Full Length Research Paper

Natural rubber/organoclay nanocomposites: Effect of filler dosage on the physicomechanical properties of vulcanizates

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Natural rubber/organoclay nanocomposites of varying filler loading [2 to 10 per hundred rubber (phr)] using derivative of tea (*Camellia sinensis*) seed oil were prepared by melt intercalation. Effects of filler dosage on the physicomechanical properties of the natural rubber (NR) vulcanizates were examined. Results of the mechanical properties indicates that tensile strength and tear properties of the modified organoclay/NR nanocomposites increases with increasing filler loading compared with the unmodified filled NR vulcanizates. Furthermore, rheological measurement showed that modified filled NR vulcanizate exhibited higher storage modulus (G') than the unmodified filled NR. The values of the weight-swelling ratio (Qt) of the modified filled nanocomposites decreased remarkably and are lower than the unmodified filled NR vulcanizate. The higher value of the chemical crosslink density of 0.629 at 6 phr for the organoclay/NR composite indicate better reinforcement of the filler-rubber matrix over the unmodified. The scanning electron microscopy revealed that incorporation of modified organoclay up to 6 phr has transformed the failure mechanism of the resulting NR vulcanizate compared to the unmodified. There is an indication that the optimum level of incorporation of sodium salt of tea seed oil is 6 phr.

Key words: Vulcanizate, physicomechanical, nanocomposite, *Camellia sinensis*, natural rubber, organoclay.

INTRODUCTION

The field of polymer-clay nanocomposites has experienced rapid growth in the past decades. This class of materials has assumed considerable importance and has been the focus of extensive investigation (Kojima et al., 1993; Gianelis, 1996; Biswas and Sinharay, 1998; Lagaly and Pinnavaia, 1999; Gianelis et al., 1999; Hasegawa et al., 2000; Pinnavaia and Beall, 2000; Pramanik et al., 2001; Kim et al., 2001; Mannias et al., 2001; Ray and Bhowmick, 2002). They are materials that consist of two or more materials with one having a dimension in the nanometer range that is, one billionth of a meter. They are material which is an embodiment of

et al., 2004; Nagi et al., 2008). In polymer nanocomposites, a few weight percent of each silicate layer of clay mineral is randomly homogenously dispersed on a molecular level in the polymer matrix. Following molding, the mechanical, thermal and barrier properties of the resulting material is superior to the virgin polymer (Usuki et al., 2002; Sinham Ray et al., 2003; Utra, 2004; Zheng et al., 2004; Zanetti and Costa, 2004; Okada and Usuki, 2006).

Clay has been used as filler for natural rubber over the years, however the reinforcing property is poor and this is largely due to the large particle size and low surface activity. In recent times, improving the reinforcing ability of clay is by altering the hydrophilic nature of clay to organophillic. This is achieved by ion exchange of the clay interlayer cations such as alkyl ammonium or

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Table 1. Recipe of the organoclay filled and unmodified filled NR nanocomposite.

Ingredients (phr)	NR/2, 4, 6, 8, 10 UTK	NR/2, 4, 6, 8, 10 MTK
Natural Rubber	100	100
Zinc Oxide	5	5
Stearic acid	2	2
Unmodified	2,4,6,8,10	-
Kaolin(UTK)	-	2,4,6,8,10
TSO-Na Modified	2	2
Kaolin(MTK)	2	2
MBT	2	2
Sulphur		

alkylphosphonium (Sharif et al., 2005). This concept of clay-based nanocomposite was first introduced by researchers from Toyota (Okada et al., 1990) who discovered the possibility of building a nanocomposite from polyamide 6 and organophillic clay. There was an expansion of the work to include various polymers such as polypropylene (Hasegawa et al., 1998., Saujarya et al., 2001), polyurethane (Wang and Pinnavaia, 1998), polyethylene terepthalate (Ke et al., 1997), silicon rubber (Burnside and Gianelis, 1995; Wang et al., 1998), poly (methyl methacrylate) Okomota et al., 2001), ethyl vinyl acetate (Zanetti et al., 2001) and many more.

It was observed in a recent report that the clay-based polymer nanocomposites prepared from china clay-based nanoclay offers better mechanical and barrier property than the often used clay, montmorillonite (Lagaron et al., 2005). Montmorillonite clay (bentonites) has been studied extensively as ideal mineral for organomodified fillers. This material is limited is supply and thus becoming expensive. However, china clay, kaolin is much in abundance and can be harnessed in this respect. Reinforcement of polymer is achieved at very low loading of filler, typically < 10 weight percent when compared to the 30 to 70 wt% filler in convectional polymer composites (Frost et al., 1999). Nanofillers may be used to substitute traditional fillers in polymeric composite as a result of their high aspect ratio (length/ diameter) and low density. In the present study, we varied the dosage of the organomodified filler in the preparation of natural rubber/organoclay nanocomposite. The main objective of this study is to investigate the effect of filler loading on the physicomechanical properties of the natural rubber vulcanizates.

MATERIALS AND METHODS

Materials

Tea seed oil (TSO) was obtained from the Mambilla substation of the Cocoa Research Institute of Nigeria. Kaolin, grade BCK was obtained from M/s English, India clays Ltd, Veli, Thiruvananthapuram, Kerala, India. Natural rubber was of the Indian standard ribbed smoke sheet (grade RSSV); sodium hydroxide (LR Fischer), hydrazine hydrate (Aldrich), zinc oxide, stearic acid, sulphur and mercaptobenzothiazole (MBT) were obtained from the open market.

Preparation of TSO-Na modified kaolin

Sodium salt of tea seed oil (TSO-Na) was synthesized by reacting 28 ml of TSO with approximately 27.5 ml of 20% NaOH in an ice bath with constant agitation for 24 h. The pH of the resulting solution was maintained at 8 - 9. TSO-Na was then introduced into a separating funnel and washed with water to remove excess base. This was then oven-dried to remove residual moisture and powdered. 2 g of TSO-Na was treated with 9.8 g kaolin, 7 ml of hydrazine and 5 ml water under vigorous agitation at 20°C. The mixture was homogenized using an ultra Schallprozessor (HIELSCHER, GMbH, UP 100 H) and the sample was dried using a freeze drier (HetroTrap-CT600e, JOUAN). The sample was powdered and labeled.

Characterization of Unmodified and TSO-Na modified kaolin

FTIR

The IR spectroscopy of both the modified and unmodified samples was determined using the Fourier Transform Infra red spectrometer (MAGNA, 560, NICOLET). In a typical experiment, about 10 mg of sample was thoroughly mixed with finely ground KBr and made into pellet to obtain a transparent disc.

XRD

The X-ray diffraction of the samples was determined using a Philips -1710 X-ray diffractometer using monochromatic Ni-filtered Cu K alpha radiation 1.5418 Å at 40 Kv and 20 mA. All the readings were taken at room temperatures. The d-spacing was calculated using Braggs equation, $n\lambda = 2d \sin \theta$, where λ is the wavelength of the 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.

Preparation of natural rubber organo-kaolin mixes

Natural rubber-organokaolin mixes of the samples were mixed according to the recipe (Table 1) on a two roll open mill for 5 to 10 min and the homogenized mixes were sheeted out.

Preparation of natural rubber vulcanizates

Vulcanizate sheets of dimension 90 mm × 90 mm ×1.5 mm were prepared by compression molding of the mixes at 140°C for 10 min on an electrically heated, semi-automatic laboratory press (model PF-A15) at 3 torr pressure.

Measurement of tensile and tear properties

Dumb-bell shaped and crescent shaped samples were cut out of the molded sheet for tensile and tear strengths measurements, respectively. The vulcanizates were measured according to

Table 2. Fatty acid profile of tea seed oil.

Fatty acids	Value (%)
Palmitic	21.8
Stearic	03.79
Oleic	60.08
Linoleic	13.01
Linolenic	02.20
Others	01.07

standard ASTM D624-86 using a universal testing machine (Hounsfield H5 KS).

Rheology of mixes

The rheology of the mixes was studied on a Paar Physical rheometer (MCR 150) at 120 °C over a range of angular frequencies.

Chemical crosslink density

The chemical crosslink density, CLD of the vulcanizates was determined following the procedure of equilibrium swelling in toluene. The volume fraction of rubber, Vr was calculated from the swollen and deswollen weights. The CLD expressed as $(2MCchem)^{-1}$ was calculated using the Flory-Rehner equation given as

$$- (\rho V_o)/M_c = [(ln\ (1-V_r)\ +V_r+\xi V^2{}_r)/\ (V^{1/3}{}_r-V_r/2]-2\rho V_o/M_n \quad (1)$$

Where, ρ is the density of the vulcanizate, V_o is the molar volume of

the solvent, M_c is the molecular weights between crosslink, V_r is the volume fraction of rubber in the swollen sample given as

$$V_r = [(D-FT)\ \rho^{-1}]/\ [(D-FT)\ \rho^{-1}{}_r+A_o\rho^{-1}{}_s] \quad (2)$$

D is the deswollen weight of the vulcanizate, F is the weight fraction of insoluble components of the vulcanizate, T is the initial weight of test specimens, ρ_r is the density of rubber, A_o is the weight of solvent absorbed under equilibrium condition and ρ_s is the density of the solvent, ξ is the polymer-solvent interaction parameter given as ξ =0.44 + 0.18V_r and M_n is the number average molecular weight of natural rubber.

Swelling behaviour

The samples of 20 mm × 20 mm × 2 mm were used to determine the swelling behavior of the vulcanizates according to ISO-1817-198. The initial weight of the samples was taken and then introduced into toluene. These were removed periodically from the bottles, the adhering solvent was cleaned from the surface and then the sample weighed immediately and then placed into the toluene again. The weight-swelling ratio, Qt was determined from the weight of the sample in the unswollen and swollen states. Qt was thus calculated using the equation

$$Q_t = \Delta M/M_n=M_t-M_o/M_o\times100 \quad (3)$$

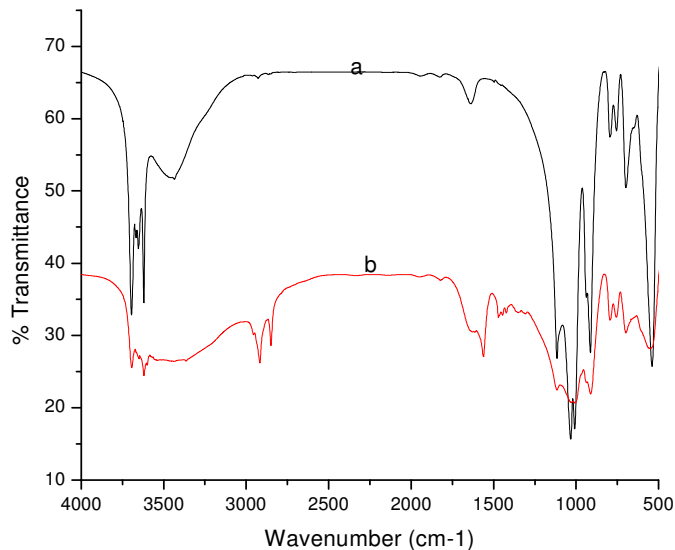Where Q_t is the weight-swelling ratio, M_t is the weight of the sample

Figure 1. FTIR Spectrum of unmodified (a) and modified (b) Kaolin.

in the swollen states and M_o the initial weights of the samples.

Scanning electron microscopy

The fracture surface of the vulcanizates was studied with JEOL 5600 LV scanning electron microscope. The fracture surface was coated with gold to prevent electrostatics charging during examination.

RESULTS AND DISCUSSION

Characterization of tea seed oil

Table 2 shows the fatty acid profile of tea seed oil. From the table, it can be seen that tea seed oil possesses long hydrocarbon chain, C18 which is a requirement for its use as an organomodifier.

Characterization of organoclay

FTIR

The FTIR spectra of the unmodified kaolin and TSO-Na modified kaolin is shown in Figure 1 in which transmittance is plotted against wave number. The spectrum of unmodified clay shows a band at 3620 cm^{-1} which is characteristics of the inner hydroxyls of the clay (Jonhson and Stone, 1990; Frost et al., 1999). This increase is as a result of the rupture of the hydrogen bonds between the kaolinite layers and the formation of new hydrogen bonds involving the inner surface hydroxyl group in the inserting molecule, a process called intercalation. Hence, the occurrence of peaks at 2920 and 2854 cm^{-1} suggests the presence of grafted organic
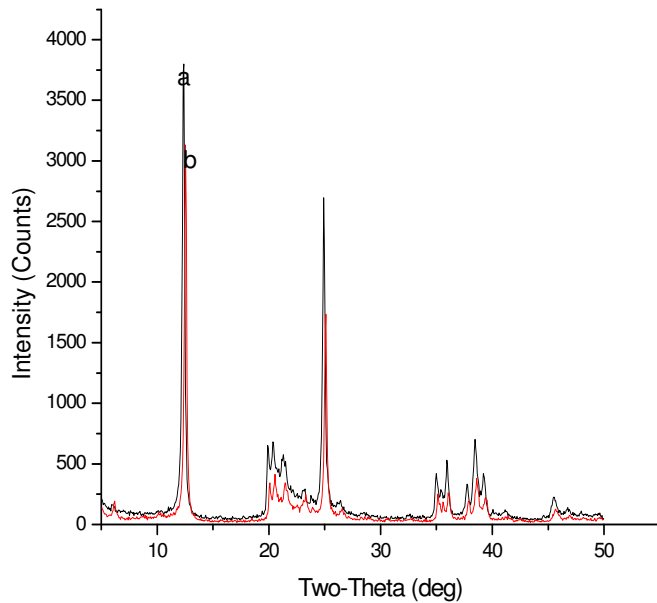
Figure 2. XRD Spectrum of unmodified (a) and modified (b) Kaolin.

Figure 3. Effect of organoclay loading on tensile strength of NR/organoclay nanocomposites.

moiety onto the clay surface (Dai and Huang, 1999).

X-ray diffraction

The XRD patterns of the pristine kaolin and modified kaolin is depicted in Figure 2. The interlayer distance was determined from the diffraction peak position in the XRD, using the Braggs equation. From the spectrum, it is evident that kaolin show a d-spacing of 7.15 Å, however in the modified clay, there is an additional peak corresponding to 14.3 Å found in the spectrum (Figure 2). This appreciable increase in the intergallery spacing is higher than some reported organoclays (Arroyo et al., 2003; Varghase et al., 2004; Wu et al., 2005). In the course of compounding the NR, there was the penetration of the chain in between the silicate layers. However, the penetration would not result in the disruption of the clay tactoids. Hence, the organomodified kaolin was predominantly intercalated by the NR as a result of the additional peak.

Mechanical properties of NR/organoclay nanocomposites

The effect of organoclay loading on the tensile and tear properties of the NR/organoclay nanocomposites was shown in Figures 3 and 4, respectively. Figure 3 shows that there was a remarkable increase in tensile strength of about 68% of the NR/orgnoclay nanocomposite with increasing filler loading. These increases were higher for the modified filled vulcanizates (MTK) than for the
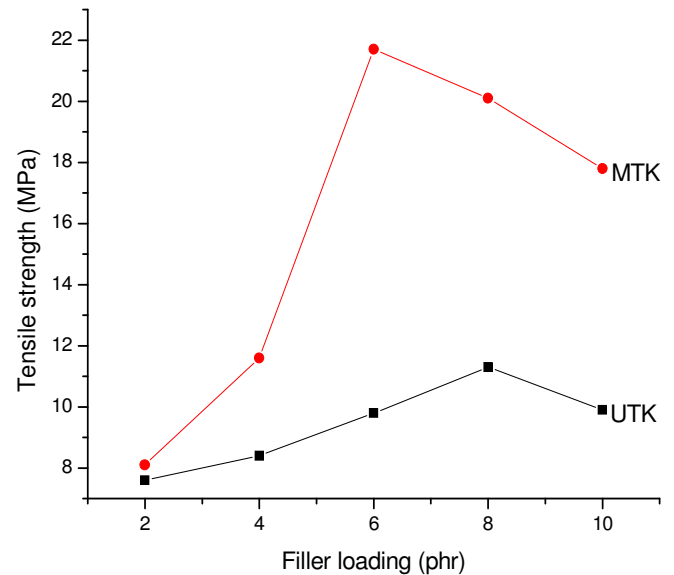
unmodified filled vulcanizates (UTK). The improvement of mechanical properties of polymer-clay nanocomposites such as tensile and tear strength are presented by some researchers (Shi et al., 1996; Shia et al., 1998). Some explanations are presented on the basis of interfacial properties and restriction of polymer chain movement. For example, it has been observed (Usuki et al., 1995) that strong ionic interaction between polymer and silicate layers, which generate some crystallinity at the interface, is responsible for the effect of reinforcement. Previous workers (Ash et al., 2002) investigated the incorporation of 5% alumina particles into a polymethylmethacrylate (PMMA) matrix and observed an increased average value of strain to stress failure of up to 600%. Ideally, for conventional composites, tensile strength increase with increasing filler loading until a maximum point is reached; whereby the filler particle are no longer adequately separated or wetted by the polymer phase.

In the present investigation, maximum value of tensile strength was achieved at 6 phr after which a fall was observed. The reduction in tensile strength after 6 phr for the modified filled vulcanizates and 8 phr for the unmodified filled NR nanocomposites may be attributed to the filler particle or the result of physical contact between agglomerates (Ishak and Bakar, 1995). Since, there is high amount agglomerate in high filler dosage composites; these agglomerates played the role of an obstacle to molecular chain movement of the NR, thereby initiating failure under stress. The tear properties for the organomodified vulcanizates also showed higher values than the unmodified filled nanocomposites and these increases linearly as a function of organoclay loading. It is interesting to note that tear strength of MTK reached
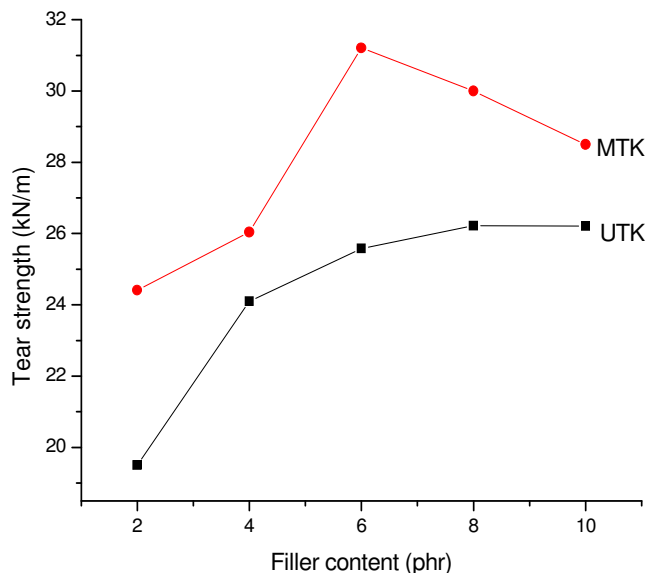
Figure 4. Effect of organoclay loading on tear strength of NR/organoclay nanocomposites.
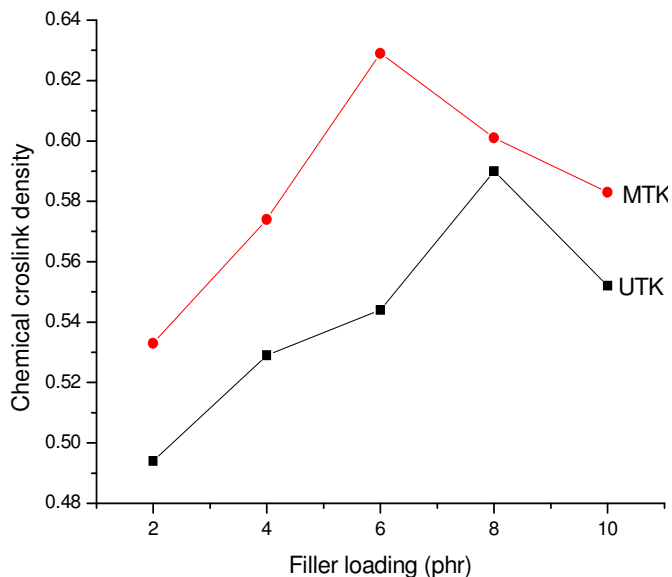

Figure 6. Effect of organoclay loading on the chemical crosslink density of NR/organoclay nanocomposites.
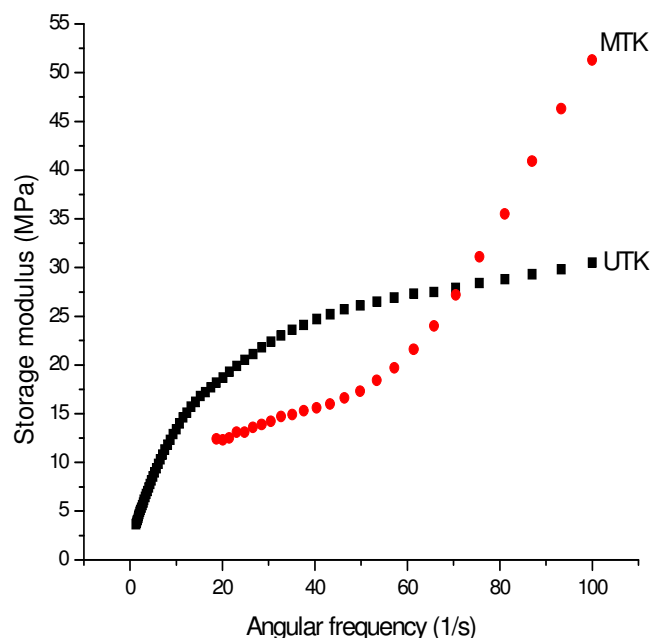

Figure 5. Storage modulus as a function of Angular frequency for organoclay filled NR (MTK-8) and unmodified filled NR (UTK) vulcanizates.

organoclay and NR. This is similar to the results reported for epoxidized NR nanocomposites containing mont-morillonite modified with octadecyltrmethylammonium (Teh et al., 2006).

Rheological properties

Figure 5 depicts the storage modulus of the NR/organoclay nanocomposite at 8 phr dosage. It is evident from the rheograph that storage modulus which is a measure of the stiffness of the polymer for MTK is higher than UTK. This likely reflects the interfacial interaction between the intercalated/exfoliated silicate layers and the polymer matrix. According to Li et al. (2003), the interfacial adhesion between the clay tactoids and the polymer matrix is remarkably improved due to the formation of partially intercalated structures.

Chemical crosslink density

Chemical crosslinking density is defined as mole of effective network chain per cubic centimeter. In the present study the value of the chemical crosslink of the organoclay filled NR compared with the unmodified filled NR is shown in Figure 6. The figure indicates that there was effective crosslinking of the filler with NR during vulcanization and this increases with increasing organoclay dosage until a maximum of 0.605 was obtained for UTK at 8 phr and 0.629 for MTK at 6 phr. This further corroborates the fact that there is better filler-rubber interaction for modified sample than the unmodified. This
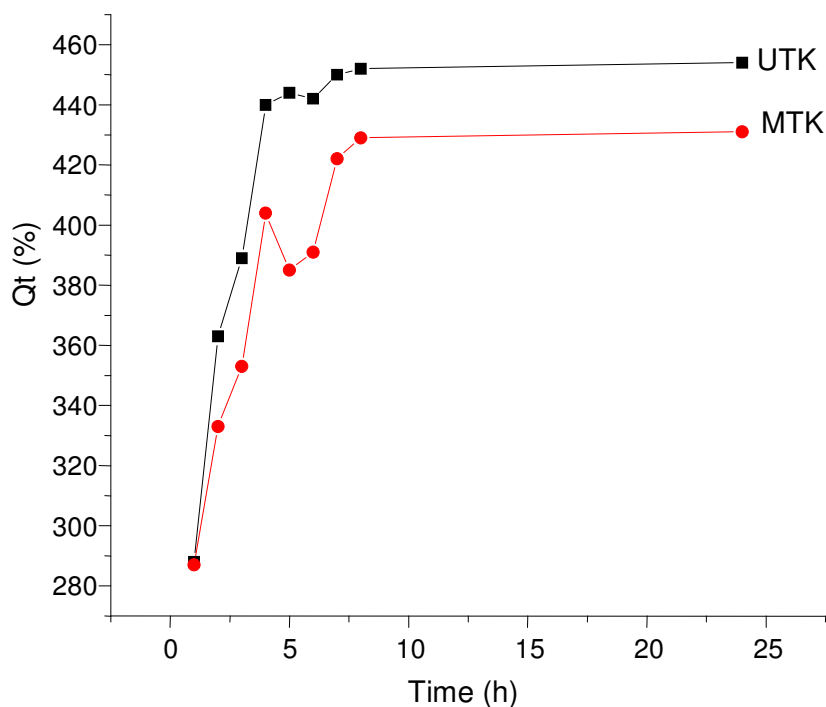
optimal value of about 32 kN/m at 6 phr. The observed improved tear strength of the organomodified sample is directly related to the intercalation process of the organomodified filled NR vulcanizates. In order words, the better reinforcement efficiency of the organoclay may be attributed to the strong interaction between the

Figure 7. Swelling index as a function of time for organoclay filled NR/MTK-8 and NR/UTK-8 vulcanizates.

also explains and support the data obtained for the mechanical properties of the organomodified NR nanocomposites.

Swelling behaviour of NR/organoclay nanocomposite

The sorption behaviour curve of nanocomposite filled with 8 phr modified organoclay and unmodified clay versus time obtained by plotting Q_t (the weight-swelling ratio) in toluene at room temperature were shown in Figure 7. It is evident that the rate of solvent uptake decreased with the incorporation of the organoclay. This trend can be attributed to the presence of the nanodispersed impermeable clay layers, which decreased the rate of transportation by increasing the average diffusion path length in the NR matrix (Peiyao et al., 2008). The organomodified vulcanizates evidently posses silicate that are uniformly dispersed in the NR; this is in contrast to the unmodified filled NR which has poor dispersion of the clay layers, hence their increased solvent uptake.

Scanning electron microscopy

Figures 8(a to d) shows the SEM micrographs of the tensile failure surfaces of the unmodified clay NR vulcanizate and modified filled NR nanocomposites. Even though there appeared to be no significant difference in

the morphology between MTK and UTK, it can be observed that the tensile fracture surface of modified filled composites exhibits rougher fracture surface consisting of tear paths compared with the unmodified composites. The observable tear lines are believed to be arrested or deviated by the organoclay particles as a result of enhanced organoclay/NR interaction (Ardhyanata et al., 2006). Similar results has been reported for NR/organoclay nanocomposites using various organomodifier (Hasegawa et al., 2000; Pramanik et al., 2001; The et al., 2004; Lagaron et al., 2005; Peiyao et al., 2008). There is however agglomeration of the organoclay at 10 phr due to poor dispersion. This also explains why there occurred a reduction in the mechanical properties after 6 phr organoclay loading.

Conclusions

The effect of filler dosage on the physicomechanical properties of tea seed oil organomodified kaolin/NR nanocomposites was examined. The following conclusions can be drawn: There was remarkable enhancement in the tensile and tear properties of the NR vulcanizates with increasing filler loading. This can be attributed to the strong rubber-filler interaction. Further, evidence of the interaction was obtained from the swelling behavior, which decreased as filler loading increases and the chemical crosslink density of the
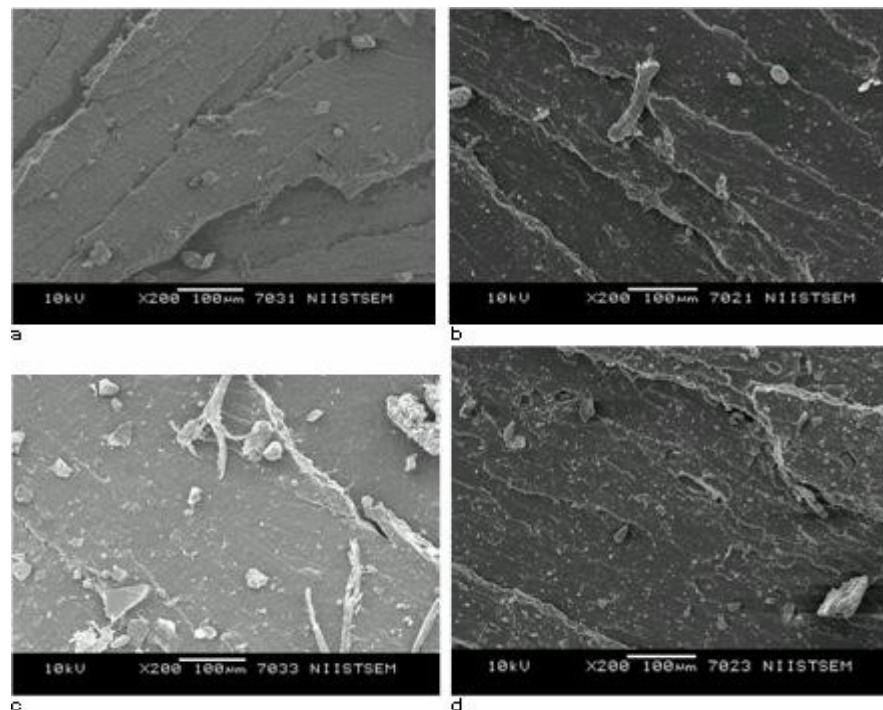
Figure 8. Tensile fracture surface of NR nanocomposites: (a) unmodified clay/NR at 6 phr (b) modified clay/NR at 6 phr (c) unmodified clay/NR at 10 phr (d) modified clay/NR at 10 phr.

nanocomposites increases with increasing dosage until an optimum of 6 phr was attained. Evidence from SEM indicates that the failure mechanism is strongly dependent on the reinforcement effect on the modified filler marked by a higher extent of filler-rubber matrix interaction.

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