The Role of Surfactant Type and Modifier Concentration in Tailoring the Properties of Chlorobutyl Rubber/Organo Clay Nanocomposites

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ABSTRACT: Nanocomposites were prepared using montmorillonite with different organic modifiers (cloisite 10 A, cloisite 15 A, and cloisite 20 A) and the effect of intercalant structure on clay morphology and chlorobutyl vulcanization kinetics was investigated. Because of its lower rigid structure the aliphatic salt was easier to intercalate into the clay galleries giving rise to a higher interlayer distance and facilitating the rubber intercalation obtaining an exfoliated structure in the nanocomposite. The vulcanization process was sensibly accelerated by this organoclay and a higher crosslinking degree was observed in the nanocomposite which gave rise to materials with improved processing and physical characteristics. The present work focuses on characterising the surfaces of organically modified MMT clays and the relationship to the final properties of their nanocomposites. Concentrating on the surface modifiers, one has to take into account their interaction with the matrix polymer, the solubility of the organic molecule adding to the complexity due to its influence. We aim to show that understanding the influence of surface characteristics is the basis for selecting the ideal organoclay for the given matrix polymer. Depending on the nature of the surfactant used for the organic modification of clay and its modifier concentration the nanocomposites exhibit difference in the properties. The organoclays used in the present study were selected to explore the effects of the amine surfactant structure on the dispersion of clay particles in chlorobutyl rubber matrix. The structure of the organic amine compound used to form the organoclay is expected to have some effect on the morphology and properties of the nanocomposites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4590–4597, 2012

Key words: nanocomposites; gas permeation; TEM; organoclay; surfactants

INTRODUCTION

At present nanocomposites based on polymer matrices and organo-layered silicates represent an interesting opportunity for the design of high characteristic materials mainly from the mechanical properties and thermal stability points of view.[1] While clay nanocomposites have been investigated in combination with many thermoplastics and thermosetting polymers, much less attention has been paid to the elastomers as matrices.[2–5] Besides increased modulus and strength, other factors such as tear properties, fracture toughness, and abrasion resistance are claimed to be improved as a result of clay addition to rubber.[6–8] Polymer–clay nanocomposites can be prepared by several methods,[9] such as *in situ* polymerization or intercalation via solution, while in the case of rubber nanocomposites also intercalation of rubber via latex compounding can be used.[10] Besides changing the properties of vulcanized rubber compositions resulting from the presence of nanoparticles, the nanofillers affect also the chemistry of vulcanization process.[11] A substantial reduction of optimum vulcanization time was observed in the presence of organoclay.[12] The effect is explained by the presence of amino groups which act as accelerator of the curing process. The incorporation of organoclay into rubber leads to a slight increase in glass transition temperature, obviously resulting from a restricted motion of the rubber chains on the intergallery space. Similar reasoning may be used to explain certain increase in temperature of thermal decomposition, although this effect may not be a consequence of higher thermal stability of the material decomposing at higher temperature but just due to a prevention of diffusion of volatile remnants immobilized between galleries.[12,13] Properties of rubber/organoclay nanocomposites were investigated for a number of rubber matrices, e.g. natural rubber (NR),[12,13] EPDM,[14,15] SBR,[16] nitrile rubber,[16] silicon rubber[16] or polybutadiene rubber.[17] An increase in

tensile strength was usually observed as expected; in most cases the increase was substantial. However, surprisingly also elongation values rose, e.g. for EPDM with organoclay.[14] Important improvement was reported regarding an increase in tear strength originated from an increased resistance to crack growth.[14,18] Similar to thermoplastic matrices, a decrease in gas permeability[14,18] and increased solvent resistance[19] was reported also for rubber nanoclay composites. The introduction of organic ions into the interlayer spacing not only render more organophylic phyllosilicates but also results in a larger interlayer spacing depending on functionality, packing density and length of organic molecule.[20] The modified clay has a greater d spacing than unmodified clay which allows the penetration of the polymer into the gallery spaces thereby providing intercalated nanocomposites. Thus the effect of amine modifiers in producing intercalated structures form an important part of the study. Moreover we have investigated the kinetics of vulcanization of chlorobutyl rubber nanocomposites which clearly shows that with the increase in clay loading the vulcanization process is accelerated. This is clearly substantiated from the calculated activation energies.

Materials

The chlorobutyl rubber (CBK 150) Mooney viscosity [ML(1+8)@125°C] 45, with Chlorine content 1.2 used in this study is from Nizhnekamsk, Russia. The layered silicates used were, Closite 15 A (Organic modifier used are dimethyl, dehydrogenated tallow, and quarternary ammonium)with a density 1.66 g/cc and modifier concentration 125 meq/100 g clay, Cloisite 20 A (Organic modifier used are dimethyl, dehydrogenated tallow, and quarternary ammonium) with a density 1.77 and modifier concentration 95 meq/100 g clay and Cloisite 10 A (Organic modifier used are methyl, benzyl, dehydrogenated tallow and quarternary ammonium was) with a density 1.9 and modifier concentration 125 meq/100 g clay were obtained from Southern Clay products, USA. Solvents used in this study were supplied by Merck limited, Mumbai.

Preparation of chlorobutyl rubber nanocomposites

Five grams of the layered silicate was swollen in cyclohexane and kept aside for 24 h. Twenty grams of chlorobutyl rubber was also swollen separately in the same solvent. The two solutions were mixed with vigorous stirring for 12 h. The nanocomposites so obtained were cast on a petri dish at room temperature to get a thin film. The solvent was allowed to evaporate at room temperature and dried in a vacuum oven at 60°C till there was no weight variation. The film so casted was mixed with the remaining quantity of CIIR on a two roll mill of 170 mm diameter, working distance 300 mm, speed of slow roll 18 rpm, and gear ratio 1 : 4 by careful control of temperature, nip gap, and time of mixing. After complete mixing the stock was passed six times through tight nip and finally sheeted out at a fixed nip gap. The CIIR composites were left for a day before vulcanization in the normal air.

Cure characterization and curing

The cure characteristics of the stocks were measured using an elastograph, "Vario" 67.98 (Gottfert; Germany) at 150°C according to ASTM 2240-93. Blanks were cut from unvulcanized sheets marked with the machine direction. Sheets of ~ 2 mm thickness were vulcanized in hot press at 150°C and 10 MPa pressure for the respective cure times, t_{90} derived from the MDR 2000 tests. Dumbbell shaped samples were cut using a die for tensile test as per ASTM specifications.

Mechanical properties

Dumbbell-shaped tensile specimens were punched out from the vulcanized sheets and the mechanical properties were studied using a Universal Testing Machine (Instron 4411; England) with a load cell of 10 kN capacity, as per ASTM D 412-68. The gauge length at the start of each test was adjusted to 30 mm and the measurements were carried out at a cross-head speed of 500 mm/min. An average of at least six sample measurements was taken to represent each data point.

Thermal studies

Thermal analysis of the layered silicate nanocomposites was performed on a TA instrument, SDT 2960 at a heating rate of 10°C/min under nitrogen atmosphere over a temperature range from room temperature to 550°C.

RESULTS AND DISCUSSION

Cure kinetics

The cure time of the nanocomposites containing all the different clays was found at different temperatures and the maximum and minimum torque values were tabulated.

According to first order kinetics

$$\ln(a - x) = -Kt + \ln a$$

The torque values obtained are proportional to the modulus of rubber

$$a - x = M_H - M_t$$
$$a = M_H - M_L$$

where M_H is the maximum torque, M_L is the minimum torque, and M_t is the torque at time t.
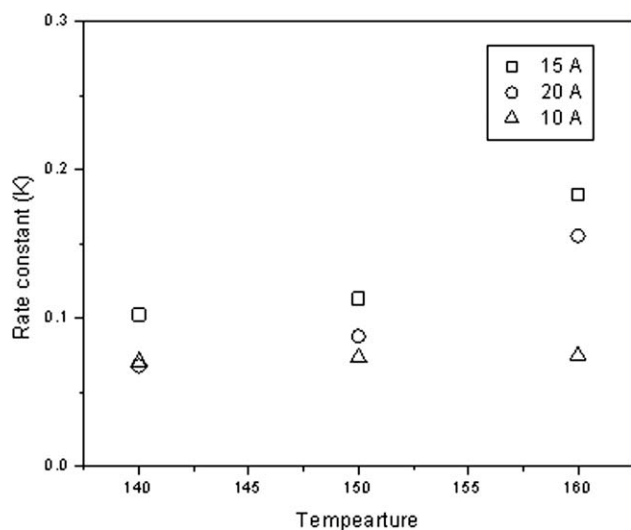
Figure 1 Plots of rate constant vs. temperature of chlorobutyl rubber nanocomposites containing various clays.

$\ln M_H - M_t$ when plotted against time a straight line is obtained whose slope gives the value of K, the rate constant at a particular temperature T. Arrhenius equation is used to calculate the activation energy of the mixes. Since t_{90} is a measure of the cure rate, it is taken as a measure of the rate of cure reaction.

$$1/t_{90} = A e^{-E/RT}$$

$$\log t_{90} = \log A - E/2.303\, RT$$

A plot of log t_{90} vs. $1000/T$ gives a straight line and from the slope of this curve, the activation energy can be calculated.

To show the accelerating effect of the aliphatic group of the organic surfactant the nanocomposites prepared using different clays were subjected to a cure kinetic study. The cure kinetics followed a first order reaction. The rate constant K was obtained at different temperatures and the value of K is found to be increasing with increase in temperature for all the nanocomposites. Figure 1 shows the variation of the rate constant of the nanocomposites containing different clays at different temperatures. From the graph it is evident that cloisite 15 A and 20 A containing aliphatic modifiers are more effective in the acceleration of the cure rate of chlorobutyl rubber nanocomposites. This is further indicated from Figure 2 which shows the variation of torque with time during the curing of the nanocomposite. Aliphatic MMT show a maximum value of torque as indicated in Figure 2. This shows that a higher crosslinking degree is obtained with aliphatic MMT clays. So these clays are better dispersed in the polymer matrix and a higher torque is necessary for this composite to flow. Thus aliphatic MMT behaves as a

catalyst for the vulcanization of CIIR. Increase in the value of K indicates the fastness of a reaction. When $\ln K$ is plotted against $1/T$, the activation energy for chlorobutyl rubber vulcanization is found. As the clay loading increases the value of activation energy decreases as shown in Figure 3 for nanocomposites containing cloisite 15 A. This shows that the aliphatic MMT clay is acting as a catalyst towards the vulcanization of CIIR.

Characterisation by XRD and TEM

In the case of cloisite 10 A only a small peak is observed at 2θ value 2.5 which shows that the clay layers are in a state of exfoliation than intercalation whereas in the case of cloisite 20 A, a slightly higher peak is observed around 2θ value 2 which suggests intercalation of polymer into the clay layers. A higher amount of intercalation is observed in the case of 15 A because of the increased d spacing of the cloisite 15 A. Moreover the peak is appearing at a much lower 2θ value when compared with the 2θ value of the pristine cloisite 15 A. In this case, the most significant compatibilizing effect was found for the clay modified with tallow only, i.e., C15A and C20A. XRD patterns in Figure 4 indicate a lower degree of exfoliation of clays with less polar treatment (C15A and C20A) in the CIIR matrix, which tends to decrease the strength and stiffness of corresponding nanocomposite. Best exfoliation is obtained with organoclays based on one long alkyl tail apparently owing to the affinity of the polymer for the silicate surface. Thus organoclays based on one long tail alkyl group (cloisite 10 A) provide more access to the silicate surface of the clay than two or more
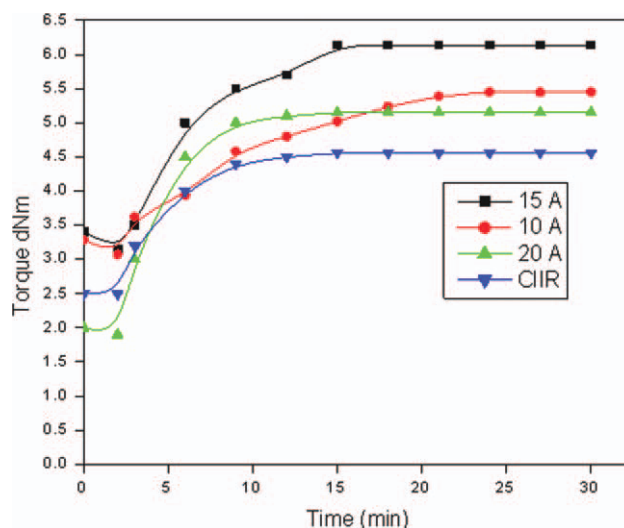

Figure 2 The effect of torque against time of the different clays. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
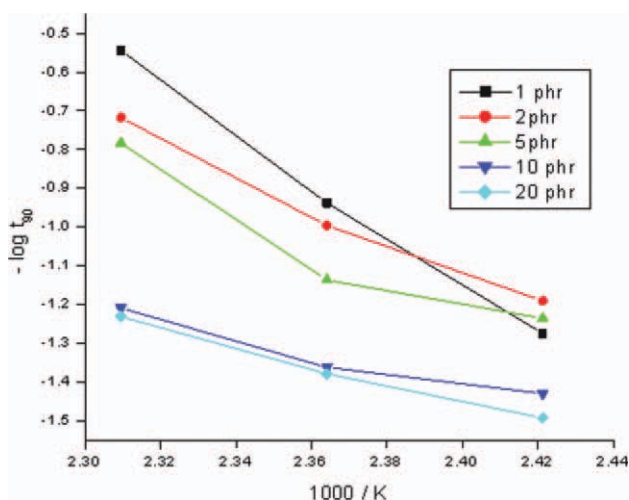
Figure 3 Activation energy plots for the nanocomposites containing cloisite 15 A. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

alkyl tails (Cloisite 15A and 20 A). XRD of 20 A composites shows greater *d* spacing than 15 A composites. This is because the excess amount of surfactant in 15 A could remain unbound in the silicate layers which in their initial state increases the gallery spacing of clays. During shear mixing this excess unbound surfactant could diffuse from the galleries thereby decreasing the d spacing. This combined with the simultaneous intercalation of the polymer molecules could have led to the decrease of d spacing in 15 A when compared with 20 A. similar XRD observations have been reported by Lakshminarayan et al.[21] in the case of fluoroelastomer and Ranade[22] et al. in the case of PETG nanocomposites containing cloisite 15 A and 20 A. Neverthless 15 A composites have better reinforcement than 20 A nanocomposites. The justification provided was that 15 A nanocomposites were highly oriented compared with 20 A resulting in more platelet- platelet interaction thereby strengthening the composite. As a result, the clay with the best compatibilizing effect does not lead to the best balance of mechanical behavior. Similar results have been reported by Kelnar et al.[23] Transmission electron micrographs (TEM) of the samples were taken in a LEO 912 Omega transmission electron microscope with an acceleration voltage of 120 k V. The specimens were prepared using an Ultracut E cryomicrotome. The TEM of the nanocomposites as shown in Figure 5 also support the above argument.

Evaluation of cure kinetics

Effects of physical structure of clay on the mechanical properties of nanocomposites

Keeping the clay same but on changing the concentration of modifier different properties have been observed for the rubber clay nanocomposite system.

When cloisite 15 A and 20 A are compared both have the same organic modifier but the modifier concentration is higher in the case of 15 A. As modifier concentration increases more will be the incorporation of amine and more will be the organophilicity of clay. So the polymer chain incorporation will be higher or most facilitated when modifier concentration is high. More the organophilicity of clay better will be the polymer filler interaction, which leads to better strength of the nanocomposites. This is reflected from the mechanical property analysis of the nanocomposites in which higher mechanical strength is exhibited by cloisite 15 A when compared with 20 A though both have the same modifier as shown in Figure 6. The reason for the enhanced mechanical property of cloisite 15 A when compared with cloisite 20 A can be attributed to the following reason. As modifier concentration increases in 15 A, the organophilicity of clay increases. So the polymer chain incorporation will be higher or most facilitated when the modifier concentration is high. More the organophilicity of clay better the polymer filler interaction which in turn leads to better strength of the nanocomposite. Keeping the clay same but changing the nature of the surfactant (10 A/15 A, 20 A) is found to affect drastically the properties of the rubber clay nanocomposite system. During intercalation of the clay with different amines the number of reacting sites in a definite amount of clay will be a constant (5 phr). So the number of amine groups reacting will be a constant. As the molecular weight increases from 15 A to 10 A the amount of clay in the nanofiller (5 phr) would be lower for 10 A than 15 A. The amount of modified clay taken is constant for all the amine modifiers (5 phr). So the number of clay particles
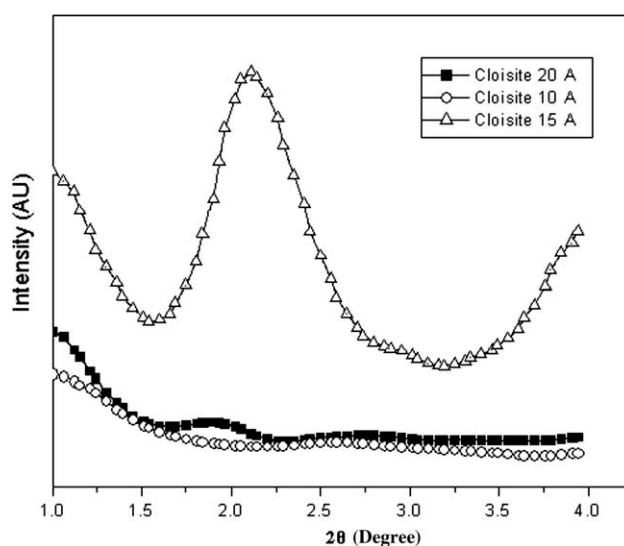

Figure 4 XRD plots of the chlorobutyl rubber nanocomposites containing 5 phr clay.
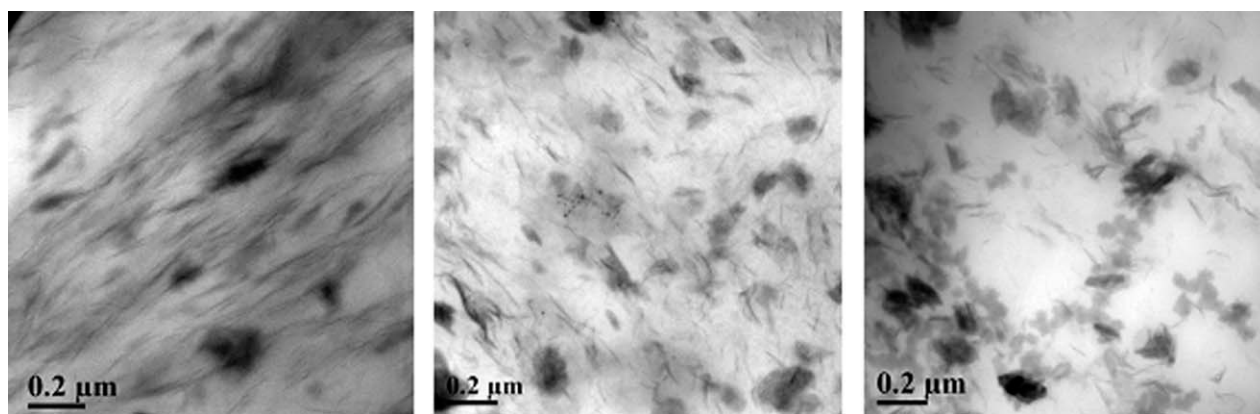
Figure 5   TEM images of nanocomposites containing 5 phr of (a) cloisite 15 A (b) cloisite 10 A (c) cloisite 20 A.

added to the rubber matrix is maximum in the case of 15 A than 10 A. In deciding the modulus of a nanocomposite two factors come to play

1. The number of particles
2. Interaction between the modified clay and the rubber matrix.

In the case of 15 A the first factor plays a major role, which is the reason for the enhancement of tensile modulus and decrease in elongation at break when compared to 20 A. In the case of an amine with higher chain length, i.e., 10 A when compared with the others the second factor is predominant causing a constant increase in modulus. So the modulus of the nanocomposites varies as 10 A > 15 A > 20 A as depicted in Figure 7. The interaction between the nano filler and the rubber matrix increases with the increase in the number of carbon

atoms in the amine chain. This is namely due to nonpolar Van der Waals type of interaction between the filler modifier and the rubber matrix. The variation in tensile strength and modulus is a function of dispersion in addition to filler rubber interaction. Since the amine chain in closite 15 A/20A contains two tallow groups, the number of carbon atoms is higher than cloisite 10 A and hence they show enhanced mechanical properties when compared to 10 A.

Of the three clays studied two (15 A and 20 A) are having aliphatic groups in the modifier whereas the clay 10 A is having an aromatic group. The modifiers used in the case of all the clays are shown in Figures 8 and 9. Lower degree of intercalation is obtained with aromatic salts as modifiers due to steric effect of the aromatic rings. The long tallow tails on the amine surfactants are made from natural oil that contains some unsaturation, i.e., double
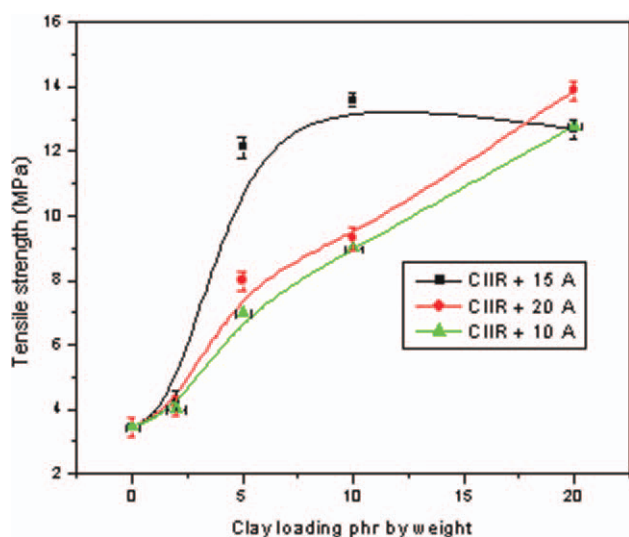

Figure 6   Effect of clay type on the tensile strength of chlorobutyl rubber nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
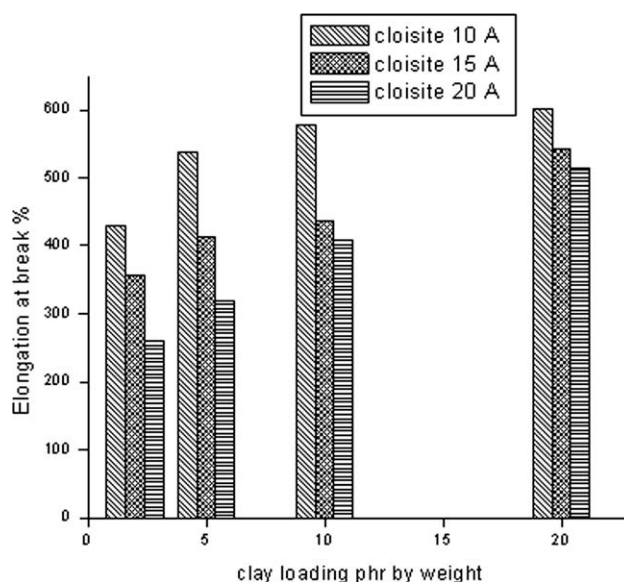

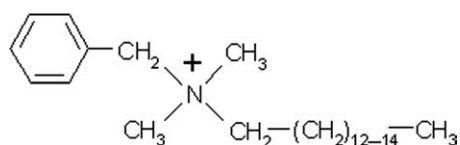**Figure 7**   Effect of clay loading on the elongation at break of chlorobutyl rubber nanocomposites.

Figure 8 Structure of the surfactant in cloisite 10 A.

bonds. This unsaturation may lead to undesired chemical reactions particularly at the high temperature used in melt processing. The substituent size (or volume) on a surfactant can affect the dispersion of clay particles in the polymer matrix. The organoclay with a broader d spacing can have much more possibility to be exfoliated in polymer/organoclay nanocomposites because polymer molecules penetrate into the gallery more easily. It is interesting to see that the material with a benzyl group also has a higher elongation at break than do the methyl or hydrogen substituted organoclays as shown by Paul et al.[24] In addition to the organoclay chemical structure, physical structure may play a role in exfoliation or intercalation in a polymer matrix. Intuitively, one might expect that the further the aluminosilicate platelets are pushed apart by ion exchange with the organic modifier (i.e., the larger the organoclay *d*-spacing) the easier it will be to obtain intercalation by the polymer. However, a recent study of nylon 6 nanocomposites showed that tensile modulus or yield strength did not increase with the d-spacing of the organoclay; if anything, the opposite trend was found.[25] This study indicated that better exfoliation stems from a good affinity of the polymer for the organoclay rather than larger platelet separation in the pristine organoclay.

Thermal properties

In the case of layered silicate nanocomposites the thermal properties do not show much improvement. It has been argued that after the early stages of thermal decomposition the stacked silicate layers could hold accumulated heat acting as a heat source to accelerate the decomposition process in conjunction with the heat flow supplied by the outside heat source. Also the alkyl ammonium cations in the organoclay could suffer decomposition following the Hoffmann elimination reaction and the product could catalyze the degradation of polymer matrices. Moreover clay itself can also catalyze the
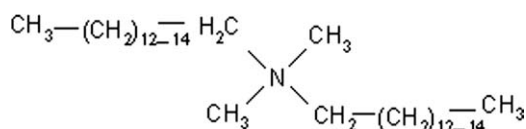

Figure 9 Structure of the surfactant in cloisite 15 A/cloisite 20 A.

Figure 10 The mechanism of degradation in the chlorobutyl rubber nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

degradation of polymer matrices. Thus it becomes obvious that the organoclay may have two opposing functions in the thermal stability of the nanocomposite, a barrier effect which could improve the thermal stability and a catalytic effect on the degradation of the polymer matrix which should decrease the thermal stability as shown in Figure 10.[26] The incorporation of clays containing aliphatic modifiers do not improve the thermal stability of the chlorobutyl rubber to a greater extend. Better thermal stability is exhibited by chlorobutyl rubber nanocomposites containing cloisite 10 A as indicated in the TGA of the various nanocomposites in Figure 11. The 15 A contains a higher amount of intercalants than 20 A which as pointed out earlier has a chance to be expelled during the shear mixing and could remain unbound in the silicate layers and thereby engage in unwanted degradation reactions between the decomposition products and the polymer matrix, which could lead to further matrix degradation and color formation in nanocomposites.[27] DTA curves of 15 A and 10 A in Figure 12 show two closely spaced curves. The first one corresponds to the degradation of the excess amine modifier (above CEC) in the clay. The second peak corresponds to the degradation of the intercalated surfactants which were stabilized by confinement within the interlayer.
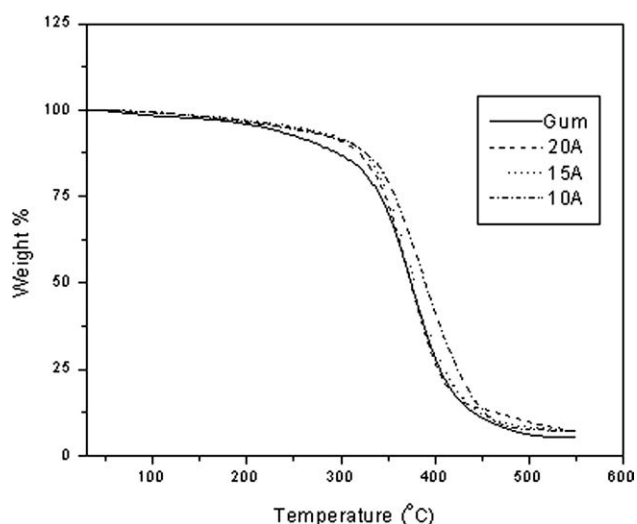

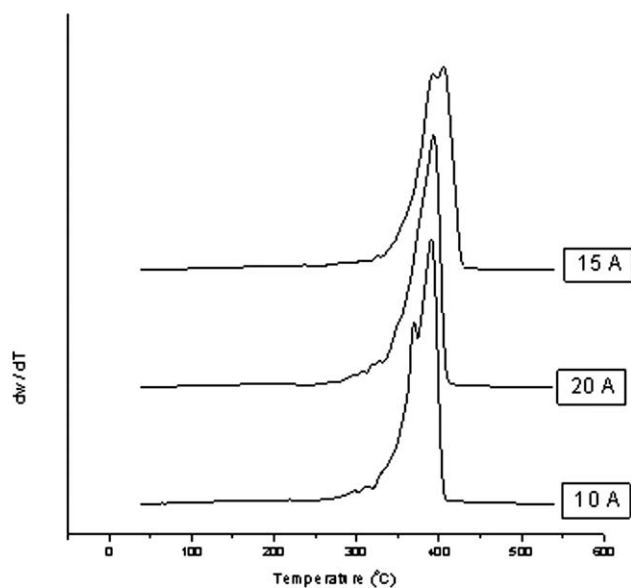**Figure 11** TG curves of chlorobutyl rubber nanocomposites containing various clays.

Figure 12 DTA curves of chlorobutyl rubber nanocomposites containing various clays.

In consequence the ammonium surfactants decomposed earlier which paved way for the degradation of the polymer.

Nitrogen permeability

The permeation of Nitrogen gas through the nanocomposite samples containing different types of clays at different loadings of nanoclay is shown in Figure 13. The figure shows that the nanocomposites containing cloisite 10 A as well as cloisite 15 A are excellent barrier materials at both lower and higher loadings. The relatively lower performance of cloisite 20 A as barrier materials can be substantiated due to the less effective dispersion in the chlorobutyl
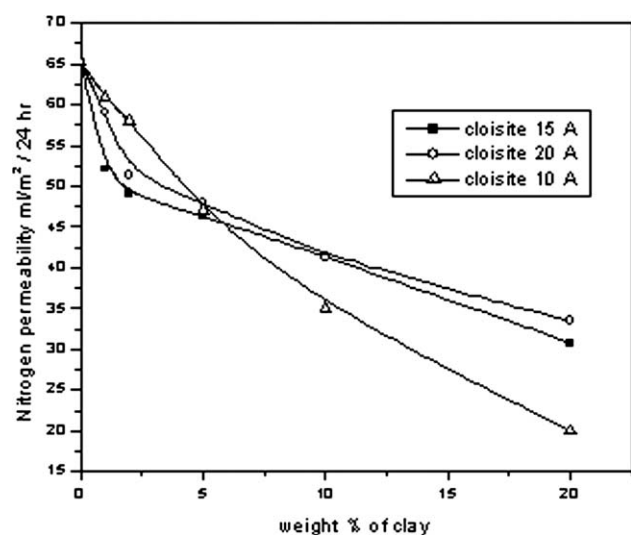

Figure 13 Permeability of Nitrogen gas through the nanocomposites containing different types of clays.

rubber matrix. These results clearly verify the choice of chlorobutyl rubber nanocomposites as effective barrier materials.

CONCLUSIONS

Chlorobuty rubber nanocomposites containing three different types of clays (cloisite 10 A, cloisite 15 A, cloisite 20 A) were prepared and the mechanical, thermal, kinetic as well as nitrogen gas permeation studies were done. The mechanical properties of nanocomposites containing cloisite 15 A were superior when compared to the other varieties of nanoclay. This can be explained due to the increased d spacing in 15 A which facilitates easier intercalation. Moreover the presence of aliphatic modifier at an increased concentration enhances the interaction between the rubber matrix and the nanoclay. The mechanical properties show that the nanoclays are promising candidates for reinforcement. Moreover the analyses of gas barrier properties reveal the effectiveness of the material to be used as barrier materials. The enhancement in properties showed by layered silicate moieties with different modifications can be explained on the basis of the type of modification and d spacing. This in turn helps in the tailoring of the properties of the layered silicate nanocomposites for a variety of advanced applications.

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