**Thermogravimetric, Differential Scanning Calorimetric and Experimental Thermal Transport Study of Functionalized Nanokaolinite Doped Elastomeric Nanocomposites**

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**Abstract**

A simple technique to synthesize and functionalize kaolinite nano-particles having analogous shape and size in single step using layered silicate micro-clay as starting material is presented. The morphology, composition, and functionalization study of the activated nanokaolinite were determined by scanning electron microscopy/energy dispersive spectroscopy, atomic force microscope, and Fourier transform infrared spectroscopy, correspondingly. Variant doping concentrations of activated nanokaolinite were doped in acrylonitrile butadiene rubber (NBR) by conventional industrial elastomeric mixing techniques to fabricate composite specimens. The accumulated data simulated that the thermal conductivity was diminished 92% by increasing 15mass% filler loading in the polymer matrix. Thermogravimetric analyzer showed that thermal stability and heat absorbing capability were remarkably augmented by increasing activated nanokaolinite concentration in the NBR base formulation. Differential scanning calorimetric study revealed that glass transition and crystallization temperatures were reduced whereas first and second melting phase temperatures were enhanced by increasing filler to host matrix ratio. Tensile strength, elongation at break, and elastic modulus at 200% elongation were remarkably improved to a level of 144, 66, and 90%, respectively with increasing filler to matrix ratio. Efficient enhancement in elastomeric hardness was also observed.

**Keywords: N**anokaolinite; Polymer-matrix composites (PMCs); Thermo-mechanical properties; Transport properties; Functionalization of kaolinite

1. **Introduction**

Elastomeric composites are widely used in variant useful applications viz. automotive, sports, electric, electronics, and aerospace industries due to their high strength to weight ratio, low density, easy processing, low cost, and many other advantages[[1-4](#_ENREF_1)]. The most commonly used elastomers are silicon rubber, ethylene propylene monomer rubber, acrylonitrile butadiene rubber, natural rubber, styrene butadiene rubber, polychloroprene rubber, and fluorinated Viton rubber [[5-9](#_ENREF_5)]. The compression molded emulsified acrylonitrile butadiene rubber (NBR) composites has shown remarkable features viz. tensile strength 200–3500psi, elastomeric hardness 20–95 shore A, elongation at break 300-650%, good tear/impact resistance, good adhesion with metals and excellent shape retention. Automobile, petroleum, and natural gas industries are the main consumers of variant NBR composite formulations. Alternation in acrylonitrile or butadiene contents defines the thermo-mechanical character of the virgin elastomer [[2](#_ENREF_2), [10-12](#_ENREF_10)]. The incorporation of appropriate nanofillers in the host polymer matrix plays an important role to attain the required set of properties to develop composites for different technologies. Carbon, silica, calcium carbonate, titania and different mineral clays are used to reinforce elastomeric matrices to tune their thermo-mechanical parameters [[11](#_ENREF_11), [13-15](#_ENREF_13)]. Layered silicate mineral clay, kaolinite (Al2Si2O5(OH)4) is one of the clay viz. extensively doped in polymer matrices (epoxy, elastomers, polyvinyl choloride, polyvinyl alcohol, etc). Nanokaolinite remarkably influences the physical and chemical characteristics of the base polymer matrix. Filler-matrix compatibility and its uniform dispersion within the host polymer are the major reinforcing parameters that drastically change the characteristics of the fabricated composites [[16-19](#_ENREF_16)]. Functionalization of the incorporated nanofillers by using appropriate chemical method is one of the procedure viz. efficiently used in academia and industry to enhance filler to matrix compatibility. Silane functionalization route in which adequate silane coupling agent is used to attach silane moiety is effective, easy, economical and environment friendly method to functionalize the incorporated reinforcements compared to other established chemical processes [[19-21](#_ENREF_19)]. Thermal stability, enthalpy changes, thermal conductivity/impedance and phase transition properties have the key importance to define the operating temperature range of the polymer nanocomposite for a specific application. Mechanical, abrasion, sorption, electrical, and dynamic mechanical properties of the rubber nanocomposite are directly altered with the variation in thermal characteristics of the composite [[20](#_ENREF_20), [22](#_ENREF_22)]. To enhance the thermal endurance and diminish the thermal transfer through the polymer matrix, nanoclays (kaolinite, hallosite, montmorillonite, bentonite, etc) have been incorporated into the host polymer matrices[[18](#_ENREF_18), [19](#_ENREF_19), [23-27](#_ENREF_23)].

The present research reports the synthesis/functionalization of kaolinite nanoparticles and its effects on the thermomechanical characteristics of NBR elastomer. The appraisal of thermal conductivity according to ASTM standards also attributed novelty to this study. Ultimate tensile strength, elongation at break, and elastomeric hardness of the fabricated nanocomposites were also executed that showed the efficient mechanical properties improvement by introducing activated nanokaolinite into the host polymer matrix.

1. **Experimental**

Silane coupling agent (SCA), 3-aminopropyl-trimethoxysilane (APTMS) and cetrimonium bromide (CTAB) were purchased from Sigma Aldrich, Germany. Nanosilica, nanokoalinite, sulphur, zinc oxide and stearic acid were acquired from Merck, Germany. MBTS (Mercapto benzo thiazoles) and TMTD (tetramethyl thiuram disulfide) were procured from Dalian Richon Chemical Co. Ltd, China. DOP and wax were bought from International petrochemicals (Pvt) Ltd, Pakistan. Emulsified acrylonitrile butadiene rubber (Kumho KNB 35L) was purchased from ABF International Corporation limited, Korea.

A silane coupling agent (SCA), 3-aminopropyl-trimethoxysilane (APTMS) along with cetrimonium bromide (CTAB) was used for the surface treatment to modify the layered silicate mineral clay (kaolinite). A specific amount of the unmodified kaolinite was added in ultra-pure water in a ratio 10:100 and the mixture was sonicated in ultra-sonication bath at 70oC and 40 KHz frequency for 30min. After that, 1 mass% CTAB was introduced in the preset mixture followed by further sonication under similar conditions for next 30min. Subsequently, 5 volume % SCA was added in the mixture and sonicated it for next three hours. Consequently, magnetic stirring followed at 1000rpm for an hour with 90oC. The sonicated solution was diluted five times to maintain its pH at 7. Centrifuge (Centurion Scientific C2 series) at 4000rpm was used to recover the nano alumino-silicate clay. The nanokaolinite sample was dried for 12h at 80oC to eradicate moisture from the specimen. The schematic flow chart for surface modification is depicted in Figure 1.

Modified nanokaolinite (NK), was integrated into the rubber dispersion kneader at 110oC for thirty minutes to uniformly disperse and diffuse the nano fillers in the host polymer matrix with reinforcement (nanosilica), plasticizers (DOP, wax), and activators (zinc oxide). The post mixing of the NK/NBR, blended rubber along with the addition of crosslinker (sulphur) and accelerators (MBTS and TMTD) in the NBR matrix was carried out on two roller mixing mill at 60oC and 40rpm roller’s speed for twenty minutes. Four pre-cured rubber composite sheets with four diverse concentrations of NK were cultivated. The base formulation of NK/NBR nanocomposite (NC1) is presented in Table 1. Four different concentrations of nanokaolinite are included as 5 mass% (NC2), 10 mass% (NC3), and 15 mass% (NC4) in the basic composition 0 mass% (NC1). The composite specimens with dimensions 100 x 100 x 3 mm3 for thermal transport analysis and tensile testing specimens according to ASTM D 412-98A, were cured on hot isostatic press at 130oC and 1500psi for 30 minutes.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| NBR  /mass% | Nanosilica  /mass% | ZnO /mass% | | Stearic Acid /mass% | | aDOP /mass% | Sulphur  /mass% | bMBTS /mass% | cTMTD  /mass% |
| 100 | 20 | | 5 | | 2 | 7.5 | 2 | 2 | 2 |
| aDOP: Dioctylphatalate  bMBTS: Mercaptobenzthiazole Disulphide  cTMTD: Tetramethylthiuram Disulfide | | | | | | | | | |

Table 1: Basic formulation of NBR composite

To appraise thermal conductivity (*TC*) of the fabricated polymer nanocomposites, an appropriate apparatus were designed and developed in-house [[3](#_ENREF_3), [6](#_ENREF_6), [11](#_ENREF_11)]. The ASTM E1225-99 was used to evaluate thermal conductivity of the rubber nanocomposites[[28](#_ENREF_28)].

Thermal stability and heat flow response of the polymer composites were characterized using Perkin Elmer Diamond TG/DTA, Japan. Heating rate and temperature range during the Thermogravimetric analysis of the specimens was 10oCmin-1 and 25- 800oC, respectively in air environment.

Perkin Elmer Diamond DSC, Japan was used to analyzed physical transformations viz. phase transitions (glass, crystallization, and melting) and specific enthalpies of the fabricated samples with heating rate 10oCmin-1 from -74 to 450oC. Both TG/DTA and DSC analyses sample mass, purge gas and material of the crucible is 5mg, Nitrogen, and ceramic respectively.

Tensile strength, elongation at break and modulus of elasticity of the polymer nanocomposites were executed using universal tensile testing machine (AG-20KNXD Plus, Shimadzu) according to the ASTM D412-98A. Shore A rubber hardness of the composite specimens were carried out using Torsee, Tokyo testing machine.

Scanning Electron Microscopy (SEM, JSM 6940A, Jeol, Japan) along with the energy dispersive spectroscopy was used to analyze the surface morphology of the post thermal conductivity tested specimens and compositional analysis of the rubber nanocomposite.

Fourier Transformation Infrared (FT-IR) spectroscopy in which Infrared spectrum measures the quantity of radiation absorbed as a function of its frequency. Four samples of KBr with 0.5% by mass of nanokaolinite were prepared for FT-IR spectrometer. To obtain these samples, Nanokaolinite were mechanically mixed to the KBr powder and pressed into discs shape. FT-IR (Perkin-Elmer Diamond 1000) was used to analyze the changes taken place on the nanokaolinite surface due to the silane treatment in the frequency range 400–4000 cm-1.

Atomic Force Microscopy (AFM) is a very high-resolution type of scanning probe microscopy with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. 5200 Jeol Atomic force microscopy, Japan was used to examine the surface topography of the functionalized nanokaolinite at the host institute.

1. **Results & discussion**

*Nanokaolinite modification confirmation*

Figure 2 shows the FTIR spectra of unmodified/modified kaolinite. The peaks at 2922.91, 2849.14, and 1463.25cm-1 indentifies the presence of trimethoxy silane moiety at the surface of nanokaolinite Experimental results reveal that the functionalization of nanokaolinite due to the attachment of silane moiety in the presence of APTMS[[29-32](#_ENREF_29)].

The average particle size observed in Figure 3a is <1μm for the unmodified kaolinite. The synthesis and modification process has successfully reduced the particle size of the clay up to 1000 times. The average particle size noticed in Figure 3(b, c) for modified kaolinite is 15nm. Another interesting thing in the morphological analysis of the nanokaolinite is that all particles have approximately similar spherical shape and size. Another advantage of this route is that both the nano-particle synthesis and modification have taken place synchronously. The EDS analysis in Figure 3d, illustrates the presence of Al (21.05), Si (32.86), and O (46.09) present in nanokaolinite (Al2Si2O5­(OH)4) that means synthesized nanoparticles maintain their original composition (unmodified kaolinite) [[20](#_ENREF_20)].

Ultrasonication at 40kHz 70oC temperature and magnetic stirring at boiling conditions provide sufficient energy to exfoliate the layered silicate kaolinite into atmost single layer sheet structure. Under the abovementioned process conditions and in the presence of CTAB and APTMS, micro kaolinite converted into very fine modified nanopowder. AFM images clear the particle size fineness (1-5nm) of modified nanokaolinite in Figure 4(a, b). The approximate average particle size observed in AFM and SEM images is less than 10nm. The measured average particle size of the fabricated modified nanokaolinite is around 5nm using SEM software. The morphology of the synthesized modified nanokaolinite is spherical.

The FTIR, SEM, and AFM analyses reveal the successful functionalization of kaolinite, which is quick easy and economically viable process for small scale as well as large scale production of the modified nanokaolinite with very fine particle size.

*Dispersion of nanokaolinite in nitrile butadiene elastomer*

Figure 5 (a, b, c) elucidates the uniform dispersion of nanokaolinite in the NBR matrix at different magnifications. It means that the surface activation of the nanokaolinite improves its dispersion efficiency within the polymer matrix resulted due to the nanoscale interaction with the polymeric molecular chains [[33](#_ENREF_33)]. Figure 7d elucidates the compositional analysis of the highest nanokaolinite incorporated composite specimen, which reveals the presence of the C, O, Mg, Al, Si, Zn, S, and Ca in the fabricated rubber formulation.

*Thermal Conductivity/Thermal Impedance Analyses*

Thermal conductivity contours of the rubber nanocomposites in the continuously increasing temperature atmosphere are depicted in Figure 6. Nanokaolinite doped nanocomposites adapt approximately a specific constant level of thermal conductivity up to utmost temperature. NC4 has acquired the lowest level due to the presence of peak nanokaolinite contents in the NBR matrix. The progressive addition of nanokaolinite in the rubber matrix effectively diminishes the thermal conductivity through the composite specimens due to the nano level interaction of the filler particle with the host matrix, high surface area, good thermal stability, and excellent heat absorbing capability of the nanokaolinite[[11](#_ENREF_11), [34](#_ENREF_34)]. This is ascribed to the endothermic phenomena occurred within the composite, viz., transpirational cooling effect due to the evaporation of aromatic oil, heat absorbed by nanosilica because of its high heat capacity, large surface area and nanoscale interaction with the polymer matrix. As clear from Figure 6 the thermal conductivity of NC4 is relative low than the other nanokaolinite impregnated rubber composites and is attributed to the uniform dispersion of the nanokaolinite in the rubber matrix. NC4 composite has 92% surplus thermal conductivity compared to NC1 rubber composite due to the utmost incorporation of the nanokaolinite into the NBR matrix which enhances the endothermic capability and reduces the back face temperature of the fabricated polymer composite [[28](#_ENREF_28), [35](#_ENREF_35), [36](#_ENREF_36)]. So, the progressive addition of nanokaolinite in the rubber matrix effectively reduces the thermal conductivity through the composite specimens due to the nano level interaction of the filler particle with the host matrix, high surface area, good thermal stability, and excellent heat absorbing capability of the nanokaolinite[[37-39](#_ENREF_37)].

Surface analysis of the post thermal transport tested rubber nanocomposites was executed using SEM and the micrographs are displayed in Figure 7 (a, b, c, d). The morphological study shows that the nanokaolinite impregnation has efficiently diminished the micro-voids generation and surface damage during the continuous heat flow. It was attributed to the excellent thermal stability and even dispersion of the nanokaolinite in the base composite formulations[[40](#_ENREF_40), [41](#_ENREF_41)].

*Thermal decomposition and Differential Thermal Analysis*

Thermal degradation of the polymer nanocomposites in air environment and temperature range of 25 to 700oC is revealed in Figure 8. The composite specimens represent approximately no mass loss at 410oC and the maximum composites mass degradation is observed in the proceeding 110oC due to the base polymer pyrolysis and molecular bond breakage. NC4 rubber nanocomposite has the supreme thermal stability in the tested temperature range among the four fabricated compositions due to the utmost nanokaolinite impregnation in the NBR matrix which has remarkable thermal stability up to high temperature. Figure 8 also illustrates the heat absorbing/exhaust capability of the rubber nanocomposites. The endothermic ability of the polymer nanocomposite is augmented with increasing nanokaolinite contents in the polymer matrix owing to the additional heat energy absorption phenomenon occurred in nanokaolinite with increasing temperature viz. evaporation of water of crystallization, silane moiety debonding, and kaolinite composition phase changes.

Table 2 illustrates that NC4 has 1, 3, and 10% additional thermal endurance at 250, 450, and 650oC, respectively as compared to base composite formulation that is attributed due to additional heat absorbing capability of the activated nanokaolinite present in the elastomeric nanocomposite[[9](#_ENREF_9), [11](#_ENREF_11), [42](#_ENREF_42)].

|  |  |  |  |
| --- | --- | --- | --- |
| Sample ID | Mass loss at  250oC / % | %Mass loss at  450 oC / % | %Mass loss at  650 oC / % |
| NC1 | 2.788±0.01 | 34.521±0.1 | 71.851±0.1 |
| NC2 | 1.489±0.01 | 54.230±0.1 | 70.085±0.1 |
| NC3 | 3.634±0.01 | 37.408±0.1 | 67.687±0.1 |
| NC4 | 1.835±0.01 | 37.165±0.1 | 61.343±0.1 |

Table 2: %Mass loss data of the rubber nanocomposites at diverse temperatures

*DSC Study*

Differential scanning calorimetric analysis of the polymer nanocomposites in the temperature range -74 to 450oC are exposed in Figure 9. It explores the effect of the nanokaolinite on the phase transition temperatures and the associated specific enthalpies. Glass transition, crystallization, first melting, and second melting phase temperatures were measured from the DSC contours and are calculated in Table 3. The reduction of glass transition temperature (~27oC) is observed in the presented data due to the 15 mass% nanokaolinite impregnation in the rubber matrix. The crystallization temperature of the rubber nanocomposites is reduced with increasing filler contents in the polymer matrix and the minimum is observed for NC4, i.e., 79.7oC. This lessening is attributed to decrease of crosslinking density of the base polymer matrix because of the nanokaolinite incorporation in the host matrix, which extends the rubbery range and reduces the crystallization point.

The phase transition temperatures of the first and second melting points of the composite specimens were improved with increasing filler concentration in the rubber matrix because of many factors viz. high heat quenching capability, uniform dispersion, good thermal stability, and nano-scale interaction of the nanokaolinite with the host polymer matrix. Table 3 also interprets that the specific enthalpies of glass transition and crystallization temperatures are diminished while first/second melting phase temperature’s specific enthalpies were enhanced with increasing the nanokaolinite in the NBR matrix. It is attributed due to the remarkable heat absorbance capability of the incorporated activated nanokaolinite in the elastomeric matrix. Additional heat energy was required to evaporate water of crystallization present in the nanokaolinite. Another way of extra heat consumption in activated nanokaolinite loaded composite specimens is debonding energy requirement to debond the silane coupling. This represents that the incorporated filler remarkably influences the phase transition temperatures and their associated specific enthalpies [[33](#_ENREF_33), [43-45](#_ENREF_43)]

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample ID | NC1 | NC2 | NC3 | NC4 |
| Glass transition temperature Tg / oC | -37.79±0.01 | -38.22±0.01 | -39.52±0.01 | -43.35±0.01 |
| Crystallization Temperature Tc / oC | 72.10±0.01 | 76.43±0.01 | 80.62±0.01 | 81.34±0.01 |
| First Melting Temperature Tm1 / oC | 156.44±0.01 | 196.12±0.01 | 197.48±0.01 | 198.61±0.01 |
| Second Melting Temperature Tm2 / oC | 365.84±0.01 | 368.56±0.01 | 373.78±0.01 | 384.90±0.01 |
| Specific Enthalpy of Glass transition / Jg-1 | 4.269±0.01 | 3.831±0.01 | 3.823±0.01 | 2.625±0.01 |
| Specific Enthalpy of Crystallization / Jg-1 | 5.772±0.01 | 6.131 ±0.01 | 6. 307±0.01 | 9.897±0.01 |
| Specific Enthalpy of First Melting Phase / Jg-1 | 17.752±0.01 | 18.113±0.01 | 19.996±0.01 | 21.135±0.01 |
| Specific Enthalpy of Second Melting Phase / Jg-1 | 237.281±0.01 | 240.028±0.01 | 252.920±0.01 | 266.935±0.01 |

Table 3: The effect of nanokaolinite on the phase transition temperatures and their respective specific enthalpies of rubber nanocomposites

*Mechanical Characterizations*

Figure 10 elaborates the effect of the impregnated on the tensile strength and elongation properties of the base polymer matrix. Tensile strength of the rubber nanocomposites is amplified 143% and elongation at break is reduces 22% with the utmost integration of the nanokaolinite into the base composite formulation (NC1) and is due to the uniform dispersion, high surface area, nano level interaction with the polymeric molecular chains, and the filler– matrix compatibility of nanokaolinite[[46](#_ENREF_46)]. The modulus of elasticity at 100 and 200% elongations were measured from the stress–strain contours of the fabricated composite specimens and are illustrated in Figure 11. It is observed that the nanokaolinite insertion in the polymer matrix efficiently enhances the Young’s modulus of NC4 rubber composite up to 81 and 90%, respectively relative to the base composite formulation (NC1). Figure 12 illustrates the effect of the filler concentration on the shore A rubber hardness. It is observed that the nanokaolinite incorporation remarkably enhanced the rubber hardness of the composite specimens due to the reduction of flow-ability of the host matrix with the nanokaolinite polymeric molecular chain linkage development [[14](#_ENREF_14), [41](#_ENREF_41), [47](#_ENREF_47), [48](#_ENREF_48)]

**Conclusions**

Polymer nanocomposites were fabricated by the modification of nanokaolinite from the untreated micro-clay followed by impregnation of the nanokaolinite with different concentrations in the rubber matrix. Nanokaolinite size, composition, structure, morphology, and activation were confirmed using SEM/EDS, AFM and FTIR techniques. It was observed that the thermal conductivity was reduced 56% at 250oC; thermal degradation was reduced 10% at 650oC; Glass transition and crystallization temperatures were diminished at 6 and 5oC respectively while the first/second melting phase temperatures were augmented 42 and 9oC, accordingly; tensile strength, elongation at break, 100 modulus, and 200% modulus were increased 143, 63, 81, and 91%, respectively; and the shore A hardness of the polymer nanocomposites were augmented up to 22% with the 15 mass% inclusion of the nanokaolinite in the base polymer composite formulation. The remarkable improvement in thermomechanical character of the NBR elastomeric matrix by introducing activated nanokaolinite advocates its applicability in the area of variant mechanical and thermal protection systems viz. aircrafts, automobile etc.

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***Figure Captions***

Figure 1. Flowchart of surface modification and synthesis of nanokaolinite

Figure 2. FTIR Spectra of unmodified/modified kaolinite

Figure 3. Surface morphology of unmodified (a) and modified (b, c) kaolinite along with its compositional analysis (d)

Figure 4. Surface topography of modified Kaolinite

Figure 5. SEM micrographs of modified nanokaolinite dispersion at variant magnifications (a, b, c) and compositional analysis of the 15 mass% loaded specimens (d)

Figure 6. Thermal conductivity of the rubber nanocomposites in the temperature range 323K to 523K

Figure 7. SEM micrographs of the post thermal transport tested rubber composites with four diverse loadings of the nanokaolinite

Figure 8. Thermal degradation of the nanokaolinite incorporated composite specimens in the temperature range 25-700oC

Figure 9. Differential scanning calorimetric contours of the polymer nanocomposites in the temperature range -74 to 450oC

Figure 10. The effect of nanokaolinite on the tensile strength and elongation at break of the polymer nanocomposites

Figure 11. The effect of nanokaolinite concentration on the 100% and 200% elastic modulus of the rubber nanocomposites

Figure 12. The effect of nanokaolinite concentration on the rubber hardness of the fabricated polymer nanocomposites