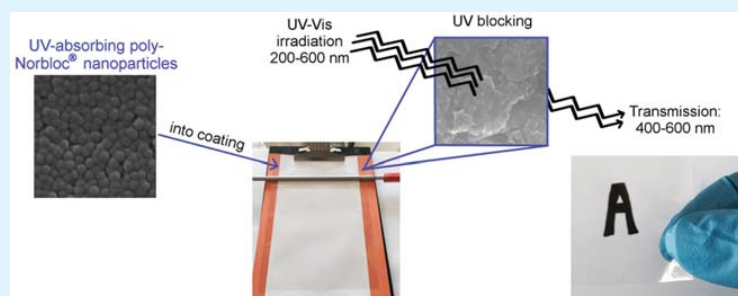


Design of UV-Absorbing Polypropylene Films with Polymeric Benzotriazole Based Nano- and Microparticle Coatings

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ABSTRACT: UV-absorbing nanoparticles (NPs) and microparticles (MPs) were prepared by emulsion and dispersion copolymerization of the vinyl monomer 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole (Norbloc (NB)) with the crosslinking monomer divinylbenzene. The effect of the initiator concentration on the size and size distribution of the polyNB (PNB) particles was elucidated. Thin coatings of the formed PNB NPs or MPs of 19 ± 2 and 200 ± 25 nm dry diameter, respectively, onto polypropylene (PP) films were then prepared and characterized. Increasing the concentration or thickness of the PNB NP or MP thin coatings on the PP films decreased their UV transmittance, up to complete UV blocking with just 2 μm of a 4% NP coating. Migration of the UV-absorbing agents from the coated PP films was not observed during three years of storage at room temperature, offering a unique solution to current problems of migration of UV-absorbing additives. The thin coatings obtained by the PNB NPs were superior to those of the PNB MPs, in that no UV transmittance or loss of optical properties of the PP films were observed for the NP coatings, while the coatings produced by the PNB MPs resulted in damaged optical properties, particularly increasing the haze, and achieved incomplete UV blocking.

KEYWORDS: microparticles, nanoparticles, polymer additives, polypropylene, thin coatings, UV absorbers

1. INTRODUCTION

Ultraviolet (UV) radiation is responsible for the photo-destruction, discoloration, and the loss of mechanical properties of polymers and plastics. In addition, UV radiation can adversely affect substances within the plastic such as food and beverages, pharmaceutical products, and household, cosmetic, and personal care products, by leading to color fading of food, accelerated oxidation of oils and fats, and loss of vitamin content in fruit juice and milk.^{1–5} Therefore, protecting light-sensitive materials against UV irradiation is an important technological demand in the vast majority of industrial fields.⁶

Protection against photodegradation can be achieved by applying a coating of UV absorbers comprising either inorganic or organic materials.^{1,7–9} One of the most important families of organic UV absorbing molecules includes a phenol functional group that participates in the dissipation of the absorbed energy by a nonradiative process,^{3,10} such as 2-(2-hydroxyphenyl)-1,3,5-triazines and 2-(2-hydroxyphenyl)benzotriazoles. The benzotriazole UV absorbers, comprising a phenol group conjugated to the benzotriazole group, are known to absorb the full spectrum of UV light and are used in a variety of plastic

products.¹¹ However, while the various types of small molecule UV absorbers are effective in inhibiting the photodestruction of the polymers to which they are added, they tend to migrate from the polymers over time or upon irregular conditions, e.g., exposure to solvents and/or high temperatures.^{12,13} This imposes a significant disadvantage, since the fabrication and processing of the polymers is performed at elevated temperatures. Cross-linked polymeric NPs or MPs based on organic UV absorbers may overcome this disadvantage, due to their insolubility and large spatial structure, which limits them from migrating while maintaining their activity. Polymeric nano- and microparticles as an additive to films will thus result in resistance to degradation upon exposure to UV light, with decreased extractability and volatility. In addition, preparation of an aqueous dispersion of these NPs or MPs, rather than utilization of volatile organic solvents, provides an environmental advantage.

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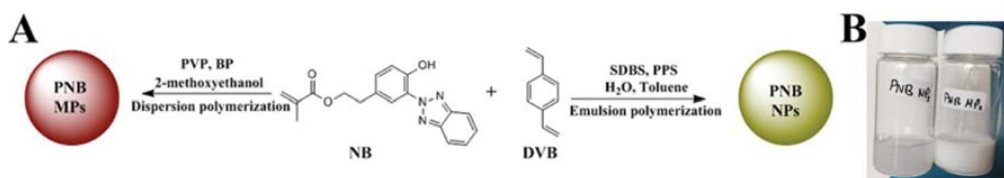


Figure 1. (A) Synthetic scheme of the PNB NPs/MPs. NB was copolymerized with divinylbenzene by emulsion and dispersion polymerization processes to obtain PNB nanoparticles and microparticles, respectively. (B) Emulsion polymerization resulted in a translucent NP dispersion, whereas the MP dispersion obtained was opaque.

Polyolefins are used for the manufacture of a wide variety of plastic products, a common example being plastic films. Plastic films such as polypropylene (PP) films are in use in packaging applications, but they also find utility in the agricultural, medical, and engineering fields. For packaging applications, for example, the optical properties (visible light transmittance, haze, and clarity) of the films are critical. Ideally, the plastic films should be UV-absorbant, while simultaneously possessing complete transparency to visible light, low haze, and high clarity values.¹⁴

Vinyl monomers are routinely used for preparing organic polymeric particles since they can be varied according to the functional side group of choice.^{15,16} This article describes the synthesis of UV blocking NPs and MPs by copolymerization of the commercial UV-absorbant vinyl monomer 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole (Norbloc (NB)) with the crosslinking monomer divinylbenzene. Thin coatings comprising the UV-absorbant NPs/MPs were then applied onto PP films. Both the nano- and microparticles produced highly UV-absorbant films, with no detected escape of UV absorbers over time. The thin coatings prepared from the PNB NPs were found to be superior to those of the PNB MPs in that the optical properties of the uncoated PP films were retained, except the transmission of UV light.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The following analytical-grade chemicals were used without further purification: 2-(2'-hydroxy-5'-methacryloxyethylphenyl)-2H-benzotriazole (Norbloc 7966, NB), divinylbenzene (80%), potassium persulfate, sodium dodecylbenzenesulfonate (SDBS), polyvinylpyrrolidone (MW 360 000), benzoyl peroxide (BP), 2-methoxyethanol, and toluene from Sigma-Aldrich. PP films (O₂ corona treated) of A4 size and 30 μ m average thickness from Dor Film Ltd., Israel. A-131-X film former (primer) (composed of modified polyethylenimine dissolved in an aqueous solution) was from MICA Corporation (Shelton, CT). Water was purified by passing deionized water through an Elgastat Spectrum reverse osmosis system (Elga Ltd., High Wycombe, UK).

Hand coater (Mayer rod) was purchased from RK Print Coat Instruments Ltd. (Litlington, Royston).^{15,17}

2.2. Methods. **2.2.1. Synthesis of PNB NPs/MPs.** PNB NPs were prepared by emulsion copolymerization of the vinyl monomer NB with the crosslinking monomer DVB, in the presence of SDBS as the surfactant and potassium persulfate as the initiator in an aqueous continuous phase, according to Figure 1A. Briefly, PNB NPs of 19 ± 2 nm dry diameter were prepared by adding 90 mL of a toluene solution containing 17.64 g of NB to a 240 mL aqueous solution containing 3 g of SDBS, 330 μ L of divinylbenzene, and 0.9 g of potassium persulfate. The mixture was then shaken at 73 °C for 18 h. The organic phase containing the toluene and excess monomers was then extracted from the aqueous phase, followed by removal of the excess SDBS from the aqueous dispersion by ultrafiltration with a Viva flow 200 system (Sartorius AG, Goettingen, Germany). The effect of the initiator

concentration on the size and size distribution of the PNB NPs was also elucidated.

PNB MPs were synthesized by dispersion copolymerization in a similar manner to as previously described by our research group.¹⁸ Briefly, PNB MPs of 200 ± 25 nm dry diameter were prepared by dissolving 22.6 g of NB, 10 g of polyvinylpyrrolidone, 1.28 mL of divinylbenzene, and 1 g of BP in 500 mL of 2-methoxyethanol. The mixture was then shaken at 73 °C for 18 h. The formed PNB MPs were then washed from excess reagents by intensive centrifugation cycles with ethanol and water.

2.2.2. Thin Coatings of the PNB NPs or MPs onto PP Films. PNB NP coated PP films were prepared by mixing a 4% PNB NP aqueous dispersion with 4% aqueous solution of the film former A-131-X (1:1 v/v) or by mixing 8% PNB NP aqueous dispersion with 4% aqueous solution of the film former (1:1 v/v). The obtained 2% or 4% PNB NP aqueous dispersion in the A-131-X polymer former aqueous solution was then spread on the 30 μ m PP films (O₂ corona treated) with a Mayer rod, followed by drying the PNB NP coating on the PP films for 3 min at 80 °C. PNB MP coated PP films were prepared similarly by mixing 4% PNB MP aqueous dispersion with 4% aqueous solution of the polymer former (1:1 v/v). The obtained 2% PNB MP aqueous dispersion in the A-131-X aqueous solution was then used for coating the PP films as described above for the PNB NPs.

2.2.3. Characterization of the PNB NPs and MPs and NP or MP Coated PP Films. Hydrodynamic particle size and size distribution of the PNB NP or MP dispersion in water were determined by dynamic light scattering (DLS) with photon cross-correlation spectroscopy (Nanophox particle analyzer, Sympatec GmbH, Germany). The mean dry diameter was determined by scanning electron microscopy (SEM) (JEOL, JSM-840 Model, Japan), by measuring 200 NPs or MPs using an image analysis software (AnalySIS Auto, Soft Imaging System GmbH, Germany). SEM images of the various films were obtained with a FEI SEM model Inspect S (JEOL, JSM-840 Model, Japan). For this purpose, coated and uncoated PP films were spread on a glass surface. The samples were then coated with iridium at reduced pressure before being viewed by SEM. UV-vis spectra of the films in the range 200–600 nm were determined in absorption and transmission modes, using a Cary 5000 spectrophotometer (Agilent Technologies Inc.). Average UV absorbance and transmission were calculated over the range of 280–380 nm. Fourier transform infrared (ATR-FTIR) analysis was performed using a Bruker platinum-FTIR QuickSnap TM sampling module A220/D-01. Powder X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (model D8 Advance, Bruker AXS) with Cu K α radiation. The thermal behavior of NB, PNB NPs and MPs, and the PNB NP and MP coated PP films were measured by thermogravimetric analysis (TGA) (TGA/DSC 1 STARe System, Mettler Toledo, Switzerland). The analysis was performed with approximately 10 mg of dried samples or films under an inert atmosphere at a heating rate of 10 °C/min.

Film thicknesses were measured on a Millitron 1204 IC (Mahr Feinmesstechnik GmbH). The optical parameters transmittance, haze, and clarity of the films were measured on a BYK Gardner haze-gard plus in accordance with ASTM D1003 "Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics".^{19,20} Mean values and standard deviations of transmittance, haze, and clarity were obtained by taking the average over several measurements (at least four measurements each).

2.2.4. Migration Test. Migration over time was determined by measuring the absorbance and transmission spectra of the PP film and PNB NP and MP coated films stored at room temperature for 2, 4, 6, 10, 14, 20, 24, and 36 months. Accelerated migration tests of the PNB NP and MP coated films were also performed by incubating a specimen of 0.5 dm² of each sample in 50 mL of 95% ethanol or 3% acetic acid for 2 h at 60 °C. Absorbance and transmission spectra of the various dried films in the range of 200–600 nm before and after the test were then taken.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the PNB NPs and MPs. The MPs and NPs were synthesized by dispersion and emulsion polymerization, respectively, as shown in Figure 1. The dispersion polymerization process begins with a homogeneous aqueous solution of the monomer, initiator, and surfactant. Upon polymerization, the initiator radicals react with the solute monomer molecules to form oligomeric radicals, which at a critical chain length precipitate as small nuclei. These nuclei then grow to the final size by a variety of mechanisms, such as agglomeration of small nuclei, polymerization of monomer in the swollen nuclei, and seeded polymerization of the monomer on the nuclei surfaces. The growing process is accompanied by adsorption of the stabilizer on the surface of the particles. The particles stop growing when all of the monomer is consumed and/or when the stabilizer forms a relatively packed coating on the surface of the particles. In this mechanism, particles ranging from ca. 0.1 up to ca. 15 μm are produced.

In emulsion polymerization, the monomer is emulsified in the continuous phase with the aid of a surfactant, while the initiator is soluble in the continuous phase. Small portions of the monomer molecules are also dissolved in the continuous phase, and the process begins with oligoradical formation. The formed oligoradicals can be absorbed by the monomer-containing micelles and, subsequently, by absorbing more oligoradicals and monomer molecules from the medium, changing the main loci of polymerization to the micelle interior. In this way, the primary particles grow gradually until the monomer is consumed or the radicals disappear. The size of the latex particles thereby produced is usually in the range of 50–300 nm.²¹

3.1.1. Effect of Initiator Concentration on the Size and Size Distribution of the PNB Particles. The effect of the initiator concentration on the size and size distribution of the PNB NPs is illustrated in Figure 2. Increasing the potassium persulfate concentration led to an increase in the diameter and

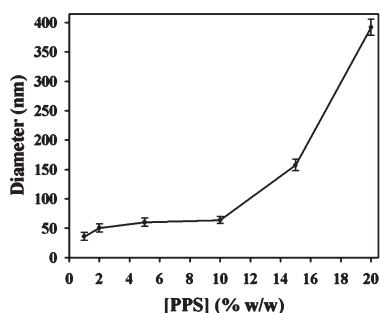


Figure 2. Effect of the initiator concentration on the size and size distribution of the PNB NPs.

size distribution of the formed PNB NPs. For example, raising the weight % of the initiator concentration from 2 to 10 and 20% increases the particle size and size distribution from 50 ± 6 to 60 ± 6 and 157 ± 10 nm, respectively (Figure 2). A similar effect of the initiator concentration on the size of the particles formed by emulsion polymerization was recently reported by Zhang et al.²² According to their explanation, increasing the initiator concentration causes an increase of oligomer radical concentration and, thus, increased the probability of particle collision, and further promoted particle coagulation, resulting in obtaining larger size particles. An opposite effect of the initiator concentration on the size and the polymerization yield of particles formed by the emulsion polymerization has also been reported.²³ It is possible to assume that increasing of oligomer radical concentration would produce more numerous, although smaller, particles.

The influence of the initiator concentration on the size of the MPs has been previously analyzed.¹⁸ An opposite effect on MPs compared to the NPs was observed, and a decrease in the average diameter of the PNB MPs was observed as the initiator concentration increased. According to Horak et al.,²⁴ increasing the initiator concentration in dispersion polymerization process causes an increase in the oligomeric radical concentration and thus produce more numerous particles but of smaller dimensions.

3.1.2. Characterization of the PNB Particles. We chose to continue our study with the smallest PNB particles obtained by the dispersion and emulsion polymerization processes. The hydrodynamic diameter of these PNB NPs dispersed in water was measured by DLS to be 54 ± 6 nm (Figure 3A), whereas the dry diameter of these NPs was measured to be 19 ± 2 nm as illustrated by the SEM image shown in Figure 3B. The difference in the particle size between these two methods are due to the fact that the SEM measurements determine the dry diameter, whereas light scattering measurements determine the hydrodynamic diameter, which takes into account swollen water molecules, water layers adsorbed on the particle surface, and Brownian motion. Similarly, the hydrodynamic and dry size and size distribution of the PNB MPs were measured to be 420 ± 40 nm and 200 ± 25 nm, respectively (Figure 3C,D). The emulsion polymerization formed a translucent dispersion of NPs, whereas the dispersion polymerization process, as anticipated, gave an opaque dispersion of MPs (Figure 1B).

3.1.3. XRD, FTIR, and TGA Measurements. The XRD pattern of the NB monomer displays clear sharp and narrow diffraction peaks typical of crystalline materials. The XRD spectrum of the PNB NPs, on the other hand, reveals a very poor diffraction pattern with two very broad peaks in the region between $2\theta = 25^\circ$ – 35° and $2\theta = 37^\circ$ – 50° , illustrating the amorphous phase of the PNB NPs (Figure 4A). A similar XRD pattern was also observed for the PNB MPs.

The FTIR spectrum of the PNB NPs is similar to that of the NB monomer, comprising of carbonyl stretches and C–H bending and stretching (Figure 4B). The efficient polymerization is indicated by the disappearance of the vinylic double bond peak at 1650 cm^{-1} and the broadening and shifting of the carbonyl peak from 1720 to 1740 cm^{-1} . The difference in the carbonyl stretching band peak location of the NB and the PNB NPs is due to the change in chemical character of these carbonyl groups, in that the carbonyl group of the NB monomer is conjugated to the vinylic double bond while that of the polymer is not. The broadening of the polymeric carbonyl peak as opposed to the monomeric one is due to the

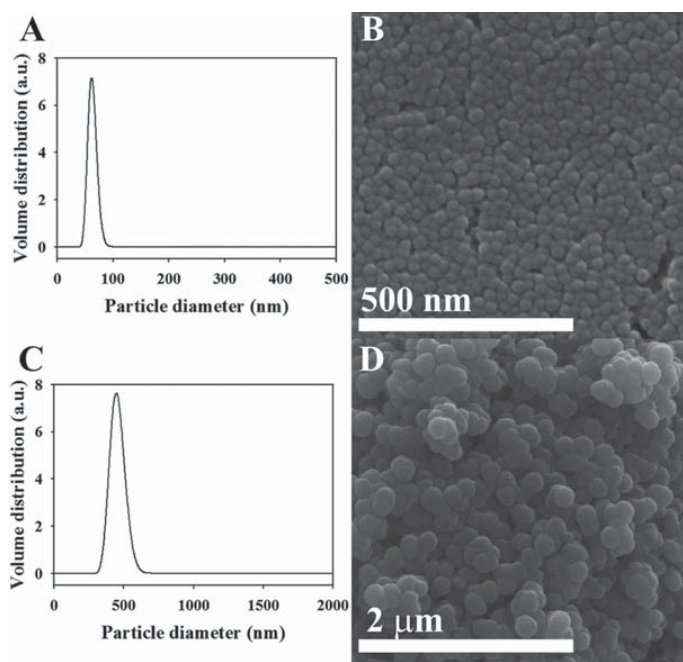


Figure 3. Hydrodynamic size histograms (A, C) and SEM images (B, D) of the PNB NPs/MPs.

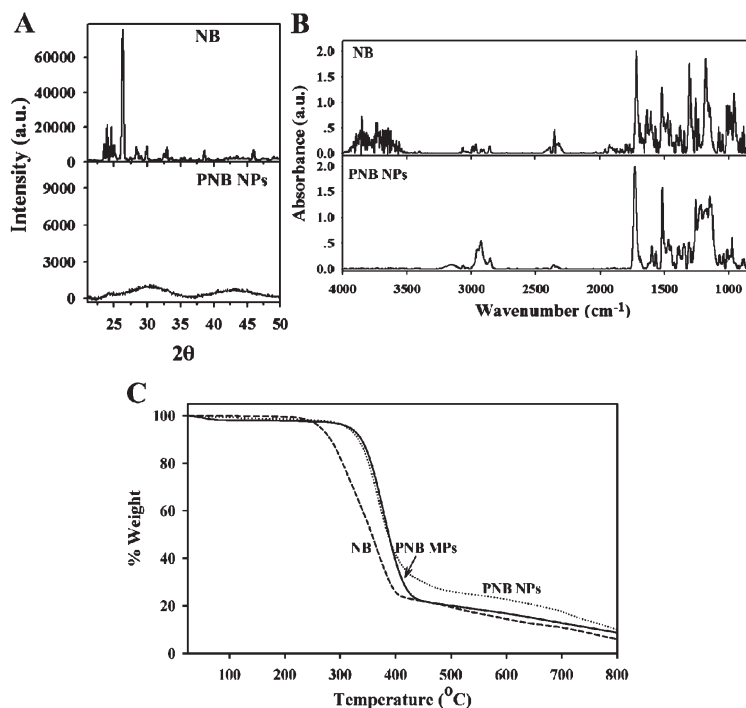


Figure 4. XRD patterns (A), FTIR spectra (B), and TGA (C) of the NB monomer and the PNB NPs.

inhomogeneous chemical environment of the polymeric carbonyl group compared to that of the monomer. Additionally, the absorption peaks at about 953 and 991 cm^{-1} corresponding

to the vinylic C–H bending band appear for the NB monomer and not for the PNB NPs, indicating the lack of residual monomer within the polymeric NPs. The peak that appears

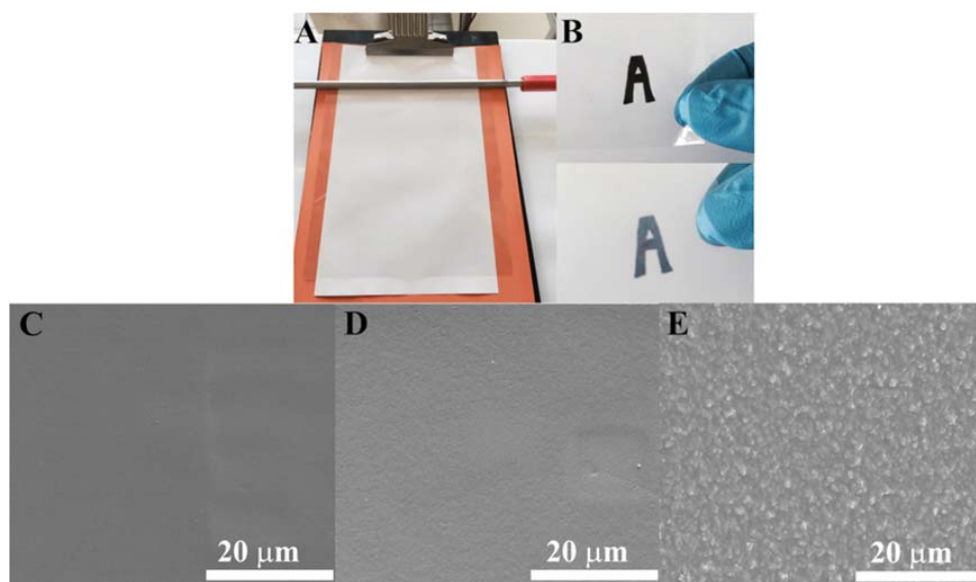


Figure 5. PP film coating and the effect on film transparency. (A) Mayer rod coating setup for coating the PP films with PNB NPs or MPs. The PP film is placed on a flat surface and a Meyer rod is pulled over the film, which leaves a uniform thin layer of the PNB NPs or MPs; (B) PNB NP coated PP film (top) and MP coated film (bottom) laid over black text, showing opacity of the MP-coated film, compare to the transparent NP-coated film. (C, D, E) SEM images of the PP film and NP coated and MP coated films, respectively. The MP coating results in significant roughness of the film compared to the relatively flat NP coating.

after polymerization at 2926 cm^{-1} corresponds to aliphatic C–H stretching. The broad peak at 3742 cm^{-1} probably belongs to the OH group of the NB monomer as well as water molecules that strongly interact with this hydroxyl group. This peak does not appear for the PNB NPs and MPs since only the external surface of the polymeric particles is exposed to water, diminishing the signal. A similar FTIR spectrum to that of the PNB NPs was observed, as expected, for the PNB MPs.

The thermogravimetric analysis (TGA) was performed to illustrate thermal stability of the NPs and MPs compared to the NB monomer (Figure 4C). The crosslinked PNB NPs and MPs degrade rapidly over a narrow temperature range, $315\text{--}415\text{ }^{\circ}\text{C}$ (mass loss of 70 wt %), followed by a slow degradation process over a wider temperature range, $415\text{--}800\text{ }^{\circ}\text{C}$ (mass loss 70–90 wt %). The NPs appear slightly more thermostable compared to the MPs. The NB monomer displays a similar degradation behavior (80% weight loss) but at a lower temperature range $280\text{--}410\text{ }^{\circ}\text{C}$. It has previously been shown that two degradation steps are observed for polymeric chains with functional side groups;^{15,16,25} therefore, two degradation steps could be anticipated. The lower degradation temperature of the NB monomer compared to that of the NPs or MPs indicates its lower thermal stability and therefore an increase in stability of the UV-absorbing crosslinked PNB particles compared to the corresponding monomer.

3.2. Thin Coatings of PNB NPs and MPs onto PP Films. UV-absorbing PP films were prepared by thin coating of the PNB NPs or MPs onto the PP films, as described in the Experimental Section. As a dispersion, the PNB MPs as well as NPs exhibit identical absorption curves, with a double peak at 300 and 335 nm, as has been previously described.¹⁸ The coating of the PNB NPs onto the PP films was performed with 2 and 4% (w/v) of the PNB NPs in the aqueous polymer

former solution. The coating of the PNB MPs was performed only with 2% (w/v) of the PNB MPs in the polymer former aqueous solution, since the 4% PNB MP aqueous dispersion was not stable due to rapid agglomeration with the change in composition of the aqueous phase. Coatings of different thicknesses were performed using a Mayer rod hand coater (Figure 5A) providing wet thicknesses of 6, 12, and $24\text{ }\mu\text{m}$. The coated films were allowed to dry, and it was observed that the NP-coated films were transparent while the MP-coated films were turbid (Figure 5B). The nanostructure of dry films was studied by SEM, showing thicknesses 1, 2, and $4\text{ }\mu\text{m}$, respectively. SEM images of the uncoated PP, and of films coated with NPs and MPs, of $2\text{ }\mu\text{m}$ thickness (originally of $12\text{ }\mu\text{m}$ wet thickness), are shown in Figures 5C, 5D, and 5E, respectively. The NP and MP thin coatings appear to be well dispersed onto the PP film. It is clearly seen that the NP coating yielded a smooth surface, while the film coated with the MPs appears quite rough. This roughness may be an additional factor affecting the optical properties of the MP-coated PP film.

3.2.1. FTIR and TGA Measurements of the Coated PP Films. The FTIR absorption spectra of the PNB NP coated PP films contain peaks characteristic of PP, polymer former, and PNB NPs or MPs (Figure 6A). Besides the peaks that corresponded to the PNB (described above), the absorption peaks at about 1375 and 1455 cm^{-1} corresponded to the C–H bending band of methyl group of PP and the absorption peaks at 1655 cm^{-1} corresponded to N–H bending band of polyethylenimine belonging to the polymer former.

The thermal stability of the PP film and PNB NP and MP coated PP films was evaluated by TGA, as shown in Figure 6B. PP and the PNB NP and MP coated films possess similar degradation behavior, i.e., rapid degradation over a narrow temperature range, $315\text{--}415\text{ }^{\circ}\text{C}$ (mass loss of 98 wt %),

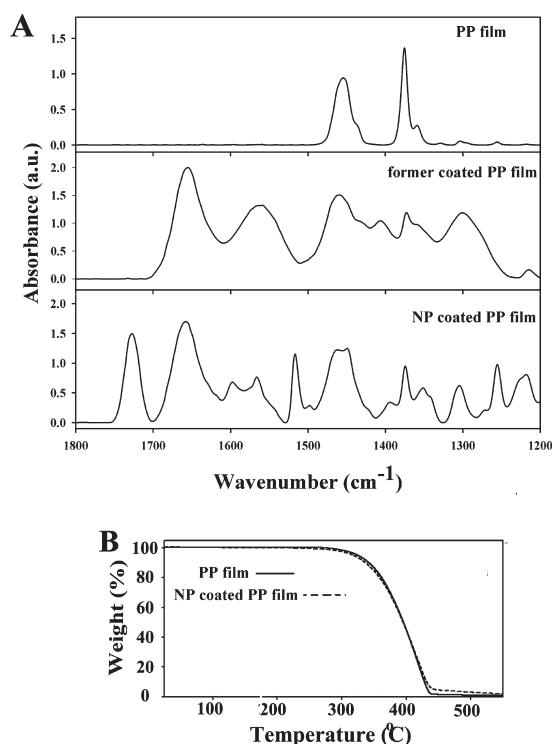


Figure 6. FTIR spectra (A) and TGA thermogram (B) of the PP film and PNB NP coated PP films.

indicating that the surface coating of the PNB NPs onto the PP films has no significant effect on the thermal properties of the PP films. The identical TGA behavior was observed for the PNB MP coated films. The NP and MP coatings are very fine, and thus their degradation was not observed when analyzing the coated films.

3.2.2. UV–Vis Light Transmission. The transmission of visible light through PP, former coated PP films, PNB NP-coated, and MP-coated films was found to be similar and between 85 and 95%, while the UV transmission was dependent on the coating (Figure 7). The transmission of

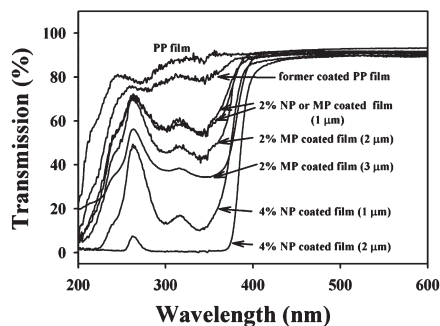


Figure 7. UV–vis transmission spectra of the PP, former coated PP films, and PNB NP and MP coated PP films. The UV transmission decreased as the concentration (%) or thickness (μm) of the NP or MP film coatings increased.

UV radiation through PP film and former coated PP films was found to be about 85 and 75%, respectively. The coating of the PP films, however, with the PNB NPs or MPs led to a significant decrease in the UV transmission. Increasing the concentration of the PNB particles or the coating thickness led to corresponding decreases in the % UV transmission. For example, thin coatings of PP films, of 2% PNB MPs, of ~ 1 , 2, and 4 μm in average thickness, decreased the UV transmission through the PP from 95% to 60, 45, and 35%, respectively (Figure 7). Similar results were obtained by substituting the 2% PNB MPs for 2% PNB NPs. Increasing the concentration of the NPs to 4% PNB particles in the aqueous polymer former solution, coatings of 1 and 2 μm in thickness decreased the UV transmission of the PP films from 95% to 20 and 0%, respectively. That is, complete blocking of UV radiation through a transparent PP film was achieved with a 2 μm coating comprising 4% PNB NPs and with only a minor reduction of 5% in the transmission of visible light. For some industrial applications, these optical properties of the polymeric film are important, for example, in transparent food wrap, plastic windows, or contact lenses. Similar results could not be obtained with the MPs, as a 4% dispersion could not be prepared (as described above).

3.2.3. Haze and Clarity. While the total transmitted visible light includes both scattered and unscattered light,²⁰ the haze is the fraction of transmitted light which scatters and deviates from the incident beam by more than 2.5° .²⁶ High haze values indicate that an object will appear milky or cloudy, when viewed through the film. Haze values for the PNB MP coated films were relatively high and averaged $33.3 \pm 8.5\%$, whereas the haze values of the PNB NP coated films averaged $\sim 3.5 \pm 0.6\%$ and were below 1% above the uncoated PP film (see Table 1). Clarity describes the degree to which fine details may

Table 1. Optical Properties of the PP Film, Former Coated PP Film, and PNB NP and MP Coated Films^a

film type	haze (%)	clarity (%)	transmission (%)
PP film	3.18 ± 0.35	93.3 ± 0.22	96.3 ± 0.22
former coated PP film	3.22 ± 0.63	96.3 ± 0.21	91.9 ± 0.22
4% NP coated film (1 μm)	3.54 ± 0.40	96.6 ± 0.41	91.0 ± 0.49
4% NP coated film (2 μm)	3.82 ± 0.91	96.9 ± 0.12	91.1 ± 0.08
2% NP coated film (1 μm)	3.2 ± 0.3	93.8 ± 0.1	95.3 ± 0.24
2% MP coated film (1 μm)	33.9 ± 6.05	96.8 ± 0.08	92.3 ± 0.58
2% MP coated film (2 μm)	24.2 ± 13.3	96.4 ± 0.64	91.9 ± 0.25
2% MP coated film (4 μm)	41.8 ± 6.25	96.8 ± 0.09	91.4 ± 0.24

^aPP film, former coated PP film, and PNB NP and MP coated films were prepared as described in the Experimental Section. % indicates the concentration of the NPs or MPs in the aqueous dispersion (w/v) used for the coating of the PP films, and μm indicates the average thickness of the NP or MP film coatings.¹⁹

be resolved in an object viewed through the film.²⁷ For all of our films, both coated and uncoated, clarity values ranged from 93 to 97% (Table 1). These high clarity values are associated with a clear and sharp image of the object. As the clarity values decrease, the object seen through the film appears out of focus and blurry.

3.2.4. Absence of Migration. Migration is the term used for the escape of additives from a polymeric host and may limit the use of additives in the plastic. As crosslinked NPs are used for covalently incorporating the UV absorbing “additive”, escape of the UV-absorbing moiety is not possible in atmospheric

conditions. In addition, identical absorbance and transmittance spectra of the PNB NP or MP coated films following 3 years of storage at room temperature, showing no migration of the MPs or NPs from the polymer former coating. The high stability of the coating was such that the coated films could also be immersed at 60 °C in 95% ethanol or in 3% aqueous acetic acid for 2 h, without affecting the UV-absorbing properties.

4. SUMMARY AND CONCLUSIONS

UV-absorbing NPs and MPs of 19 ± 2 and 200 ± 25 nm dry diameter were prepared by emulsion or dispersion copolymerization, respectively, of the monomer NB and divinylbenzene as a crosslinking monomer. The formed PNB NPs and MPs were characterized using DLS, SEM, FTIR, XRD, and TGA. Thin film coatings of different concentrations and thicknesses of the PNB NPs and MPs onto PP films were then prepared. It was demonstrated that increasing the concentration or thickness of the PNB NP or MP coatings on the PP films decreased the UV transmission of the films. The coatings of the PP films with the PNB MPs decreased the UV transmission of the PP films from 95% to 35% while those with the PNB NPs decreased the UV transmission to 0%, demonstrating complete absorbance and blocking of UV radiation, with only minor reductions in transparency compared to the original PP film. In addition, migration of the PNB NPs and MPs from the coated PP films was not observed during three years of storage at room temperature or during dipping of the coated PP films in 95% ethanol or in 3% aqueous acetic acid for 2 h at 60 °C.

The PNB NP coated UV-absorbing films that retain the optical properties of a transparent PP film, including visible light transmission, low haze, and high clarity, have great potential for industrial applications, protecting skin, eyes, and various goods against UV radiation without reducing access to visible light. Furthermore, the retention of optical properties of the films after 3 years of storage at room temperature showed high potential for long-term storage of UV-absorbant industrial products. In future work we intend to study the NP coating for protection of various industrial products against UV radiation.

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Notes

The authors declare no competing financial interest.

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