A novel method based on specific measurements for enhancing the dispersion quality of nanofillers in natural rubber latex

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Abstract

Two different fillers, namely carbon black (CB) and carbon nanotubes (CNTs) were applied in various concentrations into natural rubber latex (NRL) to investigate their dispersion within the latex itself. In this work, a novel method, the clash method as well as the conventional mechanical mixing were used to study their effect on enhancing filler dispersion in the rubber matrix. The morphology of the rubber composites was evaluated by transmission electron microscopy (TEM). The swelling measurements revealed that the degree of swelling of the composites containing 5 phr CNTs nanofiller prepared by clash method was greatly enhanced. However, the presence of CNTs, especially 2 phr nanofiller content, in the rubber composite improved the tensile strength to a great extent in case of the clash method, and reached ~ 5.90 MPa compared to neat NRL (i.e., ~ 0.80 MPa) or other nanocomposites. Thus, the obtained results based on clash method provide a promising approach

Keywords: Carbon nanotubes, Natural rubber latex, Clash method, Swelling measurements, Tensile strength

1 Introduction

Elastomers, such as natural rubber latex (NRL) are widely used in the industrial and medical domains, mainly because of its high elasticity and good mechanical properties [1,2]. To improve NRL properties, they require blending with reinforcement fillers to optimize their all-round performance in service conditions [3,4]. Carbon black and silica still remain the classical fillers for rubber purpose. Recently, nanofillers, in particularly organoclay and carbon nanotubes have received much attention for the reinforcement in polymer matrix because of their nano-dispersion. However, rubber properties are dependent on not only the filler adding, but also the level of dispersion in the polymer matrix [5]. The use of the compatibilizer such as polymer grafted maleic anhydride [6] or modified filler by organic surfactant [7,8] increases the degree of filler dispersion within the matrix by melt blending or by direct compounding or by sol-gel process [9,10]. In some cases, silane coupling agent or a functional oligomer (PP-OH) is usually added with the rubber in the mixing process in order to enhance the dispersion efficiency of the filler when the rubber possesses a non-polar group in its backbone or the filler used is a hydrophilic filler such as silica [11-14]. Many researches [15-17] focus mainly on filler dispersion and filler interaction within the rubber matrix, because they are considered the key factors to obtain excellent mechanical properties. Nevertheless, the dispersion of some fillers such as layered silicate into a polymer matrix is still very difficult because of its hydrophilic nature and its aggregates into the polymer matrix. To overcome these difficulties, filler modification or rubber treatment is required to promote filler dispersion.

In this study, a novel approach, namely the clash method was used to improve the dispersion quality of carbon black (CB) and carbon nanotubes (CNTs) fillers in NRL. The conventional mechanical mixing was also discussed for comparison. The filler dispersion within the NRL for both approaches was characterized by TEM observations. The tensile properties and the percentage swelling of the vulcanized samples were also measured.

2 Materials and methods

2.1. Materials

Natural rubber latex (NRL) with 60% of dry rubber content was purchased from Weber & Schaer GmbH & Co. KG, Ferdinandstrasse 29 - 20095 Hamburg, Germany. Carbon nanotubes (CNTs) and (ISAF) carbon black (CORAX-N220) were provided by Degussa, Germany. Dicumyl peroxide (DCP) (98%) used as a crosslinking agent, was supplied by Sigma-Aldrich. Formic acid and sodium dodecyl sulphate (SDS, 90%) were provided by Merck Chemical Co., where SDS was used as a surfactant for dispersing the nano-fillers in distilled H_2O.

2.2. Preparation of NRL-filler composites

The dispersion of the nano-fillers in the NRL is carried out by using two methods described as follows:

2.2.1. By mechanical mixing

The dispersion of 1, 2 or 5 phr (part per hundred of rubber) of the CB N220/or CNTs in 100 ml of distilled water in presence of 5 g of SDS was carried out by using ultra-turrax T25, Janke & Kunkel IKA-Labortechnik as a stirring device for 10 min at ambient temperature to obtain carbon slurry. A hundred gram of NRL was weighed in 500 ml clean beaker, and then the slurry was added to NRL with continuous stirring for 15 min at room temperature to ensure good mixing of the compounds. The coagulation process has been done by the addition of 100 ml of distilled water to the mixture followed by 10-15 ml of formic acid added to form coagulated blends. Afterwards, the coagulated blends were filtered, washed with distilled water and remained about 10 h at room temperature. The blends were then cut into small pieces and dried in vacuum oven at 60°C for 6 h to remove the excess of water and acid.

2.2.2. By clash method

In this procedure, 1, 2 or 5 phr of CB N220 or CNTs was first dispersed in 100 ml distilled water with 5 g of SDS by Ultra-turrax stirrer for 10 min to form the carbon slurry. Then it is directly transferred to stainless steel container and simultaneously, 100 g of NRL was weighed and put in another container with continuous stirring of the two containers by magnetic stirrer as shown in Fig. 1. The air compressor was turned on to give pressure of 8 bars, and then the two valves were opened at the same time. The air pressure pushed the NR latex and the carbon slurry in high speed to clash together through two parallel copper cones which their internal diameters are 0.9 mm, then the mixture of NRL/CB or NRL/CNTs were collected in the final container to be investigated as shown in Fig. 1. Afterwards, small part of this mixture was taken to carry out the morphology by TEM; while the major part was firstly coagulated and was then dried by the same processes as mentioned above in the mechanical mixing. After the drying process, the filled composites produced by the two methods were incorporated with 3 phr dicumyl peroxide (DCP) by using two-roll mill at 70°C for 10 min. The samples were then molded by placing them in a molding set comprising of 100 x 100 x 2 mm thick steel spacer placed between two Mylar papers and two steel slabs using Hydraulic Press at 170°C and under a pressure of 150 kg/cm2 for 10 min. The molding set were cooled down by tap water for 5 min. A NRL sample was also processed under the same conditions without additives and used as a blank.

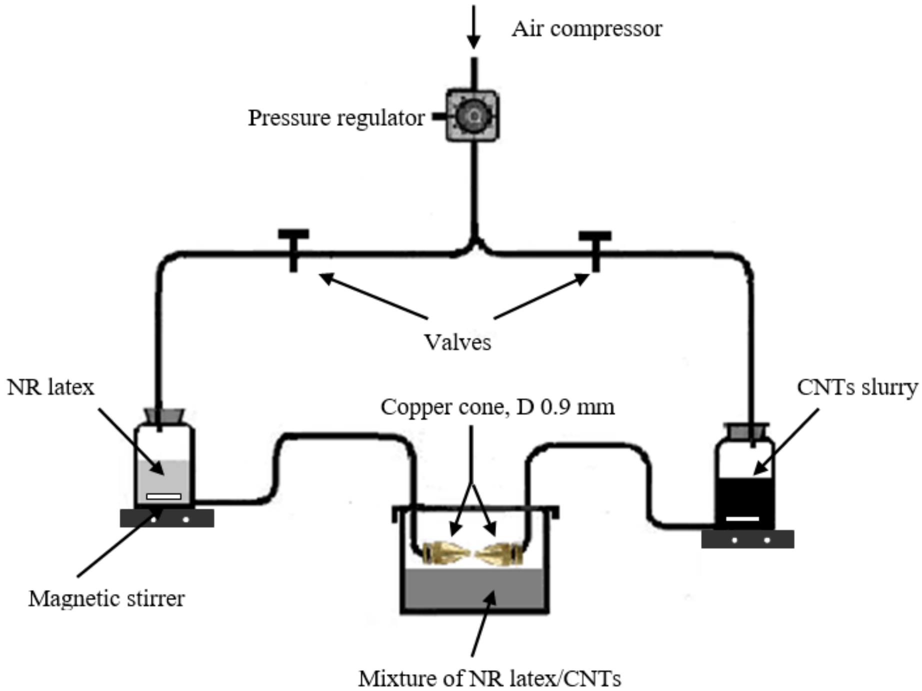

Figure 1: Schematic representation of dispersion of nanofillers in NRL by clash method.

2.3. Characterization and measurements

2.3.1. Morphology study

Morphology of composites was characterized by using transmission electron microscopy TEM-Philips CM 200 and accelerating voltage of 200 kV. Each sample has been prepared after dilution and dispersion by ultrasonics, where some drops were put in the grid surface to be investigated.

2.3.2. Swelling measurements

The samples of dimensions, 10 x 10 x 2 mm were used to determine the equilibrium swelling behavior of vulcanized NRL and its filled composites in case of mechanical and clash techniques. The initial weights of the samples were weighed, and then they were immersed in test bottle containing 50 cm^3 of toluene for 3 days at ambient temperature, and the solvent was renewed after 12 h. The swollen weight, W_s was then recorded after 24, 48, and 72 h. Finally, the samples were dried in the vacuum oven for a period of 6 h at 60 °C till constant weight. The swelling degree, S % for samples was calculated from the following equation [18]:

$$S,\% = \frac{(W_s - W_d)}{W_d} x100 \qquad (1)$$

Where W_d is the weight after drying.

2.3.3. Mechanical testing

For measuring the tensile tests of unfilled and filled NRL composites, dumbbell shaped samples were cut from the molded sheets. Tensile properties were realized by using a Dynamometer (Lhomargy DY 34 d'Adamel-Lhomargy); at a temperature of 23 ± 2°C and at a relative humidity of 50 ± 5% with a crosshead speed of 500 mm/min according to ISO 37:2017 standard. The sample length between the grips was 25 mm and its width was 4 mm. Five measurements from each sample were tested and the average values were reported.

3. Results and Discussion

3.1. Morphology study

The dispersion of nano-fillers in NRL at different filler contents was observed by TEM visualization technique in comparison between the mechanical mixing and high-speed clash methods. Fig. 2 shows that the CB and CNTs are dispersed outside the NRL matrix in case of the two mixing techniques at 1 phr filler content, except the case of NRL/CB composite where CB is located as aggregates into the matrix by clash method, as shown in Fig. 2 (b).

The degree of dispersion of nano-fillers is obviously improved at 2 phr in case of clash method, most of nano-fillers are observed within the NRL matrix, while the majority of nano-fillers are located outside the matrix in case of the mechanical mixing route as shown in Fig. 3(e) and 3(g).With increasing filler loadings up to 5 phr, it can be noticed that the nano-fillers are located inside the NRL matrix except NRL/CNTs composites in which part of fillers are observed outside the matrix in case of clash method, as shown in Fig. 4 (l). It is important to note that the filler distributions are fairly well dispersed within the rubber matrix in case of clash method rather than mechanical mixing in which the aggregates are formed outside the matrix. It can be said that the dispersion quality of nano-fillers in NRL matrix was achieved by using clash method, which exhibited unique filler-rubber dispersion based on rubber latex or emulsion as a novel technique.

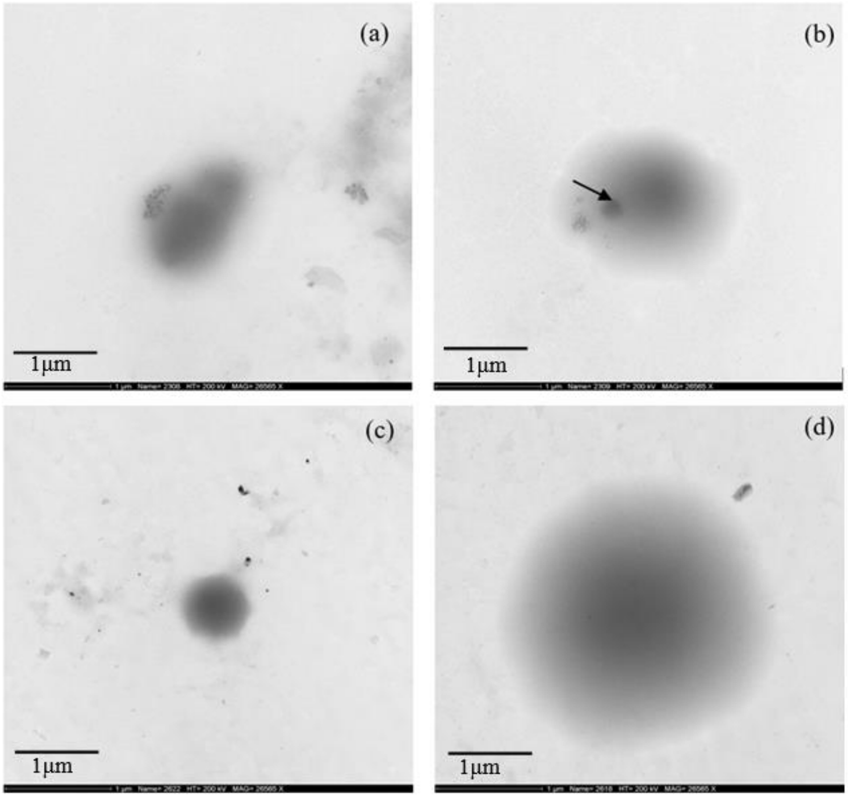

Figure 2: TEM micrographs of a) NRL/CB mechanical, (b) NRL/CB clash, (c) NRL/CNTs mechanical, (d) NRL/CNTs clash, at 1 phr of each filler at 20000x.

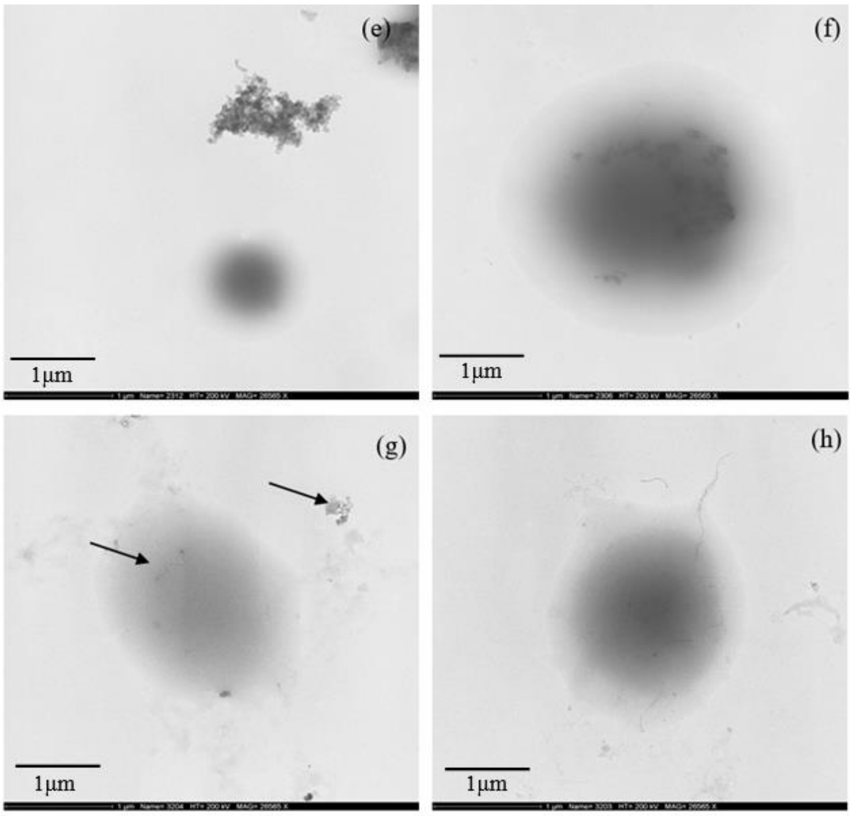

Figure 3: TEM micrographs of e) NRL/CB mech., (f) NRL/CB clash, (g) NRL/CNTs mechanical, (h) NRL/CNTs clash, at 2 phr of each filler at 20000x.

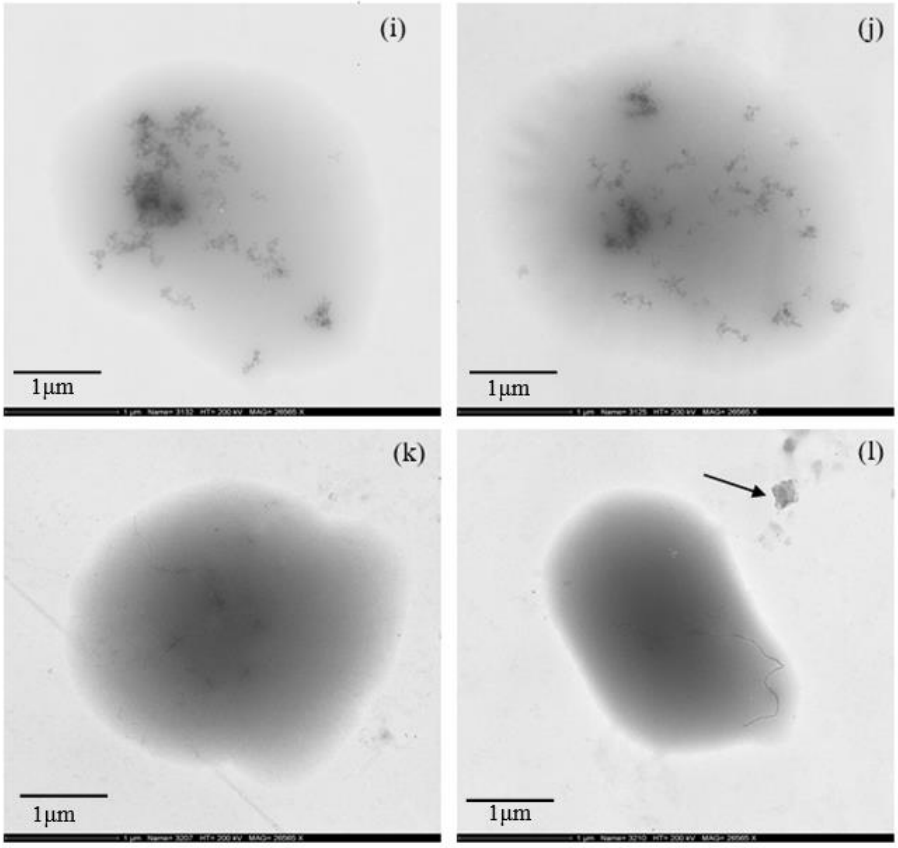

Figure 4: TEM micrographs of i) NRL/CB mech., (j) NRL/CB clash, (k) NRL/CNTs mechanical, (l) NRL/CNTs clash, at 5 phr of each filler at 20000x.

3.2. Swelling measurements

Fig. 5 presents the percentage swelling for the unfilled and filled composites with different CB and CNTs filler contents: 1, 2, and 5 phr by using the two mixing techniques. The figure shows that there were no changes in the swelling values at filler contents 1 and 2 phr in case of the two dispersing techniques. However, the swelling values were clearly decreased with increasing the filler content up to 5 phr, and that the swelling values in case of clash method were lower than those in case of mechanical mixing. The decrease in the swelling values of composites filled with CNTs filler in case of clash and mechanical techniques were about 35%and 17%, respectively, compared to those of the neat NRL, see Fig. 5(a). The enhancement in the swelling data by using the clash method may be due to the better dispersion of the CNTs and their presence in aggregates structure in the natural rubber latex. These results are consistent with that obtained in the morphology investigation. While in case of CB filler, the enhancement in the swelling behavior is limited, as can be shown from Fig. 5(b).

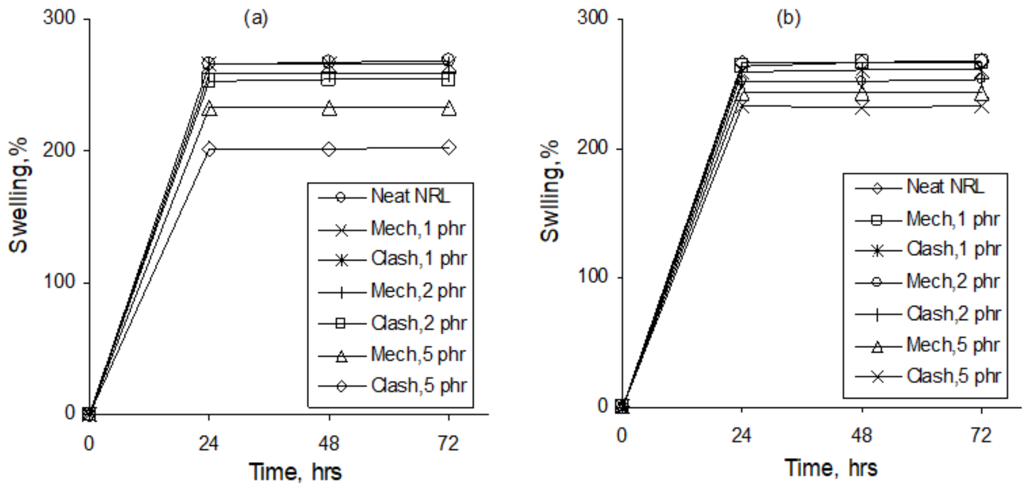

Figure 5: Swelling behaviors for unfilled NRL and its filled composites at (a) different CNTs filler contents, at (b) different CB filler contents by using mechanical and clash methods.

3.3. The mechanical properties

The tensile properties were carried out to monitor the dispersion quality of nano-fillers within the NRL matrix, as well as to evaluate the reinforcing effect in comparative study between the two mixing techniques. Figs. 6, 7, and 8 summarize the tensile properties of unfilled NRL and its filled composites at different contents of CB and CNTs fillers; 1, 2, and 5 phr by mechanical mixing and clash method, respectively. Fig. 6 shows that the tensile values of the composites filled with 1 phr content of both fillers increased than that of the pure NRL. The figure also shows that the tensile strength is enhanced for composites filled with CNTs rather than those filled with CB. In addition, the clash technique for both nanofillers is preferable to give high tensile strength values than the mechanical technique.

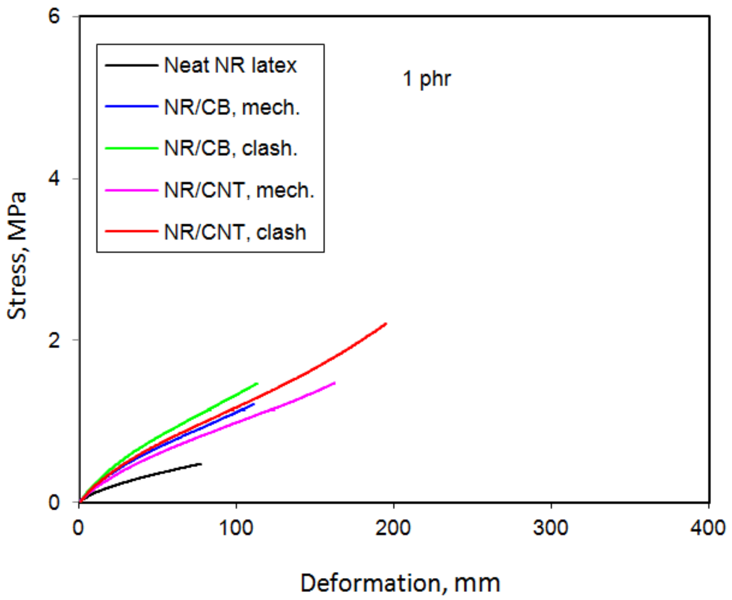

Figure 6: Tensile strength values of neat NRL and its filled composites in case of mechanical and clash methods, at 1 phr CB or CNTs filler.

On further addition of the filler content, i.e 2 phr, it can be clearly noticed that there is an extraordinary increase in the tensile values of the rubber compounds filled with CNTs, especially when the clash method is used, as shown in Fig. 7. This sharp increase may be due to better dispersion of the CNTs filler in the rubber matrix, beside that the filler-matrix interaction was achieved rather than the filler-filler interaction. These results are consistent with that reported by TEM observations in which most of the CNTs particles by clash method were observed within the NRL matrix as compared to NRL/CNTs sample by mechanical mixing as shown in TEM images Fig. 3 (g & h). The figure also showed that there is no noticeable change in the tensile values of the samples filled with 2 phr of CB when compared to those in case of samples filled with 1 phr CB either by using clash or mechanical method (see Fig. 6). This may be due to the presence of some aggregates of CB filler outside the NRL matrix, i.e lower compatibility as shown in TEM images, Fig. 2(a,b) and Fig. 3(e). On increasing nano-filler loadings to 5 phr, it can be noticed that the tensile values were decreased, particularly in case of NRL/CNTs by clash method, with respect to 2 phr filler content as shown in Fig. 8. This decrease may be explained by the formation of CNTs filler aggregates outside the matrix, as indicated in TEM image, see Fig. 4(l). For NRL/CB samples showed that there is an increase in the tensile values for the two dispersion methods because of the better nano-fillers distribution in the NRL matrix as confirmed by TEM images, see Fig. 4 (i,j).

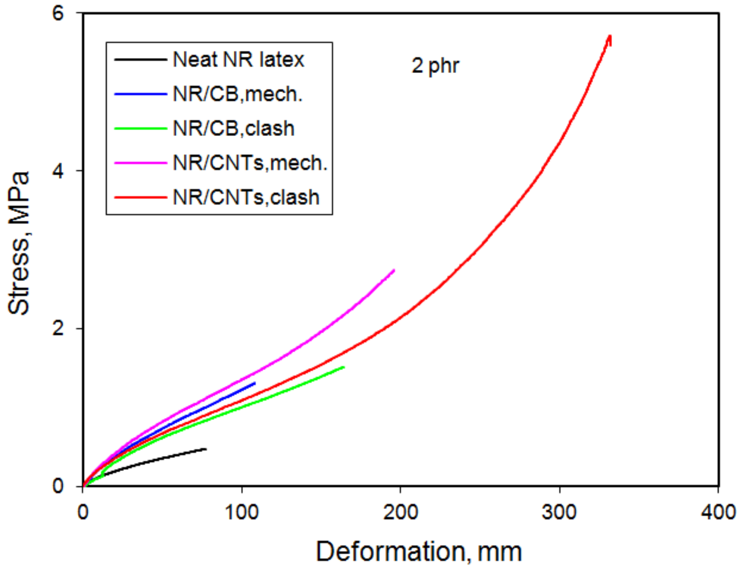

Figure 7: Tensile strengths of neat NR latex and filled NR latex composites in case of mechanical and clash dispersion methods, at 2 phr CB or CNTs filler.

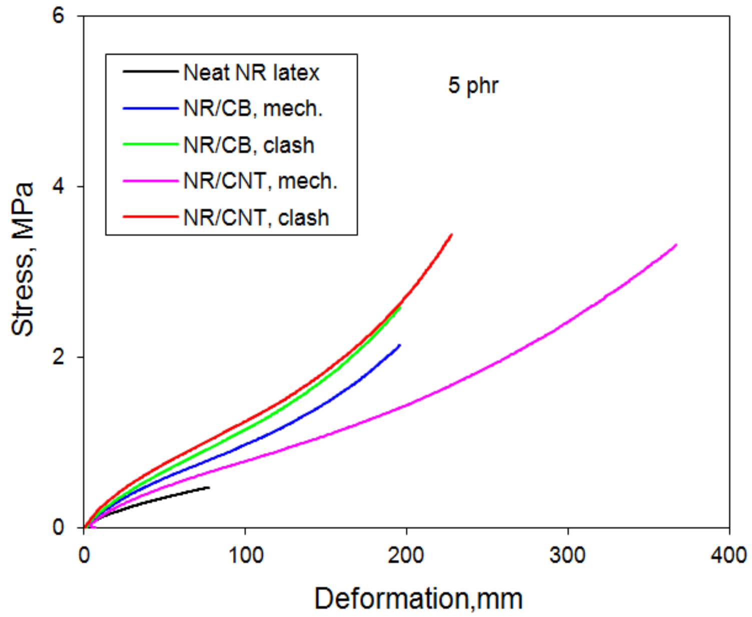

Figure 8: Tensile strengths of neat NR latex and filled NR latex composites in case of mechanical and clash dispersion methods, at 5 phr CB or CNTs filler.

4. Conclusions

The present work was revealed that the clash method was a distinct effect on the dispersion quality of nano-fillers in natural rubber latex. The swelling data show that NR latex filled with 5 phr of CNTs filler, prepared by the clash method, enhanced the swelling behavior to great extent rather than that of composites with CB filler. The results also clarify that addition of 2 phr of CNTs filler leads to an increase over 1000% tensile stress which can be attributable to quite good dispersion of the CNTs filler as well as good filler-rubber interactions. This conclusion is confirmed by TEM morphological studies.

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References

[1] Guerra N. B., Pegorin G. S-A., Boratto M. H., Roberto de Barros N., Graeff C. F-de-O., Herculano R. D. Biomedical applications of natural rubber latex from the rubber tree Hevea brasiliensis. *Materials Science and Engineering: C* Volume 126, 112126 (2021).

[2] Li X., Liu Y., Wang S., Zhang Y., Liu F., Han J. Mechanism and Characterization of Polydopamine Modified Multi-walled Carbon Nanotubes Reinforcement of Natural Rubber Latex Composites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 631, 127721, (2021).

[3] ALex R. Nanofillers in rubber-rubber blends, Rubber Nanocomposites; Preparation, properties, and applications, Chap. 9, John Wiley & sons (Asia) Pte Ltd. ISBN: 978-0-470-82345-3 (2010).

[4] Subash S., Mini K. M., Ananthkumar M. Incorporation of natural rubber latex as concrete admixtures for improved mechanical properties. *Materials Today: Proceedings*, Volume 46, 4859–4862 (2021).

[5] Kang D., Kim D., Yoon S-H., Kim Do., Barry C., Mead J. Properties and Dispersion of EPDM/Modified-Organoclay Nanocomposites. *Macromolecular Materials and Engineering*, Volume 292, 329–38 (2007).

[6] Maiti P., Hoai Nam P., Okamoto M., Hasegawa N., Usuki A. Influence of Crystallization on Intercalation, Morphology, and Mechanical Properties of Polypropylene/Clay Nanocomposites. *Macromolecules*, Volume 35, 2042-49 (2002).

[7] Sinha Ray S., Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. *Progress in Polymer Science*, Volume 28, 1539–1641(2003).

[8] Da Silva C., Haidar B., Vidal A, Miehe-brendle J., Le Dred R., Vidal L. Preparation of EPDM/synthetic montmorillonite nanocomposites by direct compounding. *Journal of Materials Science Letters*, Volume 40, 1813-15(2005).

[9] Kohjiya S., Ikeda Y. Reinforcement of general-purpose grade rubbers by silica generated in situ. *Rubber Chemistry and Technology,* Volume 73, Issue 3, 534-50 (2000).

[10] Xu H., Liu J., Fang L., Wu C. In situ Grafting onto Silica Surface with Epoxidized Natural Rubber via Solid State Method. *Journal of Macromolecular Science, Part: B,* Volume 46, Issue 4, 693-703(2007).

[11] Poompradub S., Thirakulrati M., Prasassarakich P. In situ generated silica in natural rubber latex via the sol-gel technique and properties of the silica rubber composites, *Materials Chemistry and Physics*, Volume 144, 122-31(2014).

[12] Usuki M. K., Okada A., Kurauchi T. Synthesis of Polypropylene-Clay Hybrid, *Journal of Applied Polymer Science*, Volume 63, 137-38 (1997).

[13] Cardenas M. A., Garca-Lopez D., Gobernado-Mitre I., Merino J. C., Pastor J. M, Martnez J. de D., Barbeta J., Calveras D. Mechanical and fire-retardant properties of EVA/clay/ATH nanocomposites: Effect of particle size and surface treatment of ATH filler, *Polymer Degradation and Stability*, Volume 93, 2032-37(2008).

[14] Sae-oui P., Sirisinha C., Hatthapanit K., Thepsuwan U. Comparison of reinforcing efficiency between Si-69 and Si-264 in an efficient vulcanization system. *Polymer Testing*, Volume 24, 439 – 46 (2005).

[15] Sarkawi S. S., Dierkes W. K., Noordermeer J. W. M. Elucidation of filler-to-filler and filler-to-rubber interactions in silica-reinforced natural rubber by TEM Network Visualization, *European Polymer Journal*, Volume 54, 118-27 (2014).

[16] Leblanc J. L. Rubber-Filler interactions and rheological properties in filled compounds, *Progress in Polymer Science*, Volume 27, 627-87 (2002).

[17] Frohlich J., Niedermeier W, Luginsland H-D. The effect of filler–filler and filler–elastomer interaction on rubber reinforcement. *Composites Part A: Applied Science and Manufacturing,* Volume 36, 449-60 (2005).

[18] Donghee K., Dongsik K., Sung-Hwan Y., Dongkyu K., Carol B., Joey M. Properties and Dispersion of EPDM/Modified-Organoclay Nanocomposites, *Macromolecular Materials and Engineering*, Volume 292, 329–38 (2007).