



Development of Natural Rubber-Fibrous Nano Clay Attapulgite Composites: The Effect of Chemical Treatment of Filler on Mechanical and Dynamic Mechanical Properties of Composites

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Abstract

Common nano clay fillers have layered structure. Some nano clays like Attapulgite (AT), Sepiolite have rod like fibrous structure. Compared to layered structured clay fibrous clay AT can undergo better dispersion in polymer matrix leading to better improvement in composite properties. Chemical modifications of AT are done through amine treatment as well as by amine+silane treatment to get chemically modified fillers AAT and SAT respectively. In the present investigation, nano composites are prepared using natural rubber (NR) filled with AT, AAT and SAT. Three different loadings of each filler are used namely 2.5, 5, and 10 phr (parts per hundred of rubber). Mechanical properties like tensile strength, elongation at break increase with the increase in filler loading up to 5 phr there after these properties marginally fall when loading is increased to 10 phr due to problem of filler dispersion at higher loading. However, modulus at 300% elongation and tear strength increases with the increase in filler loading up to 10 phr. Very similar trend can also be observed for composites with chemically modified fillers, AAT and SAT. But the degree of reinforcement is higher in the case of AAT and SAT compared to that of unmodified filler AT for the same filler loading. This difference is mainly due to better polymer-filler interaction and filler dispersion in the case of chemically modified clays AAT and SAT compared to unmodified AT. Tear strength of composites increases remarkably with the addition of AT and which is further enhanced when chemically modified clays AAT and SAT are added. Dynamic-mechanical analyses of different clay composites give idea about the difference in the degree of polymer–filler interaction due to chemical treatment of filler.

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Keywords: Nano clay; composite; chemical modification; mechanical properties; dynamic mechanical properties; thermal properties

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1. Introduction

In recent years there has been considerable interest in clay-polymer nanocomposites due to novel material properties they exhibit [1]. Recently, compared to well developed inorganic filler of two dimensional layered silicates (such as montmorillonite), rod like clay is attracting more attention in polymer-clay nanocomposite research. Besides its natural and unique fibrillar structure, it is believed that these rod-like nanoparticles can be more efficiently dispersed in polymer matrix than traditional layered silicates due to its weak interactions between individual particles and low exchangeable ion percentage [2,3]. In this, work, the typical rod-like fibrillar silicate attapulgite (AT) was chosen as the filler. Attapulgite is relatively less common clay filler because of its peculiar characteristics and scarce occurrence. Attapulgite is a family of fibrous hydrous magnesium silicates. The structure of attapulgite was first proposed by Bradley early in 1940 [4]. The chemical structure of attapulgite is shown in Figure 1. Its theoretical half-unit cell formula is $Mg_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ and is a natural fibrous silicate material. The formulas are written as such to indicate the two types of water present; magnesium coordinated water and adsorbed water. The structure of the mineral results in zeolite-like channels, which are approximately 3.7×6.0 and 5.6×11.0 Å wide, respectively [5]. These channels may be filled with water or organic molecules. The smallest structural unit of attapulgite is fibrillar single crystal with a length of 500-2000 nm and 10-25 nm in diameter. It is containing ribbons of a 2:1 phyllosilicate structure different from other layered silicates such as montmorillonite. Each ribbon is connected to the next by the inversion of SiO_4 tetrahedral along a set of Si-O-Si bonds and extends parallel to the X-axis to form rectangular channels. Unlike the layer-layer interaction existing in layered silicates, the interaction between AT single crystal is extremely small due to a similar line-line contact, which could result in a weak interaction and facilitate the separation of AT micro-agglomerates into single crystals upon large shear, physical and chemical modification. In addition, it has a large surface area and strong absorptive capacity that is greater than any other natural mineral [4,6]. It is well known that in order to obtain the most reinforcing effect for a polymer matrix using filler, two key criteria are: (a) strong interfacial adhesion to have sufficient stress transfer from the polymer matrix to the filler and (b) uniform dispersion of a filler in a polymer matrix [6-9]. Till date, to achieve the above mentioned criteria, researchers have focused on exchanging cations in the clay galleries with long-chain ammonium or phosphonium ions [10-12]. Alternative possible modification is thorough reaction of the surface silanol groups which are present at the edges of the nanoclays. Little work has been done on edge-modified clay may be because of the relatively small edge-silanol groups which are present in the widely used smectite type of nanoclays such as montmorillonite [13]. But in attapulgite type of clays, the surface silanol groups are relatively higher in number. Hence, in this work, modification of AT has been done by both the modification methods taking the advantage of a significant number of reactive silanol groups which are situated at the edges of its tunnel structure. The effect of different type of chemical modifications of the clay filler on the properties of NR-f clay has also been investigated.

2. Experiment

Natural rubber (NR), grade RSS 4 with ML1 + 4@120 °C = 70. Fibrous nano clay, Attapulgite Source: Ashapura Group of Companies, India. Cetyl trimethyl ammonium bromide (CTAB), 3-amino propyl trimethoxy silane (APS), Source: Merck, Schuchardt Chemicals, Germany.

2.1. Preparation of composites

NR based nanocomposites were prepared in Brabender plasticorder at 120 °C and 60 rpm rotor speed. The formulation and designations are given in Table 1.

Table 1. Formulation and designations of different samples

Formulation (phr)	Designation			
	NR	NR-AT	NR-AAT	NR-SAT
Rubber	100	100	100	100
ZnO	5	5	5	5
6PPD	2	2	2	2
Sulfur	1.5	1.5	1.5	1.5
TBBS	1.3	1.3	1.3	1.3
AT		5		
AAT			5	
SAT				5

2.2. Infrared spectroscopy (FTIR)

FTIR (Nicolet 6700, USA) within the range of 400 to 4000 cm^{-1} .

2.3. Scanning and transmission electron microscopy

SEM analysis was done using Scanning Electron Microscope (JEOL JSM-5800, Japan) and TEM analysis was performed using a transmission electron microscope (JEOL-2010, Japan) with LaB6 filament

2.4. Mechanical and dynamic mechanical properties

The mechanical properties were measured as per the ASTM D 412-98 method in a universal testing machine (Zwick Z010) and dynamic mechanical properties were measured with DMTA.

3. Results and Discussion

The spectra of different modified clays are shown in Figure 1. IR spectra of silicates contain very intense absorption bands in the range 1100–900 cm^{-1} . The IR spectra of the AT in the range 400–500 cm^{-1} exhibits a combined band due to the stretching vibrations of the Mg–O bond and the bending vibrations of the O–Si–O bond. A group of very strong bands corresponding to vibrations of the Si–O–Si bond is observed in the range 900–1100 cm^{-1} . A group of bands attributed to the stretching vibrations of the Si–OH bond in silanol groups is located in the range 3400–3700 cm^{-1} . The absence of the band at around 2850 cm^{-1} and around 2925 cm^{-1} in the unmodified clay and the appearance of these bands in the modified clay confirm the effect of modification as these correspond to stretching vibration frequencies of CH_2 groups of CTAB and APS. The peak at 1470 cm^{-1} corresponding to-NH bending also indicates the presence of amine group 1 and in turn confirms the organic modification of the clay.

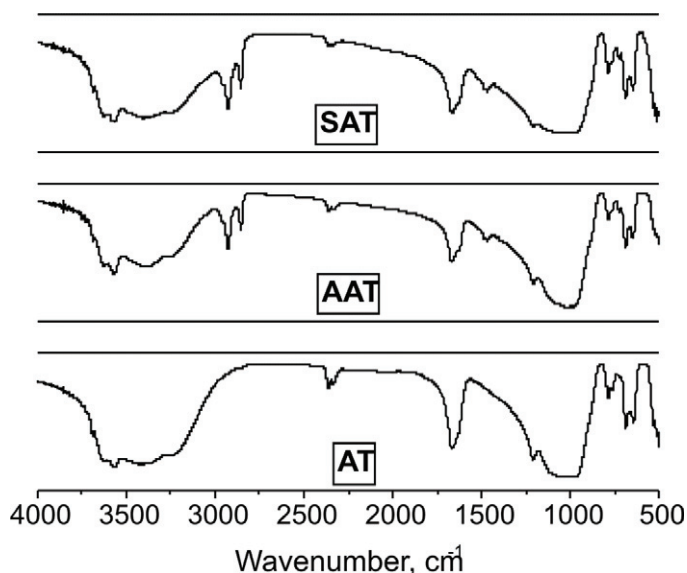


Fig. 1. FTIR of different clays

3.1. Cure-properties

Cure-properties of different nanocomposites are reported in Table 2. T_{c90} of the cure curve indicates the optimum cure time. The unmodified clay is acidic in nature which will retard the curing as reflected in T_{c90} value. T_{c90} of NRAT is longer than NR. In the case of NRAAT and NRSAT, clay modification is done with amine containing groups which are basic in nature and increase the cure rate and cause faster curing. So the T_{c90} values of those samples are much lower than NR.

Table 2. Cure properties of different nanocomposites

Sample	M_L	M_H	$M_H - M_L$	T_{s2} , min	T_{c90} , min
NR	0.27	6.12	5.85	6.23	9.03
NRAT	1.03	7.03	6.00	8.72	12.83
NRAAT	0.32	7.2	6.88	3.22	5.68
NRSAT	0.86	7.04	6.18	2.58	4.62

3.2. Physico-mechanical properties

The effect of different nanoclays on the mechanical properties of natural rubber is shown in Figure 2. NRAT, NRAAT and NRSAT register 12, 29, 37% increase in tensile strength and 46, 94, 124% increment in 100% modulus respectively. The volume fraction of rubber is also increased gradually from NR to NRAT, NRAAT and NRSAT.

The plots of storage modulus and $\tan \delta$ against temperatures are shown in Figures 3 and 4. Above the T_g , an increase in storage modulus over the neat NR is observed with all the clays. The increment in storage modulus is more pronounced in the case of NRSAT and NRAAT, followed by NRAT. Though T_g remains unaltered in the case of NRAT and NRAAT compared to neat NR, and the $\tan \delta_{max}$ value at T_g for

all clay based composites is also lower than neat NR. T_g shifts to higher temperature in the case of NRSAT. This indicates a better polymer-filler interaction.

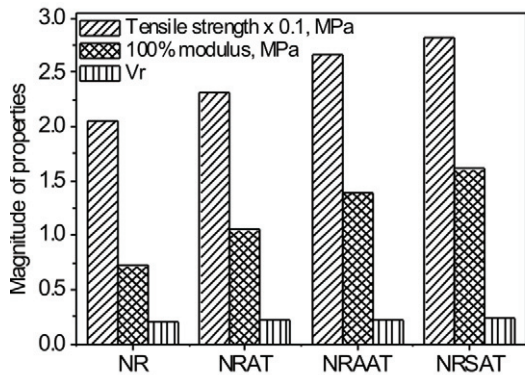


Fig. 2. Comparison of physico-mechanical properties of different nanocomposite

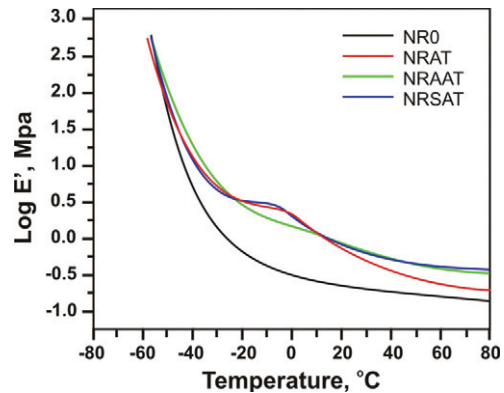


Fig. 3. LOG E' vs. temperature plot of different nano-composites

The results for TG curves for NR, NRAT, NRAAT and NRSAT are shown in Figure 5. These TG curves indicate single-stage degradation with well defined initial and final degradation temperatures and might have been a result of a random chain scission process. T_{onset} and T_{max} values for NR, NRAT, NRAAT and NRSAT are 276, 296, 282 and 286 °C and 375, 383, 381 and 381 °C respectively. Thermal properties are also better with the addition of clays.

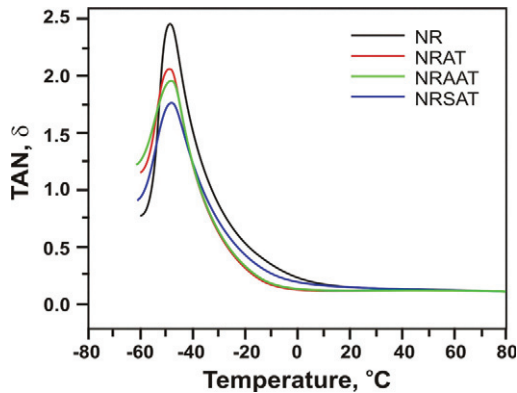


Fig. 4. Tan delta vs. temperature plot of different nanocomposites

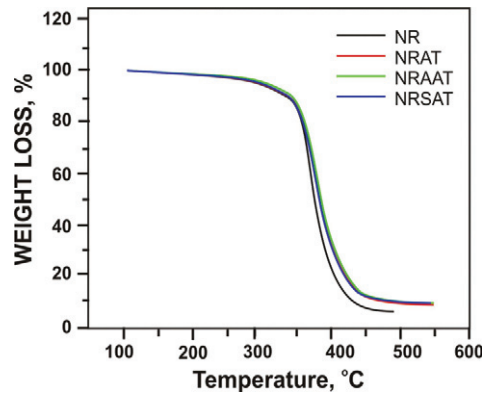


Fig. 5. Typical TG curves of different nanocomposites

The improvement of properties may be due to better dispersibility of the fibrillar clays. The fibrillar silicate single crystals possess a high degree of structural perfection and the concomitant superior mechanical properties. The strength and modulus of the single crystals are over 50 and 500 GPa, respectively; which are at least five times higher than those of conventional fibers [14].

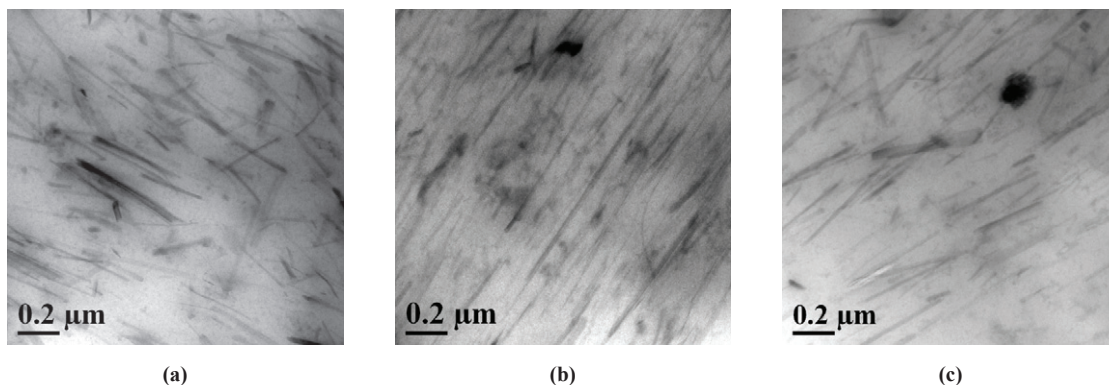


Fig. 6. TEM of (a) NRAT, (b) NRAAT and (c) NRSAT

Unlike layered silicates such as montmorillonite, fibrillar silicate is much easier to separate into single layers and subsequently can be uniformly distributed in polymer matrices. This is because the spacing among the aggregated single crystals in fibrillar silicate is much larger than that of the silicate layers in montmorillonite. As a result, the van der Waals' interaction force of the single crystals in fibrillar silicate is considerably weaker than that of the silicate layers in montmorillonite. Additionally, the clay modifications even improve the compatibility of the clay with the polymer matrix. In the case of SAT, surface $-OH$ groups are modified by silane groups which increase the compatibility of clay with the rubber even better than AAT, where only the cations inside the clay galleries are exchanged with long chain amines. Morphology also supports the same, Figures 6a-c. The dispersion is better in NRAAT and NRSAT than NRAT. NRAT shows the clay diameter of ~ 250 nm, while NRAAT and NRSAT exhibit clay diameter of ~ 100 nm and 75 nm respectively. The interfacial bonding between the silanized fibrillar silicate single crystal filler and the rubber matrix can be reasonably strong which is reflected in all properties.

4. Conclusion

The modification of attapulgite clay was done by two processes: absorption of long-chain amines and covalent functionalization with silanes. Both FTIR and TGA studies indicate successful modification of the clay. NR-AT nanocomposites were prepared. The nanocomposites show better properties compared to the standard NR compounds. Best properties can be observed in the case of SAT where both amine and silane modifications were done. Clay dispersion is better in the case of modified clays containing nanocomposites.

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