

Comparing Styrene Butadiene Rubber–Clay Nanocomposites Prepared by Melt Intercalation and Latex-Coagulation Methods

M. Salehi, M. Razzaghi-Kashani

Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, P.O. Box 14115-114, I.R. Iran

Received 13 August 2011; accepted 7 February 2012

DOI 10.1002/app.36980

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Among different methods for preparation of rubber–clay nanocomposites, melt intercalation and latex-coagulation methods are more practiced. In this study, dispersion of pristine nanoclay by the latex-coagulation method and organically modified nanoclay by the melt-intercalation method in styrene butadiene rubber were compared, based on the same amount of mineral clay in the composites. Dispersion of nanoclay was examined by X-ray diffraction before and after vulcanization, and by atomic force microscopy after vulcanization. It was shown that final structure of nanoclay in the composites was intercalated by both methods, with better dispersion resulting from coagulation of latex over mixing in the melt state.

Dynamic–mechanical–thermal analysis and tension tests were used to further assess dispersion and polymer–filler interactions. These tests confirmed better dispersion and larger interfacial area for pristine nanoclay in the latex-coagulated rubber through observing lower peak loss factor, higher growth of stress in stretching, and lower elongation at break when compared with those for the nanocomposite prepared by the melt mixing. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: rubber–clay nanocomposites; latex coagulation; melt intercalation; microstructure; atomic force microscopy; dynamic–mechanical–thermal analysis

INTRODUCTION

Rubber articles need to be reinforced by fillers for practical applications. Mineral reinforcing nanoclays such as Montmorillonite have been considered for this purpose to replace part of traditional fillers such as carbon black.^{1–3} Such partial replacement can lead to lighter weight, more effectively reinforced and environmental-friendly rubber products such as tires. Thin clay platelets with nanosize thickness, large surface area, and high aspect ratio have proved promising reinforcing effects if properly dispersed in rubber.^{4,5} Since rubber is hydrophobic but clay has hydrophilic nature, their melt-mixing is difficult unless clay is modified for better compatibility. This has been achieved by ion-exchange reactions of clays with cationic surfactants, including primary, secondary, tertiary, and quaternary alkylammonium cations.^{6–9} These organic alkylammonium cations reduce the surface energy of clay, improve wettability of clay by typical nonpolar or mildly polar rubbers, and expand the basal spacing of clay layers for better intercalation of rubber in the melt mixing.

However, this organic modification increases the cost of nanoclays. On the other hand, the latex-coagulation method has been under attention due to application of pristine hydrophilic clay, mixing process in aqueous phase, and economical advantages over other methods.^{5,10,11} Different preparation routes and characterization methods for rubber–clay nanocomposites have been reviewed, and it has been shown that the latex-coagulation method is promising in preparing such nanocomposites.¹ Formation of a “house-of-card” structure has been reported, in which the silicate layers, disintegrated by hydration, can be surrounded by rubber particles.

Intercalation of polymer into clay galleries disturbs the ordered structure of nanoclay layers from their parallel and evenly spaced arrangement. X-ray diffraction (XRD) is often used to evaluate the degree of polymer intercalation. Shifts in XRD peaks are normally used to explain the state of polymer intercalation into the clay galleries, but if XRD peaks disappear, application of other complementary techniques such as transmission electron microscopy (TEM) or atomic force microscopy (AFM) become necessary to differentiate between disordered-intercalated and fully exfoliated microstructures of clay.¹² Since TEM requires tedious preparation of microtome sections of rubbery materials, AFM has recently gained attention as an effective tool, which gives insight into microstructure of rubbery nanocomposites.^{6,12,13}

Correspondence to: M. Razzaghi-Kashani (mehdi.razzaghi@modares.ac.ir).

State of clay dispersion is normally not the same before and after vulcanization, and it may change by application of heat, pressure, and chemical reactions during rubber vulcanization due to de-intercalation of rubber chains, layer collapse, and reduction of interlayer spacing.¹⁴

There are numerous research works focusing on application of layered silicate nanoclays in styrene butadiene rubber (SBR) compounds^{2,3,15–20}. Very few of them attempted to simultaneously compare the microstructure of nanocomposites obtained by the melt intercalation and the latex-coagulation methods based on a common basis.¹⁰

The objective of this study is to compare nanoclay dispersion and final properties of SBR-clay nanocomposites prepared by the melt-intercalation method, in which application of modified nanoclay is mandatory, and the latex-coagulation method in an aqueous phase where pristine clay is preferentially used. To have a common basis for comparison, amount of mineral clay in the compounds prepared by both methods was kept the same. Therefore, weight percentage of the modified nanoclay used in the melt-intercalation method was higher, considering a large amount of modifier in this type of nanoclay. Microstructure of nanocomposites was characterized by XRD and AFM. Dynamic-mechanical-thermal analysis (DMTA) and mechanical tests in uniaxial stretching were also used to further quantify effects of the mixing method on dispersion of montmorillonite nanoclay and its compatibility with SBR which in turn affects reinforcement of rubber.

EXPERIMENTAL

Materials and preparations

SBR-1502 latex with solid content of 18% was obtained from Bandar-Imam Petrochemical Company (BIPC), Iran. SBR is a copolymer of styrene and butadiene with Styrene content of 23.5%. Pristine montmorillonite nanoclay (Cloisite Na⁺) and its organically modified type (Cloisite 15A) with about 43 wt % “dimethyl, dihydrogenated tallow, quaternary ammonium” as modifier were obtained from Southern Clay, USA. The cation exchange capacity of montmorillonite is 1.45 mEq/100 g clay.

To prepare rubber-clay nanocomposites by the latex-coagulation method, pristine nanoclay was dispersed in de-ionized water properly, and the suspension was mixed with rubber latex vigorously for 2 h by a propeller mixer. The mixture was coagulated by diluted sulfuric acid, properly washed by water, and dried in an oven for 24 h.

To prepare nanocomposites in the melt-intercalation method, the required amount of modified Montmorillonite was calculated so that the net amount of

TABLE I
Recipe of Nanocomposites

Ingredients	Phr ^a
SBR	100
Nanoclay	Variable
Zinc oxide	3.0
Stearic acid	1.0
TMTD ^b	0.1
TBBS ^c	1.0
Sulfur	1.8

^a Part per hundred of rubber.

^b Tetramethylthiuram disulfide.

^c *N-tert-butyl-2-benzothiazyl sulfonamide*.

mineral clay in the compounds prepared by both methods is the same. Then modified clay was added to laboratory-coagulated neat SBR using Brabender Type PM-2000 two-roll-mill. Other ingredients and curing agents were later added on the two-roll-mill according to the recipe shown in Table I. Accelerators and sulfur were obtained from Flexsys Company, Belgium. Stearic acid was obtained from IOI Group, Oleochemicals, Malaysia, and zinc oxide was purchased from Pars Nekoo, Iran. Compounds with 1, 3, and 5 parts per hundred of rubber (phr) of modified nanoclay were prepared by the melt intercalation (M) methods. Similar compounds with equal “mineral clay” were prepared by the latex coagulation (L) method. Although weight percentage of the pristine nanoclay in the latter method was less than that of the modified one in the former, the same numbers (1, 3, and 5) before letters “L” or “M” were used as compound nomenclature for simple comparison. Weight percentage of nanoclays in rubber compounds was kept low to avoid filler networking effects. The reference compound is the neat SBR compound with no clay. Finalized composites were vulcanized in a hot hydraulic press from Wickert WLP, Germany at 160°C with an optimum cure time obtained by an Oscillating Die Rheometer GT-7070-S2 from Gotech, Taiwan.

Test methods

Degree of intercalation of rubber into the nanoclay layers was evaluated using XRD in a scan range of $2\theta = 0.5\text{--}10^\circ$ by a Philips X-Pert Pro machine, operating with the wave-length $\lambda = 0.15418$ nm.

AFM was used to study dispersion of nanoclays in the rubber matrix on smooth surfaces of samples. For this purpose, DME SPM-Prober Station 150 with a pyramidal silicone tip resonating at 260 kHz in a soft tapping mode was applied. AFM micrographs were taken from the surface of very thin and smooth (arithmetic average of surface heights: $R_a < 0.3$ μm) samples prepared specifically for AFM studies.

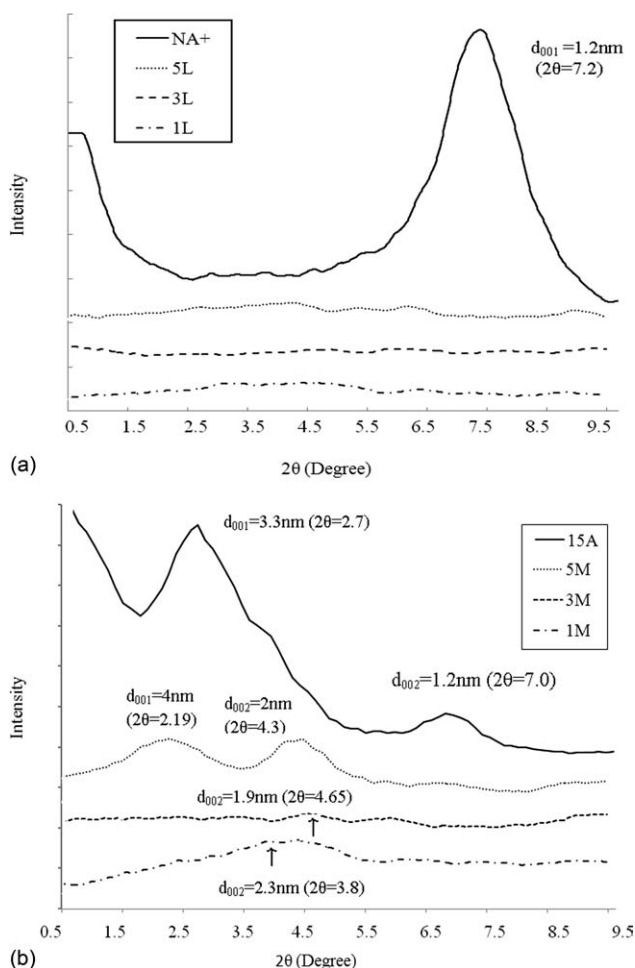


Figure 1 XRD pattern of clay and nanocomposites prepared by (a) latex coagulation (b) melt intercalation.

DMTA was performed on the samples in a single cantilever mode using Triton Tritec 2000, England. Temperature was swept from -100 to $+100^{\circ}\text{C}$ at the heating rate of 5°C , constant frequency of 1 Hz , and strain amplitude of 0.002 .

Mechanical properties of composites were compared using uniaxial tension tests at 100 mm/s stretching rate by Instron 4302, England. Reproducibility of the tests was checked using four specimens for each sample.

RESULTS AND DISCUSSION

Intercalated structure of nanoclays by XRD

XRD was used to not only compare degree of rubber chain intercalation into the spacing of nanoclay layers in both preparation methods but also study effects of the vulcanization process on the stability of clay microstructure. Figure 1(a) shows XRD graphs of Cloisite Na+ and its nanocomposites prepared by the latex-coagulation method. It can be

seen in this figure that the (001) peak for the pure clay disappeared in all three nanocomposites, meaning the silicate layers have lost their order to a fully-exfoliated and/or disordered-intercalated state. Figure 1(b) shows similar graphs for Cloisite 15A and its nanocomposites prepared by the melt-intercalation method. In this figure, samples 1M and 3M have lost the major peak (001) and reached a fully-exfoliated and/or disordered-intercalated structure, whereas the sample 5M shows shifted peaks, which are the sign of intercalated structure for the nanoclay. Therefore, nanocomposites, with at least intercalated structures, were formed in all cases at the unvulcanized state.

To investigate effects of the vulcanization process on the stability of clay microstructure in the SBR matrix, the XRD experiments were repeated for all the samples in the vulcanized state. Results for the latex coagulated composites are shown in Figure 2(a). As seen in this figure, peaks around $2\theta = 6.4^{\circ}$ have appeared which shows that some of the silicate layers are de-intercalated close to their original state.²¹ Since there are no other distinct peaks on the graphs, there is no evidence what percentage of silicate layers remain in disordered/exfoliated state. Similarly, the vulcanization process caused de-intercalation of silicate layers due to heat, pressure, and/or chemical interactions (formation of a Zn complex

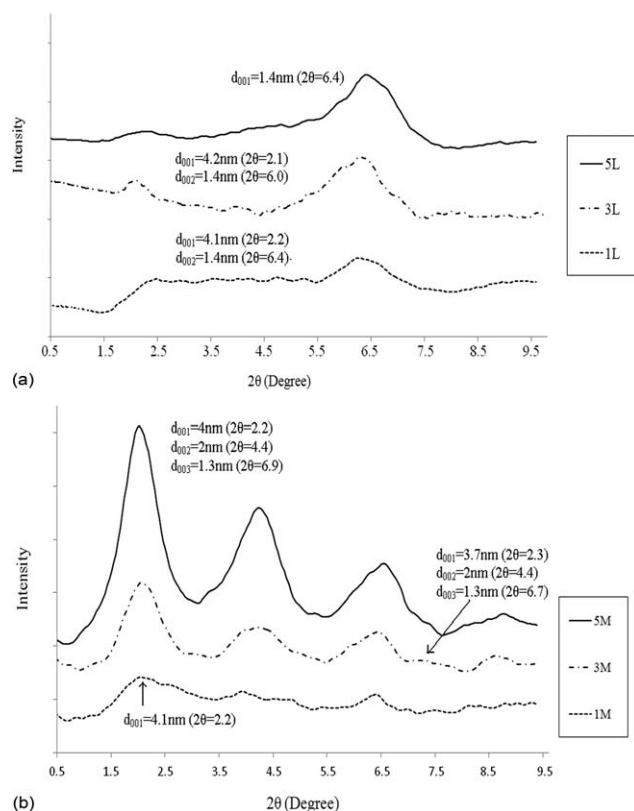


Figure 2 XRD pattern of vulcanized nanocomposites prepared by (a) latex coagulation (b) melt intercalation.

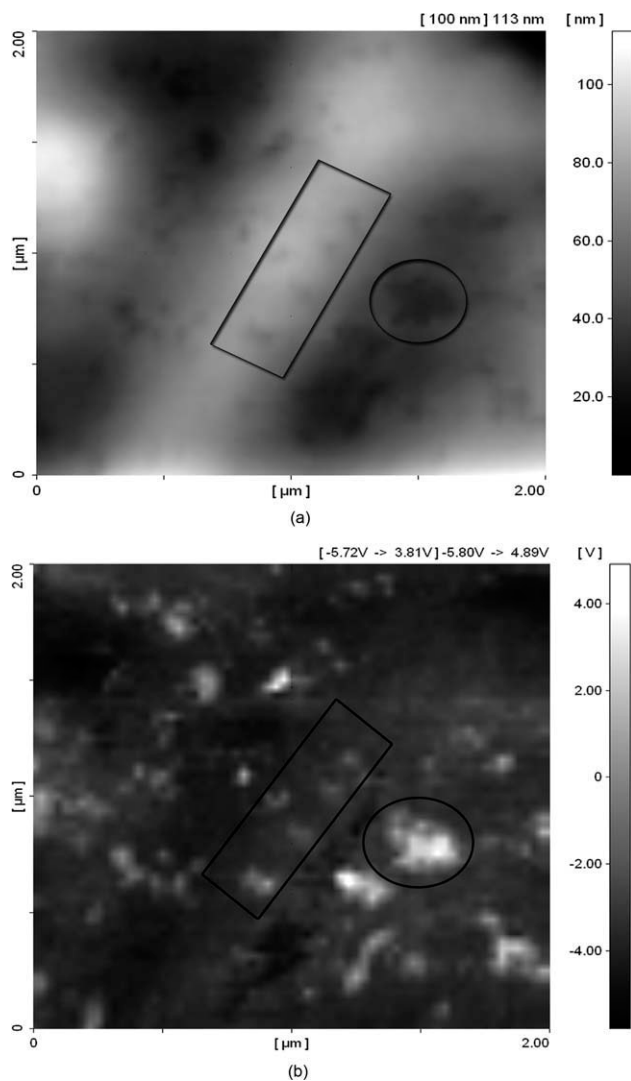


Figure 3 AFM micrographs for the melt mixed nanocomposite (5M) (a) height image (b) phase image. Circles and rectangles show areas with clay agglomerates and clay bundles, respectively.

in which sulfur and amine groups of modifier participate) in the melt-intercalated nanocomposites.^{14,21,22} This is shown in Figure 2(b), in which three distinct peaks have re-appeared for the nanocomposites after vulcanization. This is even clearer for 3M and 5M nanocomposites, which contain higher percentage of nanoclay. Re-appearance of the peaks after vulcanization induces this idea that the structure of nanoclays in the unvulcanized state was mostly disordered-intercalated rather than fully exfoliated since the latter is not reversible. From all these figures, one may conclude that the final microstructure of nanoclays samples prepared by both methods are at least intercalated, but it is difficult to compare the degree of clay dispersion in two methods from these results. Therefore, microscopic and other studies are needed to confirm these observations. For this purpose, only the nanocomposites 5L

and 5M were chosen for further microscopic and mechanical studies.

Atomic force microscopy of nanocomposites

To further evaluate the morphology of nanocomposites, AFM was performed on the samples 5M and 5L. Micrographs for the nanocomposite prepared by the melt-intercalation method are shown in Figures 3(a,b). Figure 3(a) is the height micrograph in which lighter color represents regions with more heights and vice-versa. This large but tolerable contrast was inevitable due to some waviness and height difference on the surface of specimens. Therefore, very large dark regions are in-fact valleys with low heights which must be ignored. However, some dark domains dispersed in the light region, which are correspondingly seen as light domains in the

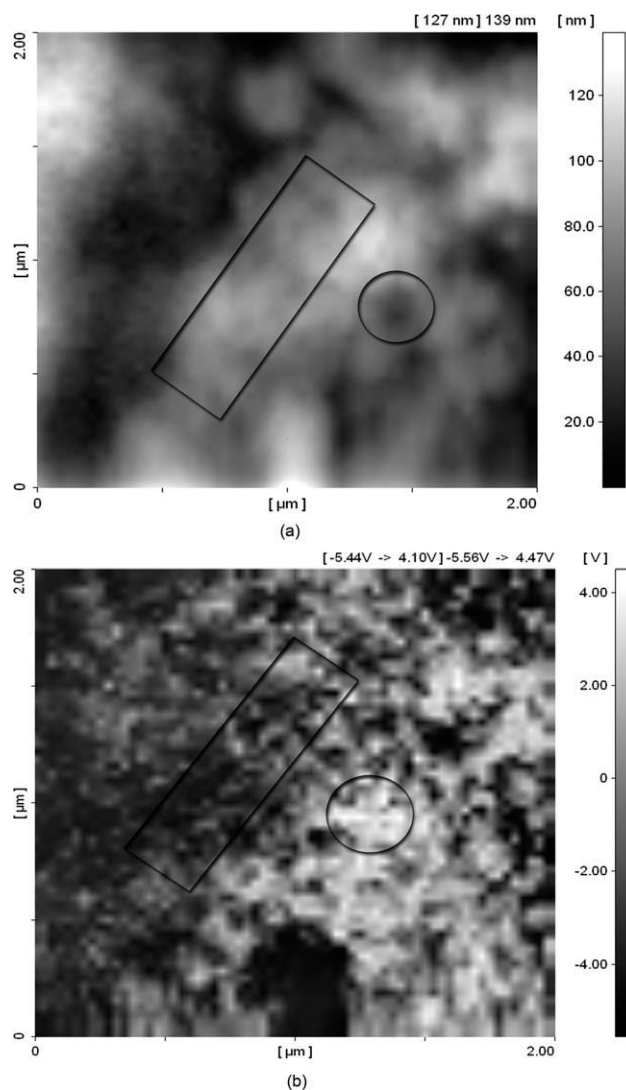


Figure 4 AFM micrographs for the latex coagulated nanocomposite (5L) (a) height image (b) phase image. Circles and rectangles show areas with intercalated and exfoliated clay structures, respectively.

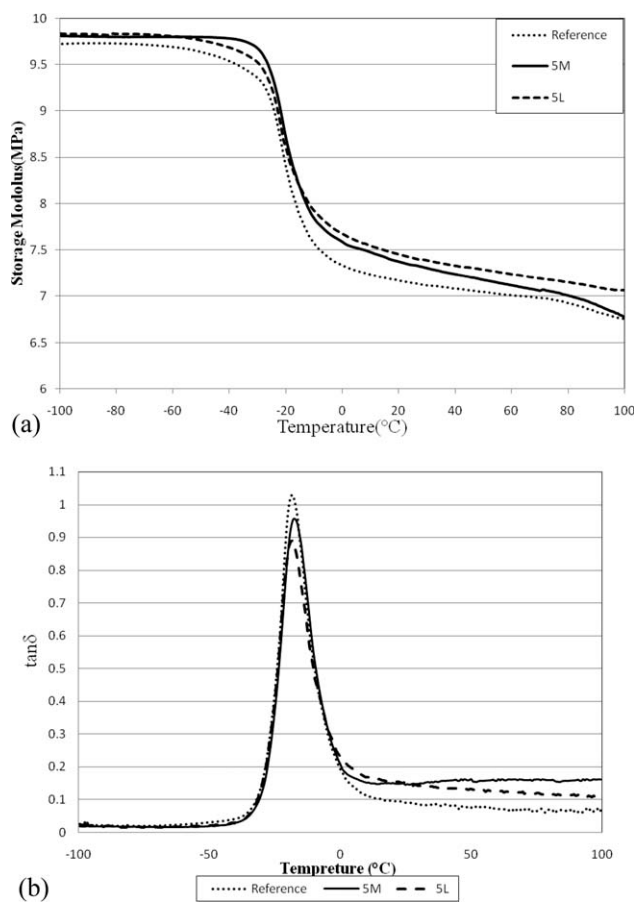


Figure 5 (a) storage modulus and (b) loss factor for 5 phr nanocomposites and the reference compound.

phase micrograph, Figure 3(b), can be distinguished and represented as nanoclay agglomerates dispersed in the rubber matrix (circles). These clay agglomerates, with clear boundaries and dimensions of few hundred nanometers segregate themselves from the matrix of rubber. In addition, some thin clay bundles, scattered around these agglomerates, are observable (rectangles).

Similar micrographs from surface of the nanocomposite prepared by the latex-coagulation method, 5L, are shown in Figures 4(a,b). In this case, nanoclays are less agglomerated as separate, dense domains as it was seen for the 5M sample, but they are more intercalated by rubber (circles). Even there are areas

TABLE II
Dynamic-Mechanical-Thermal Properties of Nanocomposites Containing 5 phr Clay and the Reference Compound

	T_g (°C)	Peak $\tan \delta$	Storage modulus @60°C (MPa)
Reference	-18.4	1.030	7.01
5 L	-18.1	0.891	7.25
5 M	-17.9	0.956	7.13

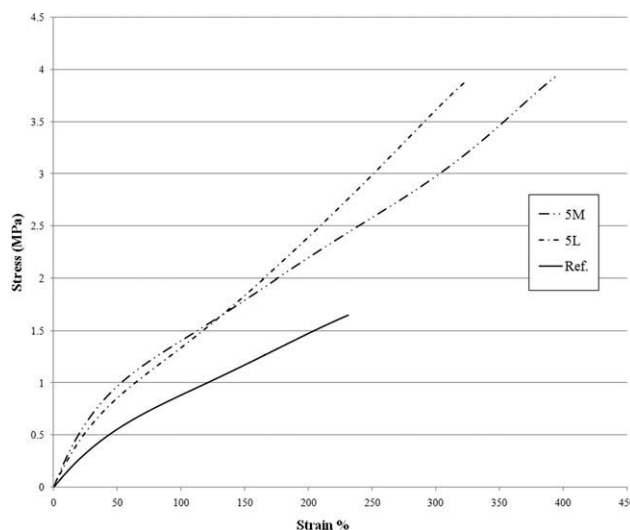


Figure 6 Representative stress-strain graphs of 5 phr nanocomposites and the reference compound.

in Figure 4a, where dark shade of exfoliated nanoclays is smeared on the light background of rubber (rectangle). Similarly, in the phase image of Figure 4b, light spots of hard nanoclays and dark spots of soft rubber are highly entangled, and it is difficult to consider them as separate phases as it was seen in the 5M sample, Figure 3b.

In general, it can be concluded that dispersion of pristine nanoclay layers in rubber was more effective by the latex-coagulation method than dispersion of modified nanoclay layers in the melt-intercalation method.

Filler-polymer interactions by DMTA

Interfacial interaction between rubber and fillers were studied by dynamic-mechanical properties of the vulcanized compounds in a temperature sweep. Results are shown in Figure 5, and important quantities are summarized in Table II. As shown in Figure 5(a), the storage modulus of both nanocomposites in the rubbery state is higher than the reference compound. Although there is a slight advantage for the latex-coagulated nanocomposite over the one prepared by the melt mixing, their storage moduli at such small strain (0.2%) are not too distinct to consider a meaningful difference. Figure 5(b) shows the loss factor ($\tan \delta$) as a function of temperature for all the samples. Rubber immobilizes in the vicinity of active fillers or in the confinement of the filler network. Reduction in the magnitude of peak loss factor (0.015 difference is considered meaningful²³) is quantitatively related to reduction in the amount of free rubber as a result of its immobilization in the presence of filler particles. Results in this figure show that nanoclays in both preparation methods are active in immobilizing the rubber chains.

TABLE III
Mechanical Properties of Nanocomposites Containing 5 phr Clay
and the Reference Compound

	Stress at 100% strain (MPa)	Stress at 300% strain (MPa)	Elongation at break (%)	Stress at break (MPa)
Reference	0.89 (0.09)	–	231 (24)	1.66 (0.17)
5 L	1.34 (0.02)	3.62 (0.03)	319 (9)	3.82 (0.09)
5 M	1.40 (0.12)	2.98 (0.13)	392 (20)	3.96 (0.25)

However, the pristine nanoclay in the latex coagulated rubber has immobilized more rubber than the organically modified nanoclay in the melt prepared composite. This can be attributed to the larger area of contact between highly dispersed nanoclay layers and rubber, better adsorption of rubber chains on the surface of pristine nanoclays in the dilute aqueous medium than in the concentrated melt state, and possibly formation of the house-of-card structure of nanoclay layers in the latex coagulated composite. There are no meaningful differences in the position of peaks on the temperature axis for the samples (0.5°C is range of error).

Mechanical properties in uniaxial tension

Representative stress–strain curves for the nanocomposites and the reference rubber are shown in Figure 6. The average and standard deviation (in the brackets) for some characteristics of this test are shown in Table III. It is clear that nanoclays have reinforced SBR as they were mixed into the rubber by both methods. However, the rate of increase in stress for the latex coagulated nanocomposite, 5L, is higher than that for the melt intercalated one, 5M. This can be attributed to better dispersion of the nanoclay, larger area of contact, and larger quantity of immobilized rubber in the former nanocomposite. The ratio of stress at 300% strain to that at 100% strain has been considered as a measure of entrapped rubber shielded from the macro-deformation by filler.²⁴ This ratio is higher for the latex-coagulated nanocomposite, showing better dispersion of nanoclay and more confinement of rubber in this case. Also there is a possibility that large amount of modifier in Cloisite 15A acts as a lubricant, contributing to the softening behavior of the composite prepared by this type of clay.

On the other hand, elongation at break for the latex coagulated sample is less, which again can be related to more immobilized rubber in this sample when compared with the melt prepared one. Tensile strength is almost the same for both nanocomposites.

CONCLUSION

In a comparative study on the latex coagulation and the melt-intercalation methods for mixing the same

amount of mineral nanoclays in the SBR matrix, it was shown that pristine nanoclay can be dispersed more effectively by the latex-coagulation method than modified nanoclay by the melt-intercalation method. AFM was successful in revealing this difference. It must be noted that to keep the amount of mineral clay the same in both nanocomposites, larger amount of the more expensive modified nanoclay had to be used. Difference in dispersion of nanoclays was further investigated by DMTA and the uniaxial tension test. DMTA showed that, as a result of better dispersion, more rubber was immobilized when it was coagulated in presence of the pristine nanoclay in aqueous state than in the melt mixing using the modified nanoclay. Results of the tension test showed that the nanocomposite prepared by the pristine nanoclay in the latex-coagulation method had higher rate of increase in stress by stretching, whereas the one prepared by the modified nanoclay in the melt-intercalation method showed a stronger softening effect and higher elongation at break as a result of less dispersed modified nanoclay. Considering lower price of the pristine nanoclay and ease of the latex-coagulation method for emulsion SBR, preparation of SBR-pristine clay nanocomposites by this method in the petrochemical industry is recommended rather than melt mixing of the modified nanoclay in the rubber industry.

The authors thank the financial support of Bandar Imam Petrochemical Company of Iran for this project.

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