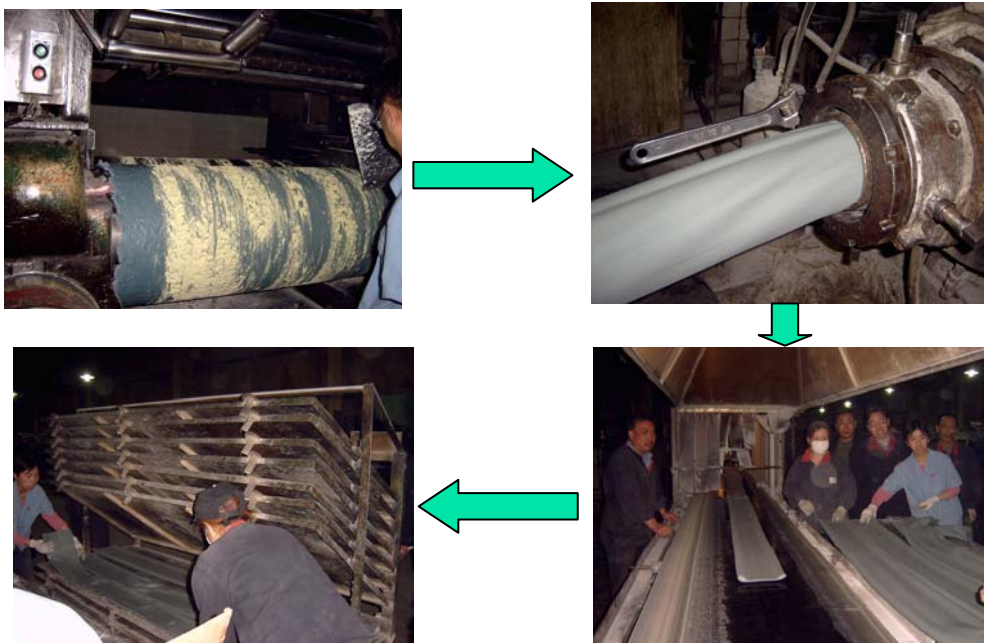| Properties	Layered silicate/SBR NC experimental inner Tube (without carbon black	Commercial NR inner tube (with carbon black)	Commerical IIR inner tube (with carbon black)
Stress at 100% strain/MPa	2.1	1.4	1.3
Stress at 300% strain/MPa	2.5	5.7	4.2
Tensile strength/MPa	14.4	16.9	10.3
Elongation at break/$\%$	725	613	667
shore A Hardness	71	53	51
Tear strength/N·m^{-1}	29.5	36.9	28.3
Permeability /10^{-17}m^{2}s^{-1}Pa^{-1}	2.21	5.17	0.946

Figure 9 Preparation of layered silicate/SBR NC experimental inner tube in factory

Table 7 Comparison of commercial road off tire materials and experimental road off tire materials conducted by a road off tire company

Properties	Commercial road off tire	Experimental road off tire (5phr clay layers in place of 5phr carbon black by factory)
Hardness Shore A	60	65
stress at 100％strain/MPa	1.6	2.5
stress at 300％strain/MPa	8.2	12.1
Tensile strength/MPa	25.3	29.3
Elongation at break/％	639	576
Tear strength/KN/m	85	107
resilience/％	33	33
Mooney Viscosity/Mv	56.6	74.00
Rolling resistance	Deformation (mm)	4.03	4.03
	Temperature rise (℃)	78.1	69.2
	Energy loss (J/r)	5.24	4.48
Gas permeability ($*10\text{-}17m2s\text{-}1Pa\text{-}1$)	11.24	9.00
Akron abrasion △V （cm3）	0.3226	0.2462
Fatigue	The time for pinprick（min）	119	64
	Crack propagation speed （mm/h）	2.75	1.5

Table 7 compared the performance of commercial road off tire materials and experimental road off tire materials conducted by a road off tire company. From table 7, it can be easily found that experimental road off tire material exhibits lower rolling resistance, lower Akron abrasion and better fatigue property.

Table 8 Comparison of commercial transport belt materials and experimental transport belt materials conducted by a transport belt company

Properties	Commercial transport belt	Experimental transport belt (30 phr layers in place of 30 phr CB)
Stress at 100% strain /MPa	1.2	2.0
Stress at 300% strain /MPa	3.1	4.2
Tensile strength/ MPa	18.5	15.9
Elongation at break / %	871	756
Shore A hardness	72	73

Table 8 compared the performance of commercial transport belt materials and experimental transport belt materials conducted by a transport belt company. It can be seen that 30 phr silicate layers introduced by nanocomposites masterbatch in place of 30 phr carbon black didn't lower the performance of transport belt materials. However, figure 10 clearly displays that the experimental materials posses better high temperature resistance than commercial materials.
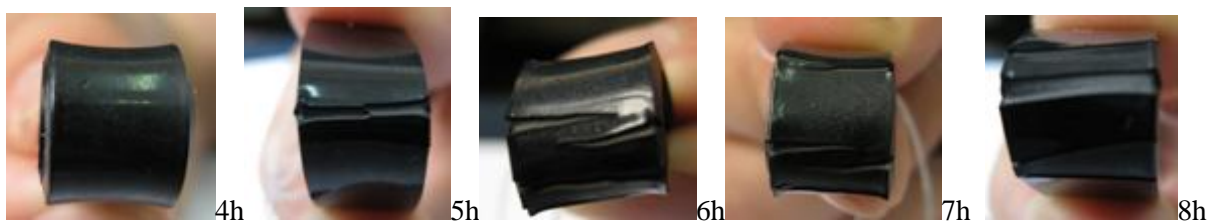
commercial transport belt materials（broken after 9h aging）
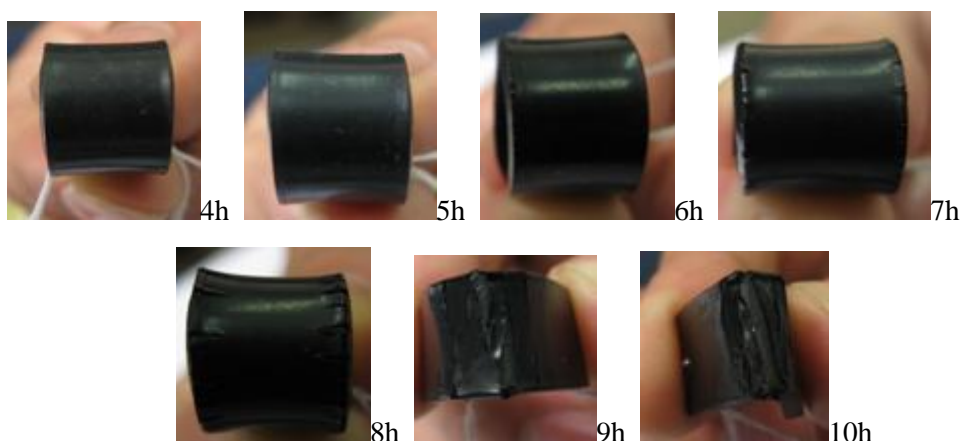
experimental transport belt materials

Figure 10 Photos comparison of two kinds of materials firstly experienced 200℃ ageing then bending

Conclusions

Layered silicate/rubber nanocomposites prepared by latex compounding method possess low cost/performance ratio, desirable properties, such as excellent tensile strength, superior gas barrier property, improved flame retardant property, outstanding anti-fatigue properties, etc. This novel and valuable material can be applied in tyre inner tube, tyre inner liner, OTR tyre tread, conveyor belts and so on.

Acknowledgements

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