

NANOKAOLIN CLAY AS REINFORCING FILLER IN NITRILE RUBBER

Preetha Nair K, Dr. Rani Joseph

Abstract — Nanocomposites were prepared by incorporating varying amounts of nanokaolin clay and vinyl silane grafted nanokaolin clay in NBR, on a two roll mill. Improvement in mechanical properties like tensile strength, elongation at break, modulus and tear strength were observed for the composites. Cure characteristics showed an increase in the cure rate of the composites. Clay rubber nanocomposites were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The increase in d spacing suggested an intercalated /exfoliated structure of clay and SEM studies showed uniform dispersion of clay in the matrix. Swelling index decreased with the increase in filler loading, as observed from the swelling studies conducted in toluene. Rubber filler interactions were also studied by strain sweep analysis. It was found that the complex modulus values increased with the clay content indicating better rubber filler interaction. Differential scanning calorimetry (DSC) studies showed that glass transition temperature (T_g) remained unchanged. Thermal studies showed that addition of clay marginally improved the thermal stability.

Index Terms—, Cure characteristics, Mechanical properties, Nanokaolin clay, Nitrile butadiene rubber, Vinyl silane grafted nanokaolin clay, Scanning electron microscopy, Thermo gravimetric analysis.

1 INTRODUCTION

Remarkable enhancement in the properties of polymers are observed on incorporation of nanofillers. With the advent of polymer nanocomposites by the Toyota group of companies, conventional fillers gave way to nano fillers. Among the nanofillers, nanoclays occupy the prime position. Now polymer clay nanocomposites (PCNs) have become one of the most promising research areas in the field of polymer science and technology. Use of clay in thermoplastics like polypropylene [1],[2],[3] polystyrene [4] etc. are widely studied. Recently rubber/clay nanocomposites [5],[6],[7] have also received special attention.

Filler reinforcement is more pronounced with non crystallising synthetic rubbers like NBR and SBR compared to NR which undergoes crystallization on stretching. In rubber reinforcement, the most important characteristic of the reinforcing filler is its small size, so that the particles have a large surface area to interact with rubber. In addition to particle size, particle structure also influence its reinforcing efficiency [8]. Among the various nano clays used the 2:1, expanding type, clay mineral, montmorillonite takes prime position. Polymer clay nanocomposites derived from organically modified MMT has been extensively studied as shown by a large number of publications on the subject [9],[10],[11],[12],[13],[14],[15],[16],[17].

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However kaolin (Al₂[Si₂O₅](OH)₄) is a 1:1 non expanding type clay with neither cations nor anions in the interlayer region. Modified nano kaolin is used in natural rubber [18] styrene butadiene rubber [19] and epoxidized natural rubber [20]. Kaolin can provide excellent reinforcement in rubber. Q Liu [21] has compared precipitated silica (PS) and nanokaolin clay (NK) in different matrices and has found that the mechanical properties like tensile strength, elongation at break and rebound elasticity are superior to PS.

Until now little study has been taken up with kaolin clay. Kaolin is very low cost, non swellable, easily available clay. In this work we report the effect of addition of unmodified and modified kaolin clay on the mechanical properties of NBR.

2 EXPERIMENTAL

2.1 Materials

Acrylo nitrile butadiene rubber grade-KNB 35L, Nanokaolin clay (Nano Caliber 100) and vinyl silane grafted nano kaolin clay (Nano Caliber 100V) are supplied by English Indian Clays Ltd. (Thiruvananthapuram). Zinc oxide (ZnO), Sulphur (S), N-Cyclohexyl-2benzothiazole sulfenamide (CBS), Tetra methyl thiuram disulphide (TMTD), Stearic acid, antioxidant HS used were of commercial grade.

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2.2 Preparation of NBR clay compounds

Compounding of NBR was done on a two roll mill as per the formulation given in Table1. NBR was masticated for 2 mts on a two roll mill (6 x 12") and the ingredients were added in the same order as mentioned. Unmodified clay (Nano Caliber 100) is represented as C and modified clay (Nano Caliber 100V) as V. The composites are designated as NBR C and NBR V compounds. Concentration of filler is also given along with the name of the compound. C and V were added in varying concentration (in parts per hundred rubber, phr). The samples were then cured at 100°C in an electrically heated hydraulic press to their respective optimum cure time at a pressure of 150 Kg/cm² in a specially designed mould to get sample sheets having thickness 1.5 mm approximately.

Table1
Formulation of NBR clay composite

INGREDIENTS	WEIGHT (g)
NBR	100
S	1.5
ZnO	4.5
Stearic acid	2.0
Clay	Varying concentration
HS	1
CBS	1
TMTD	0.25

2.3. Cure characteristics

Cure characteristics of clay filled NBR was studied using a Rubber Process Analyzer (RPA2000) as per ASTM standard D 2084-01. Important parameter like maximum torque Dmax, minimum torque Dmin, cure time T90, Scorch time T10 were determined. Cure rate index which is a measure of the rate of cure reaction is given by $CRI = 100 / T_{90} - T_{10}$

2.4 Mechanical properties

Dumb-bell shaped specimens were cut from the cured latex sheets and tensile strength, elongation at break and modulus, were determined on a Shimadzu Universal Testing Machine (AG1 series), using a cross head speed of 500mm/min as per ASTM D 412-1998. All the tests were carried out at 28+/- 20°C. Five samples were tested and their average values were taken.

Tear resistance was also carried out on a Shimadzu Auto-graph AG1 series Universal testing machine UTM, using a cross head speed of 500mm/min at test temperature 28+/- 20°C as per ASTM D 624 -1998. The tear resistances of the samples were reported in N/mm

2.5 Swelling studies:

Solvent swelling of cured rubber compounds was carried out in toluene. Samples were weighed (w_1) before immersion at 250C. After 24 hrs when equilibrium swelling was reached, the swollen samples were removed, wiped dry and again weighed (w_2). The degree of swelling was calculated using the following equation. Swelling index (100%) = $(w_2 - w_1) / w_1 \times 100$

2.4 X ray Dffraction Studies (XRD)

For characterization of clays and rubber composites XRD studies were conducted by Bruker, D8 advance model employing CuK α radiation $\lambda = 1.54 \text{ \AA}$. X-ray diffraction method gives qualitative information about the exfoliation and d spacing of clay layers in the polymer matrix compared to that of pure clay. When polymer chains are inserted in the gallery spacing of the clay layers, the interlayer spacing increases and the shifting of diffraction peaks to lower angle takes place. Diffraction peaks disappear for exfoliated structures, where silicate layers are completely and uniformly dispersed in the matrix

2.6 Scanning Electron Microscopy (SEM)

The morphology of the nanocomposites was studied using Joel Model JSM 6390LV Scanning electron microscope.

2.7 Strain Sweep Studies

The strain sweep studies at low strain amplitude were conducted on RPA. It gives information about the dispersion of filler particles in rubber matrix. The variation of storage modulus G', loss modulus G'' and complex modulus G* with change in strain amplitude can be measured on RPA

2.8 Differential Scanning Calorimetric Analysis (DSC):

To analyze the effect of clay on the glass transition temperature of NBR, DSC scan was performed. DSC measurements were performed at a temperature range of -60°C to 90°C. In the case of polymer nanocomposites DSC measurements are useful for the identification of the extent of intercalation or exfoliation of the nanoparticles in the matrix.

2.9 Thermo Gravimetric Analysis (TGA)

Thermal degradation studies involve the measurement of change in the weight of the material as a result of heating in an inert atmosphere. The integral (TGA) and derivative (DTG) thermogravimetric curves provide information about the thermal stability and extent of degradation of polymeric materials.

3. RESULTS AND DISCUSSION

3.1 Cure characteristics

Cure characteristics of NBR-C and NBR-V composites expressed in terms of optimum cure time (T90), scorchtime (T10), and cure rate index CRI and the difference in maximum and minimum torque values (Dmax-Dmin) are given in tables 2 and 3 respectively.

Table2

Cure Charecterestics of NBR C composite

Con of filler(phr)	T90	T10	CRI	Dmax-Dmin
0	3.51	1.63	53	3.145
1	3.16	1.44	58	3.439
5	3.12	1.37	57	3.327
10	3.04	1.39	60	3.543
15	3.13	1.42	58	3.556

Table3

Cure Charecterestics of NBR V composite

Con of filler(phr)	T90	T10	CRI	Dmax-Dmin
0	3.51	1.63	53	3.145
1	3.05	1.51	65	3.357
5	2.58	1.46	89	3.446
10	2.41	1.33	93	3.419
15	2.59	1.38	83	3.589

Addition of C and V in NBR shows a small reduction in scorch time and cure time of the composites. Torque values (Dmax-Dmin) of the composites show a slight increase and CRI values of the composites show considerable increase with the addition of clay.

Acidic nature of Clay activates the formation of soluble Zn ions and the Zn ions might have promoted the formation of free radicals by the accelerator in the early stages of the cross linking reaction. These free radicals can cause premature vulcanization resulting in a decrease in scorch time [22].

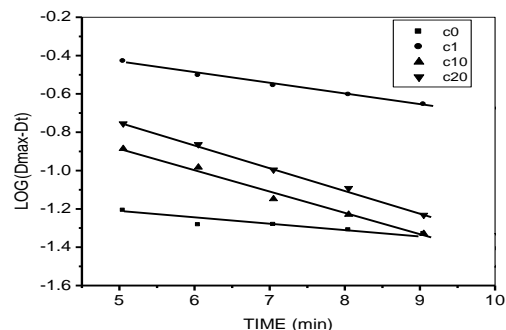
From the cure time values it is seen that NBR V composites accelerates curing reaction when compared to NBR C composites. Cure retardation in NBR C composites may be due to the absorption of curatives by the unmodified clay which will reduce the amount of curatives available for cure reaction. Higher CRI values of NBR V composites show that the unsaturated sites of vinyl group may get cross linked with that of NBR in the vulcanization. The favorable entrapment of rubber, curatives and vinyl modifier within the intercalated silicate galleries might be the reason for the accelerating effect of modified clay on curing [23]

Slight increase in torque values suggests an increase in cross linking density in the rubber phase. Swelling studies also confirm an increase in cross link density with the increase in the concentration of clay.

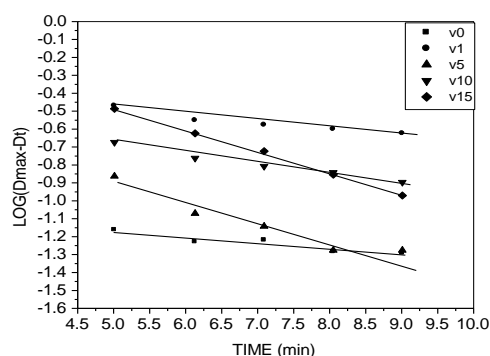
3.2 Cure Kinetics:

The plots of log (Dmax-Dt) against time for NBR C and NBR V composites are given in Fig: 3 and 4 respectively Dmax is the maximum torque and Dt is the torque at a given time.

The plots are found to be linear which proves the cure reaction proceeds according to the first order kinetics.



(a)



(b)

Fig: 1: Plot of log Dmax-Dt against time for

Mechanical Property	NBR-C composite	NBR-V composite
Tensile Strength	56% (15 phr)	32% (5 phr)
Elongation at break	30% (15 phr)	13% (5 phr)
Modulus at 300% elongation	10% (15 phr)	23% (15 phr)
Tear Strength	49% (15 phr)	33% (15 phr)

(a)
NBR C
Com-
posite
and (b)
NBR V
composite

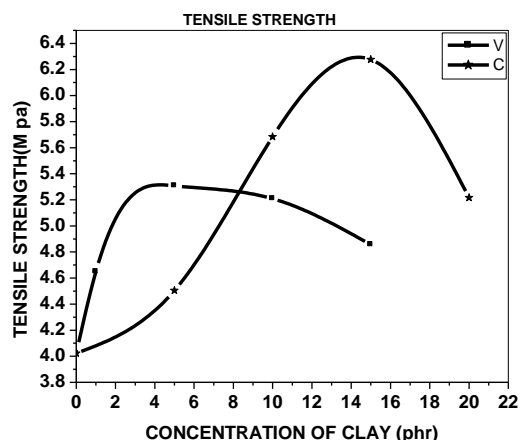


Fig:2

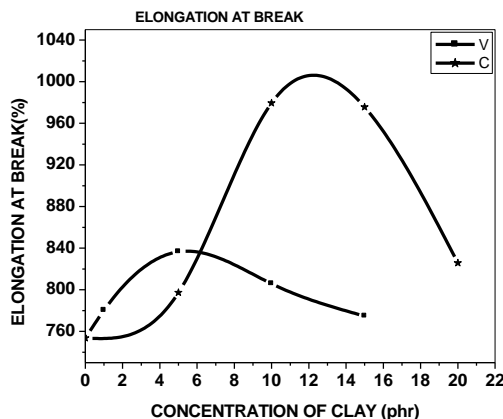


Fig: 3

3.3 Mechanical properties:

Table4
 Variation in mechanical properties of NBR clay composites

Maximum increase in mechanical properties of both the composites is given in Table 4.

Tensile strength, elongation at break, modulus and tear strength are maximum for unmodified clay composite at 15 phr. But modified clay composite gives maximum values of tensile strength and elongation at break at a lower concentration of 5 phr.

Here unmodified clay is hydrophilic and on organic modification it becomes hydrophobic. Hydrophobic clay is more compatible with NBR.

Variation of tensile strength and elongation at break of NBR C and NBR V composite is as shown in Fig 2 and 3 respectively. Both the values increases with clay loading, reaches a maximum and then decreases. For NBR V composite tensile strength and elongation at break increases up to 5 phr (32% and 13% respectively) and then decreases. But for NBR-C composite tensile strength and elongation at break reaches a maximum (57% and 30% respectively) only at 15 phr.

The increase in tensile strength may be due to the increase in interfacial area of clay platelets and good interaction between the clay platelets and NBR. Increase in interfacial area arises by intercalation or possible exfoliation of clay layers, as evidenced by XRD analysis. In kaolin clay the layers are linked through Hydrogen bonding between hydroxyl groups on the octahedral sheet and oxide arrangement of tetrahedral sheet. Even though the intercalation reactivity of kaolin is low due to hydrogen bonding between the layers, the free OH groups on kaolin can interact with the CN groups of NBR. In vinyl modified clay the vinyl groups on the surface of kaolin clay forms a bridging cross linking reaction with rubber when cured, thus giving reinforcement in properties. Decrease in tensile strength at higher loading may be due to agglomeration of clay tactoids.

Generally rigid fillers cause a significant reduction in elongation at break, but the presence of clay improves the elongation at break more than with other isotropic fillers. Better filler dispersion and strong rubber filler interaction leads to an in-

crease in elongation values. SEM images of the composites show a good dispersion of filler in NBR. When rubber filler interaction increases, rubber absorbs more energy, decoils the chain to a greater extent, leading to a chain slippage over the longer clay particles. At higher loading the elongation at break decreases because of filler aggregation. Aggregation of filler weakens the number of available reinforcing links [24]. The formation of non exfoliated aggregates at higher clay content makes these composites much more brittle.

Variation of modulus at 300% elongation of NBR C and V composites are shown in Fig4. Modulus of NBR- C composite increases upto 5phr and then remains a constant. While the modulus of NBR- V composite increases continuously with the increase in clay content. Better compatibility of modified clay and the cross linking of the vinyl group with the matrix may be the reason for this behaviour. Also nanometric dispersion of clay layers gives sufficient reinforcement leading to improved stiffness.

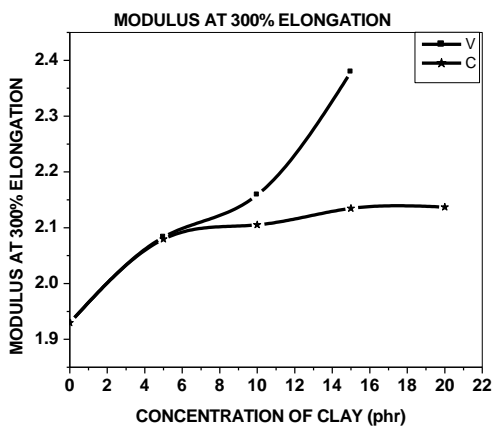


Fig: 4

Tear strength of NBR C and V composites increases with the clay loading as seen in fig 5. Tear strength is greater for the unmodified clay composite. The dispersed clay layers and small tactoids act as a barrier for crack propagation during the tear process thus increasing the tear strength.

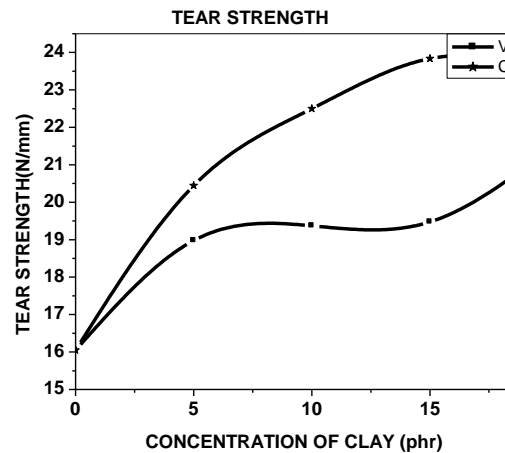


Fig: 5

Swelling studies show that the swelling index of both clay composites decreases with the addition of clay as shown in Fig: 6. The extent of cross linking is inversely proportional to the swelling index. The gum has the maximum toluene uptake at equilibrium swelling, showing that there is no restriction for toluene penetration. When the clay loading increases the solvent uptake is restricted due to the increased cross linking.

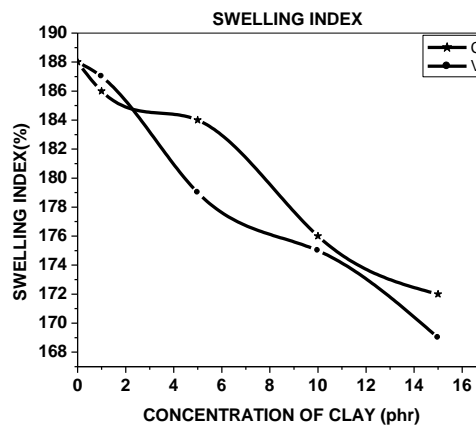
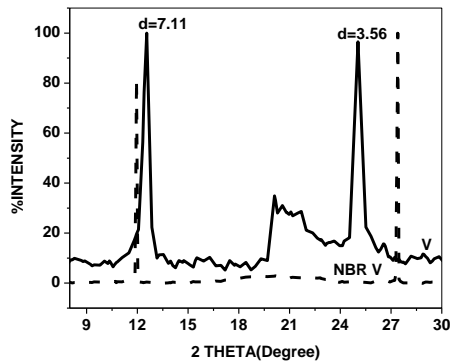
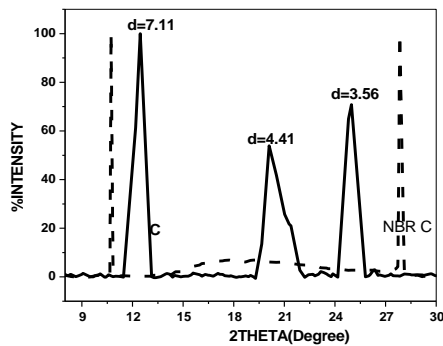


Fig:6

3. 4 XRD analysis: XRD patterns of clay and its composites are given in fig 7 The characteristic peaks of kaolin are seen around $2\theta = 12^\circ, 20^\circ$ and 25° which are assigned to the interlayer spacing of $7.12, 4.41$ and 3.56 \AA respectively.



(a)



(b)

Fig: 7 XRD of (a) NBR Vand (b) NBR C composites

XRD peak at 12° shows a shift to a lower angle in both the composites. The shift is greater for NBR C composite. Shift to lower angle indicates intercalation of NBR into the clay galleries. The increase in d spacing after curing may be due to the increase in the mobility of clay and polymer chains at the moulding temperature and pressure [25]. A small reduction in the intensity of the peak shows a disordered intercalated structure and exfoliation of some organic clay in the nanocomposite. The disappearance of the peaks between 13° and 25° in the composites show that exfoliation has taken place to some extent. Additional peaks at higher 2 theta for both the composites indicate the collapse of some intercalated structure. In the melt blended system part of the intercalated clay must have been squeezed out from the layer giving rise to some clay aggregates [25].

These observations are common in literature where MMT is used as the reinforcing filler. Amit et al [26] have worked on carboxylated NBR / Organomodified MMT composites and has shown that the intercalation is a common process from 2.5 to 10 phr organo clay mixed at 160°C . In an NBR- organically

modified MMT nanocomposite a decrease in d spacing after curing was observed [25]. For NBR /Na- MMT composite a peak appeared with a decrease in intensity compared to pristine Na MMT [24]. S.Sadhu and A K Bhowmick [27] have dealt with unmodified MMT on SBR with varying styrene content and using dicumyl peroxide as the curing agent and suggested that exfoliation has taken place in all the composites

3.5 SEM ANALYSIS:

Fig 8 and 9 are the SEM images of the tear fractured surfaces of NBR C and NBR V composites. A uniform distribution of clay particles is seen in both images. The tear pattern of NBR V composite shows a series of tear ridges parallel to the tearing direction.

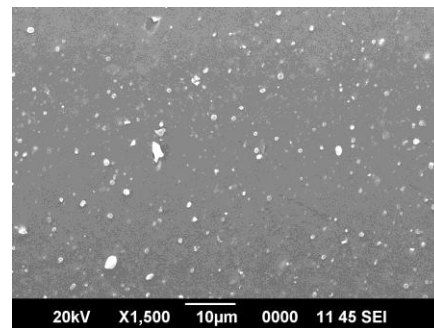


Fig:8

SEM of NBR C composite

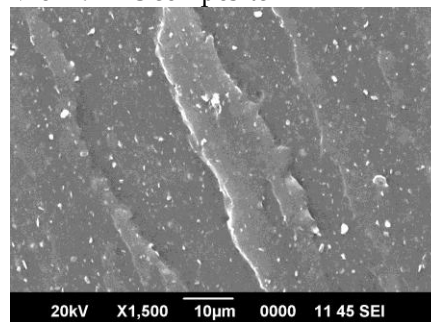


Fig:9

SEM of NBR V composite

3.6 STRAIN SWEEP STUDIES

Fig: 10 (a) and (b) shows the variation of complex modulus of the uncured NBR C and NBR V composite respectively with the strain amplitude. Strain sweep studies were conducted to study the rubber filler interaction. Complex modulus values decreased with the increase in strain. This is because formation of filler network contributes to the reinforcement in the properties of rubber. At high filler loading agglomeration of filler particles takes place leading to chain like filler structures or clusters which are termed filler networks. In kaolin composites besides the confinement of the polymer chains between

the there group CN trile

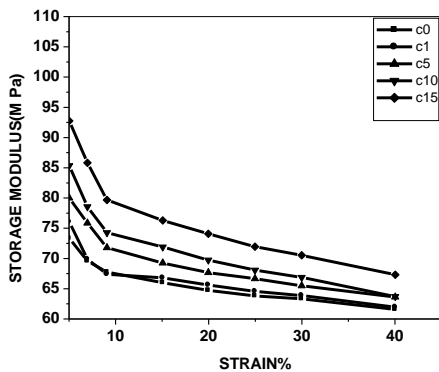
SAMPLE	Tg
NBR	-22.71
NBR C	-23.97
NBR V	-23.53

silicate layers is polar interaction between the OH of the clay and group of the ni-rubber. With the

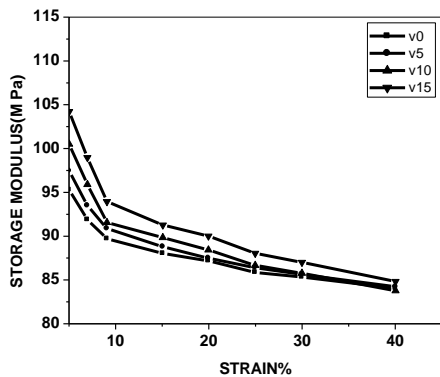
increase in strain, the filler networking is destructed leading to a reduction in complex modulus.

The complex modulus values at low strain increased with filler concentration. The enhancement of modulus with clay content is an indication of better filler-rubber interactions and hydrodynamic effect.

The increase in modulus is due to the inclusion of rigid filler particles in the soft rubber matrix. At low strain although both the clay rubber interaction and the compatibility between the clay and NBR are weak the filler -filler interaction is very strong due to filler aggregates



(a)



(b)

Fig:10 Variation of storage modulus with strain% of (a)NBR C composite and (b) NBR V composite.

3.7 DSC STUDIES:

DSC thermograms for NBR, NBR C and NBR V composites are shown in Fig: 11 and the corresponding Tgs are summarized in Table: 5. It is seen that the glass transition tempera-

tures of NBR and its composites are almost the same. So the mobility of the polymer chains are not affected by the clay layers

Table: 5
Tg of NBR and NBR clay composites

Name	T0	Tmax	Residue %	T5	T50
NBR	340.36	456	6.783	322.03	444.79
NBR 5c	341.44	456	6.45	319.15	448.63
NBR 15c	340.90	458	6.89	318.60	451.77
NBR 7v	339.12	456	12.98	304.64	448.18
NBR 15v	340.14	458	16.23	302.7	451.04

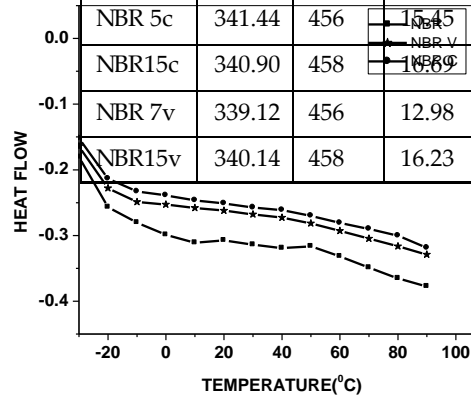


Fig: 11
DSC curves of NBR, NBR C and NBR V

3.7 Thermo gravimetric analysis

The thermal properties of the NBR Composites were studied by thermo gravimetric analysis. Table (6) shows the thermal degradation data for pure NBR and its composites.

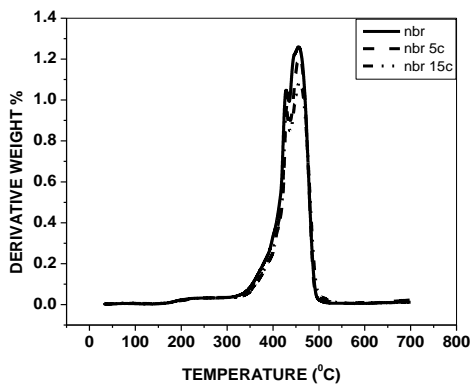
Table: 6
TGA results of NBR and NBR clay composites

At lower temperature there is no considerable change in the behavior of pure NBR and the composites. Onset of degrada-

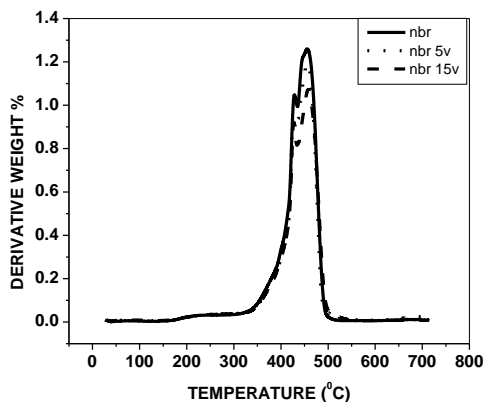
tion starts around 340°C for all the vulcanizates. Hence the samples may be considered thermally stable upto 340°C in nitrogen atmosphere.

The degradation temperature at 5% weight loss (T5) decreases with the addition of clay. NBR V composite shows greater reduction in T5 values than the unmodified clay. This shows the decomposition of vinyl chains cause faster degradation for the modified composites. Degradation temperature at 50% weight loss (T50) follows the same trend for NBR C and NBR V composites. Composites give higher value of T50 than that of pure NBR. This shows the thermal stability of NBR has improved by the presence of intercalated/exfoliated clay at temperatures above 400°C.

DTG curves are shown in Fig 17 (a&b). DTG curves show that the pyrolysis of NBR takes place in two steps. The curve exhibits a shoulder at 428°C followed by a main peak with a maximum at 456°C. The peak of the DTG curves shows the temperature corresponding to maximum degradation. The thermal degradation of rubber results in the scission of cross linking network and chain cleavage and a reduction in molecular weight



(a)



(b)

.Fig:12: DTG curves of (a) pure NBR and NBR C composite (b) pure NBR and NBR V composite

This reduces the mechanical strength and application value of rubber. It is generally believed that the inclusion of inorganic components into organic matter can improve the thermal stability. Maximum degradation temperature slightly increased from 456 to 458 in both the composites at 15 phr. So the composites have the same thermal stability. It is also observed that the amount of residue increases with the increase in clay content. The residual materials are mainly due to Zn salts and inorganic fillers.

4 CONCLUSIONS

Improvement in mechanical properties of the composites reveal that both unmodified and modified nanokaolin clay can be used as reinforcing filler in NBR. Modified clay is found to be a better reinforcing filler compared to unmodified clay.. The cure rate is increased with the addition of both clays..

The XRD characterisation of the composites show partial intercalation, but the increase in gallery gap may not be sufficient for the rubber molecules to have a strong interaction with the clay as observed from DSC analysis. The strain sweep studies shows better polymer filler interaction and SEM analysis shows a uniform dispersion of clay in the matrix. There is a small increase in the thermal stability of the system as observed from TGA.

REFERENCES

- [1] Masaya Kawasumi, Naoki Hasegawa, Makoto Kato, Arimitsu Usuki, and Akane Okada, "Preparation and Mechanical Properties of Polypropylene-Clay Hybrids", *Macromolecules*, 1997, 30 (20), pp 6333-6338
- [2] Jeong Hyun Parka, Hyung Min Leea, In-Joo China, Hyoung Jin Choia "Intercalated Polypropylene/Clay nanocomposite and its Physical Characteristics", *Journal of Physics and Chemistry of Solids* Volume 69, Issues 5-6, May-June 2008, Pages 1375-1378 14th International Symposium on Intercalation Compounds
- [3] Jian Li, Cixing Zhou, Gang Wang, Delu Zhao, "Study on Rheological Behavior of Polypropylene/Clay Nanocomposites" *Journal of Applied Polymer Science*, Vol. 89, 3609-3617 (2003)
- [4] Periyayya Uthirakumar, Min-Ki Song, Changwoon Nah, Youn Sik Lee "Preparation and Characterization of Exfoliated Polystyrene/Clay nanocomposites using a Cationic Radical Initiator-MMI Hybrid" *European Polymer Journal* Volume 41, Issue 2, February 2005, Pages 211-217
- [5] Qing-Xiu Jia, You-Ping Wub, Yi-Qing Wang, Ming Lu, Li-Qun Zhang, "Enhanced Interfacial Interaction of Rubber/Clay nanocomposites by a Novel Two-Step Method" *Composites Science and Technology* 68 (2008) 1050-1056
- [6] Wonho Kim, Byung-Suk kang, Seong-Gyuch, Chang-Sikha and Jong-

- Woo bae, "Styrene butadiene Rubber-Clay nanocomposites using a Latex Method Morphology and Mechanical Properties" Composite Interfaces, Vol. 14, No. 5-6, pp. 409-425 (2007)
- [7] Anirbanganguly, Madhuchhandamaiti and Anil K Bhowmick "Structure-Property Relationship of Specialty Elastomer-Clay nanocomposites Bull. Mater. Sci., Vol. 31, No. 3, June 2008, pp. 455-459
- [8] Renukappa, R.D, Sudhaker, S.J, "Studies on Physicomechanical and Electrical Properties of SBR-C black composites", Journal of Reinforced Plastics and Composites, August (2006) Vol25 no:11 1173
- [9] Yu-Rong Liang, Wei-Liang Cao, Xiao-Bin Zhang, Ying-Jie Tan, Shao-Jian He, Li-Qun Zhang", Preparation and Properties of Nanocomposites Based on Different Polarities of Nitrile-Butadiene Rubber with Clay", Journal of Applied Polymer Science, Vol. 112, 3087-3094 (2009).
- [10] Jin-tae Kim, Taeg-su Oh and Dong-ho Lee," Preparation and Characteristics of Nitrile Rubber (NBR) Nanocomposites Based on Organophilic Layered Clay," Polymer International Polym Int 52:1058-1063 (2003)
- [11] Jae Woo Chung, Seok Jong Han, Seung-Yeop Kwak, "Application of strain-time correspondence as a tool for structural analysis of acrylonitrile-butadiene copolymer nanocomposites with various organoclay loading," European Polymer Journal 45 (2009) 79-87
- [12] Seyed Javad Ahmadi, Christian G'Sell, Yudong Huang, Nanqi Ren, Ahmad Mohaddespour Jean-Marie Hiver, "Mechanical Properties of NBR/Clay nanocomposites by using a novel testing system" Composites Science and Technology 69 (2009) 2566-2572
- [13] Bluma G. Soares, Marlucy de Oliveira, Soraia Zaioncz, Ana C. O. Gomes, Adriana A. Silva, Kelly S. Santos, Raquel S. Mauler Nitrile Rubber/Organomontmorillonite Nanocomposites Produced by Solution and Melt Compounding: Effect of the Polarity of the Quaternary Ammonium Intercalants, Journal of Applied Polymer Science, Vol. 119, 505-514 (2011)
- [14] Meera Balachandran, Sriram Devanathan, R. Muraleekrishnan S.S. Bhagawan, "Optimizing Properties of Nanoclay Nitrile Rubber (NBR) Composites using Face Centred Central Composite Design Materials and Design xxx (2011) xxx-xxx
- [15] Lan Liu, Demin Jia, Yuanfang Luo, Baochun Guo, "Preparation, Structure and Properties of Nitrile-Butadiene Rubber-Organoclay Nanocomposites by Reactive Mixing Intercalation Method," Journal of Applied Polymer Science, Vol. 100, 1905-1913 (2006)
- [16] Rajesh Chowdhury", Electron-Beam-Induced Crosslinking of Natural Rubber/Acrylonitrile-Butadiene Rubber Latex Blends in the Presence of Ethoxylated Pentaerythritol Tetraacrylate Used as a Crosslinking Promoter," Journal of Applied Polymer Science, Vol. 103, 1206-1214 (2007)
- [17] Lan Liu, Yuanfang Luo, Demin Jia, Weiwen Fu and Baochun Guo "Structure and Properties of Natural Rubber Organoclay Nanocomposites Prepared by Grafting and Intercalating Method in Latex," Journal of Elastomers and Plastics, Vol. 38-April 2006
- [18] Rugmini sukumar, ARR Menon, "Organomodified Kaolin as a Reinforcing Filler for Natural Rubber", Journal of Applied Polymer Science, Vol 107, 3476-3483 (2008)
- [19] M. Sh. Zoromba and A. A. M. Belal, A. E. M. Ali F. M. Helaly, A. A. Abd El-Hakim, and A. S. Badran, "Preparation and Characterization of Some NR and SBR Formulations Containing Different Modified Kaolinite," Polymer-Plastics Technology and Engineering, 46: 529-535, 2007
- [20] A K Manna, D K Tripathy, P P De, S K De, M K Chatterjee, D G Peifer "Bonding between Epoxidized Natural Rubber and Clay in Presence of silane coupling agent," Journal of Applied Polymer Science vol 72, 1895-1903 (1999)
- [21] Qinfu Liu, Yude Zhang, Hongliang Xu, "Properties of Vulcanized Rubber Nanocomposites Filled with Nanokaolin and Precipitated Silica," Applied Clay Science 42 (2008) 232-237
- [22] A Shojaei and M. Faghihi, "Analysis of Structure-Properties Relationship in Nitrile-Butadiene Rubber/Phenolic Resin/Organoclay Ternary Nanocomposites Using Simple Model System, Polym. Adv Technol. 2010, 21 356-364
- [23] Mithun Bhattacharya, Anil K Bhowmick, "Correlation of Vulcanization and Viscoelastic Properties of Nanocomposites Based on Natural Rubber and Different Nanofillers, with Molecular and Supramolecular Structure," Rubber chemistry and technology Jan-March 2010 vol 83 No:1
- [24] Kader, M.A., Kim, K., Lee, Y.S., Nah, C., "Preparation and Properties of Nitrile rubber/Montmorillonite Nanocomposites via latex Blending", J Mater Sci (2006) 41:7341-7352
- [25] Dongcheol Choi, M. Abdul Kader, Baik-Hwan Cho, Yang-il Huh, Changwoon Nah, "Vulcanization Kinetics of Nitrile rubber/Layered Clay nanocomposites" Journal of Applied Polymer Science) Volume 98, Issue 4, pages 1688-1696, 15 November 2005
- [26] Amit Das, Rene' Jurk, Klaus Werner Stockelhuber, Papiya Sen Majumder, Thomas Engelhardt, Juliane Fritzsche, Manfred Kluppel and Gert Heinrich, "Processing and Properties of Nanocomposites Based on Layered Silicate and Carboxylated Nitrile Rubber" Journal of Macromolecular Science Part A: Pure and Applied Chemistry (2009) 46, 7-15
- [27] Susmitha Sadhu, Anil K Bhowmick, "Preparation and Properties of Nanocomposites based on Acrylonitrile-Butadiene Rubber, Styrene-Butadiene Rubber, and Polybutadiene Rubber" Journal of Polymer Science Part B: Polymer Physics, vol. 42, 1573-1585 (2004)

