

Organomodified Kaolin as a Reinforcing Filler for Natural Rubber

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Received 24 August 2007; accepted 29 September 2007

DOI 10.1002/app.27469

Published online 3 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: China clay (kaolin) has been modified with sodium salt of rubber seed oil (SRSO). SRSO was characterized using X-ray diffraction (XRD), infrared spectroscopy (FTIR), and differential thermal analysis (DTA). XRD of the unmodified and SRSO-modified kaolins showed an increase in the d -(001) spacing of kaolin platelets from 7.15 to 14 Å. FTIR spectroscopy indicated possible grafting of the organic moiety of rubber seed oil (RSO) onto the clay surface. DTA of the SRSO-modified kaolin indicated that the SRSO is more strongly bound in a constraint environment within the lamellae of kaolin. Natural

rubber (NR) mix containing 10 phr of SRSO-modified kaolin was found to cure faster than that of a similar mix containing unmodified kaolin. NR vulcanizates containing SRSO-modified kaolin showed considerable increase in tensile modulus, tensile strength, and elongation at break indicating its potential as an organomodified nanofiller. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3476–3483, 2008

Key words: natural rubber; kaolin; nanocomposite; rubber seed oil; organomodification

INTRODUCTION

Recently, organomodified nanoclays have emerged as a novel class of advanced reinforcing filler for the reinforcement of polymers. A unique feature of these materials is their ability to impart a rare combination of “exceptional properties” to the base polymer at very low dosages, simultaneously making the compositions economical and easily processable. In this respect, organomodified layered silicate–rubber nanocomposites need special mention, currently being the focus of intense R&D interest in academia and industry. This is quite evident from the plethora of reports^{1–5} and publications coming out recently in this area.^{6–54} Studies on organomodified clay rubber nanocomposites have been made using various elastomers such as natural rubber,^{6–18} styrene butadiene rubber,^{10,19–26,38} ethylene propylene diene rubber,^{27–32} nitrile rubber,^{19,23,33–37} fluoro elastomers,^{39–41} polyurethane rubber,^{11,42–45} butadiene rubber,^{19,20,37,46} epoxidized natural rubber,^{12,13,47} butyl rubber,⁴⁸ chlorobutyl rubber,⁴⁹ ethylene vinyl acetate rubber,⁵⁰ polychloroprene rubber,⁵¹ polysiloxane rubber,⁵² polyisoprene,⁵³ and brominated poly(isobutylene-*co*-paramethyl styrene) rubber.⁵⁴

A review of the literature on organomodified filler–rubber nanocomposites as mentioned earlier

shows that montmorillonite clays (bentonites) have been studied extensively as the ideal mineral for the preparation of organomodified fillers. As the natural deposits of montmorillonite minerals are rather limited, and as the demand for bentonites goes ever increasing, there has been considerable investigation for finding substitute products for this type of products. In this context, only scanty data is available with the relatively less expensive and abundantly available mineral kaolin.⁵⁵ It was observed in a recent report that the clay–polymer nanocomposite prepared from china clay-based nanoclay gives better oxygen barrier and water transport property than that from montmorillonite-based nanoclay.⁵⁶ Besides, the organomodifiers used are mostly of petrochemical base. Thus, majority of the reports on rubber nanocomposites indicate the use of sodium montmorillonite clay for organomodification while a few reports show the use of other layered silicates such as hectorite clay/smectite clay. The use of organomodifiers such as octyl amine, octadecyl amine, dodecyl amine, dimethyl distearyl ammonium bromide, dimethyl benzyl hydrogenated tallow quaternary ammonium, dimethyl dihydrogenated tallow quaternary ammonium, and methyl tallow bis-2-hydroxy ethyl quaternary ammonium have been reported. Many of these are expensive due to the depleting nature of their petrochemical sources. So far, reports on the use of derivatives of fatty acids based on low cost, renewable natural resources as organomodifiers for silicate fillers have not been made.

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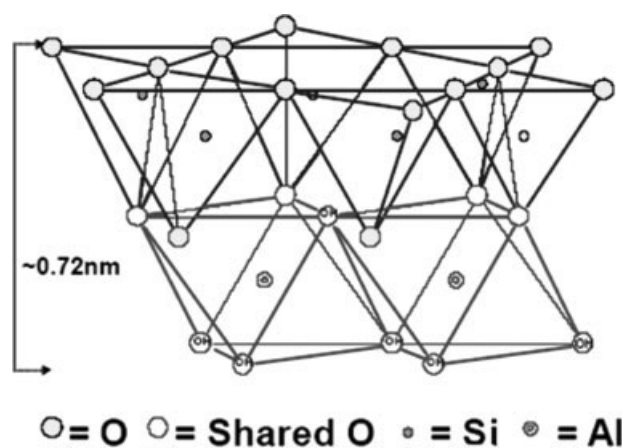


Figure 1 Schematic representation of the structure of kaolinite.

Rubber seed oil (RSO) is a byproduct of *Hevea* cultivation and is a rich source of oil that has qualities comparable to that of dry oils usually employed in surface coatings. In India, the estimated availability of rubber seed is about 30,000 MT/year, which can yield RSO to the tune of about 5000 tons/year.⁵⁷ In this study, RSO has been selected as the precursor for organomodification of kaolin, considering its uniqueness with respect to the long-chain hydrocarbon structure of its major components, renewable nature, low cost, easy availability, and amenability for organofunctionalization. Previous studies have reported the suitability of RSO and its derivatives for various applications such as surface coatings,^{58–61} diesel fuel substitute,⁶² and processing aid for rubbers.^{63,64} However, its use as an organomodifier for an inorganic filler has not been reported.

Kaolin or china clay consists chiefly of the mineral kaolinite and has been selected based on its abundant availability and low cost to favor synthesis of a product having industrial utility.

Kaolinite $[\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8]$ is a dioctahedral aluminosilicate, which is built with a tetrahedral SiO_4 sheet and an octahedral $\text{AlO}_4(\text{OH})_2$ sheet linked together by oxygen atoms. The crystal consists of several of these layers extending in a two-dimensional array, which are stacked along the *c*-axis and held together essentially by (i) hydrogen bonds between the external hydroxyls of the octahedral sheet and the basal oxygens of the adjacent layer tetrahedral sheet, (ii) van der Waal's attractive forces, and (iii) electrostatic interactions due to net fractional charges of opposite sign on each basal surface (Fig. 1). Although the surface silicate sheet of kaolinite is not particularly amenable to covalent attachment, the relatively reactive aluminol surface is similar to that in the case of montmorillonopkites and has the potential to be functionalized via Al—O—R bonds. In fact, a number of polar organic molecules such as

urea, dimethyl sulfoxide, formamide, hydrazine, fatty acid salt, potassium acetate, and so on, are reportedly able to disrupt the interlayer bonding between the adjacent siloxane and hydroxy aluminum surfaces and to penetrate the interlayer space to form a complex by hydrogen bonding to both surfaces.⁶⁵ Such a process is known as intercalation. Successful intercalation agents decrease the electrostatic attraction between the lamellae by causing an increase in the dielectric constant when the compounds penetrate between the layers.⁶⁶

In this work, a derivative of RSO has been used as a modifier of kaolin, and the effect of the modified filler on tensile properties of NR has been studied.

EXPERIMENTAL

Materials

China clay (Kaolin, grade BCK) was obtained from M/s. English Indian Clays Ltd, Veli, Thiruvananthapuram, Kerala. The physicochemical characteristics of kaolin⁶⁷ are given in Table I. RSO was obtained from M/s. Murugesan & Sons, Tamil Nadu, India, the physicochemical properties and composition⁶⁸ of which are given in Table II. Sodium hydroxide (LR, Fischer), hydrazine hydrate (Aldrich) NR (grade RSS V), zinc oxide, stearic acid, sulfur, and mercapto benzothiazole (MBT) were obtained from local suppliers.

Methods

Conversion of RSO into its sodium salt

Sodium salt of rubber seed oil (SRSO) was prepared by mixing 2.8 g of RSO with 10 mL of 20% NaOH solution along with continuous stirring and keeping for 1 day. The final pH of the resulting solution was

TABLE I
Physicochemical Characteristics of Kaolin⁶⁷

No.	Property	Value
1	Chemical assay (%)	
	SiO ₂	47.05
	Al ₂ O ₃	36.98
	Fe ₂ O ₃	0.35
	TiO ₂	0.53
	Na ₂ O	0.12
	K ₂ O	0.08
	Loss on ignition at 1025°C ± 1°C	14.49
2	Density (g/cc)	2.60
3	Particle size distribution (%)	
	<10 μm	97.21
	<5 μm	92.40
	<2 μm	62.60
4	Cation exchange capacity (mequiv NH ₃ /100 g)	2.90
5	Surface area (m ² /g)	14.30
6	pH (5% solution)	4.50

TABLE II
Physicochemical Properties and Fatty Acid
Profile of RSO⁶⁸

Properties	Value
Color (Lovibond tintometer)	22R, 23.2Y
Specific gravity (30°C)	0.916
Acid value (mg KOH/g)	43.62
Free fatty acid (%)	21.4
Saponification value (mg KOH/g)	202.9
Iodine value (g I ₂ /100 g)	136.2
Fatty acid composition (%)	
C _{16:0} palmitic acid	17.51
C _{18:0} stearic acid	4.82
C _{18:1} oleic acid	25.33
C _{18:2} linoleic acid	37.50
C _{18:3} linolenic acid	14.21
Other	0.63
Total	100.00

adjusted to 8–9. SRSO was washed with water to remove excess of NaOH. Excess water was removed by heating at 110°C for few hours in an air oven, and the product was powdered.

Synthesis of SRSO-modified kaolin in presence of water

Kaolin (9.8 g) was slowly added to a mixture-containing SRSO (2 g), hydrazine hydrate (7 mL), and water (53 mL) with vigorous stirring at 20°C. The mixture was homogenized well using an Ultra Schallprozessor [HIELSCHER, GmbH, UP 100 H], and the sample was dried using a freeze drier [HetroTrap-CT60e, JOUAN]. The sample was designated as EIK-1.

Synthesis of SRSO in absence of water

Kaolin (9.8 g) was slowly added to a mixture containing SRSO (2 g) and hydrazine hydrate (7 mL) with vigorous stirring at 20°C. The mixture was homogenized well using a homogenizer, and the sample was dried using a freeze drier. The sample was designated as EIK-2.

Characterization of unmodified and SRSO-modified kaolin

The X-ray diffraction of the samples was carried out in a Philips-1710 X-ray diffractometer using monochromatic Ni-filtered Cu K α radiation 1.5418 Å at 40 kV and 20 mA. All recordings were taken at room temperature. The *d*-spacing was calculated using Bragg's equation, $n\lambda = 2d \sin \theta$, where λ is the wavelength of monochromatic X-ray source, "*d*" is the spacing between two similar planes, θ is the

angle at which X-ray falls on the sample, and *n* is the order of reflection.

IR spectroscopy was used for the identification of the main mineral as well as the impurities (both crystalline and amorphous) in the fine fraction of kaolin. About 10 mg of the powdered sample was thoroughly mixed with finely ground KBr (~200 mg) and pelletized to obtain a transparent disc. An FTIR spectrometer (MAGNA 560, NICOLET) was used. Fifty scans at a resolution of 4° were averaged to obtain the FTIR spectra.

Thermal studies were carried out on a simultaneous TG-DTA system (SEIKO-320) using α -Al₂O₃ as the reference material. About 10 mg of the sample was heated up to 1100°C at the rate of 10°C/min under nitrogen flow of 40 mL/min. α -Al₂O₃ was used as the inert reference material, and the simultaneous DTA patterns were recorded.

Preparation of NR vulcanizates

Mixes (as given in Table III) were prepared in a Brabender Plasticorder (PLE 651) at room temperature and at rotor speed of 30 rpm. The cure time of the mixes was measured on the same instrument at 150°C at a rotor speed of 30 rpm. Test specimens were prepared by compression molding the mixes at 150°C for optimum cure time.

Tensile properties of the vulcanizates

Tensile properties of the vulcanizates were measured as per standard ASTM D-412-75 on a Universal Testing Machine (INSTRON 5500R) at a crosshead speed of 500 mm/min.

RESULTS AND DISCUSSION

Characterisation of SRSO-modified kaolin

X ray diffraction analysis

Table I shows that the kaolin under study has a Si/Al ratio of 1.08 indicating that it consists of relatively

TABLE III
Composition of Mixes

Ingredients	Mix Code		
	EIK	SRSO-EIK 1	SRSO-EIK 2
Natural rubber	100	100	100
Zinc oxide	5	5	5
Stearic acid	2	2	2
Unmodified kaolin	10	–	–
SRSO-modified kaolin, EIK 1	–	10	–
SRSO-modified kaolin, EIK 2	–	–	10
MBT	2	2	2
Sulphur	2	2	2

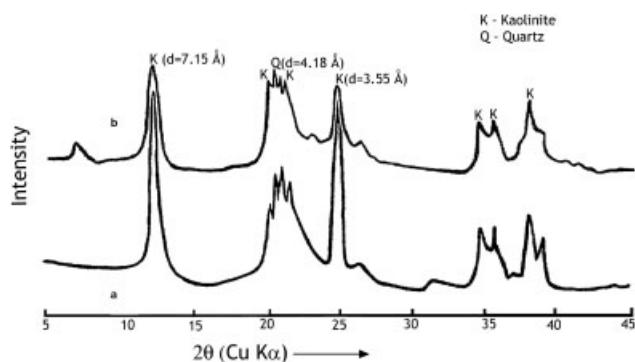


Figure 2 XRD profiles of (a) unmodified kaolin (EIK) and (b) SRSO modified kaolin (SRSO-EIK 2).

good amount of kaolinite (close to the theoretical value of one). The X-ray diffraction profiles of kaolin (EIK) before and after treatment with hydrazine hydrate and SRSO are shown in Figure 2. Figure 2 shows that in addition to the d -(001) spacing at 7.15 Å of kaolinite, the SRSO-modified kaolin shows a peak corresponding to 14 Å, which is greater than the d -spacing (13.89 Å) reported for cesium acetate–kaolinite intercalate.⁶⁹ It is reported that upon evacuation of a kaolinite–hydrazine complex, the d -(001) value decreased from 10.4 Å to 9.6 Å.⁷⁰ Because of the absence of excess hydrazine in the SRSO-modified kaolin, no peak was registered at 9.6 Å. Hence, it is possible that the SRSO has displaced hydrazine in the hydrazine–kaolinite intercalate and re-expanded the kaolinite interlayers to a larger value of 14 Å. The increase in intergallery spacing to this extent is higher than that reported for sodium monmorillonite (12.5–12.6 Å)^{7,16} and sodium fluorohectorite (12.2 Å).¹¹

FTIR spectroscopy

The FTIR spectra of unmodified kaolin and SRSO-modified kaolin (SRSO-EIK2) are shown in Figures 3

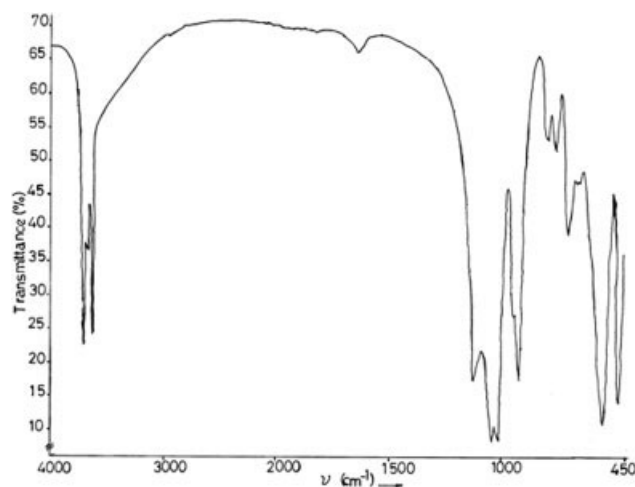


Figure 3 FTIR spectrum of unmodified kaolin (EIK).

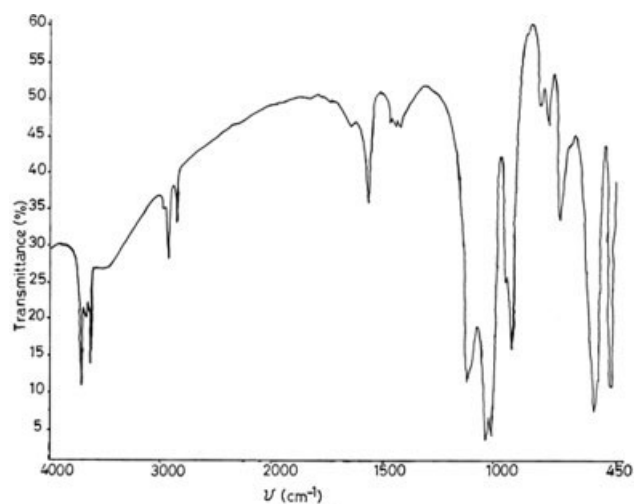


Figure 4 FTIR spectrum of SRSO-modified kaolin (SRSO-EIK 2).

and 4, respectively, in which transmittance is plotted against wave number (ν). The spectrum of unmodified kaolin (Fig. 3) shows a band at 3620 cm^{-1} , which is due to its inner hydroxyls, as reported in literature.^{69,70} The band at 3695 cm^{-1} can be attributed to the coupled vibrations of outer surface hydroxyls nearly perpendicular to the sheet. The band at 3655 cm^{-1} is due to the inner surface hydroxyl lying close to the sheet.⁶⁵ The sharp band at around 910 cm^{-1} and the weak shoulder at 938 cm^{-1} are due to the Al (VI)-OH vibrations.

Intercalation involves the rupture of some hydrogen bonds between the kaolinite layers and the formation of new hydrogen bonds (involving the inner surface hydroxyl groups) with the inserting molecule. The FTIR spectrum of SRSO-modified kaolin

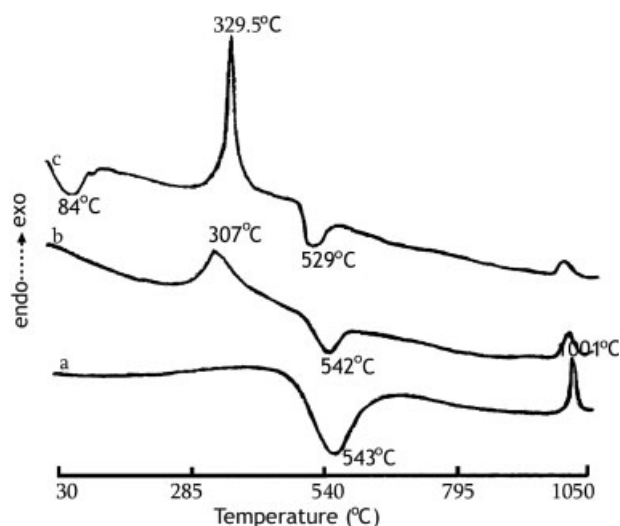


Figure 5 DTA profiles of (a) unmodified kaolin (EIK), (b) a mixture of EIK and SRSO, and (c) SRSO-modified kaolin (SRSO-EIK 2).

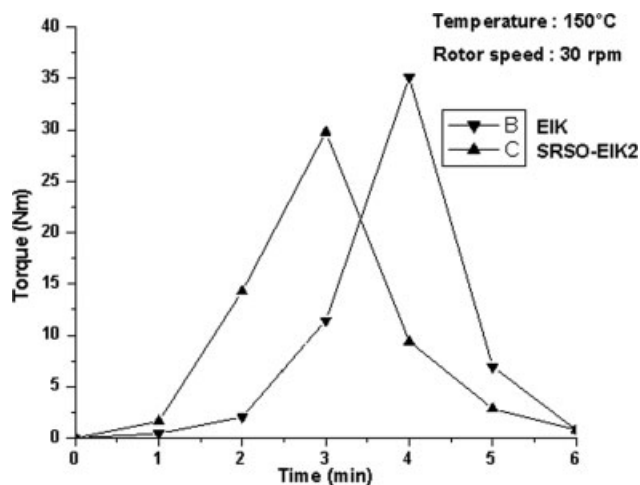


Figure 6 Brabender cure profiles of the unmodified and SRSO-modified kaolin-rubber mixes.

(Fig. 4) shows clear perturbation in the OH-stretching region (above 3620 cm^{-1}), characterized by a reduction in transmittance. This implies possible grafting of the organic moiety of RSO onto the clay surface. Also, the occurrence of bands at 2923 and 2852 cm^{-1} are indicative of the presence of grafted organic groups onto the clay surface.⁷¹

Differential thermal analysis

Further evidence for the presence of SRSO in the interlamellar spacings of the kaolinite was observed from the DTA curves given in Figure 5. The DTA profile of unmodified kaolin (EIK) (curve "a") shows an endotherm in the temperature range $530\text{--}560^\circ\text{C}$, which represents the loss of structural hydroxyls through dehydroxylation producing highly reactive metakaolin. Also, the exotherm peak at around 1001°C is due to the crystallization of the amorphous metakaolinite.⁷² Both these peaks are visible in the case of an admixture of EIK and SRSO as well as SRSO-modified kaolin but shifted to lower temperature ranges due to the presence of an impurity phase contributed by the SRSO. An additional exothermic peak at 307°C in the case of curve "b" corresponds to the elimination of SRSO from the sample. This peak, which could be attributed to the combustion of the hydrocarbon part of SRSO, is observed at 329.5°C in the case of the SRSO-modified kaolin. This provides evidence for the existence of SRSO in the interlayer region. Shifting of this peak to a higher temperature by $\sim 22^\circ\text{C}$ with respect to that of an admixture of SRSO and kaolin indicates that SRSO is more strongly bound and in a constraint environment within the lamellae and hence required more energy to decompose.

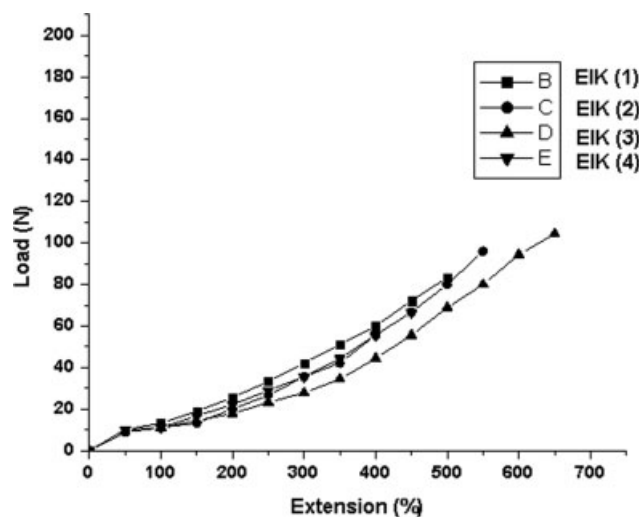


Figure 7 Load-extension plots of kaolin-filled NR vulcanizates.

Characterisation of NR vulcanizates containing SRSO-modified kaolin

Cure behavior

The cure profiles of NR mixes containing the same dosages of unmodified kaolin and SRSO-modified kaolin obtained from Brabender Plasticorder are given in Figure 6. It shows that the maximum state of cure is reached in the mix containing SRSO-modified kaolin at 3 min as against at 4 min for the mix containing unmodified kaolin. Recently, Teh et al.¹⁸ have reported faster cure in NR mixes containing low dosages of octadecyltrimethyl ammonium montmorillonite and epoxidized natural rubber (ENR 50), which has been attributed to the presence of amine functional groups in the organoclay. However, in the present system, the unsaturation sites of SRSO may

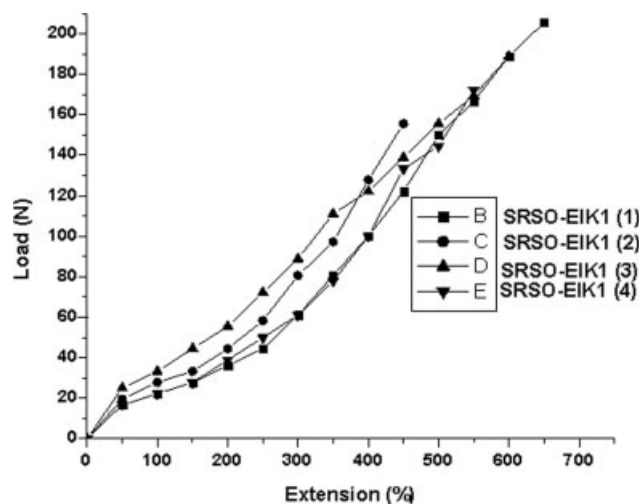


Figure 8 Load-extension plots of SRSO-modified kaolin-filled NR vulcanizates.

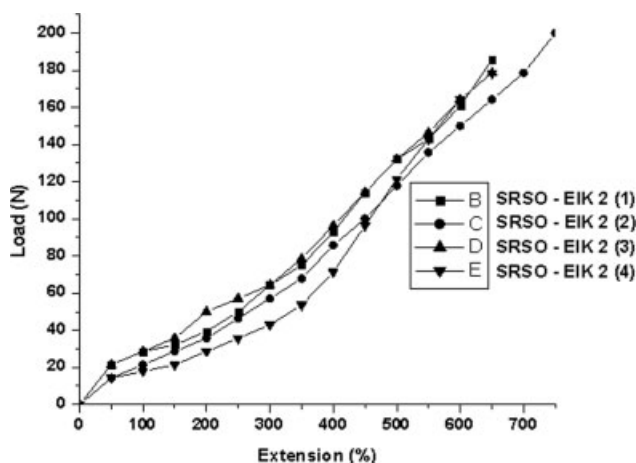


Figure 9 Load-extension plots of SRSO-modified kaolin-filled NR vulcanizates.

get cocrosslinked with that of NR in the vulcanization reaction. Besides, the alkaline nature of the SRSO-modified kaolin may accelerate this reaction.

Tensile properties of the vulcanizates

The load-extension plots of NR vulcanizates containing 10 phr each of unmodified kaolin (EIK), SRSO-modified kaolin (EIK1), and SRSO-modified kaolin (EIK2) are shown in Figures 7, 8, and 9, respectively. Table IV gives the results on tensile properties of these vulcanizates.

Figures 7–9 and the results given in Table IV show that the tensile moduli at different elongations are considerably higher for the SRSO-modified kaolin-filled NR vulcanizates as against that of the unmodified kaolin-filled NR vulcanizates. Thus, the former shows an increase in tensile modulus (at 300% elongation) by 62–107% as against that of the latter. The increase in tensile modulus may be considered as a direct indication of the reinforcing effect of a filler. Similar increase in tensile modulus has been reported for different NR nanocomposites containing low dosages of organomodified montmorillonite clays.^{7,8,11,14,15} This indicates the possibility for a high degree of interaction between the rubber and the filler, possibly resulting from the role of the

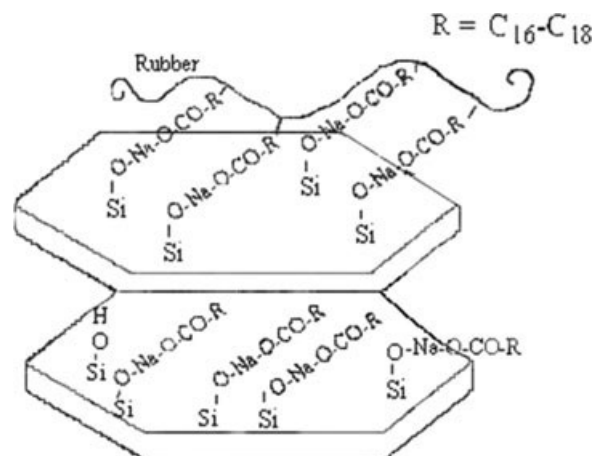


Figure 10 Plausible interactions between organofunctionalized kaolin and rubber.

organomodifier as a coupling agent between the two.

It can also be seen from the results given in Table IV that the tensile strength of the vulcanizate increases by around 98% and elongation at break by around 22% upon substitution of unmodified kaolin with the same dosage of SRSO-modified kaolin. This simultaneous increase in tensile strength and elongation at break is also analogous to that of similar results reported for NR nanocomposites containing octadecyl amine montmorillonite⁷ and methyl tallow bis-2-hydroxyethyl quaternary ammonium montmorillonite.¹⁵ The reinforcement effect of SRSO-modified kaolin as evidenced by the increase in tensile modulus, tensile strength, and elongation at break may be explained by the possible formation of a structure between kaolin and NR, shown schematically in Figure 10. It is quite possible that there could be interactions between the silanol hydroxyl groups of kaolin and the Na^+ ions of SRSO. Besides, the long-chain hydrocarbon structure of SRSO ($R = \text{C}_{16} - \text{C}_{18}$) may permit sufficient intercalation of the additive between the clay platelets. This, in turn, could increase the hydrophobicity of kaolin. Also, the presence of unsaturation sites in the alkyl group of SRSO may facilitate crosslinking reaction with that of NR during the vulcanization reaction. Thus, apart from its role as an intercalant, SRSO may act

TABLE IV
Tensile Properties of SRSO-Modified Kaolin-NR Vulcanizates

Mix Code	EIK		SRSO-EIK 1		SRSO-EIK 2	
	Mean	Variation (%)	Mean	Variation (%)	Mean	Variation (%)
Modulus-100% (MPa)	1.17	+14/-5	2.64	+26/-16	2.41	+19/-26
Modulus-300% (MPa)	3.53	+20/-21	7.29	+22/-16	5.72	+12/-12
Tensile strength (MPa)	9.7	+12/-20	19	+15/-17	19.2	+6/-7
Elongation at break (%)	553	+22/-21	568	+17/-19	675	+13/-7

as a coupling agent between kaolin and NR leading to the observed reinforcing effect.

CONCLUSION

SRSO has been synthesized and used as an organo-modifier for natural kaolin (china clay). The SRSO-modified kaolin has been characterized using XRD, FTIR, and DTA. The SRSO-modified kaolins synthesized in the presence and absence of water were used at a low dosage (10 phr) in a typical NR vulcanization system, and tensile properties of the vulcanizates were studied in comparison with that of unmodified kaolin. Considerable increases in tensile modulus, tensile strength, and elongation at break have been observed indicating the probable role of SRSO-modified kaolin as a nanofiller in NR.

The authors thank Ms. Sheeja, Department of Chemistry, Government Womens College, University of Kerala, Thiruvananthapuram, for carrying out a part of this work as partial fulfillment of her MSc dissertation project. We also thank Prof. T.K. Chandrasekhar, Director, NIST, Thiruvananthapuram, for providing the necessary facilities for this work.

References

- Karger-Kocsis, J. In *Condensation Thermoplastic Elastomers*; Fakirov, S., Ed.; Wiley-VCH: Weinheim, 2005; pp 473–488.
- Karger-Kocsis, J.; Wu, C.-M. *Polym Eng Sci* 2004, 44, 1083.
- Varghese, S.; Karger-Kocsis, J. In *Polymer Composites from Nano to Macro Scale*; Friedrich, K., Fakirov, S., Zhang, Z., Eds.; Springer: Berlin, 2005; pp 77–90.
- Mohammad, A.; Simon, G. P. In *Polymer Nanocomposites*; Mai, Y., Yu, Z., Eds.; Abington Hall: Cambridge, UK, 2006; Chapter 12.
- Utracki, L. A. *Elastomeric CPNC in Clay Containing Polymeric Nanocomposites*; Rapra Technology Ltd., Woodhead Pub. Ltd., Cambridge, UK, 2004.
- Alex, R.; Nah, C. *J Appl Polym Sci* 2006, 102, 3277.
- Arroyo, M.; Lopez-Manchado, M. A.; Herrero, B. *Polymer* 2003, 44, 2447.
- Jacob, A.; Kurien, P.; Aprem, A. S. *Int J Polym Mater* 2007, 56, 593.
- Varghese, S.; Karger-Kocsis, J. *J Appl Polym Sci* 2004, 91, 813.
- Bala, P.; Samantaray, B. K.; Srivastava, S. K.; Nando, G. B. *J Appl Polym Sci* 2004, 92, 3583.
- Varghese, S.; Gatos, K. G.; Apostolov, A. A.; Karger-Kocsis, J. *J Appl Polym Sci* 2004, 92, 543.
- Teh, P. L.; Ishak, Z. A. M.; Hashim, A. S.; Karger-Kocsis, J.; Ishiaku, U. S. *J Appl Polym Sci* 2004, 94, 2438.
- Teh, P. L.; Ishak, Z. A. M.; Hashim, A. S.; Karger-Kocsis, J.; Ishiaku, U. S. *Eur Polym J* 2004, 40, 2513.
- Varghese, S.; Karger-Kocsis, J. *Polymer* 2003, 44, 4921.
- Arroyo, M.; Lopez-Manchado, M. A.; Valentin, J. L.; Carretero, J. *Comp Sci Technol* 2007, 67, 1330.
- Wu, Y.-P.; Wang, Y.-Q.; Zhang, H.-F.; Wang, Y.-Z.; Yu, D.-S.; Zhang, L.-Q.; Yang, J. *Compos Sci Technol* 2005, 65, 1195.
- Jurkowska, B.; Jurkowski, B.; Oczkowski, M.; Pesetskii, S. S.; Koval, V.; Olkhov, Y. A. *J Appl Polym Sci* 2007, 106, 360.
- Teh, P. L.; Ishak, Z. A. M.; Hashim, A. S.; Karger-Kocsis, J.; Ishiaku, U. S. *J Appl Polym Sci* 2006, 100, 1083.
- Sadhu, S.; Bhowmick, A. K. *J Polym Sci Part B: Polym Phys* 2004, 42, 1573.
- Wang, Y.; Zhang, L.; Tang, C.; Yu, D. *J Appl Polym Sci* 2000, 78, 1879.
- Zhang, L.; Wang, Y.; Wang, Y.; Sui, Y.; Yu, D. *J Appl Polym Sci* 2000, 78, 1873.
- Sadhu, S.; Bhowmick, A. K. *J Appl Polym Sci* 2004, 92, 698.
- Sadhu, S.; Bhowmick, A. K. *Rubber Chem Technol* 2005, 78, 321.
- Schon, F.; Gronski, W. *Kautsch Gummi Kunstst* 2003, 56, 166.
- Wang, Y.-Q.; Wu, Y.-P.; Zhang, H.-F.; Zhang, L.-Q.; Wang, B.; Wang, Z.-F. *Macromol Rapid Commun* 2004, 25, 1973.
- Schon, F.; Thomann, R.; Gronski, W. *Macromol Symp* 2002, 189, 105.
- Liu, B.; Ding, Q.; He, Q.; Cai, J.; Hu, B.; Shen, J. *J Appl Polym Sci* 2006, 99, 2578.
- Acharya, H.; Pramanik, M.; Srivastava, S. K.; Bhowmick, A. K. *J Appl Polym Sci* 2004, 93, 2429.
- Zheng, H.; Zhang, Y.; Peng, Z.; Zhang, Y.; Gatos, K. G.; Karger-Kocsis, J. *Polymer* 2005, 46, 3069.
- Gatos, K. G.; Thomann, R.; Karger-Kocsis, J. *Polym Int* 2004, 53, 1191.
- Usuki, A.; Tukigase, A.; Kato, M. *Polymer* 2002, 43, 2185.
- Chang, Y.-W.; Yang, Y.; Ryu, S.; Nah, C. *Polym Int* 2002, 51, 319.
- Kim, J.-T.; Oh, T.-S.; Lee, D.-H. *Polym Int* 2003, 52, 1058.
- Nah, C.; Ryu, H. J.; Han, S. H.; Rhee, J. M.; Lee, M.-H. *Polym Int* 2001, 50, 1265.
- Wu, Y.-P.; Jia, Q.-X.; Yu, D.-S.; Zhang, L.-Q. *J Appl Polym Sci* 2003, 89, 3855.
- Nah, C.; Ryu, H. J.; Kim, W. D.; Choi, S.-S. *Polym Adv Technol* 2002, 13, 649.
- Maiti, M.; Bhowmick, A. K. *J Appl Polym Sci* 2006, 101, 2407.
- Valsecchi, R.; Vigano, M.; Levi, M.; Turri, S. *J Appl Polym Sci* 2006, 102, 4484.
- Maiti, M.; Bhowmick, A. K. *Polymer* 2006, 47, 6156.
- Maiti, M.; Bhowmick, A. K. *J Polym Sci Part B: Polym Phys* 2006, 44, 162.
- Kader, M. A.; Nah, C. *Polymer* 2004, 45, 2237.
- Chang, J.-H.; An, Y. U. *J Polym Sci Part B: Polym Phys* 2002, 40, 670.
- Kuan, H.-C.; Ma, C.-C. M.; Chuang, W.-P.; Su, H.-Y. *J Polym Sci Part B: Polym Phys* 2005, 43, 1.
- Han, B.; Cheng, A.; Ji, G.; Wu, S.-S.; Shen, J. *J Appl Polym Sci* 2004, 91, 2536.
- Song, M.; Hourston, D. J.; Yao, K. J.; Tay, J. K. H.; Ansarifard, M. A. *J Appl Polym Sci* 2003, 90, 3239.
- Wang, S.; Zhang, Y.; Peng, Z.; Zhang, Y. *J Appl Polym Sci* 2006, 99, 905.
- Varghese, S.; Karger-Kocsis, J.; Gatos, K. G. *Polymer* 2003, 44, 3977.
- Liang, Y.; Wang, Y.; Wu, Y.; Lu, Y.; Zhang, H.; Zhang, L. *Polym Test* 2005, 24, 12.
- Sridhar, V.; Tripathy, D. K. *J Appl Polym Sci* 2006, 101, 3630.
- Pramanik, M.; Srivastava, S. K.; Samantaray, B. K.; Bhowmick, A. K. *J Appl Polym Sci* 2003, 87, 2216.
- Privalko, V. P.; Ponomarenko, S. M.; Privalko, E. G.; Schon, F.; Gronski, W. *Eur Polym J* 2005, 41, 3042.
- Burnside, S. D.; Giannelis, E. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 1595.
- Jeon, H. S.; Rameshwaram, J. K.; Kim, G.; Weinkauff, D. H. *Polymer* 2003, 44, 5749.
- Maiti, M.; Sadhu, S.; Bhowmick, A. K. *J Polym Sci Part B: Polym Phys* 2004, 42, 4489.
- Rouxhet, P. G.; Samudacheata, N.; Jacobs, H.; Anton, O. *Clay Miner* 1977, 12, 171.
- Lagaron, J. M.; Cava, D.; Cabedo, L.; Gavara, R.; Gimenez, E. *Food Addit Contamin* 2005, 22, 994.

57. Ramadhas, A. S.; Jayaraj, S.; Muraleedharan, C. *Fuel* 2005, 84, 35.
58. Aigbodion, A. I.; Okieimen, F. E.; Ikhuoria, E. U.; Bakare, I. O.; Obazee, E. O. *J Appl Polym Sci* 2003, 89, 3256.
59. Aigbodion, A. I.; Pillai, C. K. S. *Prog Org Coat* 2000, 38, 187.
60. Aigbodion, A. I.; Pillai, C. K. S. *J Appl Polym Sci* 2001, 79, 2431.
61. Aigbodion, A. I.; Okieimen, F. E. *Eur Polym J* 1996, 32, 1105.
62. Perera, E. D. H. I.; Dunn, P. D. *J Rubber Res Inst Sri Lanka* 1999, 70, 11.
63. Joseph, R.; Alex, R.; Vinod, V. S.; Premalatha, C. K.; Kuriakose, B. *J Appl Polym Sci* 2003, 89, 668.
64. Nandan, V.; Joseph, R.; George, K. E. *J Appl Polym Sci* 1999, 72, 487.
65. Wilson, M. J. *A Handbook of Determinative Methods in Clay Mineralogy*; Blackie & Son Ltd: London, 1987.
66. Rouxhet, P. G.; Samudacheata, N.; Jacobs, H.; Anton, O. *Clay Miner* 1977, 12, 171.
67. Devi, C. R. Kaolin based eco-friendly catalysts for fine chemical synthesis, Ph.D. Thesis, University of Kerala, 2001.
68. Okieimen, F. E.; Pavithran, C.; Bakare, I. O. *Eur J Lipid Sci Technol* 2005, 107, 330.
69. Frost, R. L.; Kristof, J.; Horvath, E.; Kloprogge, J. T. *Langmuir* 1999, 15, 26.
70. Johnston, C. T.; Stone, D. A. *Clays Clay Miner* 1990, 38, 121.
71. Dai, J. C.; Huang, J. T. *Appl Clay Sci* 1999, 15, 51.
72. Yariv, S.; Nasser, A.; Deutsch, Y.; Michaelian, K. H. *J Therm Anal* 1991, 37, 1373.