Preparation and Properties of Nanostructured Rubber Composites with Montmorillonite

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Summary: Montmorillonite exfoliated nanoclay was prepared by treating montmorillonite with an alkyalmmonium salt. It has been characterized by FT-IR spectroscopy and thermal analysis (TGA-DTA). The nanoclay composites, in which the rubber matrix was introduced by mixing solutions of the elastomer with the organically modified clay was then compounded with carbon black filler at 2.5, 5, 10, 15 phr loading level of nanoclay. The sulfur cured rubber samples were tested against a reference compound not filled with the nanoclay. Rheometrical and scorch measurements have shown that the nanoclay increases the curing speed and reduces the scorch safety. A very high reinforcement and stiffening effect due to the nanoclay was observed especially at 5 and 10 phr nanoclay filling level and especially at low extension modulus which can be increased up to 40% its original level than in the reference compound. An anisotropic behavior has been recorded in the stress-strain curve: for instance the 50% modulus was found >20% higher when measured parallel to the alignment of the exfoliated nanoclay lamellae in comparison to the modulus perpendicular to the lamellae orientation. The compounds with nanoclay show no adverse effects in tensile strength and in tear resistance, in De Mattia crack initiation and in abrasion resistance. Nanoclay reduces also the hysteresis and heat build up of the rubber compounds.

Keywords: compounding; nanocomposites; organoclay; reinforcement; rubber

Introduction

Carbon black is one of the most common reinforcing fillers in use in rubber compounding since the beginning of the XX century.[1] Carbon black due to its unique particle dimension and shape and its special interaction with polymer matrices with physical and chemical bonding is able to produce an excellent nano-reinforcing effect that greatly enhances the mechanical properties of the bare polymer or rubber.[2–4]

Clays are in use since a very long time for the enhancement of mechanical properties of polymers and rubbers although their reinforcing effect is much less important than that exerted by carbon black. The typical approach in the utilization of clays in rubber and plastics composites was to break down clay particles aggregates into individual particles to form micro-sized fillers.[1,5]

The clays currently used as fillers in rubber compounds are usually hydrated aluminum silicates derived from the mineral kaolinite. They are distinguished into soft and hard clays for the fact that they give low or high modulus respectively to rubber compounds.[1] Soft clays are characterized for a higher level of alumina and for a content of 70–80% of particles <5 μm. Conversely hard clays are characterized by a lower level of alumina and up to 90% of particles <2 μm in diameter.[1] They are widely used in the production of rubber goods. With the traditional grinding approach of clays down to

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micro-sized fillers, also certain smectite-type layered clays belonging to the class of phyllosilicates, such as hectorite and montmorillonite cannot give better reinforcing effects in rubber compounds than more common hydrated aluminum-silicate clays.

The breakthrough in the preparation of nanosized fillers occurred in recent years[5–7] when it was discovered a way to separate the individual phyllosilicate layers with the aid of alkylammonium salts. By treating montmorillonite or related clays with the mentioned agents the layers which are kept together by Van der Waals dispersive forces are separated by the insertion of the organic molecules. For this reason the clays are also known as organoclays. The exchangeable alkaline cations which were present in the interlayer gap of montomorillonite giving hydrophilic properties to the clay are replaced by the alkylammonium molecules changing the clay nature from hydrophilic to organophilic thus permitting the clay to become much more compatible with the polymer matrix.[5–7]

A nanostructured clay is thus formed by the individual silicate layers having a thickness of 1 nm and a diameter between 30 nm and several microns, completely intercalated by the alkylammonium salt. In such a way the structure of the clay has been controlled on nanometer scale and no more on micrometer scale as it was possible with the old technology.[5,6]

In other words, the old technology involved only the micronization of the clays which means the reduction of the clay aggregated to micron-sized dimensions *without* the possibility to separate the layers. The new technology instead implies the exfoliation of the layers silicate permitting to achieve unusual morphologies in nanocomposites and therefore unusual mechanical properties in polymer-based compounds.[2]

The simplest way to introduce a nanoclay in a polymer matrix consists in the melt processing.[7] The nanoclay is added in the polymer matrix during mixing stage when the matrix was in a viscous liquid-like stage. However, with this simple approach is not possible to achieve particularly impressive reinforcing properties. In fact literature data suggest that the aid of a solvent is absolutely necessary to achieve measurable reinforcing effects due to the complete dispersion of the nanoclay.[8] Thus, the most recommendable approach in the preparation of nanocomposites involves the addition of the nanoclay into a rubber matrix dissolved in a solvent like for instance toluene.[8] In these conditions it is possible to achieve a dispersion of the nanoclay which produces an exfoliated nanocomposite. At higher loading, or when the interlayer interactions remain significant it is no more possible to talk about exfoliated nanocomposite and it is talked about flocculated nanocomposites. Only if a single polymer chain is introduced between two nanoclay layers, as a sandwich, then it is necessary to talk about intercalated nanocomposites. The astonishing reinforcing effect observed when exfoliated nanocomposites are prepared with a polymer matrix are attributed to the very high Young modulus in the nanolayer direction: up to 500 times the value of the polymer and the fact that each nanolayer offers a much more interaction with the polymer bulk in comparison to the case of a micronized aggregate.[5,6] The radius of gyration of a typical polymer has the values of tens of nm, which is the same order of magnitude of the thickness and also the diameter of certain nanoclays. Thus, a much more homogeneous phase between filler and polymer can be achieved in comparison to the morphology obtained when a micron-sized clay aggregates are dispersed in a polymer matrix. This fact implies certainly a much more filler-polymer interaction in nanocomposites which is the basis for the achievement of an excellent reinforcing effect. Furthermore, at opportune filler loadings only the filler-polymer interaction governs the reinforcing effect without the deleterious influence of the filler-filler interaction which is the basis of filler flocculation or clumping.

In this paper we explore the adoption of a montmorillonite nanoclay in a natural-rubber/SBR-based formulation. The procedure in the composite preparation adopted is practically the same described J.E. Mark and colleagues[8] involving a pre-mixing of the organoclay with the elastomers in a solvent followed by drying. The resulting nanomasterbatch was then used to prepare a common vulcanizable rubber compound for the study of the mechanical properties.

Experimental Part

Montmorillonite suspended in water was treated with a tetralkylammonium salt and collected by precipitation and filtration. The nanoclay was thus dried before use. Hereinafter the exfoliated montmorillonite will be simply referred as ''nanoclay''.

The presence of the alkylammonium in the clay was checked by FT-IR spectroscopy using a Nicolet IR300 from Thermo-Electron Corporation and the amount of alkylammonium salt picked up by the organophilic clay was measured thermogravimetrically on a Linseis apparatus (model L81+DTA).

The nanoclay was tested in a standard formulation we have already employed to test pyrolytic carbon black.[9] The testing formulation was as follows: natural rubber (SIR-20), 59.8 phr; S1712, 55.4 phr; carbon black N339, 75 phr; aromatic oil (DAE) 17 phr; stearic acid, 2 phr; zinc oxide, 3 phr; wax, 2.0 phr; TMQ, 1 phr; 6PPD, 1.5 phr; CBS, 1.8 phr; sulphur, 1.5 phr.

The nanoclay was added to a toluene solution of the required amount of natural rubber and S1712 type emulsion SBR. After stirring the solvent was distilled off under reduced pressure and the resulting nanomasterbatch was dried in an oven at 70 °C for one day before proceeding with the preparation of the composite with the other ingredients in a common internal mixer.[8]

The nanoclay was used in the above formulation at 2.5, 5, 10 and 15 phr respectively. Naturally, a ''blank'' reference compound without nanoclay was mixed as well.

After sheeting the rubber foils were rolled and passed in the mill put the roll in the same direction of motion of the rotors in order to impart a preferential direction to the filler. This operation was repeated three times before leaving to cool down the compounds. All specimens were prepared and tested according to the standard ASTM or ISO procedures using state-of-the-art equipment. In particular, rheometer curves for the cure kinetics were recorded at 150 °C for 30 minutes on an MDR2000 rheometer from Alpha Technologies. Mooney viscosity and Mooney scorch were measured on an Alpha Technologies viscosimeter. The stress-strain properties of the cured rubber compounds were measured on standard ISO dumbbell specimens using an Instron dynamometer under ISO conditions. All specimens were cured at 151 °C for 30 minutes. For each compound under testing 6 dumbbells were prepared. Three of them were cut in the direction parallel to the orientation of the sheeting and three of them were cut perpendicularly to the direction of the sheeting. The anisotropic factor σ was defined as the ratio of the modulus parallel (m_{pa}) to the sheeting over the modulus perpendicular to the sheeting (m_{pp}):

$$\sigma = (m_{pa}/m_{pp})100$$

The data obtained are the average of the three samples tested. In any case, mixing and testing for each rubber compound was repeated three times and the data reported here are the average of all the three batches (a total of 9 samples per each measurement reported).

Abrasion was measured on the DIN abrader according to the standard conditions. The heat build up of each sample was measured on a Goodrich flexometer at 35 Hz again under standard ISO conditions. The heat index was measured as the ratio between the Goodrich HBU and the hardness IRHD. Finally, angle tear and

DeMattia crack initiation tests were made as well.

Results and Discussion

FT-IR and Thermal Stability of the Nanoclay

The FT-IR of montmorillonite is dominated by a broad and intense peak at about 1060 cm^{-1} due to the Si-O-Si stretching. When montmorillonite is exfoliated and complexed with alkylammonium cations, the alkyl stretching bands appear at 2922 and 2850 cm^{-1} accompanied by a narrow band at 1470 cm^{-1} attributable to alkyl, essentially methyl groups of the ammonium salt.[10] The exfoliated montmorillonite show also a shift in the band originally located at 1060 cm^{-1} to lower energy: 1000–1010 cm^{-1}.

The TGA of the nanoclay used in the present work is shown in Fig. 1 together with the DTA curve. The material looses weight quite gradually till 251 °C because of the vaporization of residual water and vaporization of the organic salt not confined in the interlamellar region (<10% by weight). After this stage an abrupt decomposition occurs as suggested also by the exothermal transition at the DTA curve with the maximum decomposition rate at 326 °C. Under these conditions all the organic fraction present in the nanoclay is destroyed.[10] Based on the TGA curve of Fig. 1 it can be reasonable estimated that the total organic fraction in the nanoclay is about 45% by weight.

These data show that the nanoclay adopted in this work has a sufficient heat stability to be used in the preparation of a rubber compound where temperatures as high as 180 °C can be reached during mixing.

Some Observations on the Nanocomposite Preparation

One of the key problem in nanocomposite preparation with nanoclay is the preservation of the exfoliated montmorillonite layers during the mixing with the rubber matrix. If this condition is not fulfilled then any advantage derived from the application of the nanoclay in terms of reinforcement is

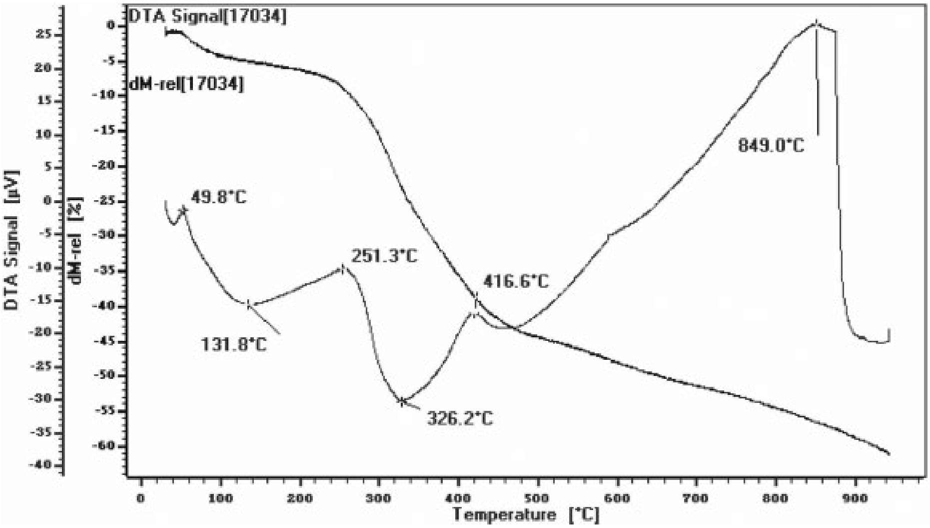

Figure 1.

TGA-DTA of the esfoliated nanoclay. The maximum decomposition rate occurs at 326 °C but a significant weight loss occurs already at about 250 °C. The total volatile matter present in the nanoclay should be about 43% by weight as deduced from the TGA curve.

lost. Therefore, the application of the nanoclay in a rubber compound cannot be done in a simple procedure because the risk of clumping, flocculation or re-aggregation of the layers is very high. Recently in literature appeared special procedures where the nanoclay is mixed with rubber latex in aqueous medium.[11,12] After drying the rubber-nanocaly masterbatch is compounded with the other usual rubber compound ingredient to make it vulcanizable. As described in the experimental section, we have preferred to adopt a more consolidated procedure first proposed by J.E. Mark and colleagues[8] consisting in dissolving the rubber matrix in toluene and adding the organoclay to the solution. This procedure ensures an adequate dispersion of the exfoliated nanoclay into the rubber matrix. The masterbatch is then recovered by distilling off the solvent and compounding it in a close mixer with other conventional compound ingredients (see the experimental section). This procedure proved to be effective in achieving unusual mechanical properties in the resulting cured nanocomposites as will be discussed in the following sections.

Cure Kinetics and Compound Viscosity

As expected, the addition of nanoclay to the rubber compound causes faster curing and reduced scorch safety. This fact is illustrated in Fig. 2, where it is possible to appreciate that the alkylammonium salt present in the nanoclay accelerates cure kinetics as observed by the reduction of the t10, t50 and t90 parameters of the rheometer curve. The acceleration of the cure

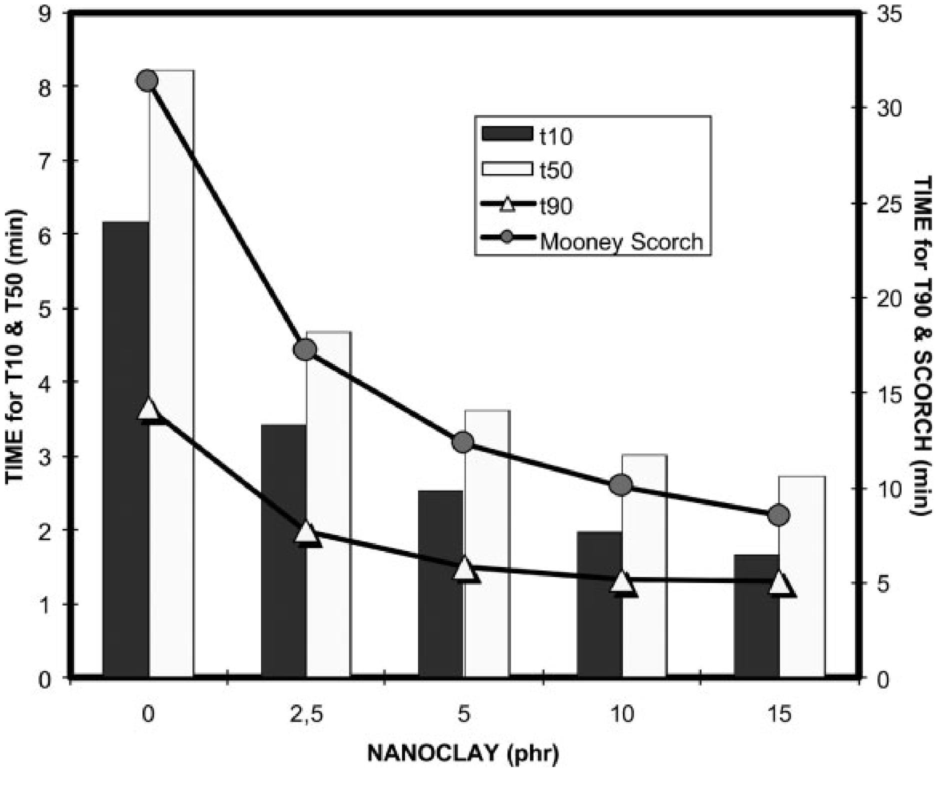

Figure 2.

Effect of the nanoclay on the cure speed of the NR/SBR standard compound. All the parameters used to measure the cure speed: T10, T50 and T90 become smaller as the nanoclay loading increases. Thus, the cure speed increases as function of the amount of nanoclay added because of the effect of the alkylammonium salt present in it which acts as accelerator. Similarly, also the scorch safety is reduced.

speed is proportional to the amount of the nanoclay added and consequently to the amount of alkylammonium salt added to the clay. Being maximum at 15 phr of nanoclay. Similarly the scorch safety at 127 °C, which was of 31.37 min, drops down to 17.21 min when only 2.5 phr of nanoclay were added (Fig. 2), and is reduced further at higher nanoclay loading. It is generally known that amines and alkaline substances accelerate the cure speed. Therefore also the alkylammonium salts do not represent an exception. If a low scorch safety may represent a processing problem, a high cure speed in general can be considered beneficial. In any case the purpose of the present work was to explore the effects of the nanoclay in a standard rubber compound without making any optimization and adjustment to the formulation.

Despite the clear effect on cure kinetics, the both the minimum torque (ML) and the maximum torque (MH) of the rheometer curves are not affected at all by the presence of the nanoclay. In fact the compound Mooney viscosity measured at 100 °C was 39.6 Mooney points for the reference compound without nanoclay and remained around 40 Mooney point also for all the samples loaded at different levels of nanoclay.

Nanoclay Reinforcing Effect

As already anticipated from the maximum torque of the rheometer curves, the addition of the nanoclay to the standard rubber compound does not cause significant changes in the tensile strength. This is illustrated in Fig. 3 where the tensile index values are reported. Made 100 the tensile of the reference compound without nanoclay, as shown in Fig. 3 the addition of the nanoclay causes only a very slight reduction of the tensile, a reduction which has the order of magnitude of 5% and which is within the experimental testing error.

Conversely, the addition of the nanoclay causes a gradual reduction in the elongation at break (Fig. 3) which grows as function of the amount of the nanoclay added. At 10 phr level the reduction in elongation is 15% less than the reference compound. The

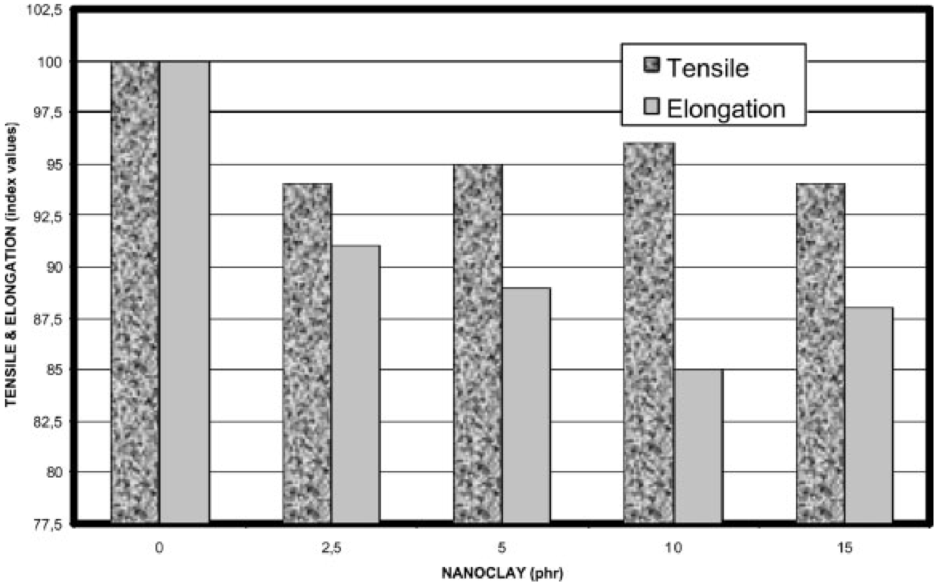

Figure 3.
The nanoclay addition does not affect significantly the tensile strength of the standard rubber compound. Instead the elongation at break is reduced significantly due to the stiffening effect offered by the nanoclay addition.

reduction in elongation at break is a consequence of the stiffening effect exerted by the nanoclay added to a certain compound. The stiffening effect can be observed both in the enhancement of hardness as well as in the significant increase in moduli especially at low extension (Fig. 4).

In fact hardness passes from a value of 61.6 points IRHD to 65 at 2.5 phr nanoclay to 65.5 and 66.5 points IRHD at 5 and 10 phr nanoclay respectively to 67,1 IRHD points at 15 phr nanoclay loading. Even more spectacular are the effects on moduli as shown in Fig. 4. At 2.5 phr nanoclay loading the moduli increase already from 13% to 22% the reference value, but the maximum effect occurs at 10 phr nanoclay level, where the 50% and 100% moduli increase about the 44% of the original value. Above 10 phr loading the properties start to fall down to the reference value. It is also remarkable to note that the reinforcing and stiffening effect is much more pronounced with the moduli at low extension (50% and 100% and is still significant at higher extension 200% and 300% but vanishes completely at the tensile strength conditions which remain the same as the reference compound as pointed out before.

By comparing Fig. 3 with Fig. 4, it is remarkable to note that at 10 phr nanoclay level, when the maximum reinforcing effect is achieved from the nanoclay contribution, also the elongation at break reaches its minimum.

The reinforcing effect is maximum at low extension when the filler-polymer interaction is at the maximum level and the nanoclay can display its better interaction with the bulk polymer matrix.[5,7] At higher elongation and under tensile condition, the mechanical properties became more dependant on the polymer-polymer interaction and the effect due to the nanoclay presence tends to vanish.

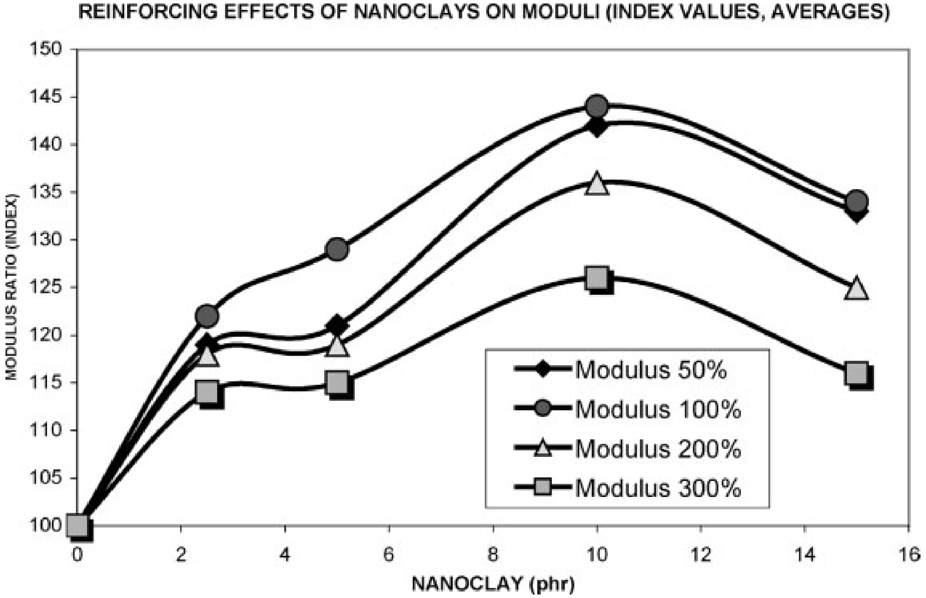

Figure 4.
The stiffening and reinforcing effect exerted from the nanoclay can be appreciated in this figure. At only 2.5 phr loading the 100% modulus increases by a factor of 1.23 over the same modulus measured on the reference compound. The maximum effect occurs at 10 phr nanoclay loading. In these conditions both 50% and 100% moduli increase by a factor >1.40 in comparison to the reference compound. The effect is more pronounced at low elongation rather than at higher elongations (see text).

In the experimental section we have defined an anisotropic factor $\sigma = (m_{pa}/m_{pp})$ 100 as the ratio of the modulus at a given extension measured parallel or perpendicularly to the sheeting direction in an open mill. Certainly, the sheeting operation adopted by us (see the experimental section) gives a preferential orientation of the nanoclay exfoliated lamellae. Thus, the testing specimens were tested with traction parallel to the orientation of the lamellae and with traction perpendicular to them. An anisotropic factor of about 110 was also found in the reference compound without nanoclay. After normalization to 100 for the reference compound, it was found a significantly higher anisotropic factor in the samples filled with nanoclay. Figure 5 provides a summary of our results. The anisotropic factor is evident at 5 and 10 phr nanoclay loading and is maximum at 5 phr loading. Again, the anisotropic factor is much more pronounced for moduli at low extension such as 50% and 100% moduli and vanishes at higher extension. For instance at 5 phr nanoclay loading the 50% modulus measured in the direction parallel to the nanoclay lamellae preferential orientation is 1.2 times higher that the 50% modulus measured on the same specimen but perpendicularly to the lamellae orientation.

Thus, the individual preferential orientation of the nanoclay lamellae provides the macroscopic effect of the anisotropic behaviour of the rubber compounds.

Other Mechanical Properties

In order to make a complete exploration of the advantages offered by the nanoclay in tailoring new rubber compounds, also angle tear, DIN abrasion and De Mattia test were run in the compounds at different nanoclay loading.

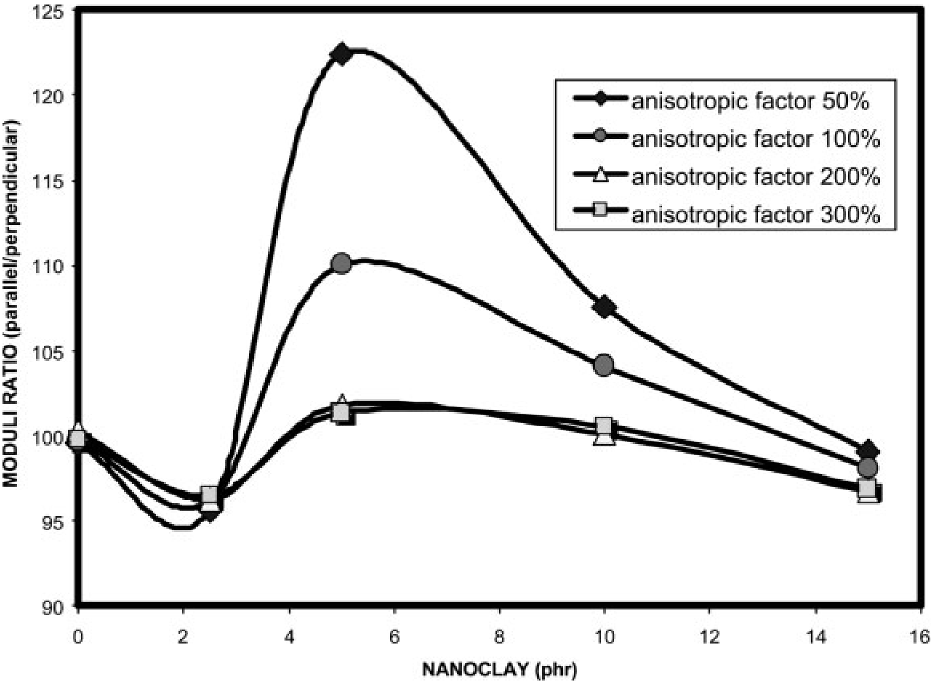

Figure 5.
The rubber compounds filled with nanoclay, after appropriate handling at the open mill show a macroscopic anisotropy especially on moduli at low extension. For instance at 5 phr loading the 50% modulus measured in the direction parallel to the nanoclay lamellae preferential orientation is 1.2 times higher that the 50% modulus measured on the same specimen but perpendicularly to the lamellae orientation.

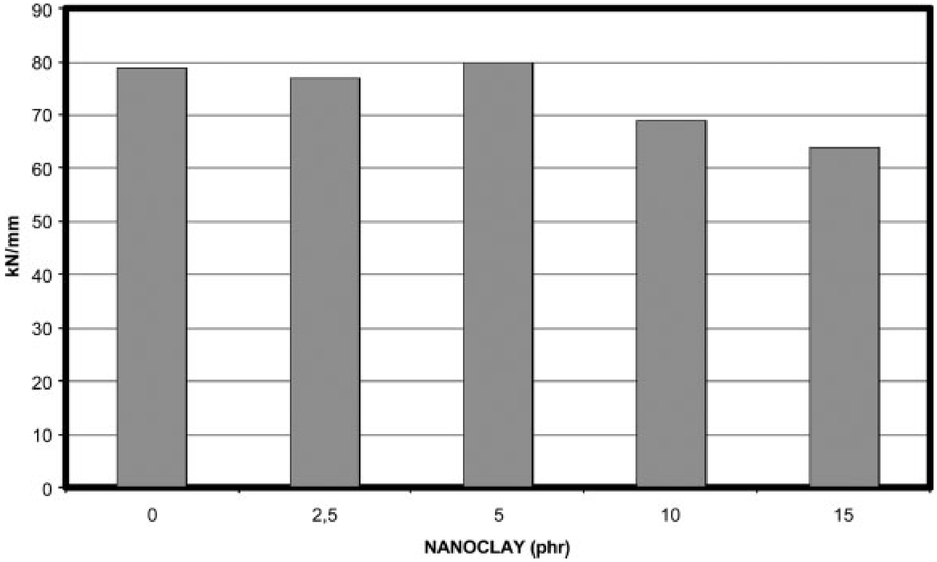

Figure 6.
Tear resistance of compound filled with nanoclay remains unchanged to 5 phr loading. Then tends to become slightly lower that the reference value but the reduction may be considered negligible.

In Fig. 6 it is shown that the tear resistance of the rubber compound filled with 5 phr of nanoclay remains at the same level as the reference compound, while a slight drop in tear resistance can be observed at 10 and 15 phr level. The drop is not so dramatic, especially at 10 phr to compromise the general performances of the rubber compound. It should be remembered that in general stiffer compounds display worse tear resistance. In the compounds with nanoclay the very high stiffening effect does not affect particularly the tear resistance. These results have been confirmed also with the De Mattia crack initiation tests: no particular differences against the reference compound without nanoclay have been detected.

In terms of abrasion resistance at the DIN abrader, no significant differences have been detected in all samples filled with nanoclay in comparison to the reference compound.

Effect of Nanoclay on Dynamic Properties

To complete our exploration on the effects of nanoclay in a NR/SBR rubber compound we looked also at certain dynamic properties such as the generation of heat under cyclic deformation. We have used the classic test of the Goodrich flexometer and the temperature increase was then divided by the hardness of the sample to have a heat index. All the data of this study are reported in Fig. 7.

It can be observed that the heat build up decreases by adding the nanoclay and the best results are already achieved at 5 phr nanoclay level. The further addition nanoclay does not affect anymore the heat index. Thus, the nanoclay offers also the beneficial effect of being able to reduce the hysteresis of a rubber compound.

The specimens used for the Goodrich test can also be used to measure the permanent set of them and hence the relative compression set. Surprisingly the compression set of the compounds loaded with nanoclay was significantly lower that the compression set of the reference compound. In fact, the latter reached a permanent set of −16,2% while all the other samples loaded with nanoclay reached a permanent set of only −10%.

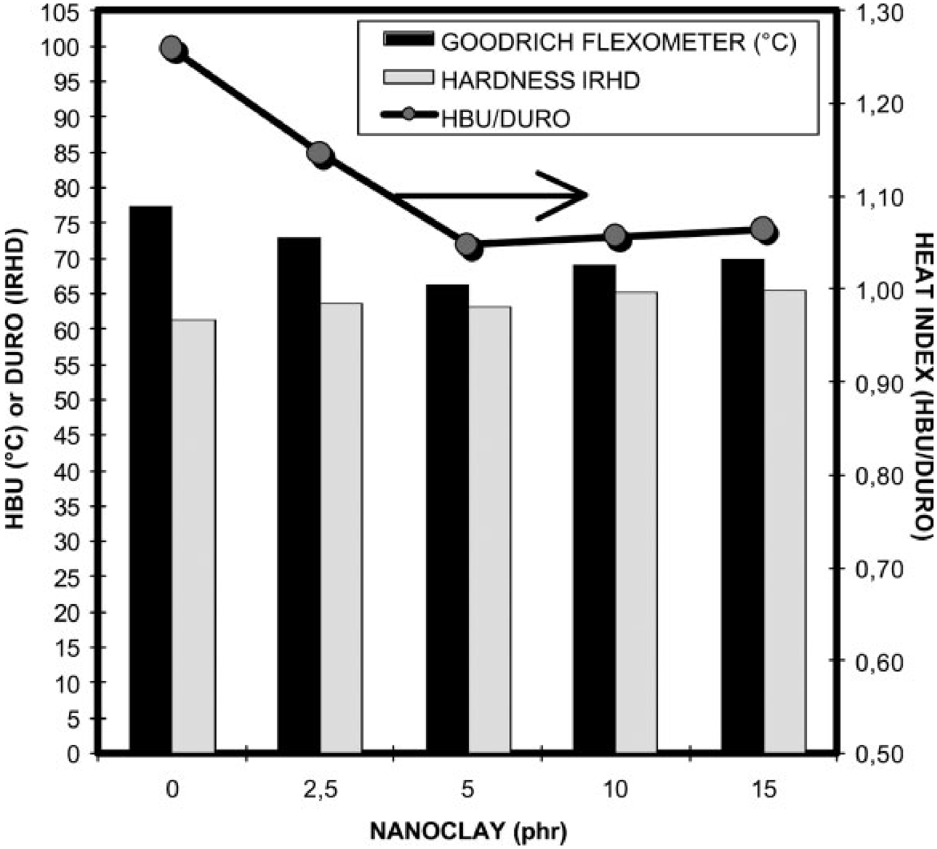

Figure 7.
At the Goodrich flexometer the compounds filled with nanoclay show lower heat build up and hence hysteresis than the reference compound without nanocaly. The heat index calculated as the ratio between the temperature jump at the Goodrich flexometer and the hardness IRHD confirms the trend to lower hysteresis for the nanoclay filled compounds.

Conclusions

The present work is only a preliminary exploration of the potentialities offered by the use of the nanoclays in rubber compound formulation. The formulation selected was a carbon black filled NR/SBR compound to which were added 2.5, 5, 10 and 15 phr of a montmorillonite nanoclay. The preparation of the rubber composite was made according to literature conditions[8] with the aid of a solvent.

The addition of the nanoclay causes an increase the in the cure rate and consequently a reduction of the scorch safety. This effect is explained by the high level of alkylammonium cations present in the exfoliated clay. Faster cure and reduced scorch safety are not necessarily deleterious effects, depending on the application they can be also desired. If these properties are undesired, an adequate adjustment of the formulation is surely possible.

The experimental data show that the addition of the nanoclay causes an impressive increase to the low extension moduli especially the 50% and 100% moduli. The maximum effect is observed at 10 phr of nanoclay loading. The low extension moduli are increased by >40% the value of the reference compound but the reinforcing effect is much less evident at much higher extension. In fact it does not affect at all the tensile strength which is maintained at the level of the control while the elongation at break is reduced significantly due to the stiffening effect of the nanoclay.

For the first time an anisotropic behavior has been observed in the rubber compounds filled with the nanoclay after having given them a specific mechanical preferential orientation. Again, the anisotropy was found more evident at lower extension rather than at higher extension.

The addition of the nanoclay does not have deleterious effects on tear resistance, on De Mattia crack initiation and on DIN abrasion.

The rubber compound filled with nanoclay show lower hysteresis, lower heat build up under dynamic conditions and significantly reduced compression set.

The best nanoclay loading level permitting to combine the advantages offered by this new filler with the maintenance of the performances of the reference compound appear to be comprised between 5 and 10 phr.

The nanoclays represent a new powerful tool in the hands of the compounders. A new era in rubber compound formulation is just started.

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