

Natural Rubber Latex Nanocomposite by Compounding Method

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Abstract:

Polymer nanocomposites represent a new alternative to conventionally (macroscopically) filled polymers. Because of their nanometer level dispersion, nanocomposites exhibit markedly improved properties compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability. Organophilic layered silicates can be dispersed in water, which acts as swelling agent due to the hydration of the intergallery cations. Several rubbers are available in latex form, which are rather stable aqueous dispersions of fine rubber particles. Hence solution intercalation of rubbers with layered silicates is a promising route to produce rubber nanocomposites.

In this study natural rubber (NR) based nanocomposites with 10 wt % natural and synthetic layered silicates were produced via the latex compounding method. As layered silicates, sodium bentonite (natural) and sodium fluorohectorite (synthetic) were selected in addition to a non-layered inert filler (English India clay) as reference material. The nanocomposites were prepared by compounding the dispersions of clays and other latex chemicals necessary for vulcanization. The vulcanized nanocomposites were subjected to mechanical, thermal and swelling tests. The silicate dispersion in the vulcanizate was studied by transmission electron microscopy (TEM) and XRD. Layered silicates registered the maximum properties compared to the reference material (commercial clay) in all aspects. Layered silicate filled NR vulcanizates exhibited a great increase in modulus and tensile strength especially with fluorohectorite. Thermal stability and solvent resistance of the nanocomposites were excellent. This was attributed to the intercalation/exfoliation of the silicates and to the formation of a skeleton "(house of cards)" silicate network in the NR matrix. Dipping characteristics of the latex nanocomposites were also analysed. The stability of latex compound and the film forming characteristics were found to be comparable to conventional filler incorporated films. Results indicate that the conventional latex compounding technique can be used to produce NR nanocomposites provided that the layered silicate can form aqueous dispersions with the NR latex.

1. Introduction

Polymer nanocomposites represent a new alternative to conventionally (macroscopically) filled polymers. Because of their nanometer size filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability (c.f.[1-3]).

The methods for the preparation of nanocomposites include *in situ* polymerization, solution and melt intercalation. Melt intercalation of high polymers is a powerful approach to produce layered silicate polymer nanocomposites. This method is quite general and is broadly applicable to a range of commodity plastics from essentially non-polar through weakly polar to strongly polar polymers. Layered silicate polymer nanocomposites are processable using current technologies. In general two types of organic/inorganic hybrids are distinguished: intercalated (polymer chains are diffused between the silicate layers preserving however some short range order of the latter) and exfoliated, (in which the silicate layers of ca. 1nm thickness are fully delaminated and dispersed in the polymer matrix). Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. Ion exchange reactions with cationic surfactants, including ammonium ions, render the normally hydrophilic silicate surface organophilic. This is the prerequisite for intercalation with many engineering polymers. The role of the alkyl ammonium cations in the "usual" organosilicates is to lower the surface energy of the silicate and to improve its wettability by the polymer. Additionally, the alkyl ammonium compounds may contain functional groups, which can react with the polymer or initiate the polymerization of monomers. This may strongly improve the strength of the interface between the silicate and the polymer (c.f [4-10])

This nano-concept is highly relevant for rubber compounds since their application requires filler reinforcement [11-20]. Vulcanized rubbers are usually reinforced by carbon black and also by inorganic minerals (talc, TiO_2 etc.) to improve the mechanical properties. Carbon black is an excellent reinforcement owing to its strong interaction with rubbers, but its presence especially at high loading often decreases the processability of rubber compounds.

Commercial clay has been used as filler for rubber many years. The reinforcing capacity of clay is poor because of its large particle size and low surface activity. On the other the hand, minerals have a variety of shapes suitable for reinforcement, such as fibrils and platelets. Layered clays are comprised of silicate layers having a planar structure of 1 nm thickness and up to 500 nm length. The layers cannot be separated from each other through general rubber processing. Since inorganic ions absorbed by clay can be exchanged by organic ions, research succeeded in intercalating many kinds of polymers and to prepare clay/polymer nanocomposites [21-24]. It has been shown that the silicate layers can be dispersed at molecular level (nanometer scale) in a polymer matrix. Rubber-clay nanocomposites were prepared from latex by a coagulation method and an improvement in mechanical properties was reported [23-24]

Here the conventional compounding technique was used to prepare nanocomposites from latex. Natural rubber (NR) latex is a macroscopic dispersion of rubber particles in an aqueous medium. Some layered silicates are suitable additives for latex, provided that they can form dispersions adequate for latex compounding. In aqueous dispersions, the clay "swells" (i.e. its layers are separated by hydration) which its good dispersion possible. In this study NR latex was compounded with dispersions of layered silicates and other

vulcanizing ingredients in order to produce vulcanized natural rubber-clay nanocomposites. Properties of the nanocomposites were compared with vulcanizates containing an inert filler (commercial, non-layered clay) used in many latex products to make them cheap.

2. Experimental

Details of the layered silicates used are given in Tables 1a. and 1b. Sodium fluorohectorite (Somasif ME-100) of Coop Chemicals, Japan is a synthetic clay, which has an ion exchange capacity of 100 meq/100g and an inter-layer distance of 0.94 nm. Sodium bentonite (EXM 757) of Süd Chemie, Germany is a purified natural clay, having an ion exchange capacity and interlayer distance 80 meq/100g and 1.24 nm, respectively. Details of the commercial clay (English India Clays, India) used are given in Table 1b. The base formulation for preparing NR nanocomposites from latex is given in Table 2. Centrifuged NR latex - high ammonia (HA) type- with 60% dry rubber content, conformed to BIS specification 5430, was supplied by Rubber Research Institute of India. Chemical composition of the NR latex has been given in Table 3. Sulphur, zinc diethyl dithiocarbamate, zinc oxide and styrenated phenol were supplied by Bayer, Germany and used in their aqueous dispersions.

10 % aqueous dispersions of layered clays were prepared in a special type of mechanical stirrer (Polytron, Switzerland). The contents were agitated at an rpm of 16,000 for 24 hours (h). Dispersion (50 %) of commercial clay was prepared by using a ball mill. The latex was mixed with the compounding ingredients according to the formulation given in Table 2 and stirred well for half an hour for a homogeneous mixture. The compounded latex is then matured (keeping overnight for uniform dispersion of added chemicals) which ensures latex films to uniform properties. The compounded latex, after removing the dirt and coarse particles by filtering through a sieve (opening: 250 micron) is then casted on raised glass plates having a dimension of 13cm x 10cm x 2mm. The casting was then allowed to dry in air till becomes transparent and then vulcanized at 70 °C for 4 h in an air circulated oven. The vulcanized samples thus obtained were kept in a desiccator before mechanical testing.

2.1. Testing

Tensile tests were performed on dumb-bell shaped specimens according to the ASTM D-412 on a Zwick 1485 universal testing machine at a crosshead speed of 50 cm per minute. Five samples were tested and the average of the values were taken. The dynamic-mechanical thermal analysis (DMTA) spectra were taken on rectangular specimens (6x 1x 0.25 cm³) in tensile mode at a frequency of 10 Hz using a Eplexor 150 N device of Gabo Qualimeter, Germany. DMTA spectra, viz E' and mechanical loss factor (tan δ) were measured in the temperature range -120 to 100 °C at a heating rate of 2 °C/min.

For swelling studies the circular specimens of 1.98 cm diameter were cut using a sharp edged circular die. The thickness of the samples were measured using a micrometer screw gauge. The initial weight was taken and the samples were immersed in toluene containing bottles and kept at constant temperature (25 °C). The samples were periodically removed from the test bottles, adhering solvents was blotted off the surface, and the samples were weighed in air tight bottles on a highly sensitive electronic balance and immediately replaced in the bottles. The time for each weighing was kept to a minimum of 30- 40 seconds in order to eliminate the error due to the escape of solvent from the samples. This procedure was continued until no more liquid uptake by the polymer was noted. The quantity of solvent absorbed was expressed in moles of solvent sorbed by 100g of the composite. Thermogravimetric analysis was done using a Thermal Analyser (Mettler Toledo TC-15, Germany) in the temperature range of 30 - 600 °C. Transmission electron microscopic

(TEM) studies were carried out with a LEO 912 Omega transmission electron microscope with an acceleration voltage of 120 keV. The specimens were prepared using a Leica Ultracut Uct Ultramicroscope equipped with a cryo-chamber. Thin sections of about 100 nm were cut with a Diatome diamond knife at -120°C .

3. Results and Discussion

3.1. Mechanical properties

Figure 1 illustrates the variation of modulus at various elongations for the different clay filled vulcanizates. There is a marginal increase in modulus, which follows the order: gum < commercial clay < bentonite < fluorohectorite. For the fluorohectorite clay filled composite, the modulus at 300 % elongation is increased by more than 5 and 2.5 times compared to the unfilled NR (gum) and commercial clay filled composites respectively.

The stress-strain curves of the vulcanizates are illustrated in Figure 2. Here also, the load at all elongations is highest for the fluorohectorite. It is worth of noting that the strain-induced crystallization of NR is not at all affected, as it is evident from the strong increase in stress after 500 % elongation. The initial high stress is due to the reinforcement of the rubber by the clay layers. However as elongation increases, ($> 400\%$) stress induced crystallization comes in to role, which increases proportionally with elongation. It is to be noted that at breaking point the curves closes together except in the case of fluorohectorite.

The nanometric dispersion of silicate layers means an efficient reinforcement, which leads to improved stiffness. The silicate layers may favour the formation of immobilized or partially immobilized polymer phases, which also increases the stiffness [1]. It is also possible that the orientation of silicate layer is responsible for the observed reinforcing effect. The low stiffening effect by commercial clay can be attributed to its high particle size and poor dispersion in the matrix.

Figures 3a to 3b depict the dynamic mechanical spectra (dynamic storage modulus E' and loss factor $\tan \delta$) as a function of temperature for the composites. There is a remarkable increase in storage modulus for both layered silicate filled composites compared to the commercial clay. The storage modulus below the glass transition temperature ($T_g = -70^{\circ}\text{C}$) is increased by 400 % for fluorohectorite and 450 % for bentonite when compared to commercial clay filled polymer. In Figure 3b the loss factor $\tan \delta$ is shown for different clay filled vulcanizates. Unlike other vulcanizates, the $\tan \delta$ curve of fluorohectorite showed a broad relaxation process from ambient temperature to 100°C . This may be due to the sliding of the intercalated silicate layers expanded by interstitial rubber [25] or may represent the relaxation of rubber fraction confined inside the layers. It is to be noted that in the case of commercial clay filled composites, which has no interstitial (confined) rubber, no such portion in the $\tan \delta$ curve can be seen. TEM photographs also support the formation of confined rubber in fluorohectorite, which will be discussed later.

The maximum of $\tan \delta$ peak reduces significantly due to the strong adhesion between NR and silicate [25]. Sliding along the intercalated interlayer is suppressed. In addition, chain slipping at the outer surfaces of the aggregates is also suppressed. Therefore the loss maximum is smallest in case of the system with the strongest filler matrix coupling (fluorohectorite).

3.2. Thermal decomposition

The thermal decomposition behaviour of NR nanocomposites is given in Table 4. At 400 °C, the percentage of weight retained is higher for the nanocomposites. This increase in thermal stability of the hybrid may result from the dispersion of the clay and from a strong interaction between the clay platelets and rubber molecules. At 450 °C, fluorohectorite filled vulcanizate is more stable than the bentonite filled version. This is due to the poor dispersion of bentonite in rubber as evidenced by TEM data (discussed later). It has been reported that hybrids with a good dispersion of organoclay are thermally more stable [20, 25]. A characteristic feature of the nanocomposites is that the thermal property improvement occurs at very low filler content, often making the obtained material cheaper, lighter and easier to process than conventional composites.

3.3 Sorption behaviour

Figure 4 shows the sorption curves of the vulcanizates, which are obtained by plotting Q_t (mole per cent uptake per 100 of the composite) in toluene at 25 °C. Note that the gum has the maximum toluene uptake at equilibrium swelling. This is expected, since there is less restriction for the penetrant to diffuse into the vulcanizate. At equal volume loading of filler, the amount of solvent absorbed at equilibrium swelling is less for the composites containing layered silicate - especially fluorohectorite - compared to that containing commercial clay. The presence of impermeable clay layers decreases the rate of transport by increasing the average diffusion path length in the specimen [26-27]. Another interesting observation from the sorption curves of the composites in toluene is the difference in the initial rates of diffusion. The initial rate of diffusion is fastest for gum followed by commercial clay filled rubber. This is because in gum compound there is no restriction for solvent molecules for penetration. However, in the commercial clay filled rubber the solvent uptake is restricted to a lower extent because of the weak interface and also due to poor clay dispersion. The relatively lower rates of diffusion at the beginning of the sorption curve for the compounds with layered silicates are due to the strong interface and also due to the orientation of the layers. During swelling the solvent can enter in the polymer along or transverse to the aligned silicate platelets. In well oriented composites, the penetration in the perpendicular direction is highly restricted. Consequently, the dimensions (thickness and diameter) of the circular specimen after the swelling will be different from that of a specimen having little or no filler orientation. In Figure 5, percentage increase in thickness and diameter (compared to the original) of the samples after equilibrium swelling are given. Here fluorohectorite registered the maximum increase in thickness after swelling where as all other composites retained more or less same thickness. Percentages increase in diameter after swelling showed a reverse trend. Composites containing well-oriented components undergo this type of anisotropic swelling, which finally leads to dimensional changes [26]. The orientation of the intercalated/exfoliated clay layers is well demonstrated by TEM pictures (see later).

The relative permeability compared to NR gum decreases in the order commercial clay (55%) > bentonite (35%) > fluorohectorite (5%). The penetration of the solvent molecule in to the composite is effectively prevented by the orientation of the clay layers. This indirectly shows that such composites are highly impermeable to solvents and gases.

3.4. Clay dispersion

The dispersion of layered silicate inside the composites was observed by TEM and are illustrated in Figures 6a to 6c, which represent commercial clay, bentonite and fluorohectorite filled NR vulcanizates respectively. In commercial silica filled composites, the filler exist as large particles. Recall that this clay was not a layered version. In bentonite

filled vulcanizate there is some level of intercalation and the silicate layers form clusters (skeleton or house of cards structure) [13]. Here it can be seen that some level of filler network is formed which might be the reason for the high compound viscosity during mixing. However, in fluorohectorite filled nanocomposites, individual layers of the silicate are well exfoliated but they still form a skeleton structure. The exfoliation and dispersion of silicate layers can be better understood from the Figures 7a and 7b. In bentonite (Figure 7a) filled composites bridging of silica nano-aggregates of very large aspect ratio forms a secondary filler network. This reinforcement structure explains the improvement in stiffness and strength. On the other hand, introduction of fluorohectorite (Figure 7b) in the NR results in a relatively large amount of exfoliated layers. Here clay layers are visible as regions of dark narrow bands within the polymer. Even though the layers are 'ceramic' in nature, because of their very large aspect ratio and nanometer thickness, they behave mechanically more like sheets of paper rather than rigid plates [28]. This increased flexibility (elastic nature) of the layers contributes to the elasticity of the rubber. It has been reported that exfoliated clay layers orient along the strain direction in elastomers [25]. This yields a further increase in the mechanical properties.

3.5. Dipping characteristics

Figure 8 shows the variation in thickness of the deposit with dwell time. In all the formulations the filler loading is 3phr. There is a sharp increase up to a dwell time of 50s and thereafter a marginal increase.

3.6. Permeability

The oxygen permeability of different silica filled composites was shown in Figure 9. It can be seen that, though the filler loading is the same (10 phr), fluorohectorite filled composite showed 50 times reduction in permeability compared to the gum compound whereas bentonite showed 35 times reduction. This is because fluorohectorite has high aspect ratio which effectively prevents the movement of the gas molecules. The impermeable clay layers mandate a tortuous pathway for a permeant to transverse the nanocomposite.

4. Conclusions

A suitable latex formulation has been designed for natural rubber latex and the conventional latex compounding method was used to produce vulcanized nanocomposites. Layered clays show excellent dispersion in NR compared to conventional composites. Layered clays filled NR vulcanizates showed a tremendous increase in modulus and tensile strength especially in the case of fluorohectorite. Dynamic mechanical analysis revealed that the layered clay filled composites possessed very high stiffness and low damping characteristics. This was traced to be a reinforcing effect owing to intercalation/exfoliation and formation of a clay network structure. Thermal stability of the layered silicates proved to be better than the commercial clay filled vulcanizates. Swelling, and TEM studies revealed some extent of orientation of the clay layers in the rubber. Exfoliation of the clay layers was demonstrated by TEM. Results indicate that the conventional latex compounding technique can be used to produce NR nanocomposites provided that the layered clay can form an aqueous dispersion compatible with NR latex compounding.

5. References

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Table 1a. Details of the synthetic layered clays.

Trade Name	Chemical name	Chemical formula	Ion exchange capacity, meq/100g	Layer distance nm
Somasif ME - 100	Na-fluorohectorite	$(\text{Mg}_{5.2} \text{Na}_{0.8}) (\text{Si}_8) \text{O}_{20} (\text{OH})_{4-x} (\text{F})_x \text{Na}_{0.8}$	100	0.94
EXM 757	Na-bentonite	$(\text{Al}_{3.2} \text{Mg}_{0.8}) \text{Si}_8 \text{O}_{20} (\text{OH})_4 \text{Na}_{0.8}$	80	1.24

Table 1 b. Details of the English India (commercial) clay.

Commercial clay	Contents Mass, %
SiO_2	45
Al_2O_3	38
Fe_2O_3 (max)	0.5
TiO_2	0.55
CaO (max)	0.06
MgO (max)	0.07
Na_2O (max)	0.25
K_2O (max)	0.1
Loss on ignition	14.5

Table 2. Formulation of the NR latex compound.

Ingredients	Wet	Dry
40% Natural rubber latex	167.0	100.0
50% ^a ZDC dispersion	2.0	1.0
50% Clay dispersion	20.0	10.0
50% Sulphur dispersion	3.0	1.5
50% ^b AO SP dispersion	2.0	1.0
5% Zinc oxide	3.6	1.8

a- Zinc diethyl dithiocarbamate (ZDC) •

b-Antioxidant(AO); styrenated phenol, (SP)

Table 3. Chemical composition of the NR latex

Constituents	Amount (mass %)
Dry rubber content	59.5- 60.5
Non rubber solids	2
Coagulum	0.05
Sludge	0.10
Ammonia	0.6 - 0.7
Volatile fatty acids	0.13

Table 4. TGA analysis of the composites

Temperature, °C	Weight retained, %		
	Clay	Bentonite	Fluorohectorite
300	97.01	97.51	96.99
350	94.85	94.76	94.82
400	54.31	63.66	63.63
450	15.86	15.11	18.28
500	11.12	7.17	10.00
550	10.98	6.95	9.90
600	10.76	6.82	9.78

Captions to figures

Figure 1. Moduli at different elongations for the clay filled nanocomposites.

Figure 2. Stress-strain curves of the clay filled nanocomposites.

Figure 3a. Complex storage modulus (E') as a function of temperature for clay filled nanocomposites.

Figure 3b. Mechanical loss factor ($\tan \delta$) against temperature for clay filled (nano) composites.

Figure 4. Swelling behaviour of the clay filled (nano) composites in toluene at 25°C.

Figure 5. Increase in thickness and diameter (percentage) of the specimen at equilibrium Swelling in toluene at 25 °C.

Figures 6a-c. TEM pictures of the different silicate filled (nano) composites
6a) commercial clay, 6b) bentonite, 6c) fluorohectorite

Figures 7 a-b. Low magnification TEM pictures of the layered silicate filled
Nanocomposites 7a) bentonite 7b) fluorohectorite

Figure 8. Variation of dwell with film thickness of various silicate filled nanocomposites.

Figure 9. Oxygen permeability for different silicate filled nanocomposites.

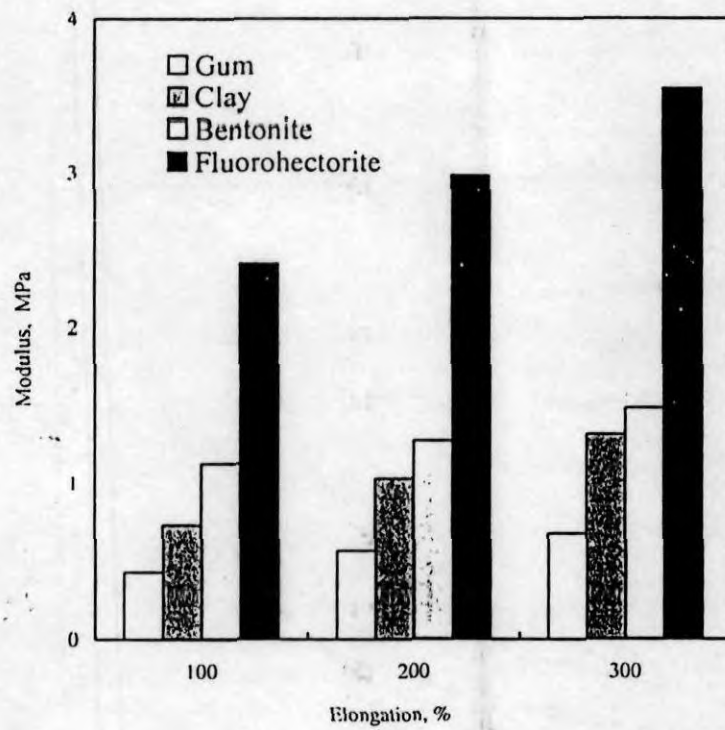


Figure 1.

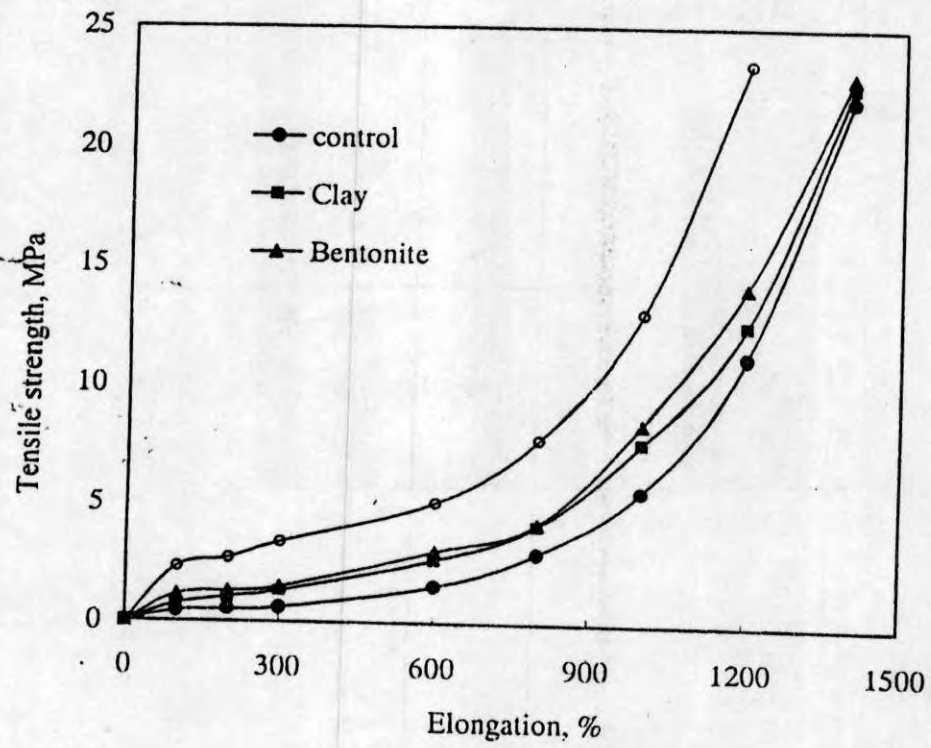


Figure 2.

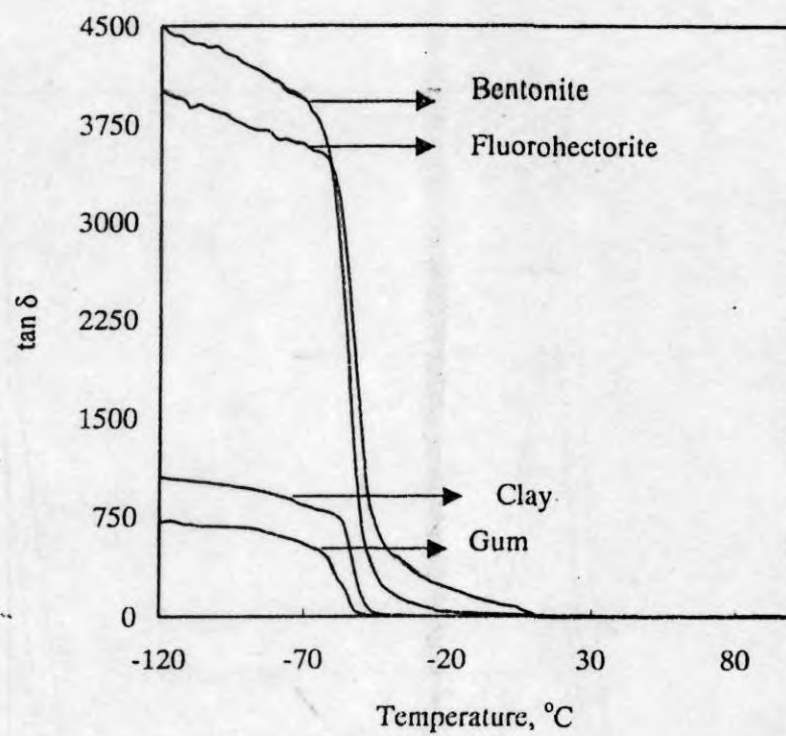


Figure 3a.

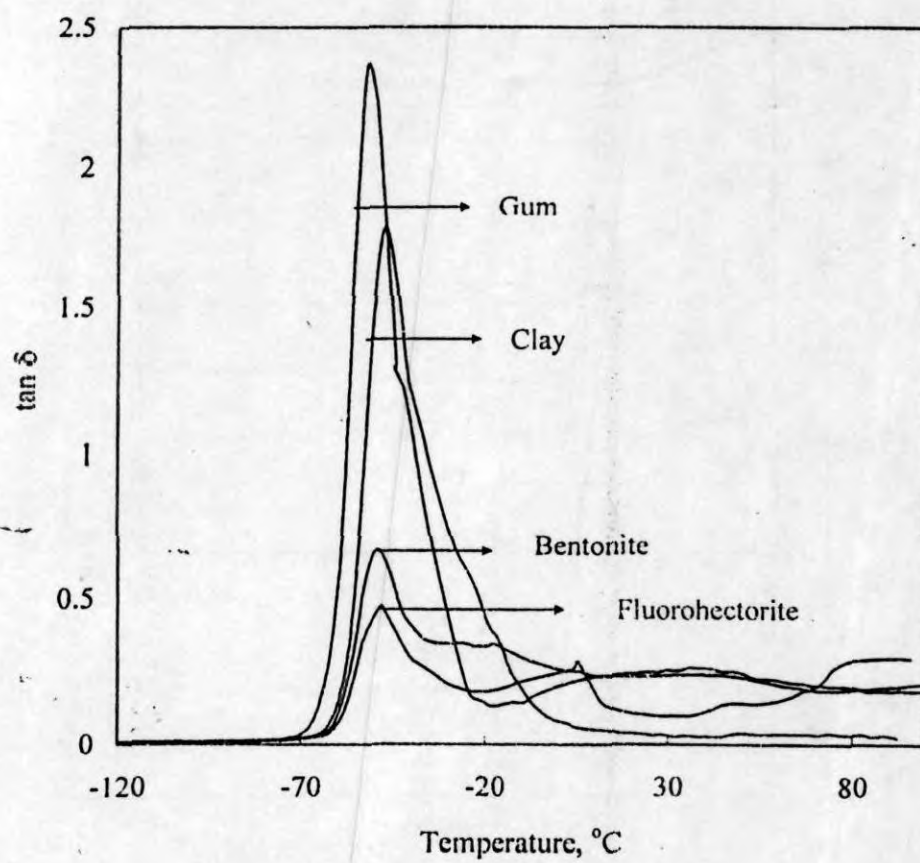


Figure 3b.

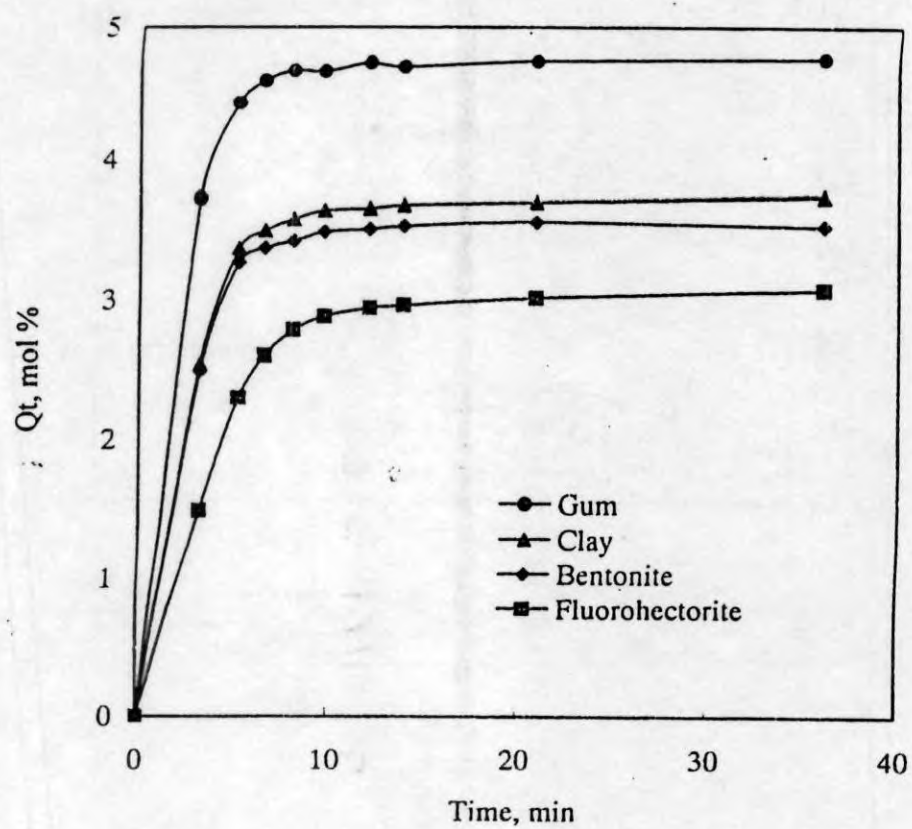


Figure 4.

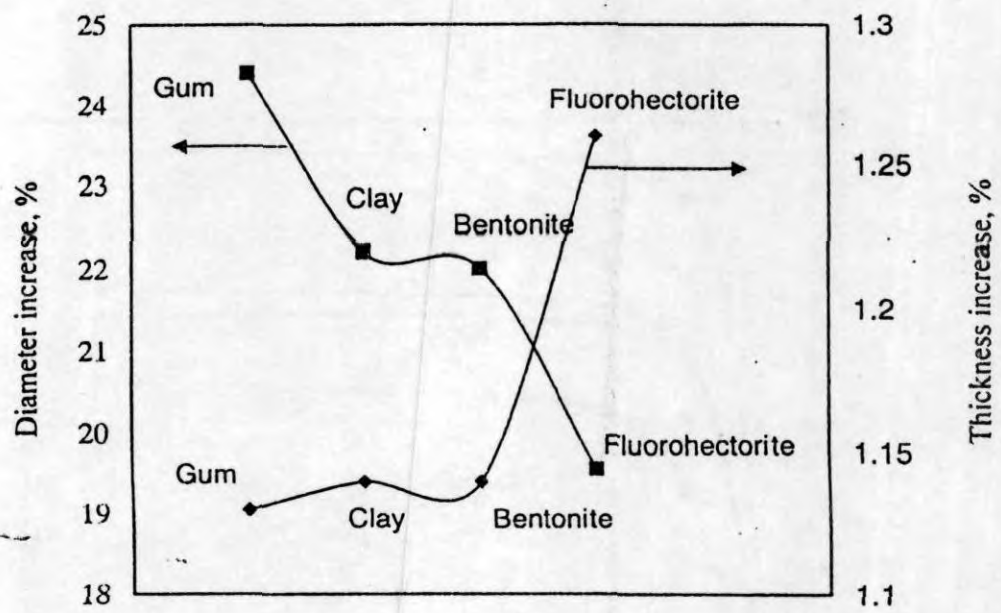


Figure 5.

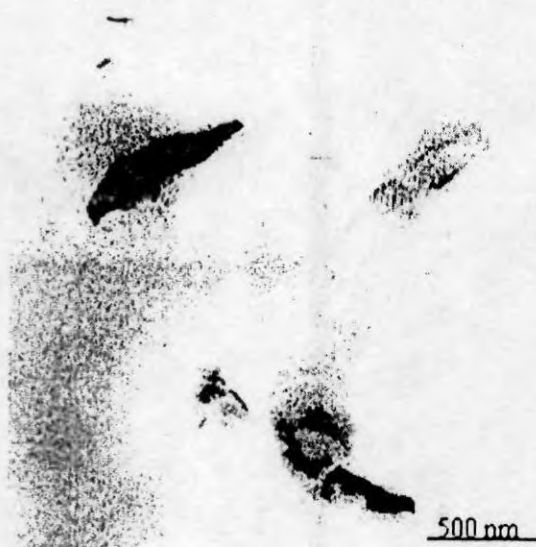


Figure 6a

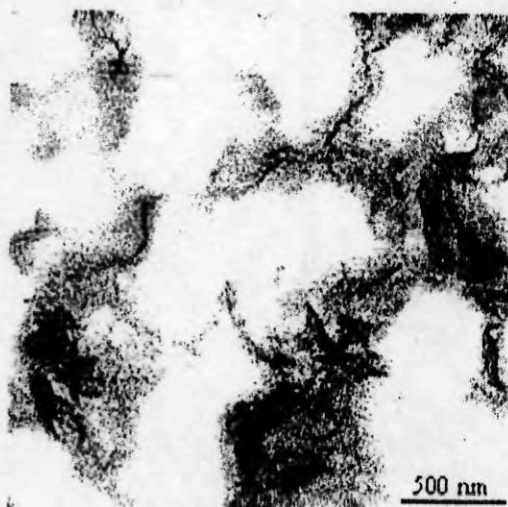


Figure 6b



Figure 6c

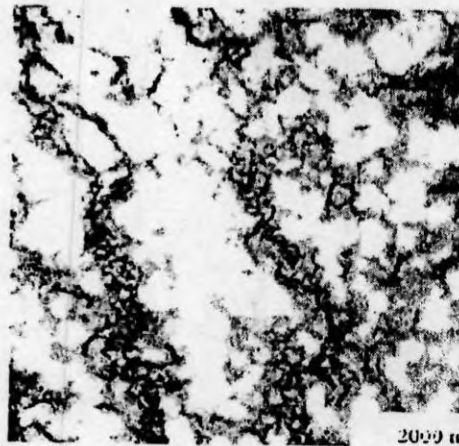


Figure 7a

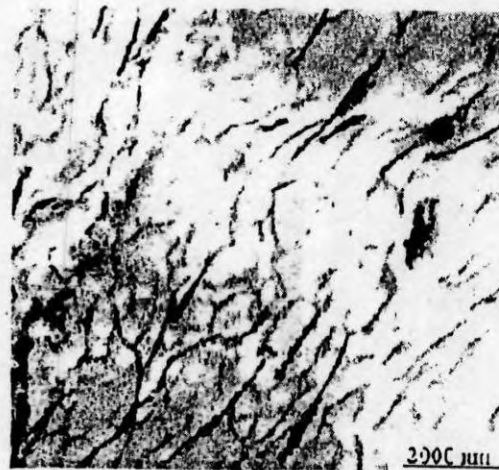


Figure 7b

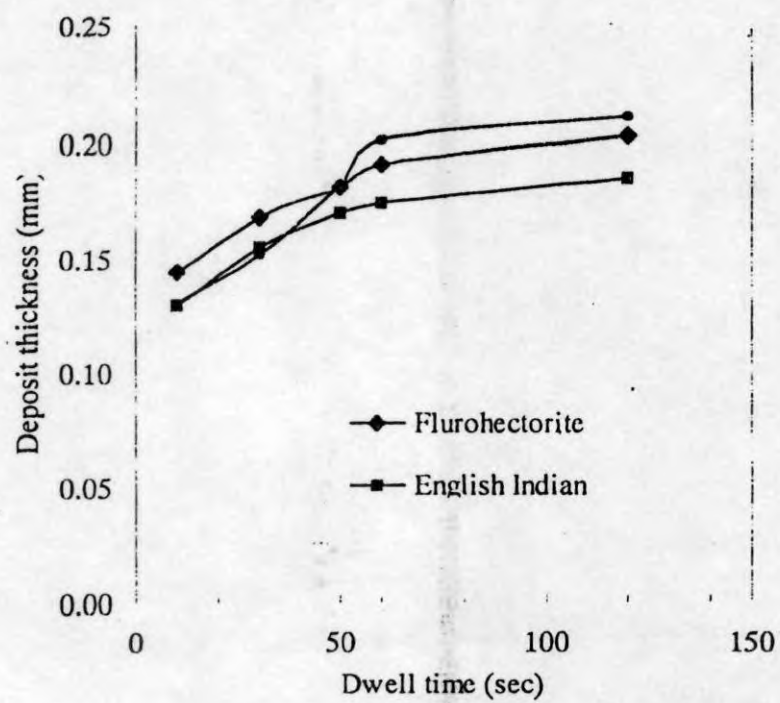


Figure 8.

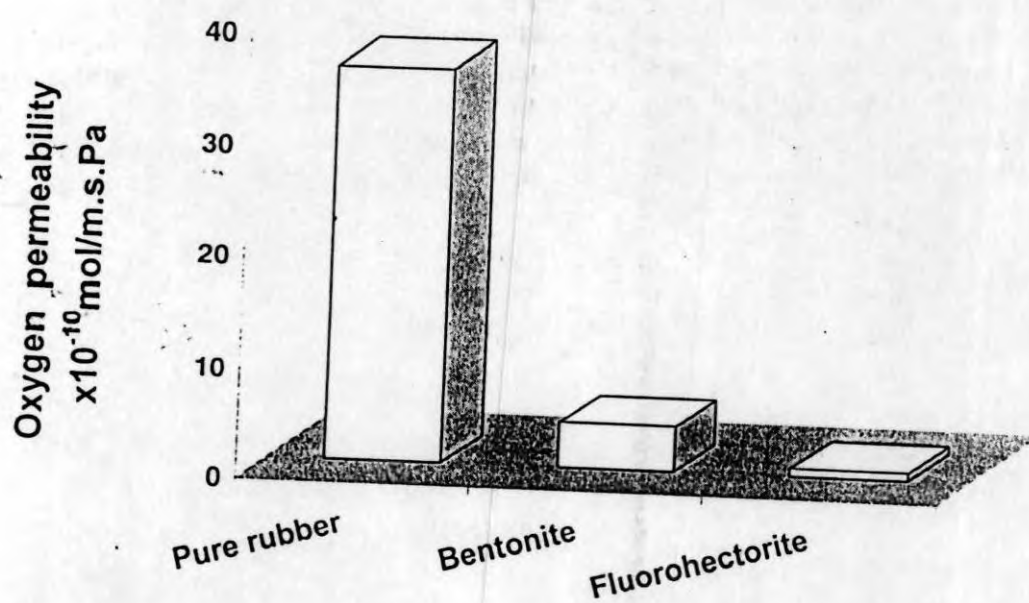


Figure 9.