Research Article

Lina Cui, Canyi Huang, Hong Xia, Yiping Qiu, and Qing-Qing Ni*

Transparent ultraviolet-shielding composite films made from dispersing pristine zinc oxide nanoparticles in low-density polyethylene

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Abstract: This work proposes an approach to fabricate flexible transparent ultraviolet (UV)-shielding membrane by casting method, which uniformly disperses pristine zinc oxide nanoparticles (NPs) in low-density polyethylene (LDPE). The critical conditions for film fabrication, such as casting temperature, LDPE concentration in the solution, dissolution time, NP concentration, and post hot press cooling processes, are systematically studied. It is found that the casting temperature needs to be close to the melting temperature of LDPE, namely, 115°C, so that transparent film formation without cracks can be guaranteed. NP agglomerates are suppressed if the polymer concentration is controlled below 6%. For good dispersion of NPs, LDPE has to be swelled or unentangled enough in the solution. When the NPs are well dispersed in the LDPE film, the film can completely shield UV light while allowing high transmissivity for the visible light. As the concentration of NPs in the film increases from 4 to 6%, the transmissivity of the film decreases, the tensile strength increases, and the tensile failure strain decreases.

Keywords: inorganic nanoparticle, dispersion, polymer, solubility, UV spectrum tailoring

1 Introduction

Nanoparticles (NPs) are popularly utilized for the property promotion and functionalization of polymeric materials for advantageous electrical, optical, or mechanical properties [1–3] in more than past two decades. Zinc oxide (ZnO) NPs have been used in developing functional devices, catalysts, pigments, optical materials, cosmetics, and UV absorbers [4–6]. The biggest challenge is how to uniformly disperse NPs in polymers for better functional performances [7]. If there is serious NP agglomeration in composites, the functions of inorganic–organic composites would be hindered as Li and coworkers reported [8]. UV photon is high-energy thermal waves [9], which reach the earth’s surface more than before because of the increased ozone depletion as indicated by Yoo et al. [10] and Xie et al. [11]. The UV photons can not only cause serious injuries to the skin which might eventually result in skin cancer as Hacker et al. reported [12], but also provide radiative heat which may consume much energy to regulate temperature in space [13]. More and more attention has been paid for shielding UV photons in recent years [14]. Feng et al. [15] and Li et al. [16] fabricated transparent UV-shielding composites using cellulose, though the material is hard for large-scale production. Han et al. [17] used 60 nm NPs mixed into a polymer, and finally the NPs were agglomerated into 600 nm clusters. Complete UV-shielding performance would appear when the NP concentration reached above 7%, which would influence the transparency to visible light. Wang et al. [18] fabricated similar functional materials by mixing inorganic NPs with polymers, which also had a high NP concentration about 0.5 mol/mL. UV-shielding materials also can be a good candidate for passive cooling, which have the cooling function without any kinds of energy...
input. Li et al. fabricated opaque textile for outdoor personal cooling by shielding UV and high-energy visible lights [19]. Gamage et al. have shown that UV-shielding and visible transparent materials are good candidates for passive cooling to save energy consumption [20].

The most common methods reported fabricating UV-shielding materials are combining polymer and inorganic semiconductor NPs. In order to improve the compatibility between NPs and polymers, surface treatments have been applied to modify the surface properties of NPs [21]. However, these treatments have the potential to induce adverse effects on the catalytic, optical, or magnetic properties of the surface-treated NPs. This may greatly influence the intended performance of the composites. Jiang et al. reported that the coating processes of NP may be phased out because of their possible high-cost or harmful effects [22]. El-Naggar et al. employed the core/shell structure to improve the agglomeration of ZnO NPs; however, the characteristic absorption peaks of the NPs were shielded [23]. In addition, Hong et al. reported reduced catalytic activity of coated ZnO NPs [24]. Therefore, direct doping of pristine NPs into the polymer could be preferable if one could achieve uniform dispersion of the NPs in the polymer when optimal mixing strategies could be adopted [25]. Mackay et al. reported that thermodynamically stable dispersion of NPs into a polymeric liquid enhanced the dispersion of NPs by increasing the enthalpy gain of the solution system [26].

Solution methods relatively easily achieve an even dispersion of NPs in polymers, especially those without a melting temperature or with a high molten viscosity as reported by Zarrinkhameh et al. [27]. In recent decades, various approaches have been attempted for the dispersion of NPs in polymers, including solution dispersion, mechanical blending, and in situ polymerization with NPs reported by Guo et al. [28], each method has its own advantages and disadvantages reported by Ray et al. [29]. Polyoxylenfins are synthesized via addition polymerization and thus have a relatively high degree of polymerization, which results in high molten viscosity [30]. Moreover, they are hard to dissolve in a solution without high temperature and long durations due to the saturated chemical structures, thus leading to poor affiliation with most of the organic solvents. Therefore, polyoxylenfins solutions are often highly dilute in the published literatures. Blackadder and Schleinitz dissolved low-density polyethylene (LDPE) in n-dodecane, p-xylene, and decalin solvents at 0.1, 0.375, 0.75, 1.00, and 1.5 wt% to obtain single crystals [31]. Kong et al. reported the use of 0.7 wt% of polyethylene (PE) solution to determine the routes of solution fractionation [32]. Wong and coauthors dissolved LDPE at 1.1–6.5 wt% to convert plastic waste from solid to liquid to transport it via feeding pipelines [33].

However, in the published literature, reports on the range of PE concentrations and experimental conditions in which pristine inorganic NPs can be well-dispersed are scarce. NP diffusion in a polymer solution is largely dependent on the viscosity of the solution which is also dependent on the polymer concentration and temperature, in addition to the dissolution time of the polymer solution. Thus, a systematic study was conducted to determine the optimal casting temperature, LDPE concentration, and dissolution time for uniform dispersion of inorganic NPs in LDPE using the solution-casting method. This ZnO NP/LDPE composite film exhibits spectrum selective properties for shielding UV and diminishing transmittance of visible light and thus could be potentially used as a passive cooling material for the purpose of energy conservation. Therefore, the transmissivities of the films with different NP concentrations were also evaluated.

2 Experimental

2.1 Preparation and characterization of samples

LDPE pellets (AS: 9002-88-4) with a melting index of 25 g/10 min were purchased from Aldrich Chemistry. ZnO NPs with an average diameter of 90 nm were provided by Rhawn Company in Shanghai, China. In the sample preparation, first, the ZnO NPs were dissolved in 12 g of xylene [34] (Achillas et al.) by sonication for 12 min at a frequency of 22 kHz in an ultrasonic cell disruptor (Scientz-IID) with a 6-mm-diameter probe in a glass column at an ambient temperature. Then, the LDPE pellets were added into the solution in the glass column using a magnetic stirrer and heated in oil bath. Once the solution was homogenized after stirring for sufficient time at a high temperature, it was casted to form a primary film. Finally, the thickness of the casted film was adjusted by hot pressing and cooling down. The conditions for film fabrication are presented in Table 1.

From the above experiments, we were able to select a set of optimal conditions, i.e., 3.2% LDPE–xylene solution, 105°C dissolution temperature and 322 h dissolution time, and 115°C in vacuum oven for the formation of casted films with reasonably good particle dispersion. Using these conditions, we selected three NP concentrations,
4, 5, and 6% ZnO NPs considering the flexural strength reported by Wu et al. [35], to optimize the transmissivity of the flexible films with balanced performance of UV-shielding and transparency for visible light.

The surfaces of the films were examined using a field-emission scanning electron microscope (SEM: Zeiss MERLIN, Oberkochen, Germany). The transmittance tests for the cooling films were conducted using an UV-visible-near-infrared (UV-Vis-NIR) spectrophotometer (Yokogawa Model AQ6375B). Films were tensile-tested at 25°C and 60% relative humidity using a universal testing machine (Model Instron Microtester 5948) at a gage length of 10 mm and specimen width of 2 mm at a strain rate of 0.10/minute; with a load cell of 100 N capacity. Thermal properties of the films were determined using differential scanning calorimetry (DSC) in nitrogen on a machine Model CCTA DSC25. The specimens were equilibrated at −80°C for 2 min and then heated at 10°C/min to 300°C at which they were isothermal for 2 min, and then cooled down at 10°C/min to −80.00°C.

### 3 Results and discussion

#### 3.1 Principles for material selection

PE is a semicrystalline polymer with long molecular chains [30]. Selecting the proper solute is critical for the dissolution of PE. According to the Gibbs–Helmholtz equation [36]:

$$\Delta G_m = \Delta H_m - T \Delta S_m$$  \hspace{1cm} (1)

where $\Delta G_m$, $\Delta H_m$, and $\Delta S_m$ denote the changes in Gibbs free energy, enthalpy, and entropy on mixing, respectively, and $T$ denotes the absolute temperature. A negative $\Delta G_m$ indicates that the mixing process occurs spontaneously. In a good solvent, Shenoy et al. reported that the interactions between the polymer and solvent are favorable to the interactions between individual polymer segments [37]. This results in the expansion of polymer coils. If the distance between the neighboring polymer chains is larger than the diameter of the NPs, both the solvent molecules and NPs can penetrate the polymer according to Choi et al. [38]. Contrarily, in a poor solvent, the coil collapses. In the transition from a good solvent to a poor solvent, a so-called $\theta$-solution is formed, and the corresponding temperature is called $\theta$-temperature, at which $\Delta G_m = 0$ [36]. In other words, at $\theta$-temperature, the interaction between the polymer segments is equally favorable to that between the solvent and polymer segments. This indicates that the polymer chains are in a stable state, thus allowing the NPs to travel freely if the distances between neighboring polymer segments are larger than the NPs size [26].

For semicrystalline polymers, dissolution is an endothermic process [36]. In addition, the enthalpy of the LDPE solution can be calculated using the Hildebrand solubility principle equation [39]:

<table>
<thead>
<tr>
<th>Group</th>
<th>Temperature of casting (°C)</th>
<th>Concentration of LDPE:xylene (%)</th>
<th>Duration of dissolution (h)</th>
<th>Temperature of oil bath (°C)</th>
<th>Concentration of ZnO:LDPE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>5</td>
<td>96</td>
<td>105</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>75</td>
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<td></td>
<td>105</td>
<td></td>
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<tr>
<td></td>
<td>115</td>
<td>115 (in vacuum)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>115 (in vacuum)</td>
<td>2.4</td>
<td>156</td>
<td>105</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>6.1</td>
<td></td>
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<td></td>
<td></td>
<td>7.0</td>
<td></td>
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<td></td>
<td></td>
<td>8.1</td>
<td></td>
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<td></td>
<td></td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>115 (in vacuum)</td>
<td>3.2</td>
<td>90</td>
<td>105</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 1: Conditions for film formation experiments
\[ \Delta H_m = V_m \varphi_1 \varphi_2 (\delta_1 - \delta_2)^2 \]  

(2)

where \( V_m \) denotes the volume of mixture or solution; \( \varphi_1 \) and \( \varphi_2 \), the volume fractions of solvent and solute, respectively; and \( \delta_1 \) and \( \delta_2 \), the solubility parameters of the solvent and solute, respectively. According to the Hildebrand solubility principle, the enthalpy of the solution could be minimized if the solubility parameters of the solvent and solute are close to each other. This could make the dissolution relatively easy. Since the solubility parameter of LDPE is 7.9–8.1 (cal \(^{0.5}\) cm \(^{-3}\)) \(^{1/2} \) [36] and that of xylene is 8.75 (cal \(^{0.5}\) cm \(^{-3}\)) \(^{1/2} \) [36], xylene was chosen as the solvent to dissolve LDPE.

For the different concentrations of the LDPE solution in 12 g of xylene, the enthalpies are all positive, as presented in Table 2, which were calculated using equation (2). According to the Gibbs–Helmholtz equation, the bigger the enthalpy of the solution, the more difficult the dissolution of the polymer in xylene. That means that a higher temperature or additional entropy should be provided to the solution system, which would make the changes in Gibbs free energy close to zero or a negative value [36]. Therefore, the solution needs to be heated to a temperature close to the melting point of the polymer to dissolve its crystalline region. The boiling point of xylene is 144.3°C [34], and the dissolution was performed in an oil bath at 105°C ± 3°C. Moreover, the solution should be kept at the temperature, namely 105°C, for a long time with a magnetic stirrer at the bottom of the beaker to provide additional entropy to the solution system according to Mackay and coworker’s points [26].

### 3.2 Effect of casting temperature

Figure 1 presents the films formed at different casting or volatilization temperatures ranging from 5°C to 115°C. At 5°C, the casted film looked like fine powder (Figure 1), and at 50°C, it appeared as a white opaque pancake-like film with cracks on the surface. At 75°C, the film looked like a combination of white powder, white pancake, and semitransparent film. At 105°C, a white opaque uniform film was formed. The films presented in Figure 1e and f were formed in vacuum oven and ordinary oven, respectively, at 115°C. Both were relatively transparent and uniform, although the film formed in air in a regular oven appeared slightly yellowish possibly due to oxidation.

The morphologies of the films formed at different temperatures revealed the states of the molecules in the solution during the volatilization of the solvent. As discussed in the previous section, mixing the polymer with the solvent is a spontaneous process when \( \Delta G_m < 0 \). This could only occur when the temperature was sufficiently high, according to equation (1) [36]. When the solution temperature was low, the polymer molecules tended to exhibit phase separation with the solvent and thus formed clusters of polymer molecules in the solution, which then became polymer particles after the evaporation of the solvent. As the temperature increased, the molecules had higher affiliation with the solvent and thus were less and less likely to exhibit phase separation in the solution. Even if some degree of phase separation still existed, the molecules on the boundaries between the neighboring domains of polymers were likely entangled. Thus, the polymer particles formed at higher temperatures, for example, 50–75°C, were stuck together, forming a powdery cake. These films could develop cracks due to the differential shrinkage of the different parts of the film caused by the uneven distribution of the polymer phases. As the casting temperature increased, exceeding the \( \theta \) temperature, the polymer molecules in the solution exhibited good solubility and thus did not demonstrate phase separation during the evaporation of the solvent [36]. This made the casted film transparent and free of cracks.

### 3.3 The solubility of LDPE in different concentrations

To determine the proper concentration for the dissolution of LDPE with reasonably good dispersion of the NPs, a systematic experiment was conducted at LDPE concentrations of 2.4, 3.8, 6.1, 7.0, 8.1, and 9.0 wt%. Such concentrations are close to those presented in Table 2. The surface morphology and particle cluster sizes of the films are presented in Figure 2. The film surfaces became rougher as the LDPE concentration increased. More importantly, the peak size of the NP cluster also increased from 0.8 to 2.3 \( \mu \)m as the LDPE concentration increased from 6.1 to 9.0%. Below 6.1%, the peak cluster size of 0.8 \( \mu \)m was maintained, regardless of the concentration reduction, which similar to what is reported by Ali et al.

<table>
<thead>
<tr>
<th>Items</th>
<th>Solution (LDPE in xylene)</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE (wt%)</td>
<td></td>
<td>0.78</td>
<td>1.47</td>
<td>2.27</td>
<td>3.01</td>
<td>3.75</td>
<td>4.50</td>
</tr>
<tr>
<td>( \Delta H_m ) (cal)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Obviously, when the LDPE concentration increases, the enthalpy $\Delta H_m$ of the polymer solution will be increased as shown in Table 2 ($\Delta H_m$ increases almost five times for polymer concentration increasing from 2 to 10 wt%), which means a higher temperature and longer time will be required for the same degree of solubility of LDPE in the solution according to equation (1). This would hinder the dissolution of the polymer, increase the solution viscosity, and inhibit the dispersion of the NPs [41]. It is noteworthy that the films were prepared with a dissolution time of 156 h at 105°C, which may not be sufficiently long for the complete dispersion of individual NPs, as discussed in the subsequent section. In our later experiments, we greatly prolonged the dissolution time and were able to achieve satisfactory dispersion of NPs with peak diameter similar to that of the individual NPs. Evidently, this result implies that a concentration below 6% is preferred for a good initial dispersion of the NPs. In the following experiment, we selected 3.2% of LDPE and prolonged the dissolution time for further dispersion of the NPs.

### 3.4 Effects of duration on the solubility of LDPE and dispersion of NPs

In the process of mixing polymer and NPs, it is necessary to completely dissolve the polymer in the solution. Thus, the polymer solution has to be stirred long enough at a sufficient temperature to increase the entropy, according to equation (1). To determine the proper dissolution time, a solution with 4 wt% of ZnO/LDPE and 3.2% of LDPE/xylene was prepared in 105°C oil bath and stirred for different hours to produce the casted films (see Group 3 in Table 2). The left column of Figures 3a–e presents the states of the casted films after dissolution for 90, 120, 188, 202, and 322 h, respectively. The casted film dissolved for 90 h has large, isolated blocks (Figure 3a). As the duration increased, the areas of the isolated blocks become flatter and larger first (120 h) and then gradually formed larger number of smaller blocks (188 h), which started to merge into larger and more continuous pieces (202 h) until forming a whole smooth piece (322 h). The middle and right columns of Figure 3 present the SEM images and size distributions, respectively, of NPs in the hot-pressed films corresponding to the casted films for various dissolution hours. In the SEM images, the NP clusters were identified, and their sizes and numbers were measured. The particle agglomerate sizes became smaller and smaller as the dissolution time was prolonged until the peak particle or cluster sizes (60 nm for the 322 h group) reached that close to the individual particle size (90 nm), as presented in the right column of Figure 3.

Another way of determining the degree of NP dispersion in LDPE is the measurement of the transmissivity of the film to thermal radiation. In principle, the transmissivity of incident light can be reduced by either Rayleigh
scattering or Mie scattering which is dependent on the particle sizes [42]. Rayleigh scattering occurs due to the existence of particles with a size parameter $X < 1$, calculated as follows [43]:

$$X = \frac{2\pi r}{\lambda}$$

where $r$ denotes the spherical particle radius, and $\lambda$ denotes the wavelength of incident light. According to this principle, particles with diameters of 90–120 nm

![Figure 2](image-url)
Figure 3: Effect of dissolution time on ZnO NP dispersion in LDPE; (a–e) the left column presents the ZnO/LDPE casted films, the middle column presents the SEM images of the hot-pressed ZnO/LDPE films, and the right column presents the corresponding particle size distributions; (f) the transmissivity curves of the ZnO/LDPE films after the different dissolution times.
are suitable for the preparation of a transparent passive cooling film with Rayleigh scattering. In this study, the NPs utilized had an average diameter of 90 nm, which could have strong Rayleigh scattering, thus ensuring good shielding against radiation in the UV region (10–400 nm) if dispersed well. Figure 3f presents the transmissivities of the films. For the films formed with 90 and 122 h dissolution times, the transmissivities for thermal radiation were high in the whole wavelength range. For the films formed with 188 h dissolution time, the transmissivity of radiation below 400 nm wavelength was substantially reduced, whereas that for the films with 202 h dissolution time was further suppressed significantly. For the films with 322 h dissolution time, the thermal radiation in the UV range was almost completely blocked. This result corresponds well to the particle size reduction pattern. In summary, as the dissolution time increased, the bonding force between NPs in an agglomerate could be diminished by continuously increased entropy provided by the solution system, resulting in reduced agglomerate sizes, which is reported in article by Jancar et al. [44]. Consequently, the film became more effective in shielding the light, especially in the UV region. This indicates that the film with good NP dispersion could have good spectrum selective properties and thus promising passive cooling performance as passive cooling materials.

The mechanism for the effect of dissolution time on NP dispersion may be explained using Figure 4. Polymer dissolution and NP dispersion are the two partially overlapping but somewhat consecutive processes in casting a homogeneous ZnO NP-doped LDPE film. The former must occur first for the latter to proceed. In the beginning of the dissolution, the polymer molecules form clusters of about 1 mm diameter (according to our visual observation), which originated from the pellets of solid polymer before dissolution. And, the NPs agglomerated into clusters of about 0.8 µm diameter, which contain hundreds of NPs (Figure 4a) due to initial mechanical blending and mixing. The polymer clusters were from the melting and dissolution of the semicrystalline polymer pieces. In such a relatively highly concentrated polymer solution, polymeric molecular entanglement is inevitable. These entangled chains can be gradually stretched at a high temperature in a proper solvent. Moreover, polymer molecular chains can diffuse toward low-concentration regions or boundaries between the polymer clusters, although this process could be very slow due to the high viscosity of the solution. In the current study, the films casted after the dissolution time of 202 h or longer could form a relatively complete film. This indicates that LDPE chains in the neighboring clusters reached out or diffused out to bridge or bond the clusters together to form a more homogeneous film. In addition, the diffusion of polymer molecular chains toward the boundaries could effectively create larger intermolecular distance between the polymer molecules near the NP agglomerates and thus accelerate the diffusion of the NPs into the polymeric gel. Only after that could the ideal dispersion of the NPs be fulfilled. In this study, the ideal NP dispersion was achieved in 322 h. Vigneshwaran et al. dispersed surface-treated 40 nm ZnO NPs in HDPE and shielded about 65% of UV because the NPs agglomerated into about 1 µm clusters [45]. Xiong et al. reported that total UV-shielding could be achieved with NP concentration higher than 7 wt% in a ZnO/poly(styrene butylacrylate) latex composite film [46], while 4 wt% was sufficient for complete shielding of UV in the current study. Obviously, the performance of our ZnO/LDPE composite films is better than those reported in literature.

As the polymer cluster started to dissolve at 188 h, the NPs began to diffuse into the polymer, and the agglomerates started to diminish [44]. The dispersion of the agglomerated NPs in the polymer solution is determined by two factors, namely, the van der Waals forces holding the NPs together and the Brownian motion for the diffusion of the NPs to move toward the direction of lower particle concentration [47]. The diffusion coefficient, \( D \), for spherical NPs can be calculated using the Stokes–Einstein equation [48]:
$D = \frac{kT}{3\pi\eta d}$ (4)

where $k$ denotes the Boltzmann constant; $T$, the temperature in Kelvin; $\mu$, the viscosity of the polymer solution; and $d$, the particle diameter. As the NPs in the agglomerated clusters diffuse toward the polymer matrix due to the Brownian motion, the diffusion rate relates positively to the temperature and negatively to the polymer solution viscosity and the particle diameter. Cui et al. also interpreted the dispersion of NPs in the liquid–liquid interface, like a transition from diffusive to confined dynamics was manifested by intermittent dynamics [49]. In the current study, we have quite small NPs (90 nm) and quite high concentration of LDPE (3.2%), which results in slow NP diffusion. Consequently, good dispersion was only achieved after quite a long dissolution time (322 h) at an elevated temperature.

Of course, the dissolution time in the current study is not necessarily optimal because some other factors such as dissolution temperature and LDPE concentration could greatly influence the process. According to equation (1), when temperature increases, $\Delta G$ will be decreased and thus stretching out of polymer chains would be more preferable leading to a shorter optimal dissolution time in addition to the increased diffusion coefficient discussed above. Lowering the LDPE concentration could also facilitate diffusion process for both the polymer and the NPs since it could greatly reduce the viscosity of the solution, leading to a reduced dissolution time.

### 3.5 Optimizing the transmissivity of spectrum selective film

The transmittance of UV photons through an NP-doped membrane is mainly affected by the NP concentration and film crystallinity. Films doped with 4, 5 and 6% ZnO NPs were tested to determine the effect of particle concentration on the transmissivity of the films.
The transmissivity of the UV-shielding films with a thickness of 0.12 ± 0.05 mm could shield total UV lights, which is a better performance at a relative lower NP concentration, and the transmissivity decreased as the NP concentration increased in the visible light region (Figure 5a). However, the difference tended to diminish with the increase in wavelength as the light scattering effect changed with the size parameter X of the NPs, which is inversely proportional to the wavelength according to equation (3).

The transmissivity of the films is also closely related to the crystallinity of the film [50], which is determined by the cooling condition after hot pressing the casted film. A higher NP concentration did not result in a higher crystallinity (37.5, 37.8, 37.5%) for 4, 5, 6% NPs shown in Figure 5c). Figure 5b presents the transmissivity of the hot-pressed ZnO nanofilms which were quenched or cooled at an ambient temperature right after hot pressing. The transmissivities of the two films are different in the visible light region and almost the same in the UV region. The DSC curves revealed that the crystallinity of the quenched film (32.3%) was substantially lower than that (37.5%) cooled at an ambient temperature (Figure 5d). Jordan with coworkers described the crystallinity in different processing influenced by temperature [51]. In general, a quenched film is likely to have smaller crystals and lower crystallinity due to a much shorter time for the crystals to grow, thus leading to high transmissivity compared with an ambient temperature-cooled film.

### 3.6 Mechanical performance of films

The mechanical property of the films is presented in Figure 6 and Table 3. The failure strains of the NP-doped films decreased from 80 to 15% with an increase in the NP concentration from 4 to 6 wt%, respectively. Conversely, the tensile strength increased with the increase in the NP concentration as reported by Wang et al. [52]. It seems that the mechanical properties of the films changed from being typical ductile materials to relatively brittle materials due to failure mechanism change from localized plastic deformation to more defects-dominant failure. This could be observed in SEM images (see Figure 7) of the films which show as the NP concentration increased, the distance between neighboring NPs decreased drastically and thus could possibly increase probability of containing weak spots in the specimen. On the other hand, the tensile strength and failure strain of the film were much lower for the quenched film compared with the film cooled at an ambient temperature due to creases or nano-cracks generated by quenching on the surface of the quenched film as shown in Figure 7.

### 4 Conclusions

To make a spectrum-selective or UV-shielding ZnO NP-doped film with uniform dispersion of the NPs and ideal transmissivity for spectrum tailoring, a systematic study was conducted to determine the critical parameters for film fabrication (e.g., casting temperature, polymer concentration, and dissolution time). It was found that the casting temperature has to be maintained at 115°C or above in vacuum to ensure the formation of a transparent and uniform film without oxidation. For proper initial dispersion of the NPs in the polymer solution, the LDPE concentration should be lower than 6%. For a uniform and complete dispersion of individual NPs, the dissolution time has to be sufficiently long for the polymer molecules to unentangle first, which could allow the diffusion of the NPs into the polymer gel, thus resulting in a homogeneous NP dispersion. Only when the NPs are well-dispersed will the film have ideal shielding against UV light, while allowing a reasonable amount of visible light to be

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tensile stress (MPa)</th>
<th>Young's modulus (MPa)</th>
<th>Failure strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4% ZnO films</td>
<td>7.6</td>
<td>5.4</td>
<td>79.3</td>
</tr>
<tr>
<td>5% ZnO films</td>
<td>9.7</td>
<td>2.3</td>
<td>29.6</td>
</tr>
<tr>
<td>6% ZnO films</td>
<td>10.8</td>
<td>3.9</td>
<td>7.3</td>
</tr>
<tr>
<td>6% ZnO films (quenched)</td>
<td>5.1</td>
<td>1.5</td>
<td>6.9</td>
</tr>
</tbody>
</table>
transmitted. The transmissivity of the films can be optimized by changing the concentration of doped NP and the crystallinity of the film through quenching. The mechanical properties of the UV-shielding films were altered from ductile to relatively brittle by varying the NP concentrations.

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Conflict of interest: The authors declare no conflict of interest regarding the publication of this paper.

References


Figure 7: SEM images of the ZnO-LDPE films. (a) 4% ZnO NP; (b) 5% ZnO NP; (c) 6% ZnO NP; (d) the high magnification of 6% ZnO NP film cooled with ambient temperature of post hot press; (e) 6% ZnO NP film quenched of post hot press.


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