The influence of pre-compounding techniques and surface modification of nano-silica on the properties of thermoplastic natural rubber

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Abstract. Thermoplastic natural rubber (TPNR) nanocomposites based on epoxidized natural rubber (ENR) and polypropylene (PP) blends filled with 2.5 wt% nano-silica (SiO₂) were prepared using a two-step compounding process to improve the dispersion of SiO₂ in TPNR. The effects of the compounding techniques, *i.e.*, solid pre-compounding and latex pre-compounding processes of SiO₂ and ENR, and surface modification of SiO₂ on the morphological, mechanical, and thermal properties together with the crystallization behavior of PP phase in ENR/PP blends were demonstrated. Scanning electron microscope (SEM) results showed that latex pre-compounding of SiO₂ and ENR gave finer dispersion and distribution of SiO₂ particles in the TPNR matrix as compared with the solid pre-compounding technique. Also, the superior mechanical properties and thermal stability of the blends were achieved by using the latex pre-compounding technique. Moreover, surface modification of SiO₂ by organosilane was found to enhance crystallization rate and the degree of crystallinity of PP phase in the TPNR, leading to an improvement in the strength and mechanical properties of the ENR/PP blends. These results agree well with the morphological properties that presented a good dispersion and distribution of silane-modified SiO₂ particles in the TPNR matrix.

Keywords: nanocomposites, nano-silica, thermoplastic natural rubber, latex pre-compounding, solid pre-compounding

1. Introduction

Development of thermoplastic elastomers (TPEs) by mixing natural rubber (NR) biomaterial with crystalline thermoplastics provides a new material called thermoplastic natural rubber (TPNR). This type of material has drawn the interest of the scientific community because it is an eco-friendly renewable resource material, which can be recycled, reused, and reprocessed while retaining the key characteristics of both thermoplastics and natural rubber, namely high mechanical strength and elasticity, respectively. Compatibility between NR and thermoplastics is one

of the key factors affecting the properties of the TPNR. A high degree of compatibility results in high mechanical properties of this material [1, 2]. Beyond using NR in its normal state, chemically modified natural rubber, *i.e.*, epoxidized natural rubber (ENR) [3–5], maleated natural rubber (MNR) [6, 7], and natural rubber-graft-poly(methyl methacrylate) (NR-g-PMMA) [1, 8, 9], have also been frequently utilized to prepare TPNRs. The main aim of the chemical modification was to improve the thermal resistance of the rubber phase and the compatibility between natural rubber and thermoplastics. Furthermore,

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some properties of TPNRs, including dimension stability, thermal resistance, gas barrier, mechanical, electromagnetic, and microwave absorbing properties, can be augmented through the addition of certain particulate particles, including nanoclay [10, 11], carbon nanotubes [12, 13], alumina nanoparticles [14], nickel zinc ferrite nanoparticles [15, 16] and nano-silica [3, 17]. With proper dispersion and distribution of these fillers in the rubber and thermoplastic phase, high interfacial areas between the filler particles and polymer surfaces can be achieved. This leads to the enhancement of the most important strength and electrical properties of composite materials. Unfortunately, the homogeneous dispersion of nanoparticles in the polymer matrix is rather difficult to achieve due to higher filler-filler than filler-polymer interactions during processing, causing the formation of aggregates and large agglomerates in the polymer matrix. These agglomerates may act as defects and weak spots which diminish the final properties of the nanocomposites. Several attempts and feasibility studies have been made to establish a suitable method to overcome this problem. These include surface modification of nanoparticles [18–20], exploitation of the silane coupling agent [21, 22], and an ultrasonication-assisted mixing method [23]. Incorporation of nanofiller into rubber latex or latex compounding is one of the eco-friendly strategies that has been frequently used to obtain a finer dispersion of nanoparticles in the rubber matrix without using solvent [20, 24–31]. This technique comes with various advantages, including a simple preparation process and the fact that it is non-toxic, low cost, and energy-efficient since the procedure is done by simple mixing of nanoparticles in a water suspension with rubber latex at very low viscosity [28]. It has been reported that the clay layers were successfully exfoliated and homogeneously dispersed in the polymer matrix by using the latex compounding method [28, 29]. In addition, NR/silica nanocomposites were prepared using the latex compounding method. It was found that the synergistic effect of ball milling and modification of nano-silica could simultaneously increase the dispersibility of silica and improve the interaction between silica and NR, which would, in turn, improve the performance of the NR composites [30]. Also, the benefits of the latex mixing process in polymer blend nanocomposites have been reported in the preparation of a natural rubber (NR)/high-density polyethylene (HDPE) blend filled with

graphene oxide (GO) [31]. It was found that the stacked GO platelets were successfully exfoliated in NR by using the latex mixing process prior to melt-blending with HDPE, which thereafter provided good compatibilization efficiency in the immiscible NR and HDPE blends.

Nano-silica (SiO_2) is one of the promising fillers for polymer nanocomposites due to its reactive high specific surface area, which can act as a reinforcing filler and nucleating agent [32–34]. In our previous study, the solid compounding process was used to prepare nano-silica filled ENR/polypropylene (PP) nanocomposites. Beyond this, the mixing sequence of nano-silica into ENR/PP blends was investigated [3]. It was found that the pre-compounding of nano-silica in ENR prior to melt-mixing with PP could provide finer dispersion of nano-silica in the polymer matrix. This led to enhanced mechanical properties, damping, and thermal stability of the blends. To further enhance the potential properties of ENR/PP nanocomposites, in this work, the latex pre-compounding technique was used to prepare ENR mixed SiO_2 prior to melt-blending with PP to form ENR/PP TPNR nanocomposites. The influence of pre-compounding techniques and surface modification of nano-silica on morphological and mechanical properties together with crystallization behavior of the ENR/PP TPNR nanocomposites were investigated.

2. Materials and methods

2.1. Materials

Polypropylene (PP), El-Pro[®]P700J, manufactured by Thai Polypropylene Co., Ltd. (Rayong, Thailand), was used as a thermoplastic matrix to prepare ENR/PP TPNR. It has a melt mass-flow rate (MFR) of 12 g/10 min (230 °C and a deadweight of 2.16 kg) according to ISO 1133. Epoxidized natural rubber (ENR) latex with an epoxidation level of 35 mol% epoxide and dry rubber content (DRC) of 20 wt% was prepared in-house *via in situ* performic acid epoxidation, as described elsewhere [35, 36]. In brief, the *in situ* epoxidation was carried out by mixing NR latex (1.00 mol) with performic acid (PA) with a molar ratio of NR:PA = 0.35:0.5 at 50 °C for about 12 h. The obtained ENR latex was then coagulated using ethanol, washed, sheeted out, and dried in a vacuum oven at 40 °C for 72 h. The dried ENR was then used to prepare the ENR/PP blends both with and without nano-silica. The nano-silica (SiO_2) used was AEROSIL[®] 380, manufactured by Evonik Degussa

Figure 1. Chemical structure of 3-methacryloxypropyl trimethoxysilane (MPTS).

(Rheinfelden, Germany) with an average particle size of 7 nm. 3-methacryloxypropyl trimethoxysilane (Dynasylan® MEMO or MPTS) was manufactured by Evonik Degussa (Rheinfelden, Germany), with its molecular structure shown in Figure 1. Formic acid and hydrogen peroxide were manufactured by Univar Canada Ltd., Van Horne Way Richmond, Canada.

2.2. Surface modification of silica nanoparticles

The MPTS-modified SiO₂ (MPTS-SiO₂) nanoparticles were prepared using a previously reported procedure [20]. Briefly, MPTS was first hydrolyzed in a mixture of distilled water/ethanol = 5/95 wt% at pH 5–6, stirred continuously for 2 h. The hydrolyzed silane solution was then slowly added into the SiO₂ suspension (in 95 wt% ethanol) with a weight ratio of silane:SiO₂ = 1:10. The mixture was then continuously stirred for another 2 h and separated by centrifugation. It was then washed multiple times with ethanol and followed by distilled water in order to remove chemical residues. The MPTS-SiO₂ product was eventually freeze-dried for 48 h and was then dried in a vacuum oven at 110 °C for 24 h and stored in a desiccator before use. The grafting of MPTS on nano-silica surface confirmed by Fourier transform infrared (FTIR) analysis has been reported in our previous study [3]. It was found an additional peak of C=O stretching vibration in the MPTS moiety of MPTS-SiO₂ at 1720 cm⁻¹ indicating the successful grafting of MPTS molecules on the SiO₂ surface.

2.3. Preparation of ENR-nanosilica masterbatches

Two different types of nano-silica (SiO₂), *i.e.*, unmodified SiO₂ and MPTS modified silica (*i.e.*, MPTS-SiO₂), were used at a fixed loading at 5 wt% of ENR. The preparation of ENR-nano-silica masterbatches was employed as follows:

Latex pre-compounding technique: 1.0 wt% of SiO₂ or MPTS-SiO₂ was firstly dispersed in deionized water, with sonicating for about 30 min. Then, 5 wt% of the silica suspension was added into the ENR latex with 35 mol% epoxide and DRC of 20 wt%. The mixture was vigorously stirred at room temperature for 2 h and then coagulated by adding ethanol. After washing with ethanol several times, the coagulum was then dried in a vacuum oven at 40 °C for 72 h.

Solid pre-compounding technique: 5 wt% of SiO₂ or MPTS-SiO₂ was firstly mixed with dried ENR in an internal mixer (Charoen Tut, Samutprakarn, Thailand) at 80 °C for 6 min with a rotor speed of 60 rpm. After that, the masterbatch was removed from the mixer and cooled down to room temperature.

2.4. Preparation of TPNR nanocomposites

ENR-SiO₂ or ENR-MPTS-SiO₂ masterbatches (52.5 wt%) from the solid pre-compounding and latex pre-compounding techniques were mixed with 50 wt% of PP at 180 °C for 6 min in an internal mixer with a rotor speed of 60 rpm to gain 50/50 ENR/PP TPNR. The TPNR without SiO₂ was also prepared with the same mixing procedure as the reference material. After coming out of the mixing chamber, the samples were cooled down to room temperature and grounded to form granules with an average size range from 2 mm to 4 mm using a Bosco plastic grinder (Bosco engineering, Samutprakarn, Thailand). The TPNR samples were finally fabricated into dumbbell-shaped test specimens (type 2 dumbbell-shaped specimens according to ISO 37) using a TII-90F thermoplastic injection molding machine (Welltec, Machinery, Hongkong, China), at 180 °C with a screw

Table 1. Sample codes and composition of TPNR and its nanocomposites.

Sample code	Compounding technique	Type of nano-silica	ENR content [wt%]	PP content [wt%]	Nano-silica content [wt%]
TPNR	—	—	50.0	50.0	—
s-TPNR-SiO ₂	solid	unmodified	50.0	50.0	2.5
s-TPNR-MPTS-SiO ₂	solid	modified with MPTS	50.0	50.0	2.5
l-TPNR-SiO ₂	latex	unmodified	50.0	50.0	2.5
l-TPNR-MPTS-SiO ₂	latex	modified with MPTS	50.0	50.0	2.5

speed of 90 rpm and a mold temperature of 30 °C. Table 1 shows sample codes and the composition of all TPNR samples in this study.

2.5. Characterizations

The morphological properties of various TPNR samples were examined using a scanning electron microscope (SEM), Hitachi S-4800 and JSM-5200 SEM (JEOL, Tokyo, Japan) at an accelerating voltage of 10 kV. The samples were firstly cryogenically fractured in liquid nitrogen. The fractured surfaces were then dried in a vacuum oven at 40 °C for 3 h and then sputter-coated with gold-palladium before examination by SEM. To study the surface morphology, ENR and PP phases in ENR/PP blends, the fractured surface was etched by extraction with chloroform at room temperature for 24 h to remove ENR phase before being dried and sputter coated.

The tensile properties of the TPNR and its nanocomposites were tested using an H10KS Universal testing machine (Hounsfield Test Equipment, Redhill, UK) fitted with a 500 N load cell and operated at a constant 500 mm/min cross-head speed according to ISO 37.

Differential scanning calorimetry (DSC) was performed by using a DSC7 (Perkin-Elmer, Buckinghamshire, UK). The samples were first incorporated in an aluminum pan and then heated from ambient temperature to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The test was maintained at this temperature for about 5 min in order to eliminate the previous thermal history. It was then cooled down to 20 °C. The heating test was again performed by raising the temperature from 20 to 200 °C with the same heating rate of 10 °C/min. The degree of crystallinity (X_c) of the PP phase in the ENR/PP blends was calculated based on the melting enthalpy of the second heating thermogram [37], as laid out in Equation (1):

$$X_c[\%] = \frac{m_c \Delta H_m}{m_p \Delta H_0} \cdot 100 \quad (1)$$

where ΔH_m is the melting enthalpy measured in the heating experiments, ΔH_0 is the theoretical value of enthalpy of 100% crystalline PP, which was 207.1 J/g [32], m_c is the mass of the sample, and m_p is the mass of PP in the blend sample.

The X-ray diffraction (XRD) analysis of the PP phase in the ENR/PP TPNR and its nanocomposites was carried out by using an X'Pert MPD, Philips X-ray

diffractometer (Philips, Almelo, The Netherlands) with a Cu K α radiation wavelength of 0.154 nm. Diffraction patterns were operated at 40 kV and collected in reflection-mode geometry from 5 to 35° 2 θ .

Thermogravimetric analysis (TGA) was performed using an STA 6000 (Perkin-Elmer, Norwalk, CT, USA) to determine the degradation temperature (T_d) of TPNR and its nanocomposites. About 10 mg samples were heated from ambient temperature to 800 °C with a heating rate of 10 °C/min under a nitrogen atmosphere.

3. Results and discussion

3.1. Dispersion of nano-silica in TPNR nanocomposites

Unmodified SiO₂, MPTS modified SiO₂, and fracture surfaces of TPNR nanocomposites prepared by solid and latex pre-compounding techniques reinforced by unmodified SiO₂ and MPTS modified SiO₂ were examined by SEM, and the results are shown in Figure 2. From our previous work [3], pre-compounding of nano-silica in ENR phase prior to mix with PP provided the morphology of nano-silica dispersed mainly in the ENR phase of the ENR/PP blend. In this study, the encapsulated structure of nano-silica in the ENR phase was assumed. It can be seen that a large agglomeration of unmodified SiO₂ particles was formed in the ENR phase for the unmodified SiO₂ filled TPNR nanocomposite prepared using solid pre-compounding (Figure 2c). However, in Figure 2d, the unmodified SiO₂ pre-compounded in ENR using the latex pre-compounding technique prior to preparation of the TPNR nanocomposites showed finer dispersion of nanoparticles in the ENR phase. This could be attributed to the much lower viscosity of the ENR latex during the incorporation of nano-silica particles while forming the ENR masterbatch. Also, the distances between the ENR particles in water media allow the SiO₂ particles to get closer to the rubber molecules than when prepared by the solid mixing technique (*i.e.*, in Figure 2c). This resulted in finer dispersion and distribution of SiO₂ particles in the ENR matrix with the latex mixing method. Therefore, the SiO₂ in the ENR phase exhibited a more uniform dispersion in ENR than that of the solid pre-compounding method.

In Figures 2e and 2f, it is clear that the size of nanoparticles in the ENR matrix was reduced in the TPNR with MPTS modified SiO₂ surfaces as compared with the unmodified SiO₂ for both solid and latex

Figure 2. SEM images of unmodified nano-silica (a), MPTS modified nano-silica (b) with a magnification of 10000× and unextracted TPNR nanocomposites with a magnification of 20000×: s-TPNR-SiO₂ (c); l-TPNR-SiO₂ (d); s-TPNR-MPTS-SiO₂ (e); and l-TPNR-MPTS-SiO₂ (f).

pre-compounding samples. In fact, the incorporation of MPTS-SiO₂ via the latex pre-compounding showed the finest dispersion of silica nanoparticles in the TPNR. This could be attributed to the chemical modification of SiO₂ with MPTS modifying the surface properties of SiO₂ from a hydrophilic to a hydrophobic nature, resulting in the surface of the silica

particles being covered by hydrophobic functional groups. This results in lower filler-filler interactions among the neighboring filler particles. This also leads to an enhancement in the compatibility between SiO₂ and the ENR and, therefore, also the PP in the ENR/PP blends. The hydrophobicity of MPTS-SiO₂ particles was verified by floating in water. It was

Figure 3. Images and model representation of hydrophilic groups at the SiO_2 surface (sink in water) and hydrophobic groups at MPTS modified SiO_2 surface (*i.e.*, MPTS- SiO_2) (float in water).

found that the MPTS modified SiO_2 particles floated on the water surface while the unmodified SiO_2 particles sunk to the bottom of the container, as shown in Figure 3. The functional groups at the surface of unmodified SiO_2 and MPTS modified particles are also shown in this figure.

3.2. Mechanical properties

Figure 4 shows typical stress-strain behaviors of TPNR and its nanocomposites with two different incorporating techniques of SiO_2 (*i.e.*, solid and latex pre-compounding techniques) and two different types of nano-silica (*i.e.*, unmodified and MPTS modified SiO_2). Also, the tensile properties in terms of Young's modulus, tensile strength, and elongation at break are summarized in Table 2. It can be seen that all types of TPNRs exhibited a combination of plastic and elastic behaviors during deformation according to the specific behaviors of thermoplastic elastomers. Furthermore, the addition of nano-silica into ENR and the ENR/PP blends led to lower strain but higher strength at break as compared with the blend without silica. This might be due to the materials having more rigidity in the presence of nano-silica.

Figure 4. Stress-strain curves of TPNR and its nanocomposites with pre-compounding technique and surface modification of nano-silica.

In Figure 4, it can also be seen that the TPNR nanocomposites prepared by the latex pre-compounding technique had higher tensile strength and lower elongation at break as compared with those prepared using the solid pre-compounding technique. This can be attributed to better dispersion of nano-silica in the

Table 2. Tensile properties of TPNR and its nanocomposites with different pre-compounding technique and surface modification of nano-silica.

Samples	Young's modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
TPNR	299±10	10.47±0.35	156±15
s-TPNR- SiO_2	292±12	10.83±0.60	134±25
s-TPNR-MPTS- SiO_2	227±9	11.42±0.45	115±10
l-TPNR- SiO_2	289±5	11.94±0.20	94±13
l-TPNR-MPTS- SiO_2	226±5	13.09±0.18	61±15

Figure 5. Schematic representation of compatibilization effect in TPNR filled with unmodified SiO₂ and MPTS modified SiO₂.

ENR and hence in the TPNR, causing the enhancement of the stress transfer between filler and the matrix leading to superior strength properties. In Figure 4 and Table 2, a dramatic improvement in tensile strength is clearly seen upon the addition of MPTS-SiO₂ into the ENR/PP blend, particularly with the ENR masterbatch blend prepared using the latex pre-compounding technique (I-TPNR-MPTS-SiO₂). This might be attributed to higher compatibilization between the polymer phase in TPNR and SiO₂ nanoparticles *via* grafted MPTS molecules. This might cause the formation of the immobilized chains of ENR and PP on the surface of MPTS-SiO₂, as shown in the proposed model in Figure 5.

In order to understand more deeply the morphological properties of TPNR filled with nano-silica, SEM was performed, and the results are shown in Figure 6. It should be noted that the ENR phase in ENR/PP TPNR was extracted by etching with chloroform. Typically, the improvement of compatibility between different phases causes the reduction of interfacial

tension, which has a great influence on the decreased droplet sizes of the blend morphology [1, 5, 31]. In Figure 6, it is clear that dual-phase co-continuous morphology is seen in all samples, indicating phase separation of the blends due to immiscibility between ENR and PP phases. It is also seen that the TPNR-SiO₂ nanocomposites had smaller ENR domains where there were holes or cavities (Figures 6b–6e), as compared with the TPNR without filler (Figure 6a). This could imply that the SiO₂ particles could prevent the coalescence of the ENR phase during processing and bring about an improvement in the compatibility between ENR and PP phases. Moreover, the TPNR filled with MPTS-SiO₂ (Figures 6c and 6e) showed finer grain morphology than those of the unmodified SiO₂ filled TPNR (Figures 6b and 6d). This is attributed to higher interfacial adhesion and compatibility between different phases of the blends (*i.e.*, ENR and PP) together with the MPTS-SiO₂ filler particles. Also, partial entanglement between PP/MPTS-SiO₂ and ENR/MPTS-SiO₂ could

form immobilized chains at the filler-polymer interface. Therefore, the grafted organosilane on the MPTS-SiO₂ surfaces could act as an effective compatibilizing agent of the ENR/PP blends, as shown in the schematic diagram in Figure 5. Hence, the greatest improvement of the phase morphology is to be found in the TPNR with MPTS-SiO₂.

In Table 2, it can be seen that the addition of nano-silica in TPNR caused a slight reduction of Young's modulus in the TPNRs. This reduction was more pronounced in the TPNR with MPTS-SiO₂. This might be due to grafted MPTS molecules on the SiO₂ surface causing softening of the silica particles, leading to a decrease in the modulus of nano-silica

Figure 6. SEM images of TPNR and its nanocomposites with a magnification of 500×: TPNR (a); s-TPNR-SiO₂ (b); s-TPNR-MPTS-SiO₂ (c); l-TPNR-SiO₂ (d); and l-TPNR-MPTS-SiO₂ (e).

particles and hence also of the TPNR. The reduction of Young's modulus upon adding modified SiO_2 into the polymer matrix has been found in stiffened materials, such as HDPE [36] and PP [37]. However, it was found that the difference in the pre-compounding techniques did not affect the magnitude of Young's modulus of the TPNR nanocomposites.

3.3. Thermal properties

The thermal stability of TPNR and its nanocomposites with 2.5 wt% of nano-silica (*i.e.*, SiO_2 or MPTS- SiO_2) was determined by thermogravimetric analysis (TGA) in a nitrogen atmosphere, as shown in Figure 7. A summary of the TGA data is shown in Table 3. All the samples showed two decomposition steps, including decomposition of ENR phase at around 395–403 °C and decomposition of PP phase at around 462–475 °C. In this work, it is clear that the addition of SiO_2 particles into ENR/PP blends significantly increased initial decomposition temperature (IDT) as well as the decomposition temperature

(T_d) of both ENR and PP phase indicating improvement in thermal stability of the TPNR nanocomposites. It is also seen that the T_d of TPNR nanocomposites filled with MPTS- SiO_2 are slightly higher than that of unmodified SiO_2 . Moreover, the latex pre-compounding of MPTS- SiO_2 in TPNR gave slightly higher T_d than that prepared by the solid pre-compounding technique. The increased thermal stability of TPNR can be explained by the enhancement of compatibilization between ENR and PP phases *via* the formation of immobilized chain (*i.e.*, PP/ MPTS- SiO_2 and ENR/MPTS- SiO_2) as discussed earlier.

3.4. Crystallization behavior of the TPNR nanocomposites

Besides the filler-polymer interaction that affects the mechanical and thermal properties of the TPNR nanocomposites, the strength properties are also governed by the molecular orientation of semi-crystalline PP phase through the crystallization process. Figure 8 shows cooling and heating DSC thermograms of TPNR and its nanocomposites with different pre-compounding techniques and surface modification of nano-silica. Also, Table 4 summarizes the crystallization temperature (T_{pc}), crystalline melting temperature (T_{pm}), and degree of crystallization (X_c) of PP phase in ENR/PP TPNR and its nanocomposites. In Figure 8a, it is clear that the cooling DSC thermograms indicate the crystallization temperature (T_{pc}) of the PP phase in pure ENR/PP TPNR at 107 °C (Table 4). It can also be seen that the T_{pc} of PP phase in ENR/PP TPNR with unmodified SiO_2 shows a

Table 3. Thermal properties of TPNR and its nanocomposites with different pre-compounding technique and surface modification of nano-silica.

Samples	IDT [°C]	T_d [°C]	
		ENR	PP
TPNR	368.70	395.03	462.47
s-TPNR- SiO_2	372.54	400.83	472.29
s-TPNR-MPTS- SiO_2	373.63	401.95	473.73
l-TPNR- SiO_2	377.18	401.05	470.86
l-TPNR-MPTS- SiO_2	375.39	402.42	474.49

Figure 7. TGA (a) and DTG (b) curves of TPNR and its nanocomposites with different pre-compounding technique and surface modification of nano-silica.

Figure 8. Cooling (a) and heating DSC thermogram (b) of TPNR and its nanocomposites with different pre-compounding technique and surface modification of nano-silica.

Table 4. Crystallization temperature (T_{pc}), crystalline melting temperature (T_{pm}) and degree of crystallization (X_c) of PP phase in ENR/PP TPNR and its nanocomposites with different pre-compounding techniques and surface modification of nano-silica.

Samples	T_{pc} [°C]	T_{pm} [°C]	ΔH_m [J/g]	X_c [%]
TPNR	107.0	154.7	44.4	42.8
s-TPNR-SiO ₂	107.6	155.2	42.1	42.7
s-TPNR-MPTS-SiO ₂	104.5	151.7	43.6	44.2
l-TPNR-SiO ₂	106.0	154.5	42.2	42.5
l-TPNR-MPTS-SiO ₂	103.0	150.5	43.8	44.4

similar value to the TPNR without silica (*i.e.*, pure TPNR), in concurrence with earlier studies [3, 17]. However, the crystallization peaks (*i.e.*, T_{pc}) of the PP phase in the TPNR nanocomposites with MPTS-SiO₂ were significantly shifted to lower temperatures (*i.e.*, 104.5 °C in s-TPNR-MPTS-SiO₂ and 103 °C in l-TPNR-MPTS-SiO₂). This implies the interference of nucleation of the PP phase in the ENR/PP blend in the commencement of the crystallization because of the MPTS-SiO₂ nanoparticles. That is, the grafted MPTS on nano-silica surfaces might cause partial absorption of PP chains on the silica surfaces by chemical and physical interaction as well as chain entanglement and hence retard the crystallization process. This might disturb the rearrangement of the chain-folding mechanisms of PP segments to crystallize. This is why the retardation of the nucleation process of the PP phase in the MPTS-SiO₂ filled ENR/PP TPNR nanocomposite occurred, as indicated by the lowest T_{pc} (Table 4). This phenomenon has

also been found in the HDPE phase in the NR/HDPE blend compatibilized with graphene oxide (GO) [31] and maleic anhydride grafted polypropylene (mPP)/layered silicate (OLS) hybrids [38].

Figure 8b shows the heating DSC thermograms of pure TPNR and its nanocomposites. The double crystalline melting peaks are seen clearly in all samples, which indicates the presence of monoclinic α -form and hexagonal β -form of PP crystallites [39], respectively. It is also seen that the crystalline melting temperature (T_{pm}) of the PP phase in the ENR/PP blend filled with unmodified SiO₂ prepared by solid and latex pre-compounding techniques are similar to that of the T_{pm} of pure TPNR. However, the addition of MPTS-SiO₂ into the ENR/PP blend caused markedly decreased T_{pm} , corresponding to the reduction in the size of spherulite in the crystalline PP phase, explaining the imperfect crystals of PP [40]. It is worth noting that the degree of crystallinity (X_c) of the PP phase in the ENR/PP TPNR was slightly increased upon the addition of the MPTS-SiO₂. However, similar X_c was observed in the pure TPNR, and unmodified SiO₂ filled TPNR, both prepared by solid and latex pre-compounding techniques. The increase in the degree of crystallinity of the PP phase in the ENR/PP TPNR with MPTS-SiO₂ could be explained by the higher dispersion capacity of the MPTS-SiO₂ nanoparticles in the ENR and eventually some in PP phases, which caused an increase in the effective number of nuclei available to promote crystallization and hence increased the degree of crystallinity.

3.5. X-ray diffraction (XRD) analysis

Figure 9 shows XRD patterns of the PP phase in ENR/PP TPNR and its nanocomposites with different pre-compounding techniques and the surface modification of nano-silica. The peaks at $2\theta = 14.0$, 16.8 , 18.5 , 21.3 , and 21.8° correspond to the α -form peaks of PP at (110), (040), (130), (111) and (041) planes were observed, respectively. Also, the β -form of PP at the (300) plane was observed in all samples at $2\theta = 16.0^\circ$. This result correlates well to the double melting peaks of DSC thermograms (Figure 8b). It is seen that all the TPNR samples did not show any new peak location; they remained nearly unchanged, as compared to the peaks of pure TPNR. This indicates that different pre-compounding techniques and surface modification of SiO_2 did not affect the crystalline structure of the PP phase in the ENR/PP blend. This concurs with our previous study [3]; that is, the addition of 2.5 wt% nano-silica in 50/50 ENR/PP blends did not change the XRD diffraction pattern of PP crystalline. Therefore, the enhancement of mechanical and thermal properties of 50/50 ENR/PP TPNR filled with 2.5 wt% nano-silica should be attributed to the uniform dispersion of nano-silica particles, strong filler-polymer interactions, and the degree of crystallinity of the PP phase.

4. Conclusions

Various properties of the 50/50 ENR/PP TPNR with 2.5 wt% of unmodified and MPTS modified nano-silica particles (SiO_2 and MPTS- SiO_2 , respectively)

Figure 9. XRD patterns of TPNR and its nanocomposites with different pre-compounding technique and surface modification of nano-silica.

prepared using latex and solid pre-compounding techniques were investigated. The effect of the processing method and surface modification of nano-silica on phase morphology, mechanical properties, thermal stability, and crystallinity of the PP phase in the ENR/PP blend was studied. It was found that the finer dispersion of nano-silica was found in the blends using the ENR-silica masterbatch prepared using the latex pre-compounding technique. This leads to an increase in mechanical properties and thermal stability of the ENR/PP TPNR nanocomposites. In addition, the highest degree of dispersion of nano-silica was achieved by the addition of ENR mixed with MPTS- SiO_2 . This resulted in superior mechanical properties for the TPNR nanocomposites filled with MPTS- SiO_2 . This can be ascribed to the increased interfacial interaction between the polymer matrix and nano-silica particles, causing a strong filler-polymer interaction and improvement of compatibilization between the different polymer phases (*i.e.*, ENR and PP) and filler particles (*i.e.*, MPTS- SiO_2), leading to the ability of filler to support stresses transferred from the polymer matrix. The thermal stability of the TPNR nanocomposites was also significantly improved in the presence of MPTS- SiO_2 .

Furthermore, a higher degree of crystallinity in the PP phase in ENR/PP TPNR with MPTS- SiO_2 particles was observed, while the different pre-compounding techniques and introduction of SiO_2 did not show any significant change in the degree of crystallinity in the PP phase. Moreover, the XRD results indicate that the crystalline structure of the PP phase in the 50/50 ENR/PP blends was not affected by the addition of 2.5 wt% nano-silica (SiO_2 or MPTS- SiO_2). Therefore, we suggest that the ENR/PP TPNR nanocomposites with finer dispersion and distribution of nano-silica with superior mechanical and thermal properties could be obtained *via* the latex pre-compounding technique together with the use of surface modified nano-silica.

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