

## **EFFECT OF ULTRASONIC TREATMENT ON THE TENSILE PROPERTIES OF THERMOPLASTIC NATURAL RUBBER (TPNR) NANOCOMPOSITES**

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### **ABSTRACT**

This paper discussed the effect of ultrasonic treatment time on the tensile properties of TPNR nanocomposites. Melt compounding technique was employed to prepare thermoplastic natural rubber (TPNR) nanocomposite. The ultrasonic bath was used to improve the filler-matrix interfacial adhesion. TPNR nanocomposites were prepared in the ratio of (70:20:10) from polypropylene (PP), natural rubber (NR) and liquid natural rubber (LNR) as a compatibilizer, with 4% organophilic montmorillonite (MMT). The composites samples were prepared using in-situ method at the optimum processing parameter of 180°C with 100 rpm mixing speed and 13 minutes processing time. The clay layers were found to be separated further with ultrasonic treatment as compared to the sample without ultrasonic treatment as exhibited by X-ray diffraction. Young's modulus, tensile strength and elongation at break of TPNR nanocomposites increased with ultrasonic treatment. The optimum result was achieved at 3h, the enhancement of these properties confirms by the fact that ultrasonic treatment can promote the dispersion of the clay in TPNR also it improves the compatibility of clay filler and the TPNR matrix.

### **INTRODUCTION**

The enhanced mechanical properties of nanoclay/polymer nanocomposites with a relatively light weight compared with conventional polymer-based composites have attracted the focus of researchers in the last decade. A relatively small amount of nanoclays, typically in the range of 3–5 wt % [1,2], is enough for the enormous improvements in the mechanical and thermal properties of the nanoclay/polymer nanocomposites. These improved mechanical properties are mainly depended on the fine dispersion of nanoclay platelets inside the nanoclay/ polymer nanocomposites. Uniform nanocomposites can only be achieved through high-shear mixing techniques such as high-speed dissolvers, extensive ultrasonic, grinding or high pressure mixing [3]. Ultrasonic oscillations produce shear to promote good dispersion of nanoparticles in the polymer matrix or intercalation and exfoliation of clay. Despite the considerable number of studies concerned with the preparation, characterization and properties of polymer/clay nanocomposites, no report has been published regarding the processing of TPNR nanocomposites using continuous ultrasonic effect. In this paper, thermoplastic

natural rubber /nanoclay composites were made subjected to different ultrasonic times. The influence of ultrasonic treatment on the interlayer distance between the nanoclay platelets also, the tensile properties of thermoplastic natural rubber nanocomposites are examined.

## **EXPERIMENTAL METHOD**

### *Materials*

Polypropylene with a density of 0.905 g/cm<sup>3</sup> and natural rubber were supplied by Propilinas (M) and Guthrie (M) Sdn. The layered silicate used in this study was NanolinDK from Zhejiang Fenghong Clay Chemicals, Inc. It is an alkyl ammonium modified montmorillonite with cation-exchange capacity of 115-120mmol/100g, Polypropylene-graft-maleicanhydride, Mn=3.900(GPC), Mw=9.100(GPC), supplied by SIGMA-ALDRICH, Germany. Liquid natural rubber (LNR) was synthesized in our laboratory from the natural rubber by using photochemical oxidation technique.

### *Composite Preparations*

The nanocomposites samples were prepared using indirect technique (IDT). This involves mixing the nanoclay with LNR and then treated first by ultrasonic bath (70Watts, 42KHz+1-6%) for different time (1 hour, 3 hours and 5 hours). Then the TPNR nanocomposite were compounded using melt blending in a ratio of 10, 20 and 70 wt% using LNR as a compatibilizer, NR and PP, respectively with 4 wt% clay. The mixing of the composites was done in the internal mixer (Haake Rheomix OS) at temperature of 180 °C with a rotor speed of 100 rpm and 13 min mixing time.

### *Characterization*

#### *X-ray diffraction*

The model of equipment used was D8 advance with radiation source from CuK<sub>α</sub> generated at energy 40 KV and current of 30 mA, which emits wavelength of 15.4 nm. X-ray diffraction was done at small angles (0-10°) to determine the degree of clay intercalation.

#### *Tensile properties*

Tensile properties were measured using Testometric universal testing machine model M350-10CT with 5 kN load cell according to ASTM 412 standard procedure using test specimens of 1 mm thickness and crosshead speed 50 mm min<sup>-1</sup>. At least five samples were tested for each composition, and the average value was reported.

## RESULTS AND DISCUSSION

### Dispersion of nanoclays using ultrasonic

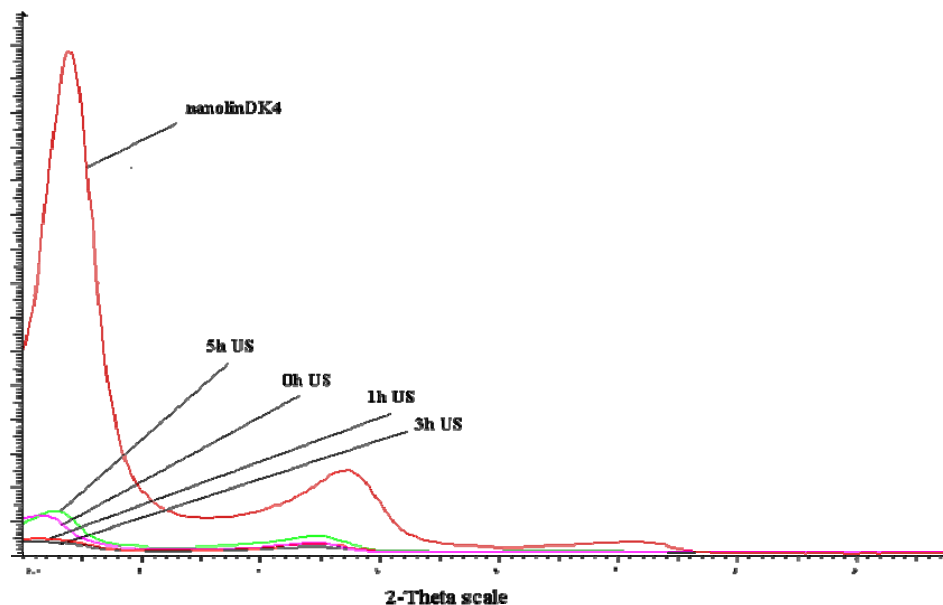


Figure 1: XRD patterns of TPNR nanocomposites with different time ultrasonic time (1 hour, 3 hours and 5 hours) without coupling agent.

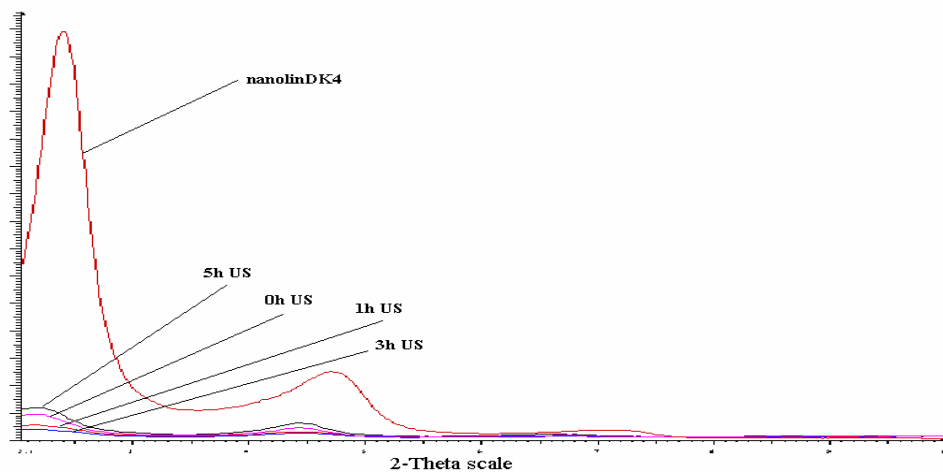


Figure 2: XRD patterns of TPNR nanocomposites with different time ultrasonic time (1 hour, 3 hours and 5 hours) with constant percentage of coupling agent (12% PP-g-MA).

The XRD diffraction patterns of TPNR nanocomposites are shown in Figures 1-2. X-ray diffraction profiles of clay and TPNR nanocomposite prepared at different ultrasonic time, in term of Bragg's equation  $n\lambda=2d\sin\theta$ . It is observed from the figures

that the spacing ( $d_{001}$ ) of nanolin DK4 is 3.6 nm. For TPNR nanocomposites without and with ultrasonic treatment the d-spacing increased, the best results were achieved at 1 hour and 3 hours ultrasonic for TPNR nanocomposite without or with coupling agent (PP-g-MA), no peaks were detected for the composites at this treatment time, the absence of peak may imply that the distance between the clay layers in the TPNR was too large to be detected by X-ray analysis, so that the rate of diffusion of polymer chains were increased, which allow to homogeneous dispersion of clay inside the matrix, revealed by decreased in the intensity of diffraction peak, which related to presence of an intercalated and delaminated configuration, it was also found that intensity of the peak increased at 5 hours, these means the d-spacing of TPNR nanocomposites were decreased with increased ultrasonic treatment, this is a direct evidence of tendency of clay to agglomerate inside the matrix with increase of Ultrasonic time, as a result the polymer chains experience more difficulty diffusing into the agglomerates and the clay interlayer.

*Effect of Ultrasonic time on the mechanical properties of TPNR nanocomposites*

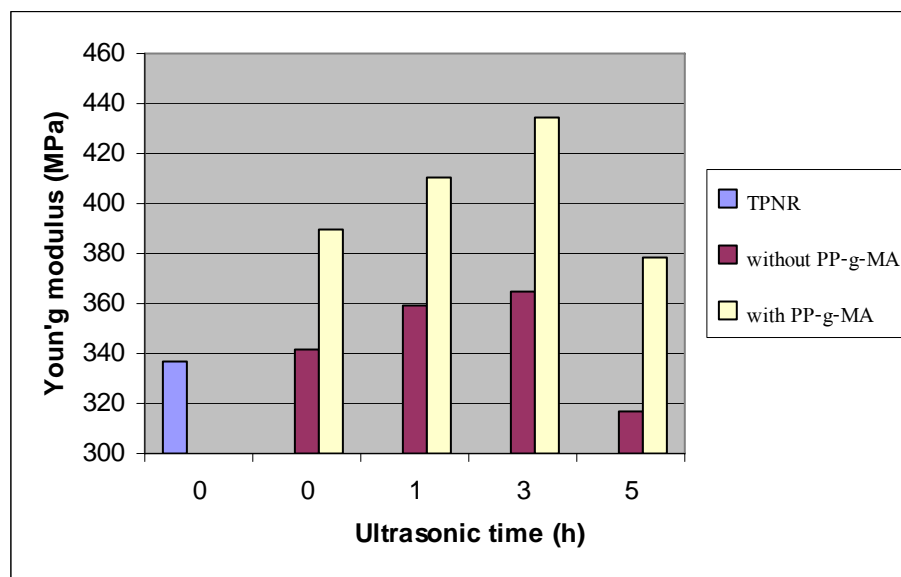


Figure 3: Young's modulus of TPNR nanocomposites with different time of ultrasonic ( 1 hour, 3 hours and 5 hours) without and with coupling agent (PP-g-MA).

The Young's modulus of TPNR and TPNR nanocomposites are shown in Fig 3. It was found that the Young's modulus of TPNR nanocomposites increased with ultrasonic time compared to the sample without ultrasonic treatment. The maximum Young's modulus of TPNR nanocomposites was obtained at 3 hours ultrasonic treatment without and with coupling agent which increased 8.06 % and 28.9%, respectively. At this time the clay particle aggregations become smaller under ultrasonic which ultimately leads to the increase of the interface action due to better overall dispersion of nanoclay inside

polypropylene and natural rubber, also increase the interlayer space in the clay, as a results, the dispersion of layers in a polymer matrix can be much improve when they are subjected at ultrasonic time [5]. After 3 hours the Young's modulus decreased owing to lower degree of dispersion and lower degree of polymer-clay surface interactions.

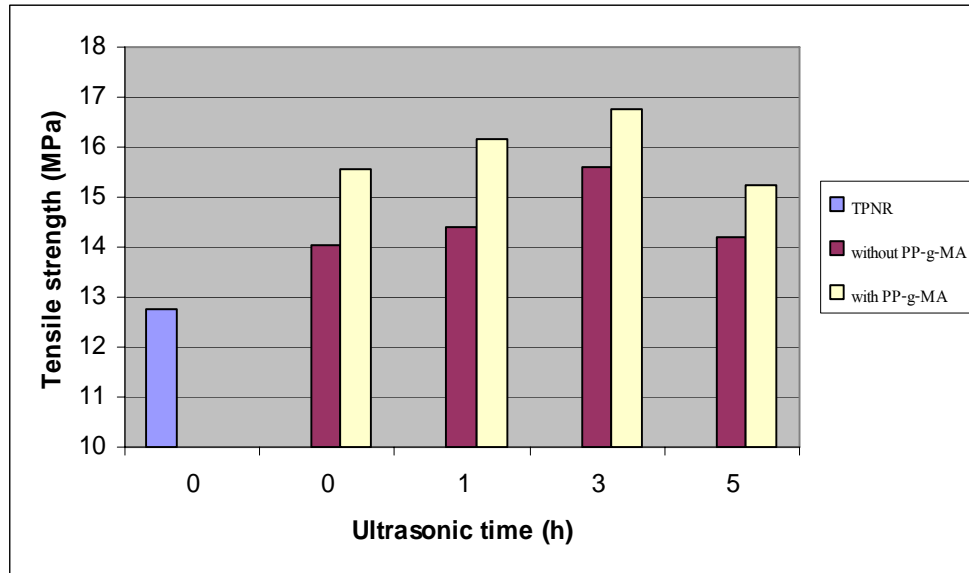


Figure 4: Tensile strength of TPNR nanocomposites with different time of ultrasonic (1 hour, 3 hours and 5 hours) without and with coupling agent (PP-g-MA).

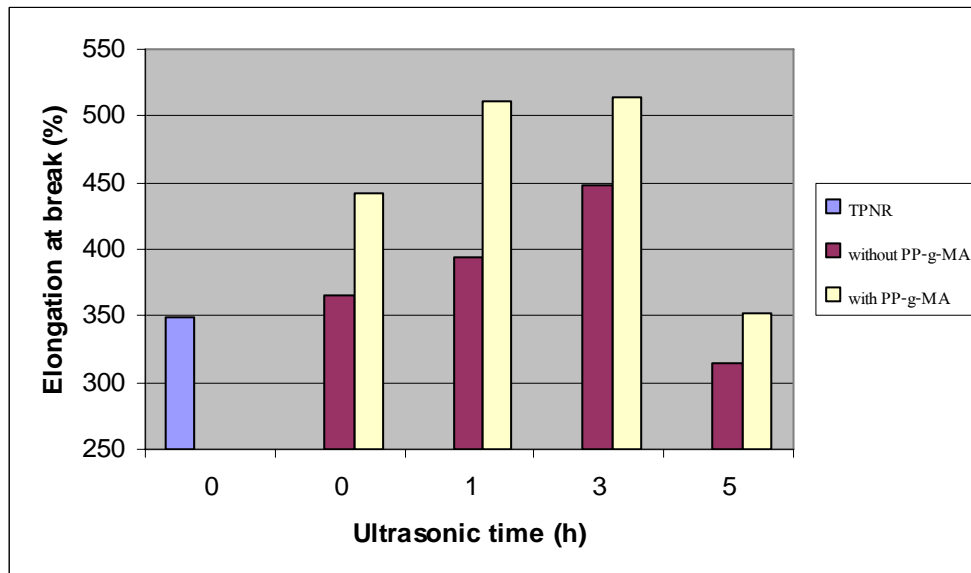


Figure 5: Elongation at break of TPNR nanocomposites with different time of ultrasonic (1 hour, 3 hours and 5 hours) without and with coupling agent (PP-g-MA).

The tensile strength of TPNR and TPNR nanocomposites are shown in Figure 4. It was also found then the of tensile strength of TPNR nanocomposites improved with ultrasonic treatment compared to that without ultrasonic treatment. The optimum results of the tensile strength archived at 3 hours, which increased by 22% and 31%, without and with coupling agent, respectively, compared with TPNR. This improvement can attributed to the mobilization of the macromolecular chains by the filler, which increases their ability to adapt to the deformation , but at higher ultrasonic time as 5 hours, there is lower degree of clay-polymer interaction, therefore the clay act as stress concentrators and tends to decrease the strength of the material [6].

The improvement of TPNR nanocomposite elongation at break at 3 hours ultrasonic treatment is as shown in Fig 5. It is increased to 28.3% and 46.9%, without and with coupling agent, respectively, can be probably attributed to the PP crystallization effect induced by organoclay filler. Good dispersion of clay inside the matrix, nano scale filler is believed to become a nucleating agent that will contribute more uniformly to the sperulite growth [4]. After that the elongation at break decreased due to decrease clay effective as a nucleating agent, this means that the ultrasonic treatment influenced the nucleating process of nucleated TPNR.

From the results obtained, the tensile properties of TPNR nanocomposites improved without and with coupling agent as ultrasonic treatment can aid the enhancement of the mechanical properties in the TPNR nanocomposites with properly controlling the sonicating time. Ultrasonic treatment is a form of vibration that provides energy for polymer chains and nanoclay platelets to escape from the surrounding restraining force of polymer. Extra energy is given to the nanoclay platelets to move around when sonicating the nanoclay/LNR mixture. If there is not enough energy given to the nanoclay/LNR mixture, the nanoclay platelets cannot escape the restraining force within LNR since the aid for dispersion is limited. On the other hand, if too much energy is given to the nanoclay platelets to move around, then the frequency of collision between single nanoclay platelets will be increased. Therefore, an optimum sonicating time must be achieved in order to obtain the maximum dispersion ability. The size of the nanoclay agglomerations (clusters) are reduced in accompanying with the increase of the number of nanoclay clusters when the optimum sonicating time is reached. Therefore, the surface area for the interaction between the nanoclay clusters and the TPNR is increased and provides the maximum reinforcement. If further increasing of the sonicating time beyond the optimum value, the size of the nanoclay clusters will start growing and therefore the number of the nanoclay clusters will then decrease. Thus, the surface area for the interaction between the nanoclay clusters and the TPNR is reduced and the mechanical properties of the composites are adversely affected.

## CONCLUSION

Ultrasonic treatment achieved a rapid intercalation and exfoliation of clay inside a matrix. This is supported by XRD study indicating an increase of d-spacing. The tensile properties of thermoplastic natural rubber nanocomposites were substantially improved

after ultrasonic treatment and the optimum results are achieved at three hours. However, by prolong time of ultrasonic treatment more than 3 hours resulted in particles aggregate and has caused significant reduction in tensile properties.

### ACKNOWLEDGEMENTS

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