Morphology and thermal stability of nano titanium dioxide filled natural rubber prepared by latex mixing method

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Abstract. This paper deals with the morphology and thermal stability of nano Titanium Dioxide (TiO_2) filled natural rubber composites. This study also suggests a new method of incorporating TiO_2. Aqueous dispersions of nano TiO_2at the loadings of 0, 2, 4, 6 and 8 phr were dispersed in natural rubber latex, the resulting compounds were then dried prior to mixing it with other ingredients on a two-roll mill. By applying this technique, the homogeneity of the compound is significantly improved. This can be clearly seen from the morphology observed. Adding TiO_2 results in shifting the decomposition temperature and char residue irrespective of the loadings of nano TiO_2.

1. Introduction

It is a well-known fact that the addition of rigid filler particles, even in small amounts, to a rubber, strongly influences its mechanical behaviour [1]. Currently, researchers have faced complications with the use of white fillers in rubber composites. As for silica, it is mostly incompatible with rubber especially natural rubber. It requires an addition of compatibilizers or coupling agents, which complicates the processing method and subsequently increases production cost. Meanwhile, calcium carbonate and clay play major roles as non-reinforcing fillers, which result in deterioration of the mechanical properties [2-4]. Therefore, new filler materials need to be determined to maintain acceptable properties.

Titanium Dioxide (TiO_2) is widely used as filler in many polymers because of the improved physical and mechanical properties it yields [5-7]. The nature of TiO_2 has great influence on the reinforcement and thermal stability of polymer composites. As reported by Meera et al. [8], they elucidated that TiO_2 do not possess any active hydroxyl groups on their surface unlike silica particles that have available surface hydroxyl groups. This could provide a less tendency to form aggregate which leads to a better dispersion of the TiO_2 accompanied with strong interfacial adhesion between matrix and fillerin the polymer composites.

In this regard, nano TiO_2 has received special interest as filler in the rubber matrix because of their specific properties. Incorporation of a small amount of nano TiO_2 into the rubber matrix has been

largely unexplored.The aim of this work is to incorporate nano TiO_2 in natural rubber composites together with the suggestion of a new route of dispersing nano TiO_2. By applying this method, the homogeneity and respective thermal stability of the compound is expected to improve.

2. Materials and Methods

2.1. Materials

The formulation used in this study is listed Table 1. Low ammonia type Centrifuged Natural rubber latex (LATZ type), bentonite clay and Disodium 2,2'-methylene-bis-naphthalene sulphonate **(**Tamol**)** were supplied by Zarm Scientific (M) Sdn. Bhd., Penang, Malaysia. Nano $TiO_2$was purchased from Sigma-Aldrich Co., LLC., USA., with the size ranging from 15 – 40 nm(TEM), 4.26 g/ml in density, surface area of 35 – 65 m^2/g (BET), and more than 99.5% purity based on an analysis of trace materials [9]. Other compounding ingredients, such as zinc oxide, stearic acid, N-cyclohexyl-benzothiazyl-sulphenamide(CBS),   N-2-Propyl-N'-phenylenediamine(IPPD),   and   sulfur   were purchased from Bayer (M) Ltd.

Table 1. The formulation used in this study.

Ingredients	Amount (phr)
Natural Rubber	100
ZnO	5
Stearic acid	2
CBS	0.5
IPPD	2
Sulfur	2.5
Nano TiO_2	0, 2, 4, 6 and 8

2.2. Preparation of the composites

Figure 1 illustrates the diagram for the compounding preparation of natural rubber composites**.** The aqueous dispersion of nano TiO_2 was prepared by using a mechanical ball mill**.** The compositions of 40 parts **(**w/w**)** of nano-sized TiO_2, 2 parts **(**w/w**)** bentonite clay as a colloidal stabilizer, 1 parts **(**w/w**)** of Disodium 2,2'-methylene-bis-naphthalene sulphonate**(**Tamol**)** as a dispersion agent and 57 parts **(**w/w**)** of distilled water as the medium, were added to the jar of the ball mill**.** Then, the whole mixture was kept on the ball milling machine for 24 hrs at the rotation speed of 10 rpm**.** Later, the dispersion form of nano TiO_2 was stored in an amber glass bottle to prevent from self photo-oxidation process**.**
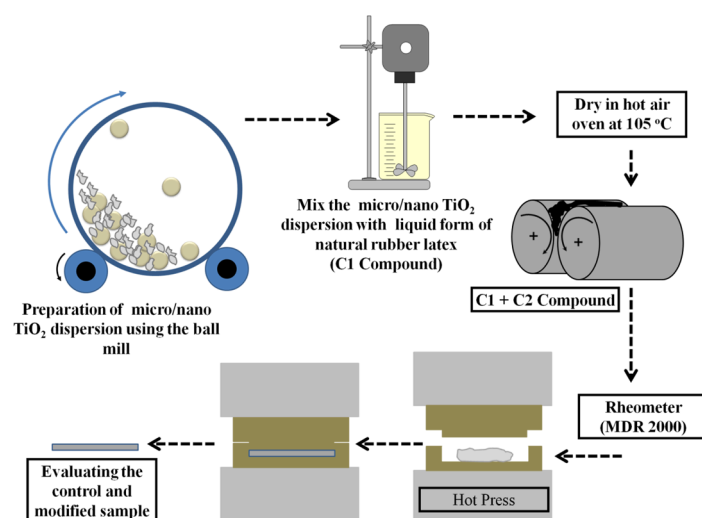

Figure 1. Schematic illustration representing the preparation of the composites.

The compounding preparation was done by mixing the centrifuged natural rubber latex with the aqueous dispersion of nano TiO_2. The mixture was agitated mechanically for 8 hrs in order to ensure the homogeneity. Subsequently, this colloidal mixture was poured into a glass tray and dried in hot air oven at 100ºC for 8 hrs to remove all the water (C1 compound). Ultimately, the dried sheet of C1 compound was compounded with other additives on the laboratory size two-roll mill (Model XK-160). The final compound was later tested for its curing characteristics by using a Monsanto Moving Die Rheometer (MDR 2000). The compounds were subsequently compression-moulded using a stainless steel mould at 150°C with a pressure of 10 MPa using a laboratory hot-press based on the respective curing times.

2.3. Morphological studies
The examination of nano TiO_2 particles was carried out using Transmission Electron Microscope (TEM) model Philips CM12 and the images were analysed using Docu version 3.2 image analysis. The dispersion of nano TiO_2 in natural rubber matrix was captured through tensile fractured samples using a scanning electron microscope (SEM) model Zeiss Supra-35VP. The fractured pieces were coated with a layer of gold palladium to eliminate electrostatic charge build-up during examination.

2.4. Thermogravimetric analysis)TGA(
Thermogravimetric analysis of nano TiO_2filled natural rubber composites was carried out with a Perkin-Elmer Pyris 6 TGA analyser. The sample was scanned from 30ºC to 600ºC at the nitrogen air flow of 30 ml/min with heating rate of 20ºC /min.

3. Results and Discussion

3.1. Morphology
Figure2 shows the TEM image of nano TiO_2 particles. It was visibly seen that nano TiO_2 particles are in rod- or elongated shapes and are far smaller than other commercial fillers such as silica, calcium carbonate and etc., indicating that high reinforcement and thermal stability can be attained by incorporating nano TiO_2.
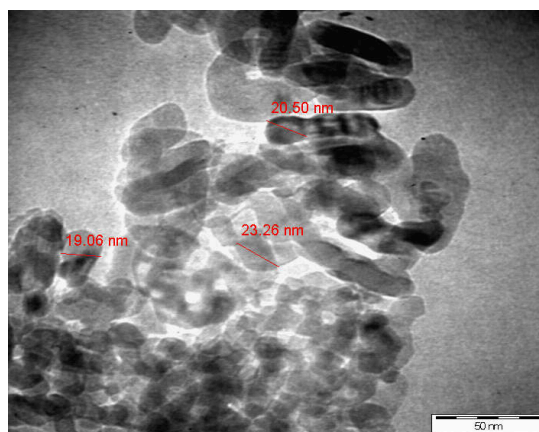

Figure 2. TEM micrograph of nano TiO_2 at 35,000× magnifications.

The dispersion of nano TiO_2inside the natural rubber matrix can be visibly seen in Figure 3. Nano TiO_2 was dispersed homogenously in the rubber matrix, indicating that using the new route for preparing the composites results in better dispersion. The homogeneity of the composites is significantly improved; especially with loading up to 6 phr. Well-dispersed nano TiO_2 is responsible for the improved thermal stability which will be discussed in later session.
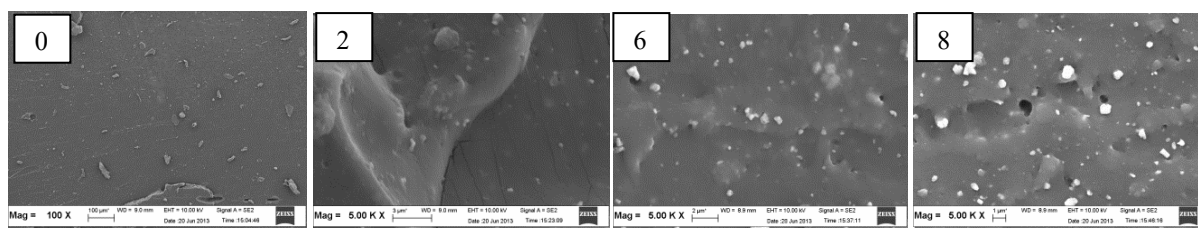
Figure 3. SEM micrographs of nano TiO$_2$ filled natural rubber composites at 0, 2, 6 and 8 phr of nano TiO$_2$ (35,000× magnifications).

3.2. Thermo gravimetric analysis

Thermo gravimetric analysis measures the amount and rate of the mass transition of a sample as a function of temperature in a certain atmosphere. Such analysis is used primarily to determine the thermal stability and compositional properties of materials. The thermal decomposition behaviour and derivative weight thermo grams of nano TiO$_2$ filled natural rubber composites are shown in Figure 4. The decomposition temperatures at various weight loss stages and char residue are also listed in Table 2. Two regions of degradation were subsequently observed. The initial minor weight loss at around 180–200ºC was associated to the presence of volatile matter such as stearic acid and absorbed water at around 300ºC [10]. The major stage in the degradation of the composites started at about 330ºC and was completed at around 450ºC. This is attributed to the degradation of natural rubber segment. The degradation of the natural rubber segment is sensitive to the presence of the oxidized structure as well as the depletion of sulphidic cross-link in natural rubber [11].
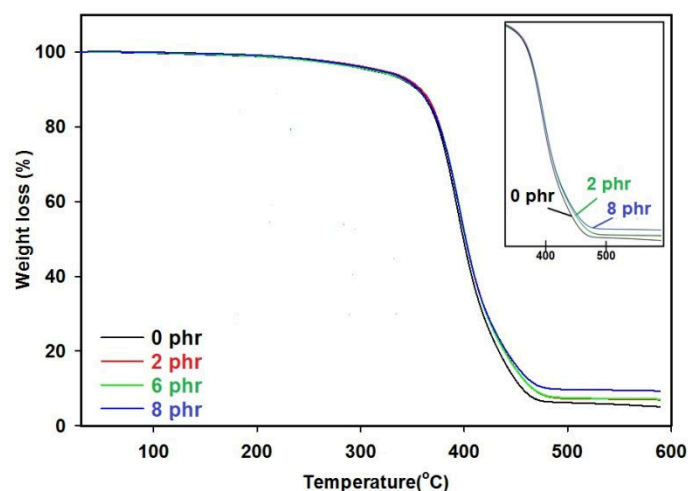

Figure 4. TGA curves of nano TiO$_2$ filled natural rubber composites.

Table 2. Thermal stability parameters of nano TiO$_2$ filled natural rubber composites.

Nano TiO$_2$ loading (phr)	Temperature at 10% weight loss (ºC)	Temperature at 50% weight loss (ºC)	Temperature at 70% weight loss (ºC)	Weight res. (%)
0 phr	348.21	401.14	415.51	2.53
2 phr	350.15	402.81	418.21	3.16
6 phr	354.91	403.74	421.22	7.45
8 phr	359.28	405.24	424.57	9.22

It is interesting to note that the decomposition temperature at 10%, 50%, and 70% weight loss of natural rubber composites was greatly influenced by the presence of nano TiO$_2$. It was found that the decomposition temperature clearly differed from the earlier stages of decomposition. Introducing nano TiO$_2$ into the natural rubber composites greatly affected their thermal stability. The decomposition

temperature of the composites showed further improvement at the decomposition temperatures above 50% of weight loss. Nano TiO_2 do not possess any active hydroxyl groups on their surface unlike silica particles that have available surface hydroxyl groups. This could provide a less tendency to form aggregate which leads to a better dispersion of the TiO_2 accompanied with strong interfacial adhesion between matrix and fillerin the rubber.

From this point of view, highly compatibilized nano TiO_2 filled natural rubber composites and better thermal resistance are formed. As a result, more pronounced thermal stability is observed in the presence of nano TiO_2. Furthermore, the char residue of all composites was influenced by introducing of nano TiO_2. This is simply due to the fact that the amount of filler was varied; thus keeping the char residue mostly changed. According to Chakraborty et al. [12], the amount of char is very much dependent on the type and amount of filler. The difference in filler amount mainly concerns the char formation.

4. Conclusions
The following conclusions can be presented:
1. Rod or elongated shape of nano TiO_2 is clearly seen in TEM image, indicating that high contact area and thermal stability can be attained by incorporating nano TiO_2.
2. Applying new technique of incorporating nano TiO_2in the natural rubber matrix has greatly influenced on the dispersion of nano TiO_2. This is visibly seen in the SEM images.
3. The thermal decomposition temperature of the rubber has shifted to a higher temperature when nano $TiO_2$is used, indicating that more heat is needed to decompose the sample.

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