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Effects of coagent incorporation on properties of ultrafine fully vulcanized powdered natural rubber prepared as toughening filler in polybenzoxazine

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Abstract

Ultrafine fully vulcanized powdered natural rubber (UFPNR) is a renewable material that is promising for industrial application as a toughening filler in polymer matrix. In this work, effects of coagent on properties of UFPNR produced by radiation vulcanization and spray-drying was systematically investigated, in which trimethylol propane trimethaacrylate (TMPTMA) was used as coagent. The crosslinking density of UFPNR could be enhanced by increasing radiation dose from 50 to 350 kGy and it was further enhanced by using TMPTMA as coagent during the production process. UFPNR with the smallest particle size of 3.9 ± 1.8 μm and highest thermal stability ($T_{d5} = 347°C$) could be obtained by using TMPTMA with the highest content of 9 phr. The results suggested that polymer chains of natural rubber were more packed into smaller particle as they were more crosslinked by the coagent. Finally, an application of UFPNR as a toughening filler in polybenzoxazine was demonstrated. The highest impact strength improvement of 20% was achieved by incorporation of 3 phr UFPNR in polybenzoxazine.

KEYWORDS
coagent, polybenzoxazine, radiation vulcanization, toughening filler, ultrafine fully vulcanized powdered natural rubber

1 | INTRODUCTION

Natural rubber (NR) is a natural and renewable material, extracted from the *Hevea brasiliensis* tree, with the main component of cis-1,4-polyisoprene polymer. NR in original form is sticky and non-elastic.[1–4] Therefore, its application is limited. To extend application of NR, it is subjected for vulcanization process to crosslink molecular chains of NR. Vulcanized NR is more heat stable and more elastic than original NR.[1] So far, there are three main techniques of vulcanization. The three techniques are sulfur vulcanization, peroxide vulcanization, and radiation vulcanization. Comparing to other two techniques, radiation vulcanization possesses many advantages, such as inherently clean technology, no oxidative degeneration in polymer, and less energy consumption as

it is operated at room temperature.[5,6] For radiation vulcanization of NR, radiation energy is absorbed by NR molecules. After that, radiolysis of NR molecules occurs, generating NR radicals. The crosslinking structure of NR is then formed with the recombination of the radicals. Furthermore, the vulcanized NR can be spray-dried into a powder form, which is called ultrafine fully vulcanized powdered natural rubber (UFPNR).[7] UFPNR is a type of ultrafine fully vulcanized powdered rubber (UFPR), which can be defined as an elastomeric rubber particle possessing a high degree of crosslinking upon radiation process. The material has a size of particle or particle aggregate in the range of 50–20,000 nm.[8] UFPNR is a renewable material that is promising for industrial application as a toughening filler in polymer matrix. It is expected to be an alternative material to replace the use of petroleum-based UFPR from styrene-butadiene, nitrile-butadiene, and so forth.[8–18]

During radiation vulcanization, coagent can be used to further enhance the crosslinking of NR. The use of coagent can also reduce the radiation dose to be used. Thus, the degradation of NR induced by the high radiation dose can be inhibited.[19] Normally, coagent used in the radiation vulcanization is organic molecules with acrylate groups. The examples of coagent are trimethylolpropane trimethaacrylate, ethyleneglycol dimethacrylate, and phenoxy ethyl acrylate.[20] It was reported that coagent could improve physicomechanical properties during radiation vulcanization of acrylic rubber/styrene butadiene rubber blend.[19]

In this work, effects of coagent on properties of UFPNR produced by radiation vulcanization and spray-drying was systematically investigated for the first time, in which trimethylol propane trimethaacrylate (TMPTMA) was used as coagent. The radiation dose in the range of 50–350 kGy and coagent content in the range of 1–9 phr were used in the production process. Physical, chemical, and thermal properties of the UFPNR were characterized by swelling analysis, scanning electron microscopy (SEM), infrared spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The properties of UFPNR produced by using different contents of coagent were compared and discussed. Finally, an application of UFPNR as a toughening filler in polybenzoxazine was demonstrated. Polybenzoxazine is a phenolic-type thermoset that have been used as a matrix for composites in many applications such as electronic packaging,[21] self-lubricating and friction materials,[22] and aerospace industries.[23] However, polybenzoxazine has been reported to show relatively low toughness and resistance on impact due to its rigidity of the chemical structure. In this work, we

demonstrated that UFPNR could be used as a filler to improve the toughness of polybenzoxazine.

2 | EXPERIMENTAL SECTION

2.1 | Materials

NR latex (60 wt% of dry rubber content) was obtained from the Rubber Research Institute of Thailand. The coagent, trimethylol propane trimethaacrylate (TMPTMA, purity >75%) was obtained from the Tokyo Chemical Industry Co., Ltd. (Japan). Bisphenol A (AR grade) was supplied by the PTT Phenol Co., Ltd. (Bangkok, Thailand). Paraformaldehyde (AR grade) and 3,5-xylidine (AR grade) were obtained from the Merck (Darmstadt, Germany) and Panreac Quimica S.A. (Barcelona, Spain), respectively. All chemicals were used as received without further purification.

2.2 | Preparation of UFPNR

In the first step, the NR latex was diluted from 60 wt% of dry rubber content to 20 wt% of dry rubber content by using distilled water. Then, it was subjected for radiation vulcanization using an electron beam accelerator module MB 10–50, facilitated by the Thailand Institute of Nuclear Technology, with the output power of 10 meV and 50 kW and a dose rate of 10 kGy/min. Different radiation dose of 50 to 350 kGy was applied. After radiation vulcanization, the samples were processed into UFPNR by using a Buchi Mini Spray Dryer Model B-290 (Switzerland) with an inlet temperature of 150°C. The flow meter valve was set to 667 L/h and the pump output was set to 4.5 ml/min of feed flow pumping into the nozzle. Finally, the UFPNR was collected at the bottom part of the cyclone unit. To study effects of coagent incorporation, TMPTMA was added to the diluted NR latex and the mixtures were stirred for 15 min before subjecting for radiation vulcanization. The amount of added TMPTMA was varied in the range of 1–9 phr. For this experiment, the radiation dose was fixed at 350 kGy.

2.3 | Preparation of benzoxazine resin

Benzoxazine resin (BA-35x) was prepared by mixing bisphenol A, paraformaldehyde, and 3,5-xylidine with a molar ratio of 1:4:2 and then the mixtures were continuously mixed in an aluminum pan at 120°C for 40 min. After that, the benzoxazine resin solidified at room temperature. By using a mortar and pestle, the solid benzoxazine resin was

ground into a fine powder of about 100–250 μm (sieve analysis) and kept in a refrigerator for future use.

2.4 | Preparation of UFPNR-filled polybenzoxazine

Various contents (0–9 phr) of UFPNR were gently added and mixed with the benzoxazine resin at a temperature of 120°C for 20 min in a propeller mixer to obtain a well dispersed molding compound. Then, the mixtures were compressed in a compression molding at 200°C for 4 h under a hydraulic pressure of 15 MPa to obtain fully cured polybenzoxazine, following the previous report.[24] Finally, the fully cured specimens were air-cooled down to room temperature and ready for characterization.

2.5 | Characterizations

The swelling and crosslinking degree of UFPNR was determined by dissolution in toluene at room temperature for 24 h. First, the dried weight of UFPNR sample was recorded as W_1 before it was immersed in toluene (ρ_s = 0.87 g/cm^3, V_1 = 106.5 cm^3/mol) for 24 h. Then, the weight of swollen UFPNR was immediately recorded as W_2 before it was dried in a vacuum oven at 70°C for 24 h. Finally, the weight of dried UFPNR was recorded as W_3. The swelling ratio (Q), gel fraction, molecular weight between crosslink (Mc), and crosslinking density (CLD) of UFPNR were calculated according to Equations (1), (2), (3), and (4), respectively.[25,26] The density of rubber (ρ_r) is 0.91 g/cm^3 and φ_r is the volume fraction of the polymer in the swollen stage. χ_{12} is the polymer–solvent interaction parameter, which was equal to 0.393 and N is the Avogadro number of $6.02214179 \times 10^{23}$.

$$Q = \frac{(W_2 - W_1)/\rho_s}{W_1/\rho_r} \quad (1)$$

$$\text{Gel fraction} = \frac{W_3}{W_1} \quad (2)$$

$$M_c = \frac{-\rho_r V_1 \left(\varphi_r^{1/3} - \frac{\varphi_r}{2}\right)}{\text{Ln}(1 - \varphi_r) + \varphi_r + \chi_{12}\varphi_r^2} \quad (3)$$

$where\, \varphi_r = \frac{1}{1+Q}.$

$$\text{CLD} = \frac{\rho_r N}{M_c} \quad (4)$$

A scanning electron microscope (SEM, JEOL JSM-6400) with an accelerating voltage of 3 kV was used for observing morphology of UFPNR. The samples were coated with a thin gold layer by using an ion sputtering device (JEOL JFC-1200). Image J program was used for measuring the particle size.

Fourier-transform infrared (FT-IR) spectrometer (Spectrum GX, Perkin Elmer) with an attenuated total reflection (ATR) accessory (Waltham, Massachusetts, United States) was used for examining molecular structure of UFPNR. A scan range of 4000–400 cm^{-1} with a total scan of 32 and resolution of 4 cm^{-1} was employed for the analysis.

A thermogravimetric analyzer (TGA, TGA1 Module, Mettler-Toledo) was used for examining thermal stability of UFPNR. The sample weight was in the range of 8–12 mg. The measurement was conducted, under a nitrogen atmosphere with a flow rate of 50 ml/min, by heating the samples from 25 to 850°C with a heating rate of 20°C/min.

The glass transition temperature of UFPNR was examined by using a differential scanning calorimeter (DSC, DSC1 Module, Mettler-Toledo). The sample weight was in the range of 5–10 mg. the measurement was conducted, under a nitrogen atmosphere and cooling system by using a liquid nitrogen, by heating the samples from −100 to 25°C with a heating rate of 10°C/min.

The impact strength of UFPNR-filled polybenzoxazine was tested by using an Izod pendulum impact tester, following the standard method of ASTM D256. The samples were cut into size of $50 \times 12.5 \times 3$ mm^3 and clamped into the pendulum impact test fixture while notch side facing the striking edge of the pendulum on the Izod impact tester.

3 | RESULTS AND DISCUSSION

3.1 | Effects of radiation dose on swelling and crosslinking degree of UFPNR

The swelling and crosslinking degree of UFPNR produced by radiation vulcanization and spray drying were investigated by analyzing its swelling ratio, gel fraction, molecular weight between crosslink, and crosslinking density. Radiation dose ranging from 50 to 350 kGy was applied to produce UFPNR with different swelling and crosslinking properties. The plot in Figure 1(A) shows the decreased swelling ratio of UFPNR as the radiation dose increased. On the contrary, the gel fraction of UFPNR gradually increased by using higher radiation doses. These results indicated that there was more insoluble polymer fraction in UFPNR produced by using higher radiation doses.[27] Radiation vulcanization induced inter-molecular crosslinking in UFPNR.[28] Therefore, it
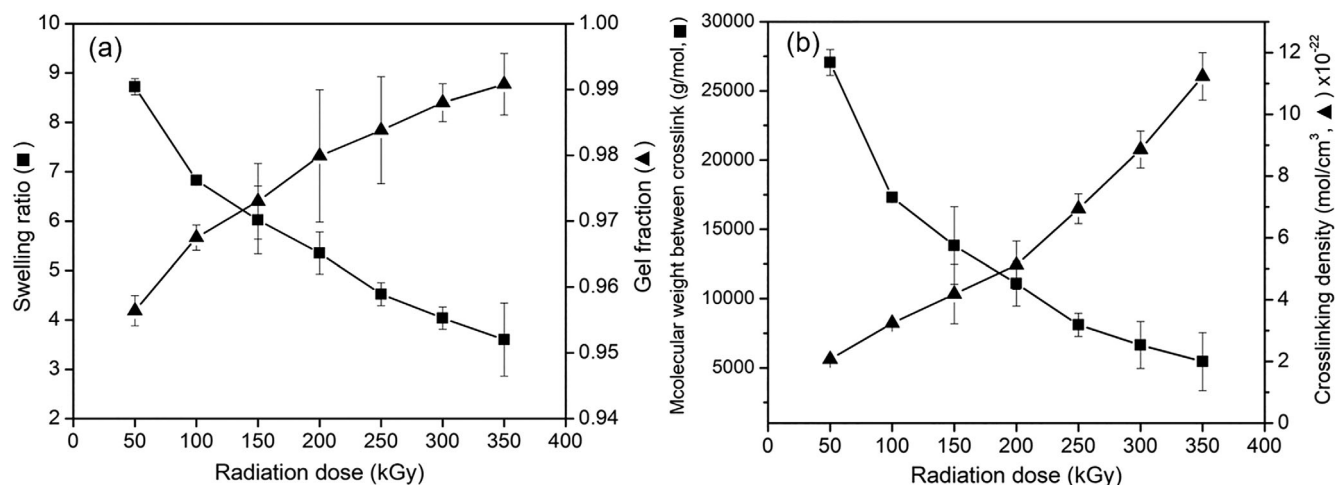
FIGURE 1 Swelling ratio-gel fraction (A) and molecular between crosslink-crosslinking density (B) of ultrafine fully vulcanized powdered natural rubber (UFPNR) prepared with different radiation doses
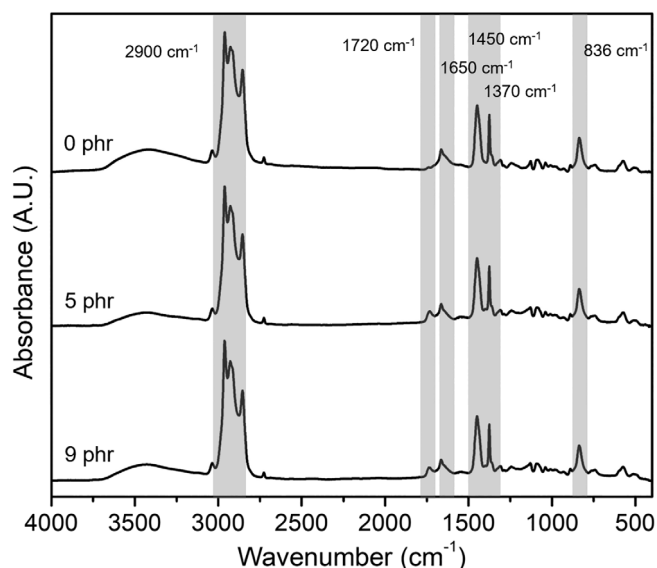

FIGURE 2 Swelling ratio-gel fraction (A) and molecular between crosslink-crosslinking density (B) of ultrafine fully vulcanized powdered natural rubber (UFPNR) prepared with different contents of trimethylol propane trimethaacrylate (TMPTMA)

was less swellable and less soluble in the solvent. The enhancement of inter-molecular crosslinking in UFPNR could be confirmed by the plot in Figure 1(B). The molecular weight between crosslink of UFPNR became lower at higher radiation doses. This was due to the shortening of polymer chain as it was more crosslinked, as stated in the Flory–Rehner theory.[25,26] At higher radiation doses, NR absorbs more energy.[29] Consequently, more free radicals are generated in polymer chains of NR. The unstable free radicals react with other carbon atoms in the chains, forming a crosslinking structure of NR. The plot in Figure 1(B) shows the increased crosslinking density in UFPNR upon the increased radiation dose.

3.2 | Effects of coagent on swelling and crosslinking degree of UFPNR

Effects of coagent on swelling and crosslinking degree of UFPNR were investigated by incorporation of TMPTMA during the production process. In this study, the radiation dose was fixed at 350 kGy. The content of TMPTMA was varied in the range of 1–9 phr. The swelling ratio and gel fraction of UFPNR regarding the content of TMPTMA are presented in Figure 2(A). The results showed that there was a decrease in swelling ratio and increase of gel fraction of UFPNR, as the content of TMPTMA increased. It could also be observed in Figure 2(B) that the molecular weight between crosslink of UFPNR became lower, but its crosslinking density became higher. These results indicated that TMPTMA enhanced the crosslinking degree of UFPNR. It should be noted that the excess content of TMPTMA (i.e., 11 phr) caused the phase separation before irradiation process, as TMPTMA was not soluble in NR solution. The phase separation occurred due to the domain of the high local concentration of this coagent. Consequently, the reactivity of the coagent could be decreased according to the steric hindrance effect.[30] We found that the crosslinking density of UFPNR decreased as the concentration of TMPTMP increased from 9 to 11 phr (data not shown).

3.3 | Effects of coagent on molecular structure of UFPNR

The molecular property of UFPNR produced by radiation vulcanization at 350 kGy and spray drying was analyzed by using an infrared spectroscopy. Figure 3 shows infrared spectra of UFPNR produced without using coagent

and UFPNR produced by using TMPTMA coagent with the contents of 5 and 9 phr. All spectra showed absorption bands at 836 and 1650 cm^{-1}, attributed to =CH— out of plane bending and C=C stretching vibration of NR, respectively.[5,6] The observed bands at 1370 and 1450 cm^{-1} were attributed to CH$_3$ deformation and CH$_2$ asymmetric stretching, respectively.[5,6] The peaks around 2900 cm^{-1} were attributed to the CH$_3$ and CH$_2$ asymmetric and symmetric stretching vibrations.[5,6] The peak around 3400 cm^{-1} was corresponded to N—H stretching vibration of amide groups from the existing proteins in NR.[31] Upon the coagent addition, the spectra showed additional band at 1720 cm^{-1}, corresponding to C=O stretching vibration of coagent molecules. The results suggested that the coagent was successfully incorporated into the structure of UFPNR. The reaction mechanisms for the network formation of UFPNR by using TMPTMA coagent was proposed in Figure 4. Under the radiation process, free radicals of NR were generated due to the excitation of NR molecules with radiation energy.[5] With the presence of coagent, the free radicals in the NR chains could react with carbon double bonds in the coagent molecules. A three-dimensional network structure of NR was formed as the coagent could act as multimodal crosslinking centers, connecting NR chains together.

3.4 | Effects of coagent on morphology and thermal properties of UFPNR

The microscopic morphology of UFPNR produced by radiation vulcanization at 350 kGy and spray drying was explored by using SEM. Figure 5 illustrates SEM micrographs of UFPNR produced without using coagent and UFPNR produced by using TMPTMA coagent with the contents of 1–9 phr. The results showed that the average particle size of UFPNR produced without using coagent was 8.5 ± 3.0 μm and it was systematically decreased upon the increased contents of incorporated coagent. The smallest particle size of 3.9 ± 1.8 μm was obtained by using 9 phr TMPTMA. The results suggested that polymer chains of NR were more packed into smaller particle as they were more crosslinked by the coagent.

The thermal properties of UFPNR produced by radiation vulcanization at 350 kGy and spray drying were explored by using TGA and DSC. Figure 6 shows TGA curves and DSC curves of UFPNR produced without using coagent and UFPNR produced by using TMPTMA coagent with the contents of 1–9 phr. As presented in Figure 6(A), the degradation temperature at 5% weight loss of UFPNR produced without coagent was 341°C and it was systematically increased to 342, 345, 346, 346, and 347°C, upon the increased contents of coagent from 1 to 3, 5, 7, and 9 phr, respectively. In the field of polymer science, degradation temperature at 5% weight loss is commonly used to evaluate thermal stability of polymer.[3,6,29] The results suggested that TMPTMA coagent enhanced the thermal stability of UFPNR, due to the higher molecular crosslinking of NR. However, the cogent did not significantly altered the glass transition temperature (T_g) of UFPNR, that is, T_g around −63 to −62°C as can be observed in Figure 6(B).

3.5 | Application of UFPNR as toughening filler in polybenzoxazine

In this last section, an application of UFPNR as a toughening filler in polybenzoxazine was demonstrated. The
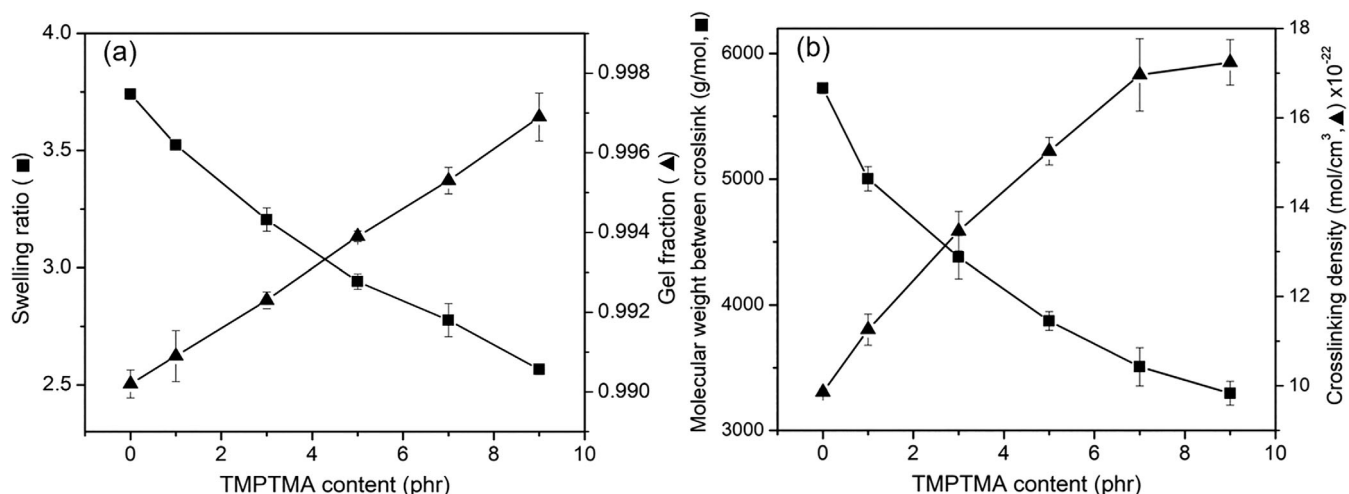
FIGURE 3 Infrared spectra of ultrafine fully vulcanized powdered natural rubber (UFPNR) prepared with different contents of trimethylol propane trimethaacrylate (TMPTMA)
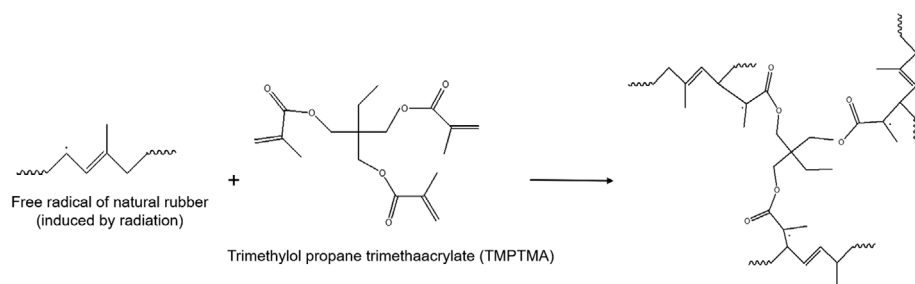
FIGURE 4 Network formation of ultrafine fully vulcanized powdered natural rubber (UFPNR) by using trimethylol propane trimethaacrylate (TMPTMA) as a coagent
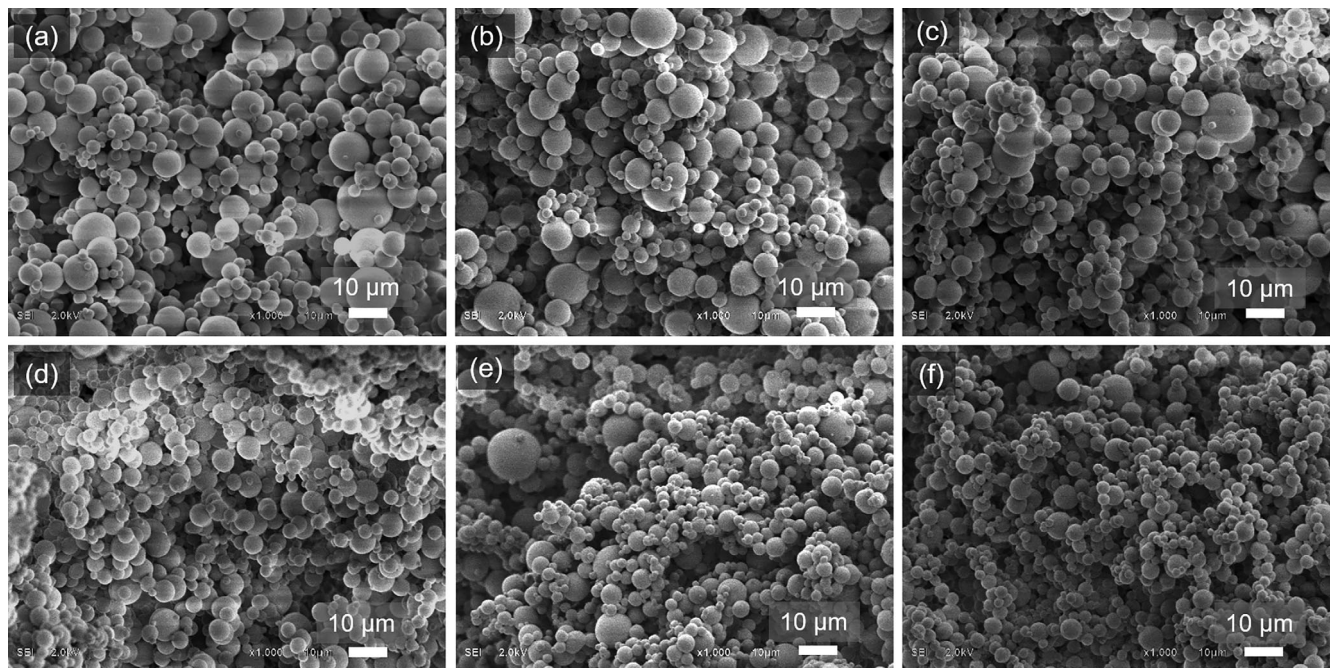

FIGURE 5 Scanning electron micrographs of ultrafine fully vulcanized powdered natural rubber (UFPNR) prepared with 0 (A), 1 (B), 3 (C), 5 (D), 7 (E), and 9 phr (F) trimethylol propane trimethaacrylate (TMPTMA)
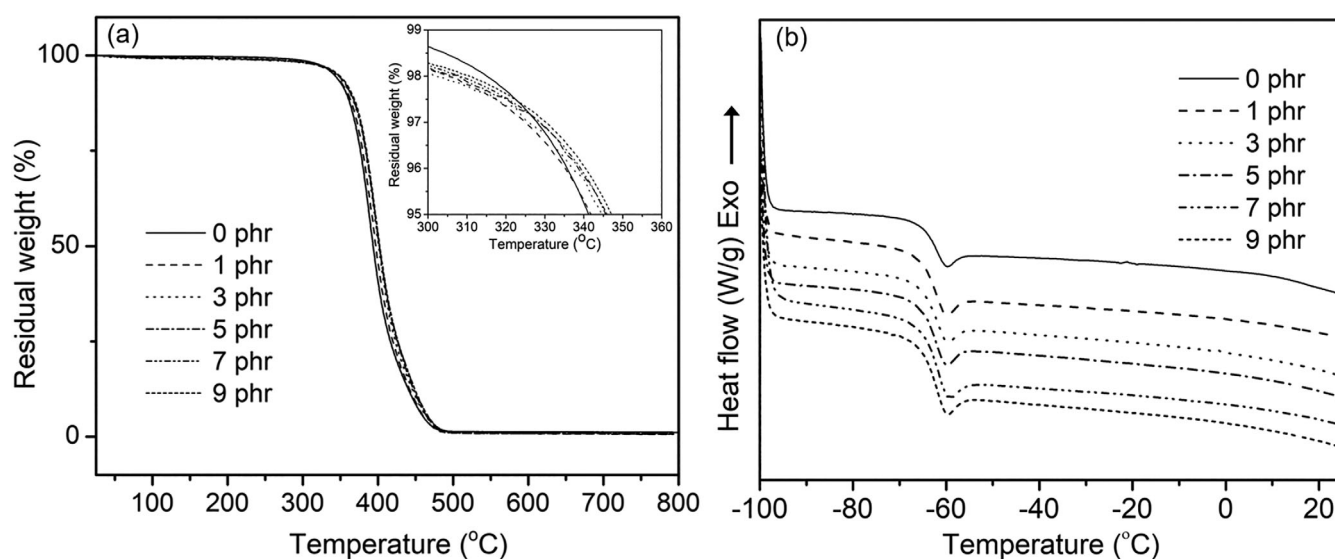

FIGURE 6 Thermogravimetric analysis curves (A) and differential scanning calorimetry curves (B) of ultrafine fully vulcanized powdered natural rubber (UFPNR) prepared with different contents of trimethylol propane trimethaacrylate (TMPTMA)
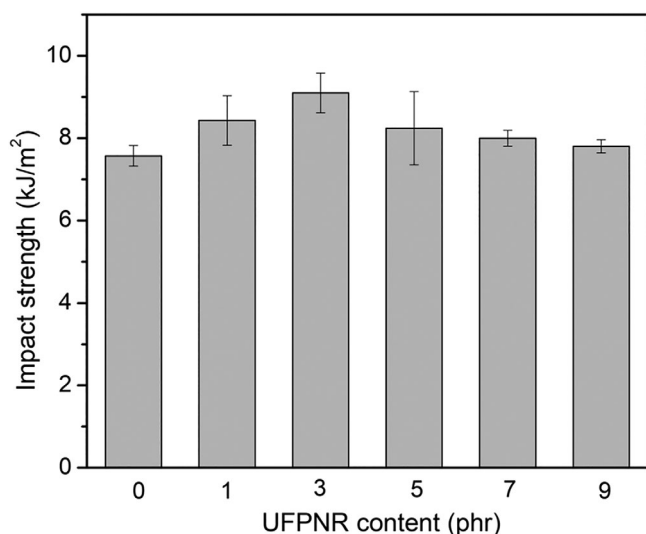
of 20% was achieved by incorporation of 3 phr UFPNR in polybenzoxazine.

FIGURE 7 Impact strength of polybenzoxazine filled with different contents of ultrafine fully vulcanized powdered natural rubber (UFPNR)

UFPNR prepared by using 9 phr TMPTMA with radiation dose of 350 kGy was used for the application. Various contents of UFPNR were incorporated into the polybenzoxazine matrix. The results in Figure 7 showed that the impact strength of neat polybenzoxazine was 7.57 ± 0.25 kJ/m^2. With the UFPNR addition of 1 and 3 phr, the impact strength of polybenzoxazine could be improved for 11.36% and 20.21%, respectively. The increased impact strength of polybenzoxazine was corresponded to the energy absorption mechanism of UFPNR, resulting in crazing and deformation of the polymer matrix.[9,32] However, excess contents, that is, 5, 7, and 9 phr, of UFPNR caused a reduction of impact strength improvement. This might be due to the decreased dispersion of UFPNR in polybenzoxazine, resulting in a crack and air gap in the matrix.[33,34]

4 | CONCLUSIONS

UFPNR was successfully produced by radiation vulcanization and spray drying. The crosslinking density of UFPNR could be enhanced by increasing radiation dose from 50 to 350 kGy and it was further enhanced by using TMPTMA as coagent during the production process. UFPNR with the smallest particle size of 3.9 ± 1.8 μm and highest thermal stability ($T_{d5} = 347°C$) could be obtained by using TMPTMA with the highest content of 9 phr. The results suggested that polymer chains of NR were more packed into smaller particle as they were more crosslinked by the coagent. Finally, an application of UFPNR as a toughening filler in polybenzoxazine was demonstrated. The highest impact strength improvement

CONFLICT OF INTEREST
The authors declare no conflicts of interest.

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