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Reinforcing Effect of Organo-Modified Fillers in Rubber Composites as Evidenced from DMA Studies

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Abstract: The use of organically enhanced kaolin clay as reinforcing filler for NR (natural rubber) and blends of NR with NBR (nitrile-butadiene rubber) and poly BR (butadiene rubber) system were investigated on the basis of DMA (dynamic mechanical analysis). Kaolin clay was modified using a chemical complex of HH (hydrazine hydrate) and SRSO (sodium salt of rubber seed oil). Intercalation of SRSO into kaolin under optimized condition showed an inter-lamellar layer expansion to 4.668 nm, compared to the characteristic d_{001} XRD (X-ray diffraction) peak of pristine kaolin at 0.714 nm. The morphology, visco-elastic behavior, modulus property, polymer miscibility and T_g (glass transition temperature) of nano-kaolin filled NR and its blend with synthetic rubbers have been studied in detail. DMA showed a diminution in tanδ peak height and a modulus shift in correspondence with increased CLD (crosslink density). Pure NR shows only ~1% increase in storage modulus (E') while adding nanoclay rather than micron sized pristine clay under experimental conditions, because of the feeble interaction between filler and matrix, as compared to blend. An increment of ~76% and ~117% in E' was recognized by the addition of 4 wt% nanoclay in blends such as BR mK and NBR mK. With loss modulus (E'') pure NR shows only ~7% decrease while adding nanoclay, compared to blend. A decrement of ~54% and ~55% in E'' by the addition of 4 wt% nanoclay in BR mK and NBR mK blends were observed. As a whole, DMA was performed to figure out the effect of surface modification enabling to materialize composite.

Key words: Reinforcement, rubber, cross link density, storage modulus, loss modulus, damping factor, surface modification.

1. Introduction

Reinforced elastomers are being pragmatic in many commercial applications to accommodate better end-use property, because of their phenomenal mechanical property. Majority of rubber products commercially favorable are filler reinforced and sulphur vulcanized. Reinforcement generally can be assessed based on the improvement in strength, modulus and other failure properties. NR (natural rubber) exposits good strength even without fillers, due to its instinctive stream crystallizing behavior. However, most of the tonnage rubbers such as SBR (styrene butadiene rubber), BR (butadiene rubber) and EPDM (ethylene propylene diene monomer) require reinforcement for achieving strength. The blending of two or more types of rubber is an effective mode for preparing materials with admirable properties which are absent in the component rubbers. Incorporation of filler can amend the static and dynamic, mechanical behavior of elastomers [1-4].

Since rubber products generally undergo dynamic loading during service, their DMA (dynamic mechanical analysis) is very important [5]. It is principally used for evaluating the mechanical properties such as storage modulus (E'), loss modulus (E'') and tanδ of viscoelastic materials like polymeric composites whose properties exhibit time, temperature and frequency dependence [6-8]. The E' measures the stored energy, depicting the elastic portion, and the E'' measures the mechanical energy converted to heat through viscous frictional forces, representing the viscous portion. The effect of tanδ was studied to comprehend the extent of polymer miscibility and damping characteristics (internal friction). Nano-filler reinforcement causes a decrease in tanδ value [9].

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DMA also administers the T_g (glass transition temperature) of polymer, which is the temperature indicative of relaxation in a polymer where a material switches from glassy to rubbery state. In the glass transition, the storage modulus decreases dramatically and the loss modulus reaches a maximum. The maximum of tanδ peak gives the T_g. The dynamic mechanical properties of polymer layered silicate nanocomposites rely upon the separation of silicate layers [10, 11].

For the last few decades, layered silicates have attracted much interest as filler for elastomer industry, which erect potential application in automotive, home appliances, construction industry etc. Because of high swelling characteristics and high cation exchange capacity, works are going in Montmorillonite, quantitatively [12]. However, kaolinite, a typical 1:1, platy hexagonal type clay mineral is a less studied variety in this context. Unique properties of kaolinite such as high degree of crystallinity, shape and size combined with its relative affluence in nature make it an attractive alternate material for developing nanocomposites. The modulus of nano-composite of NR, filled with bentonite/hectorite has increased due to the enhanced surface interaction between polymer and filler.

Clay surface is hydrophilic in nature and is compatible with only hydrophilic polymers so as to be modified as organophilic and hence hydrophobic. Clays can be made organophilic via organo-functionalization, wherein their hydroxyl groups react with organosilane. Earlier studies in the area of kaolin intercalants adorned that molecule possessing both proton-donor and proton-acceptor group can easily be intercalated [13]. Many of these are rather outrageous in price because of the depleting nature of their petrochemical source; hence there is an obligation to peek inward for alternate source preferably based on low cost renewable natural resource. Abundantly available natural resources like kaolin and RSO (rubber seed oil), which are inert, non-toxic, eco-friendly and cost-effective, have been used in the present study.

The improvement in tensile strength of NR-SBR blend composites associated with increased CLD (crosslink density) was studied by Varkey et al. [4]. The properties such as storage modulus, loss modulus and damping properties of vulcanized NR and its blends with polybutadiene and nitrile rubber, in presence of pristine and organomodified kaolin, as reinforcing filler were investigated in the present study.

2. Materials and Methods

2.1 Materials

Kaolin, grade BCK (Best Coated Kaolin) was purchased from M/s EICL (English India Clays Limited), Veli, Thiruvananthapuram, Kerala, India. Laboratory grade NaOH and HH (hydrazine hydrate, Sigma Aldrich) were used. RSO was purchased from Murugesan & Sons, Virudhunagar 626001, Tamilnadu, India. NR (Grade II, Ribbed Smoked Sheets, RSS-5) and synthetic rubbers such as polybutadiene rubber and nitrile rubber were purchased from the local market. Commercial grades of rubber chemicals such as zinc oxide (White seal; ACPL-P999), sulfur (Rub-O-Sulf), MBT (mercaptobenzothiazole, PILCURE) and stearic acid (Lubstric; Godrej Industries Ltd.) were obtained from M/s. Ceyenar Chemicals, Kottayam, India.

2.2 Organo-Functionalization of Kaolin with HH and SRSO

SRSO (sodium salt of rubber seed oil) was prepared by reacting 28 g of RSO with 100 mL of 20% NaOH in an ice bath with continual stirring for 12 h. The mixture was conserved for one day. The pH of the final solution was maintained at 8-9. SRSO thus obtained was washed with cold water in order to abolish surplus alkali content and then centrifuged at 2,000 rpm for 10 min. The SRSO residue separated out was freeze-dried, in Hetro-Trap-CT60e, JOUAN to remove residual moisture, powdered and stored. The modification of kaolin was rendered by way of two steps, first step using a pre-intercalant and then using SRSO as an organo-modifier. In the pre-intercalation process 1 g kaolin was reacted with 25 mL of 60% HH in a closed ampoule by continuous sonication in Branson 3510 system, for one day at room temperature, causing ~95% completion of reaction. The sample thus prepared was freeze-dried, in Hetro-Trap-CT60e, JOUAN, powdered, characterized and used for further intercalation process. Intercalation of SRSO on kaolin was done by slowly adding 5 g SRSO to a solution of 19.6 g kaolin in 40 mL of 60% HH and 106 mL distilled water taken in 500 mL plastic beaker, and continuously stirred at room temperature in REMI MOTOR type RQ-122 operating at 50 Hz and 220 V, for five days at 2,000 rpm, giving almost maximum intercalation. The sample was freeze-dried, in Hetro-Trap-CT60e, JOUAN and stored.

2.3 Characterization of SRSO Modified Kaolin

The powder XRD (X-ray diffraction) measurements were carried out on a XEUSS SAXS/WAXS system with Fit 2D software using a Genix micro source from Xenocs operated at 50 kV and 0.3 mA with Cu $K\alpha$ (1.5406 Å) radiation. To get the well refined spectrum, samples were exposed to XRD for 10 min. All the measurements were done in the transmission mode between a range of 2θ (3° to 60°). Particle size distribution analysis of kaolin and SRSO modified kaolin was done using DLS (dynamic light scattering), Malvern system. The powder sample was taken in water and sonicated for 30 min in order to achieve maximum dispersion. The analysis was done at a temperature of 25 °C. SEM (scanning electron microscopic) analysis of samples was done in ZEISS, EVO 18 special edition system operated at 20 kV. Those particles, which lied flat on the substrate and which got aggregated were scrutinized by SEM. The sample containing grid was sputter coated with gold and kept in vacuum chamber. SEM micrographs of the samples were taken at magnifications ranging from 500× to 20,000×.

2.4 Compounding and Testing of Vulcanizate

Compounding of rubber-clay composite was done in a two-roll open mill mixer according to ASTM-D-3182-94 method. The mixes were cured in compression type hydraulic press at 150 °C for the optimum cure time (t_{90}) at a pressure of 100 kg/cm^2. The cured compounds cooled under room temperature and the material is used for further testing. The formulations of compounds expressed as parts per hundred of rubber (phr) are given in Table 1.

The state of dispersion of clay particles in the nanocomposite was investigated using SEM which was conducted on ZEISS, EVO 18 special edition system operated at 20 kV to analyze the fracture behavior of composites. The fracture ends of specimens were mounted on aluminum stubs and gold coated to avoid electrical charging during examination. Swelling study of samples was done on the basis of Flory-Rehner equation. A test piece of known weight was cut from the press-molded rubber sample. The sample was mesmerized in pure toluene at room temperature in order to allow the swelling to reach diffusion equilibrium. At the end of this period the test piece was removed, the loose solvent rapidly removed by blotting with filter paper and the swollen weight immediately measured. The samples were dried in vacuum to constant weight and the desorbed weight was taken. The SI (swelling index) of test specimens was calculated using the formula $[(W_1 - W_2)/W_2] \times 100$, where W_1—swollen weight, W_2—initial weight. Thermal degradation measurements of vulcanizates were done in Perkin Elmer, Pyris diamond TG/DTA system. The TGA apparatus permits continuous weighing and recording of changes in weight of a reaction system on heating from room temperature to 700 °C at a rate of 20 °C/min in nitrogen atmosphere. DMA measurements were carried out on strips with a

Table 1 Formulation of mixes.

Sample code	NB	Synthetic rubber (BR/NBR)	ZnO	Stearic acid	Filler	MBT[c]	Sulfur
	(phr)						
NR 0	100	-	5	2	-	2	2
NR K[a]	100	-	5	2	4	2	2
NR mK[b]	100	-	5	2	4	2	2
BR K[a]	80	20	5	2	4	2	2
BR mK[b]	80	20	5	2	4	2	2
NBR K[a]	80	20	5	2	4	2	2
NBR mK[b]	80	20	5	2	4	2	2

[a]: kaolin as filler;

[b]: Modified kaolin as filler;

[c]: Mercapto benzo thiazole.

Table 2 Means and methods of testing.

Compound testing	Method
Reinforcement characterization	Swelling study (in toluene)*
Thermal degradation	Thermogravimetry
Filler-filler and rubber-filler	DMA
Filler distribution	SEM

* Flory-Rehner equation.

dimension of 4 mm width, 20 mm length, 0.2 mm thickness, over a temperature range of -90 to 50 °C at a frequency of 1 Hz under tension mode on TRITEC 2000B instrument. Means and methods of testing are given in Table 2.

3. Results and Discussion

3.1 XRD

Powder XRD of pristine kaolin and its modified forms are shown in Fig. 1. The d_{001} peak at $2\theta = 12.32°$ of pristine kaolin (d = 0.714 nm) has diminished considerably and new peaks have developed at lower 2θ in intercalated system (BCK + HH + SRSO). The SRSO modified kaolin showed a high intense peak at d_{001} = 4.668 nm and low intense peak at 1.513 nm which are greater than ever reported values so far and are stable at room condition. The X-ray spectrum of SRSO modified kaolin was obtained very next to the reaction and taken after a period of 30 days marks the stability of system [14].

In order to probe the morphological hierarchy developed in the clay/rubber binary component system, wide angle spectrum of composites also have been analyzed a range of $2\theta = 5°$ to 30°, which has been figured out in our previous paper [14]. It can be seen that the basal spacing of nano kaolin filled elastomers shows a shift in the d_{001} peak towards left as compared to the micro kaolin filled system with change in intensity. The shifting of the d_{001} peak to the low 2θ region stipulates the substantial layer separation associated to the clay intercalation. The reason is accredited to the long alkyl chains from the fatty acid salt, creating more interlayer space where the intercalation of rubber chain is becoming more facile.

3.2 CLD

Experimental results of SI and CLD of different composites are given in Table 3. For filled composites it is found that the CLD has increased and shows an increment in value with nano filler. Among rubber, NBR-NR blend was found to show high CLD, by

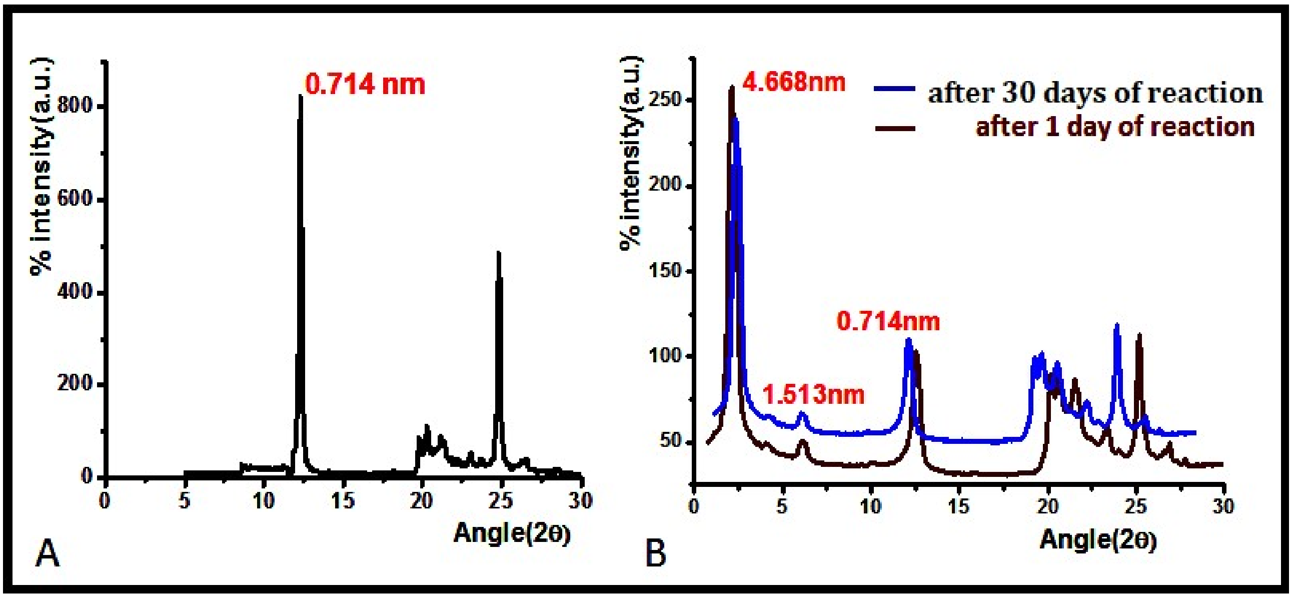

Fig. 1 XRD of kaolin (A) and SRSO modified kaolin (B).

Table 3 Swelling study in toluene.

Composition	SI	CLD
NR 0	460.5	0.165
NR K	398	0.167
NR mK	386.5	0.192
BR K	482	0.162
BR mK	392	0.188
NBR K	314.5	0.205
NBR mK	305	0.229

virtue of polar-non polar interaction, rather than BR-NR and pristine NR system. SI of composite is found to be decreasing with the addition of clay and shows further decrease with nano-clay. From the result it is found that the SI is reversely proportional to CLD. Rubber in the pristine state has maximal solvent uptake capability, because in such state the degree of crosslink against solvent mobile zone is less. As rubber gets crosslink with nano clay, its most of tunnels are occupied and solvents are restricted to enter into it. As the clay becomes nano sized from micron, its propensity for agglomeration brings down and it became finer and dispersed towards rubber and hence increased CLD. The increase in CLD is by the reason of increased surface area of filler while intercalation, whereby with maximum area can interact the rubber and other curatives. SI is a direct measurement of CLD, the smaller the SI, the higher the CLD.

3.3 SEM

Morphology is a major factor for filler dispersion determined in rubber. NR with strong molecular polarity has higher surface tension. Fig. 2 shows the fracture morphology of NR and blend composites. Filler is entering into the cross-linked network of rubber. While comparing the filler it can be seen that the treatment of organomodifier, SRSO, favors the distribution and dispersion of filler particles more uniformly, from which its homogeneous nature is indicative. Unmodified kaolin gets dispersed poorly because of free unreacted hydroxyl groups present on its surface which promotes aggregation through

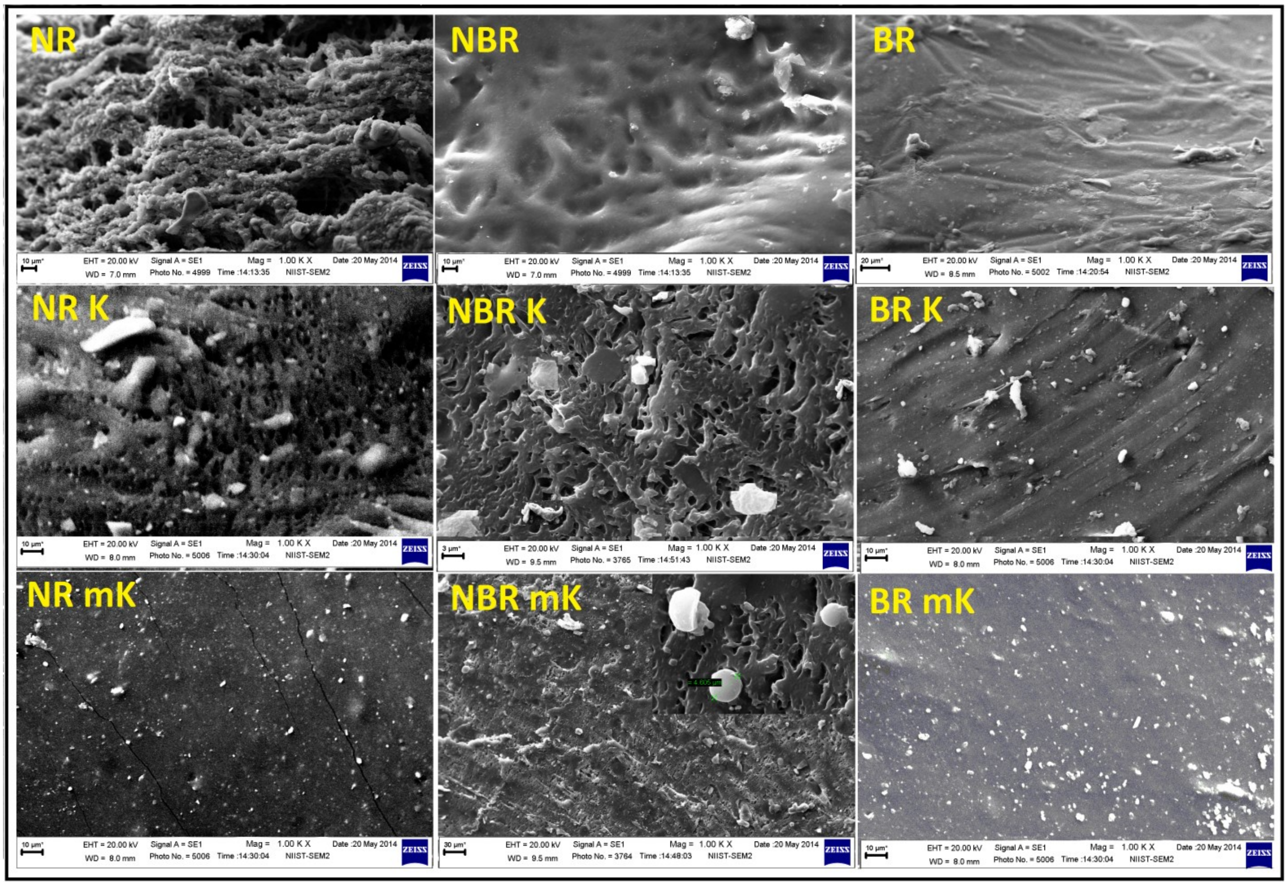

Fig. 2 **SEM of neat NR and its blend composites containing kaolin and modified kaolin.**

hydrogen bonding. The formation of exfoliated or delaminated composite is well evident from the fracture morphology pictures. From the images it is clear that in the case of pristine kaolin composite, the filler-filler interaction is more predominant, but in the case of modified kaolin composite, the filler-rubber interaction is more predominant.

3.4 Thermal Analysis

The T_{10} and T_{85} values of composites were shown in Table 4 and the thermographs between a temperature range of 0 to 700, 250 to 400 and 400 to 600 °C are shown in Fig. 3. It can be seen that the blend system is more thermally stable than the single system. As the decomposition starts, the composite with SRSO modified kaolin is found to be least thermally stable, because of the incorporation of organic content which enhances the decomposition. The incorporation of SRSO modified kaolin causes shifting of decomposition temperature towards left (lower temperature) in the case of both blend and single system. But as the temperature goes on the decomposition nature gets changed with respect to the cross-linked network stability. The NR-NBR blend is of highly cross-linked system which is found to be more thermally stable too. The nanolevel organomodified filler causes enhanced crosslinking which causes the composite to be more stable. But in the case of single system other than blend, the effect is not much seen.

3.5 DMA

The dynamic mechanical response of vulcanized NR and its blend system containing pristine and organo-modified layered silicates are presented here, measured to examine the degree of filler-filler and

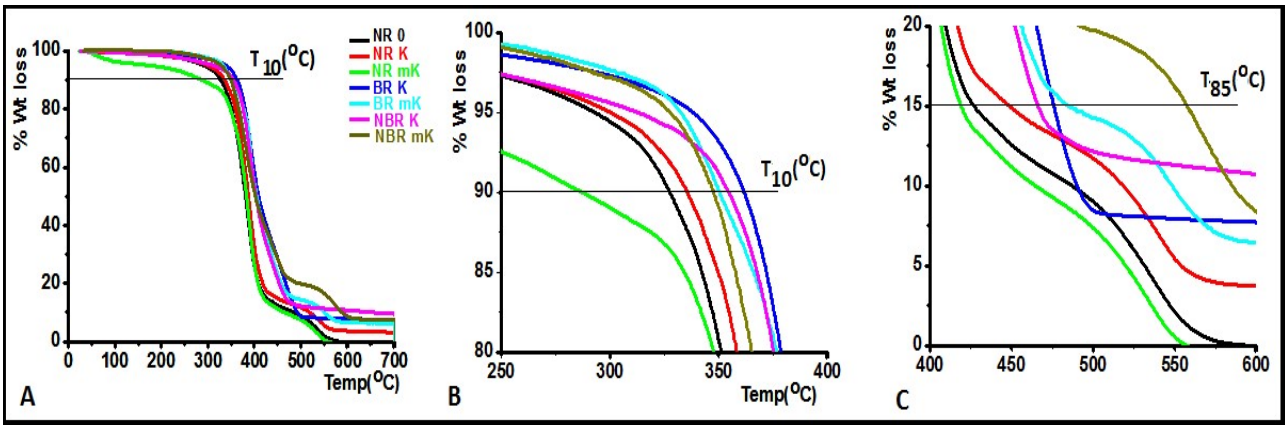

Fig. 3 Thermographs of composites between the temperature range of (A) 0 to 700 °C; (B) 250 to 400 °C; and (C) 400 to 600 °C.

Table 4 Decomposition temperature of composites.

Sample code	T_{10} (°C)[a]	T_{85} (°C)[b]
NR 0	327.0	426.0
NR K	335.5	447.3
NR mK	286.7	418.8
BR K	361.5	475.3
BR mK	350.2	483.2
NBR K	354.4	465.8
NBR mK	347.7	557.1

[a] Temperature for 10% decomposition.

[b] Temperature for 85% decomposition.

filler-matrix interaction. The elastomer chains get intercalated into the layered structures of silicate and hence reinforce the composite, resulting in the change in modulus and damping behavior. The reinforcement generally can be assessed based on the improvement in strength, modulus and other failure properties. The viscoelastic properties of composites depend upon crystallinity, polarity, extent of cross linking, etc. Storage modulus, loss modulus and damping factor are the paramount results retrieved from DMA.

3.5.1 Storage Modulus

The variation of storage modulus with temperature between ranges of -100 to 65 °C of different composites is given in Fig. 4. The storage modulus The E' connects with the elastic modulus of the material. The E' of nanocomposite is higher than unmodified and unfilled system, which indicates its influence on elastic property. The enhancement in modulus with the addition of filler is associated with the stiffness of the material and depicts the dispersion of filler. Higher storage modulus indicates better dispersed and more exfoliated system. Pure NR shows only ~1% increase in storage modulus while adding nanoclay rather than micron sized pristine clay under experimental conditions because of the weak interaction between filler and matrix, compared to blend. An increment of ~76% and ~117% in E' by the addition of 4 wt% nanoclay in BR mK and NBR mK blends was observed.

3.5.2 Loss Modulus

The E'' relates to the energy loss due to viscous dissipation. It is the viscous modulus of polymeric material. Loss modulus (E'') curves as a function of temperature for neat NR and its blend composites containing kaolin and modified kaolin were shown in Fig. 5. E'' shows a high value for gum sample compared to the filled nanocomposites. Clay incorporation decreases the E'', which indicates the lower heat

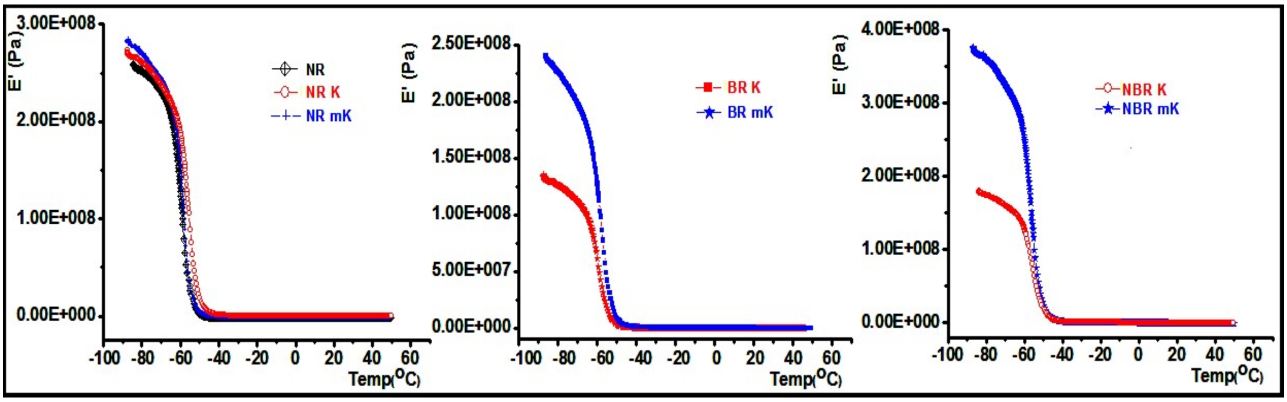

Fig. 4 Storage modulus (E') curves as function of temperature for neat NR and its blend composites containing kaolin and modified kaolin.

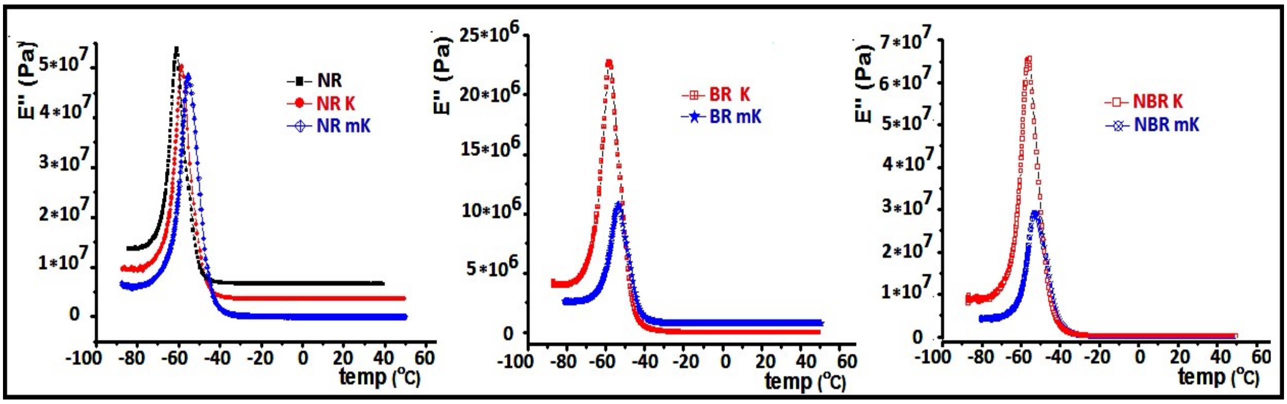

Fig. 5 Loss modulus (E'') curves as a function of temperature for neat NR and its blend composites containing kaolin and modified kaolin.

dissipation (heat build-up) in the clay reinforced nanocomposites compared to that of gum compound. The results show that pure NR (only ~7%) slightly decreases the loss modulus while adding nanoclay under experimental conditions because of the weak interaction between filler and matrix, compared to blend. A decrement of ~54% and ~55% in E'' by the addition of 4 wt% nanoclay in BR mK and NBR mK blends were noticed. T_g can be calculated from tanδ value, as the maximum of peak giving T_g, it is found that on adding nano filler the peak height gets pull down and T_g gets increasing.

3.5.3 Damping Factor

It is seen that the nanofiller reinforcement caused a decrease in tanδ value, which can be interpreted in terms of the restricted mobility of polymer chains due to their confinement in the layers of the silicates. The decrease in tanδ is the result of the reduction of the amount of polymer being deformed during strain oscillation and thus reduces the amount of dissipated energy in the dynamic transition and this may be due to the greater amount of polymer in the intercalated stacks. However, NR peak height gets down while it blended with synthetic rubber, the effect is further more in the case of nitrile rubber, because of its polar nature [14].

The important dynamic mechanical values of composites are summarized in Table 5. Highest storage modulus is found with the composite NBR mK, which may be by the reason of interaction between polar rubber and polar filler.

3.5.4 T_g and Polymer Miscibility

T_g of composites was calculated from both tanδ and E'' analyzed under DMA. Introducing nano filler into rubber will proportionally increase the density of composite and be the reason of restriction towards

Table 5 DMA values of pristine and blend NR composites.

Composition	E' (Pa)	E'' (Pa)
NR 0	2.83258E + 08	5.24871E + 07
NR K	2.90276E + 08	5.19577E + 07
NR mK	2.92886E + 08	4.84875E + 07
BR K	1.3557E + 08	2.27516E + 07
BR mK	2.40053E + 08	1.04575E + 07
NBR K	1.75432E + 08	6.54943E + 07
NBR mK	3.79702E + 08	2.93877E + 07

Table 6 Glass T_g from DMA.

Composition	T_g (°C) from E''
NR 0	-59.225
NR K	-58.1875
NR mK	-55.425
BR K	-58.325
BR mK	-58.1
NBR K	-55.45
NBR mK	-55.3875

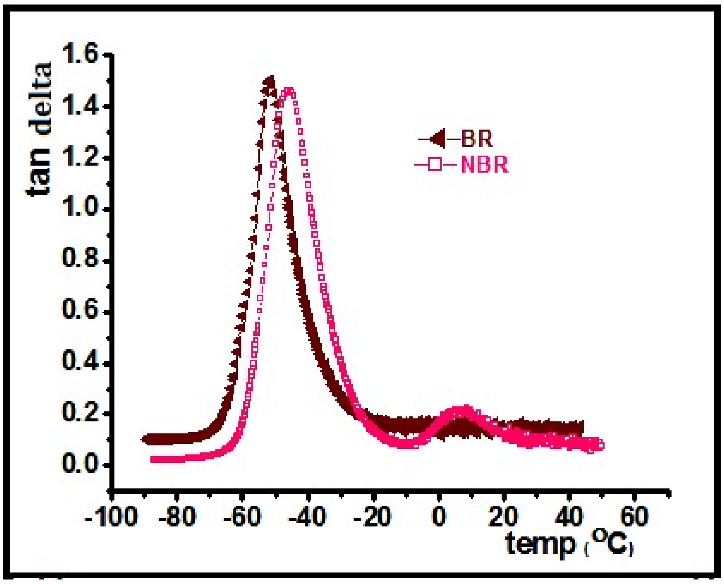

Fig. 6 Tanδ curves of NR-BR and NR-NBR blend composite as a function of temperature.

molecular motion within the material and hence increased T_g. From Table 6 given below it is found that as usual T_g calculated from E'' curves is lower than those from tanδ curves. Within a comparison between pure NR and NR blend, it is seen that the glass transition of NR-NBR blend is high because of better polar-nonpolar interaction. In the case of nitrile rubber two transitions are commenced, first T_g is because of glass transition and the second T_g is because of ionic transition. The polar group of nitrile rubber comes in an intermolecular interaction with hydroxyl group of filler and hence the ionic interaction gives a new transition above the glass transition. Blending may produce polymer whose modulus-temperature curve may show one or two transition regions. If the polymers blended are completely compatible, then the blend behaves like an ordinary amorphous polymer with a single transition region and an intermediate T_g. Tanδ curves of NR-BR and NR-NBR blend composite as a function of temperature are shown in Fig. 6, from which the polymer miscibility nature can be easily predicted.

4. Conclusions

Kaolin has been organo-modified with SRSO and characterized with wide angle X-ray spectroscopy. Intercalation of SRSO into kaolin showed inter-lamellar layer expansion to 4.668 nm, compared to the characteristic d_{001} XRD peak of kaolin at 0.714 nm. The basal spacing of nano kaolin filled elastomers shows a shift in the d_{001} peak towards left as compared to the kaolin filled system with change in intensity. The dispersion of modified filler in rubber is at most uniform as compared to pristine filler. CLD is found to show increase with filled composite and shows increment in value with nanofill. By virtue of polar-nonpolar interaction NBR-NR blend shows highest CLD rather than BR-NR blend. The extend of intercalation/exfoliation of layered silicates in polymer will be obtained from DMA, and cause change in modulus and damping behavior. As the spacing between the silicate layers increases the storage modulus (E') increases and the damping peak corresponding to the T_g broadens. Higher storage modulus indicates better dispersed and more exfoliated system. DMA was performed to evaluate the effect of surface modification. It is found that at the experiment conditions the organoclay gets better dispersion and morphology in the rubber matrix, which leads to best dynamic mechanical properties. In the case of NR two transitions were observed, because of glass transition and ionic transition. The reinforcement generally can be assessed based on the improvement in strength, modulus and other failure properties.

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References

[1] Ngo, T. T., Kohl, J. G., Paradise, T., Khalily, A., and Simonson, D. L. 2015. “Improving Mechanical Properties of Thermoset Biocomposites by Fiber Coating or Organic Oil Addition.” *Int. J. Pol. Sci.* Volume 2015, Article ID 840823. https://doi.org/10.1155/2015/840823.

[2] Barlow, C. 2014. *The World Rubber Industry, Business & Economics*. London, New York: Routledge, pp. 95-7.

[3] Onyeagoro, G. N. 2013. “Reactive Compatibilization of Natural Rubber (NR)/Carboxylated Nitrile Rubber (XNBR) Blends by Maleic Anhydride-Grafted-Polyisoprene (MAPI) and Epoxy Resin Dual Compatibilizers.” *Int. Ref. J. Eng. Sci.* 2 (3): 7-16.

[4] Varkey, J. T., Augustine, S., Groeninckx, G., Bhagawan, S. S., Someswara Rao, S., and Thomas, S. 2000. “Morphology and Mechanical and Viscoelastic Properties of Natural Rubber and Styrene Butadiene Rubber Latex Blends.” *J. Pol. Sci: Part B: Pol. Phy*. 38 (16): 2189-211.

[5] Das, R., Kumar, R., and Kundu, P. P. 2014. “Damping Evaluation of Linseed Oil-Based Engineering Elastomers by Vibration Response Method.” *Polymer Science.* Volume 2014, Article ID 840397. https://doi.org/10.1155/2014/840397.

[6] Schon, F., Thomann, R., and Gronski, W. 2002. “Shear Controlled Morphology of Rubber/Organoclay Nanocomposites and Dynamic Mechanical Analysis.” *Macromol. Symp.* 189 (1): 105-10.

[7] Xiang, P., Zhao, X. Y., Xiao, D., Lu, Y., and Zhang, L. 2008. “The Structure and Dynamic Properties of Nitrile-Butadiene Rubber/Poly(Vinyl Chloride)/Hindered Phenol Cross-Linked Composites.” *J. App. Pol. Sci.* 109 (1): 106-14.

[8] Chonkaew, W., Mingvanish, W., Kungliean, U., Rochanawipart, N., and Brostow, W. 2011. “Vulcanization Characteristics and Dynamic Mechanical Behavior of Natural Rubber Reinforced with Silane Modified Silica.” *J. NanoSci. Nanotech* 11 (3): 2018-24.

[9] Babu, B. G., Selvaraj, D. E., Srinivas, R., Prakash, B. G., Prakash, R. V., Muthupandi, E., and Balakumar, R. 2012. "Analysis of Relative Permittivity and Tan Delta Characteristics of Silicone Rubber Based Nano-composites." *International Journal of Scientific Engineering and Technology* 1 (5): 201-6.

[10] Iroh, J. O., and Longun, J. 2012. "Viscoelastic Properties of Montmorillonite Clay/Polyimide Composite Membranes and Thin Films." *J Inorg Organomet Polym* 22 (3): 653-61.

[11] Koo, C. M., Kim, M. J., Choi, M. H., Kim, S. O., and Chung, I. J. 2003. "Mechanical and Rheological Properties of the Maleated Polypropylene-Layered Silicate Nanocomposites with Different Morphology." *J.App. Pol. Sci*. 88 (6): 1526-35.

[12] Hoidy, W. H., Ahmad, M. B., Mulla, E. A. J., and Ibrahim, N. A. 2009. "Synthesis and Characterization of Organoclay from Sodium Montmorillonite and Fatty Hydroxamic Acids." *Am. J. App. Sci*. 6 (8): 1567-72.

[13] Frost, R. L., Kristof, J., and Horvath, E. 2010. "Vibrational Spectroscopy of Intercalated Kaolinites. Part I. App. Spect. Reviews." *Int. J. Prin. Meth. Appl*. 23: 130-47.

[14] Raji, V. V., Ramakrishnan, S., Sukumar, R., Brahmakumar, M., and Menon, A. R. R. 2015. "Kaolin Modified with Sodium Salt of Rubber Seed Oil as a Reinforcing Filler for Blends of Natural Rubber, Polybutadiene Rubber and Acrylonitrile-Butadiene Rubber." *Polym. Int.* 64 (1): 1585-93. doi: 10.1002/pi.4956.