Research Article

Synthesis, Characterizations, and Thermochromic Properties of VO₂ Particles Grafted with PSS:PEDOT

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Vanadium dioxide (VO₂) particles were modified by grafting with poly(styrene sulfonate) (PSS) and poly(3,4-ethylenedioxythiophene) (PEDOT) via surface-initiated atom transfer radical polymerization (SI-ATRP). Critical transition temperature (Tᵥ) of the modified VO₂ ranging between 77 and 79°C was obtained. After mixing with acrylic-based emulsion, dispersion of the VO₂ particles in the polymer matrix was significantly improved. The visible light transmittance through the composite films above 75% was maintained if a concentration of the modified VO₂ particles loaded into acrylic polymer film was no greater than 1.0 wt%. The NIR transmittance through the acrylic/VO₂@PSS:PEDOT also dropped by 9-10%, compared with that of the pure acrylic film (without any particles). Finally, glass substrates coated with the acrylic/VO₂@PSS:PEDOT composite films could reduce the temperature inside a model house by 5-6°C, compared with that of the control system (pure acrylic coating film without VO₂ particles). Overall, this work demonstrated that it was possible to improve the dispersion of VO₂ particles in polymer films without sacrificing its NIR shielding ability by grafting the surface of VO₂ particles with PSS:PEDOT chains, while providing the optimum grafting density and particle loading.

1. Introduction

Vanadium dioxide, particularly in the form of monoclinic crystal structure (VO₂(M)), is one of the most interesting types of thermochromic materials. This is because the critical phase transition temperature (Tᵥ, 68°C) [1] of VO₂ is the lowest, compared to those of other thermochromic materials [2]. The transition temperature of VO₂ can also be further reduced by doping it with chemicals such as molybdenum (Mo) [3], niobium (Nb) [4], fluorine [5], and tungsten [1]. At a temperature above Tᵥ, VO₂(M) is transformed into a tetragonal/rutile phase, accompanied with a decrease in spectral transmittance in the near infrared (NIR) region [6, 7]. Considering this interesting behavior, the feasibility of utilizing VO₂ as a coating layer on glass to enhance the energy efficiency in buildings has been explored. Practically, thin films of VO₂ can be coated onto glass substrates by several techniques including sputtering [8], chemical vapor deposition (CVD) [9], pulsed-laser deposition [10], and ion implantation technique [11]. However, these techniques usually require complex and expensive equipment. Alternatively, if the VO₂ material can be prepared in the form of particles, it is possible to develop polymer/VO₂ composite [1, 12–15], which can be further applied onto glass substrates by less complex techniques such as spray coating [16] and lamination [1, 12].

Despite the above advantages, some challenges have yet to be resolved. These include the fact that the NIR shielding efficacy of the VSO₂-based film is usually achieved at the expense of its optical transparency [6, 7]. This is related to the poor dispersion of VO₂ particles in many polymer matrices [17]. In this regard, surface modification
of VO\textsubscript{2} particles was undertaken to deal with the above problem.

Synthetic routes and structure-property relationships of polymer-grafted nanoparticles have been reviewed by Kumar and coworkers [18]. Efficacy of the grafted nanoparticles, for the enhancements of mechanical and optical properties of polymer nanocomposites, depends on many factors including the grafting density (\(\sigma\)), length of the grafting chains (\(N\)), length of the matrix chains (\(P\)), and the \(P/N\) ratio (\(\alpha\)). Besides, the roles of size and shape of nanoparticles upon crossover of polymer chains and properties of the nanocomposites also deserve a consideration and have yet to be clarified.

Few studies concerning the surface modification of VO\textsubscript{2} particles have been reported in the open literature; however, all those works focus on the improvement of oxidation stability and the enhancement of photocatalytic activity of the materials [13–17, 19, 20]. For example, by coating the VO\textsubscript{2} particles with a polyethylene (PE) layer, the stability of the VO\textsubscript{2}@PE particles against oxidation improved while the thermochromic behavior of the metal oxides was still maintained. Li et al. [19] prepared one type of core-shell VO\textsubscript{2}@TiO\textsubscript{2} nanoparticles and reported that the chemical stability was enhanced by the TiO\textsubscript{2} shell. After carrying out the surface modification, the transmittance values (\(T_{\text{trans}}\) and \(\Delta T_{\text{trans}}\)) of the VO\textsubscript{2} particles increased from 7.35% and 6.93% to 27.46% and 17.63%, respectively.

However, enhancing the NIR shielding property of VO\textsubscript{2}-based film without sacrificing its optical transparency remains a challenge. In this study, it was proposed that if the VO\textsubscript{2} particles were grafted with a kind of special material, for the enhancements of mechanical and optical properties of polymer nanocomposites, depends on many factors including the grafting density (\(\sigma\)), length of the grafting chains (\(N\)), length of the matrix chains (\(P\)), and the \(P/N\) ratio (\(\alpha\)). Besides, the roles of size and shape of nanoparticles upon crossover of polymer chains and properties of the nanocomposites also deserve a consideration and have yet to be clarified.

2. Experiment

2.1. Materials. Vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}, >98% pure), (3-aminopropyl) triethoxysilane (APTES, >99% purity), N,N,N′,N′-pentamethyldiethylenetriamine (PMDETA, 99%), copper (I) bromide (CuBr, >99% purity), \(\alpha\)-bromoisobutyryl bromide (BIBB, C\textsubscript{4}H\textsubscript{6}Br\textsubscript{2}O, >99% purity), and sodium 4-vinylbenzenesulfonated (SSNa, C\textsubscript{6}H\textsubscript{4}NaO\textsubscript{3}S, >90% purity) were obtained from Sigma-Aldrich Co., Ltd. Citric acid (>99% purity) and methanol (99.8%) were obtained from Loba Chemie Pvt. Ltd. Tolueno (analytical grade), chloroform (analytical grade), and ethanol (analytical grade) were obtained from Merck Co., Ltd. Triethylamine (TEA, >99% purity), 2,2′-bipyridyl (Bpy, >99% purity), and 3,4-ethylenedioxythiophene (EDOT, >98% purity) were obtained from TCI group Co., Ltd. An acrylic-based emulsion (PLITOC HDT 12 from Synthomer), used as a binder for preparing polymer/VO\textsubscript{2} composite films, was supplied by the RPSC Chemicals Co. Ltd. All chemicals were used without further purification.

2.2. Synthesis of VO\textsubscript{2}@PEDOT:PSS Particles. PEDOT and PSS chains were sequentially grafted onto VO\textsubscript{2} particles through a “grafting from” approach via a surface-initiated atom transfer radical polymerization (SI-ATRP) mechanism. A schematic diagram, illustrating the chemical structures and synthetic route for preparation of PEDOT:PSS-grafted VO\textsubscript{2} (designated as VO\textsubscript{2}@PEDOT:PSS), was proposed and is shown in Figure 1.

Basically, the synthesis is divided into 5 steps, as briefly described below. Firstly, a monochinuc phase VO\textsubscript{2} particles were prepared via hydrothermal and calcination techniques using vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) and citric acid (C\textsubscript{6}H\textsubscript{8}O\textsubscript{7}) as raw materials and reducing agent, respectively. More details concerning the reaction conditions and procedures for these have been well described in our previous report [1]. After that, the VO\textsubscript{2} particles were grafted with the silane coupling agent (APTES) to introduce amine functional groups onto the surface of VO\textsubscript{2} particles. Again, more details concerning this reaction step have been reported elsewhere [25]. Next, \(\alpha\)-bromoisobutyryl bromide (BIBB), which served as an initiating species for ATRP, was anchored onto the VO\textsubscript{2}@APETS particles. The reaction was proceeded via a condensation between the amine groups of APTES moieties and the acyl-bromide group of BIBB. After that, PSS chains were grafted from the surface of VO\textsubscript{2} particles via a SI-ATRP of sodium styrene sulfonate (SS-Na). The polymerization was carried out under different reaction times, ranging from 12 to 24 h. Accordingly, the polymerized products (polystyrene sulfonate-grafted VO\textsubscript{2} particles) were designated as VO\textsubscript{2}@PSS-12,
VO$_2$@PSS-16, VO$_2$@PSS-20, and VO$_2$@PSS-24, respectively (see Table 1).

Finally, EDOT monomer was polymerized on the surface of VO$_2$@PSS particles via an oxidative polymerization mechanism, utilizing the PSS shell layer as a dopant and template for the reaction. Likewise, the final products (VO$_2$ particles grafted with PSS : PEDOT) were designated as VO$_2$@PSS : PEDOT-12, VO$_2$@PSS : PEDOT-16, VO$_2$@PSS : PEDOT-20, and VO$_2$@PSS : PEDOT-24, respectively. More details regarding the synthesis of these particles are fully described in the supplementary information file (available here).

### 2.3. Preparation of Polymer/VO$_2$ Composite Films.

To prepare the polymer/VO$_2$ composite films, different types of VO$_2$-based particles, including the neat VO$_2$, the VO$_2$@PSS : PEDOT-12, and the VO$_2$@PSS : PEDOT-24 were mixed with an acrylic-based emulsion. Depending on the concentration of particles to be loaded, a given amount of VO$_2$ particles (0.03 g, 0.06 and 0.09 g) were dispersed in 15 g of the acrylic emulsion (PLIOTEC HDT 12) in a beaker and then placed in an ultrasonic bath and kept stirred for 150 min. The above mixtures were then coated onto a glass substrate (10 × 10 cm$^2$) by using a bar coater. The final film thickness was controlled by selecting a suitable rod bar (with a specified gap between the rod and substrate of 80 nm). The coating was left overnight to allow complete drying.

### 2.4. Characterizations.

Changes in chemical functional groups on the surface of the VO$_2$ particles were monitored by using Fourier transform infrared spectroscopy (FTIR, Thermo, DSC-1) and the X-ray photoelectron spectroscopy (XPS, AXIS ultra DLD), equipped with Avantage Data System software. The XPS data were collected in the V 2p, O1s C1s, N 1s, S 2p, and Si 2p binding energy regions.

Crystal structures of the modified VO$_2$ particles were examined by using an X-ray diffractometer (XRD, Bruker AXS D8-Discover) in the 2$\theta$ range of 10–80°, using Cu-K$\alpha$ radiation (\(\lambda = 1.54178\) Å). The accelerating voltage and the current used were 40 kV and 40 mA, respectively. Thermogravimetric analysis (NETZSCH, TGA 209 model) was used to determine thermal stability and weight composition of the
VO₂-based particles. For TGA measurement, approximately, 8 mg of each sample was used and was scanned over temperatures ranging between 25°C and 800°C under nitrogen gas and a heating rate of 10°C/min. From the obtained TGA thermograms, grafting density (δ) of the final product (VO₂@PSS: PEDOT particles) was determined, using equation (1), which was adapted from the work of Babu and Raghavachari [26]

\[
(\frac{W_{200-800}}{M_{3100}} - W_{VO_2}) \times 10^6 \frac{\mu mol/m^2}{},
\]

where δ is the grafting density, \(W_{200-800}\) is the percentage weight loss of polymer chains in the grafted VO₂, S is the surface area of VO₂ particles determined by BET technique (15.9887 m²/g), \(W_{VO_2}\) is the percentage weight loss of VO₂ particles before grafting, and M is the molar mass of the immobilized molecules (the grafting chains).

In addition, thermal behaviors of VO₂ particles and polymer/VO₂ composites were investigated by differential scanning calorimetry, using DSC 204, NETZSCH instrument. Typically, about 8 mg of the sample was used and the specimens were scanned over temperatures ranging between 25°C and 800°C, under nitrogen gas atmosphere, at a heating rate of 10°C/min.

The morphology of VO₂ particles and the acrylic/VO₂ composite films were examined by using the scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) techniques. The TEM experiment was carried out by using a JEOL JEM-2100 (JEOL, Peabody) microscope with an accelerating voltage of 200 kV. The TEM specimen was prepared by dispersing 1 mg of the VO₂ particles in 10 ml of ethanol, followed by sonication for 30 min. The solution was then dropped onto a copper specimen for 30 min. The solution was then dropped onto a copper grids and dried at 60°C. The TEM experiment was carried out by using a JEOL (JSM 6610LV) machine, equipped with a secondary electron detector and energy-dispersive X-ray detector (EDX). The accelerating voltage used was 10-30 kV. The sample was coated with gold prior to carrying out the TEM experiment.

Size of the VO₂-based particles was analyzed by using SEM and dynamic light scattering (DLS) techniques, respectively. The DLS analysis was carried out by using a Zetasizer instrument (Nano-ZS90, Malvern, UK), at a measurement angle 173 backscatter (NIBS default). The samples were prepared by dilution and sonication of the sample in an aqueous solution before putting into disposable cuvettes. The average hydrodynamic diameter was determined by taking an average of 11 runs, and the duration for each run was 10 sec. Each analysis is the average of results from three consecutive measurements.

Optical properties of the acrylic binder films, containing different types and concentration of VO₂-based particles, were tested by using a UV/visible/NIR spectrophotometer (Shimadzu, UV-3100). The percentage of light transmittance and reflectance of the 2 × 2 cm² film samples in the wavelength ranging between 200 and 2500 nm was investigated and calculated in accordance with the ISO 9050 standard method.

Heat shielding ability of polymer composite films containing VO₂ particles was tested by using a model house, equipped with an infrared lamp, thermocouples, and glass windows. More details concerning the experimental setup of this equipment has already been described in our earlier report [1]. Changes of temperature inside the house chamber was then monitored and followed as a function of time and the types of polymer/VO₂ window films.

3. Result and Discussion

3.1. Structural Characterizations of VO₂ Particles. Figure 2 shows overlaid FT-IR spectra of the various types of VO₂ particles, including the neat VO₂, the VO₂@APTES, VO₂@Br, VO₂@PSS, and VO₂@PSS: PEDOT. A broad absorption band centered around wavenumbers ranging between 3200 cm⁻¹ and 3600 cm⁻¹ and a sharp absorption peak at 1630 cm⁻¹ can be noted from all spectra. These bands are assigned to the stretching vibration of hydroxyl groups (OH) on the VO₂ particles and the bending vibration of H-O bonds from the absorbed moisture, respectively [27–29]. After grafting with APTES, an intensity of a broad absorption band ranging between 3350 and 3650 cm⁻¹ increased significantly. This can be ascribed to N-H stretching of NH₃ group in the APTES [30]. New peaks at 1400 cm⁻¹, 1100 cm⁻¹, and 984 cm⁻¹ also emerged (sample (b) in Figure 2). These are attributed to the vibration of the Si-CH₃ bond, the asymmetric stretching of the Si-O bond, and the stretching of the Si-OH bond, respectively.

To verify the existence of BIBB moieties on the surface of modified VO₂ particles (VO₂@Br), in this study, an XPS technique was used. From Figure 3, the presence of characteristic peaks in the XPS spectra at the binding energy of 68.25 eV and 182 eV was noted. These can be ascribed to the Br 3d and Br 3p orbitals, respectively. [31] The C 1s peak in the XPS spectrum was further analyzed by deconvolution. From Figure 4(a), the presence of a deconvoluted peak at 287.6 eV, representing the O=C-N group [5], can be noted. This indicates that the VO₂@APTES particles were successfully grafted with the BIBB initiator via an amide linkage.

The BIBB moieties on the surface of these particles were then used as an initiator for the polymerization of the sodium styrene sulfonate (SSNa) monomer. From FTIR analysis, the absorption peaks at 1175 cm⁻¹ and 1038 cm⁻¹, which are attributed to asymmetric and symmetric stretching vibration of the SO₂ groups in the monomer [24, 32], were observed, respectively (see the inset in Figure 2). Moreover, from the XPS spectrum of this product (sample (b) in Figure 3), peaks at 167.5 eV and 1070.5 eV, which represent the binding energy of the S 2p and Na 1s orbitals, can be noted. The intensity of the C 1s peak at the binding energy 284.5 eV also increased. This indicates that the surface of the modified VO₂ particles was covered with more hydrocarbon component. In Figure 4(b), four deconvoluted peaks at the binding energy of 284.6 eV, 285.5 eV, 286.4 eV, and 287.6 eV were also noted. These can be assigned to C=C, C=C/C=H, C-O/C=S, and C=O/C=S bonds, respectively. In
addition, direct evidence supporting the presence of a PSS amorphous organic layer on the surface of the modified VO$_2$ particles can be seen from the TEM images of the products (Figure 5). The above results confirm that the monomer was successfully grafted on the VO$_2$ particles.

Finally, after reacting the VO$_2$@PSS particles with the EDOT monomer, the FTIR spectrum of the final product (VO$_2$@PSS : PEDOT) (sample (e) in Figure 2) shows additional absorption peaks at 1541 cm$^{-1}$, corresponding to C=C stretching of the thiophene rings in the PEDOT repeating units. Absorption peaks at 1358 cm$^{-1}$ (C-C stretching of SO$_3$H), 1217 cm$^{-1}$, 1093 cm$^{-1}$ (C-O-C stretching), and 982 cm$^{-1}$ (C-S stretching) representing the PSS chains were also noted [4]. Consideration of the XPS spectra...
Figure 4: Continued.
Figure 4(c) shows that the intensity of the deconvoluted XPS peaks (C=O/C=S and C=O/C=S bonds) increased after grafting with the EDOT. This suggests that the monomer was polymerized on the surface of the VO\textsubscript{2} particles via the PSS shell, which served as both a template and a dopant.

Figure 6 shows SEM images of VO\textsubscript{2}-based particles. The particles are in a spherical shape, and sizes of the individual
Figure 7: DLS intensity size distribution curves for VO₂-based particles.

Table 2: Parameters from DLS analysis of VO₂-based particles.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Range (nm)</th>
<th>Major peak (D_h) (nm)*</th>
<th>Range (nm)</th>
<th>Minor peak (D_h) (nm)</th>
</tr>
</thead>
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<tr>
<td>VO₂</td>
<td>100-1000</td>
<td>475</td>
<td>4000-6500</td>
<td>5245</td>
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<tr>
<td>VO₂@PSS-12</td>
<td>100-900</td>
<td>280</td>
<td>3000-6500</td>
<td>5083</td>
</tr>
<tr>
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<td>70-900</td>
<td>295</td>
<td>3000-6500</td>
<td>5385</td>
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<tr>
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<td>70-1050</td>
<td>436</td>
<td>100-900</td>
<td>5025</td>
</tr>
<tr>
<td>VO₂@PSS : PEDOT-24</td>
<td>250-1050</td>
<td>563</td>
<td>70-250</td>
<td>149</td>
</tr>
</tbody>
</table>

*The values of \(D_h\) are corresponding to the peak positions on DLS intensity size distribution curves.

Figure 8: DSC thermograms of various VO₂-based particles: (a) the neat VO₂, (b) VO₂@PSS, and (c) VO₂@PSS: PEDOT; note that the dot lines represent the second heating thermograms for each sample.

Table 3: The critical transition temperature \(T_c\) and grafting density values of VO₂ particles and derivatives.

<table>
<thead>
<tr>
<th>Materials</th>
<th>(T_c) (°C)</th>
<th>Grafting density (chains/nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO₂</td>
<td>73.3</td>
<td>—</td>
</tr>
<tr>
<td>VO₂@PSS-12</td>
<td>76.9</td>
<td>n/a</td>
</tr>
<tr>
<td>VO₂@PSS-16</td>
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<tr>
<td>VO₂@PSS : PEDOT-12</td>
<td>79.6</td>
<td>6.51</td>
</tr>
<tr>
<td>VO₂@PSS : PEDOT-16</td>
<td>77.8</td>
<td>7.05</td>
</tr>
<tr>
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<td>77.8</td>
<td>5.35</td>
</tr>
<tr>
<td>VO₂@PSS : PEDOT-24</td>
<td>77.8</td>
<td>7.16</td>
</tr>
<tr>
<td>PSS</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>PSS : PEDOT</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>
particles are in the range of 3000 and 5000 nm. Morphological changes of the VO₂ particle surface after grafting with polystyrene sulfonate (PSS) chains were noticed. This can be used as the evidence indicating the presence of polymer coating on VO₂ particles. In addition, results from dynamic light scattering analysis (DLS curves) of the various samples are presented in Figure 7. Some parameters derived from the DLS analysis, including size distribution and size at the maximum intensity of the major peaks \(D_h\) for those particles, are also summarized in Table 2. In this study, since the VO₂-based particles were agglomerated and exhibited multimodal characteristics, no further attempts were made to determine the average size of the particles from the above techniques.

### 3.2. Thermal Properties of the Modified VO₂ Particles

Figure 8 shows DSC thermograms of the various types of VO₂ particles. An endothermic peak at 73°C can be observed from the thermogram of the neat VO₂. This refers to the critical transition temperature \(T_c\) of the monoclinic VO₂. The critical transition temperature \(T_c\) of grafted products (VO₂@PSS) shifted slightly to a higher temperature ranging between 76.9°C and 79.6°C (Table 3). This was most likely due to the presence of grafting polymer chains on the surface of the VO₂ particles, which affected the heat transfer and the onset of the phase transition temperature of the VO₂. After polymerization with the EDOT monomer, the critical transition temperature of the products (VO₂@PSS:PEDOT) still existed and those ranged between 77.8°C and 79.6°C.

Notably, after grafting of the VO₂ particles with PPS chains, an additional peak, centered at around 164-174°C, was observed. This peak also existed in a thermogram of PSS homopolymer (see also the inset in Figure 8). The transition temperature of this peak is much lower than the melting peak of PSS, which is around 450°C [33]. Interestingly, after running a second heating DSC scan, the above peaks disappeared. The similar effect was observed by Zhou et al. in a study on temperature-dependent microstructure of PEDOT/PSS films [34]. Accordingly, the above peak was described to the release of water during heating. Finally, after polymerization of EDOT monomer, the position of this peak shifted to the lower temperatures (ranging between 145.1 and 147.2°C, see also Table 3). A similar trend was noticed in the case of PSS homopolymer and PSS/PEDOT blend systems (which were polymerized without the presence of VO₂ particles). In our opinion, the above changes were related to changes in polarity and hydrophilicity on the surface of VO₂@PSS particles after coupling with the polymerized PEDOT chains.

Figure 9 shows TGA thermograms of the synthesized PSS:PEDOT and various types of VO₂ particles. The thermogram of the PSS:PEDOT shows three major transitions including an initial weight loss, which occurred at a temperature below 110°C, owing to the loss of some absorbed moisture. The second transition occurred over temperatures ranging between 250°C and 400°C, and that was attributed to the elimination of the sulfonate groups (-SO₃⁻) attached to the styrene rings in the PSS molecules [35, 36]. The third
transition occurred over temperatures ranging between 300°C and 550°C, and that was attributed to the degradation of the polymers (PEDOT [28] and PSS [32, 37] chains).

By contrast, the neat VO₂ particles were thermally stable up to 900°C. TGA thermograms of the intermediates, which included VO₂ particles functionalized with silane (VO₂@APTES) and VO₂@APETS treated with the BIBB initiator (the so called VO₂@Br), show a gradual weight loss transition over temperatures between 120 and 600°C. This can be ascribed to the loss of functional groups on the surface of the chemically modified VO₂ particles. Finally, after grafting with PSS followed by coupling with PEDOT molecules, all these transitions can be observed from the TGA thermograms of the final product (VO₂@PSS:PEDOT).

Figure 10: Backscattered electron SEM images of polymer composite films containing different types and concentrations of VO₂ particles: (a) acrylic/VO₂ (1.0 wt%), (b) acrylic/VO₂ (1.5 wt%), (c) acrylic/VO₂@PSS:PEDOT-12 (1.0 wt%), (d) acrylic/VO₂@PSS:PEDOT-12 (1.5 wt%), (e) acrylic/VO₂@PSS:PEDOT-24 (1.0 wt%), and (f) acrylic/VO₂@PSS:PEDOT-24 (1.5 wt%).
In this regard, the grafting density of the final products was determined using equation (1), and the results are summarized in Table 3. Notably, grafting density values ranging from 5.35 to 7.16 chains/mm² were obtained, and the values changed with the polymerization time in a nonlinear fashion. In our opinion, the above effect can be ascribed to the nature of the SI-ATRP mechanism. The longer the reaction time, the greater the monomer conversion [38]. This led to the higher degree of particles covered by grafting chains [39]. Moreover, the mechanism of SI-ATRP is basically a kind of controlled free radical polymerization, which means that the length of the polymerized chains also gradually increased with the reaction time [40]. In this regard, it was possible that both parameters contributed to the number of chains per area (the grafting density values) of the VO₂@PSS:PEDOT reported in this study. It is also worth mentioning that the grafting density values of the modified VO₂ particles in this study are relatively high compared to those of the Fe₃O₄ nanoparticles grafted with poly(methyl methacrylate) chains, reported by Babu and Raghavachari [26]. In our opinion, the discrepancy was attributed to the different sizes and surface areas of the particles used. Specifically, the surface area of VO₂ (15.9887 m²/g) is relatively low compared to that of the Fe₃O₄ nanoparticle (115 m²/g).

3.3. Morphological, Optical, and Thermochromic Properties of Polymer/VO₂ Films. Figure 10 shows SEM images of acrylic polymer composite films loaded with 1 wt% of different types of VO₂ particles. It can be clearly seen that voids or gaps in the interface between particles and the polymer matrix disappeared after the neat VO₂ particles were replaced by the VO₂@PSS:PEDOT particles. This indicates that the state of compatibility between the acrylic polymer
and the grafted VO₂ improved. In addition, from the EDX dot maps (Figure 11), greater dispersion of the particles in the acrylic polymer matrix can also be noticed.

The optical properties of acrylic film containing different types and concentrations of VO₂-based particles are presented in Figures 12 and 13. The percentage visible light transmittance and near infrared (NIR) transmittance of acrylic composite films containing different types and concentrations of VO₂-based particles are shown in Figures 12 and 13, respectively.
Vis) through the acrylic polymer film dropped from 87% to 81-82%, after loading with 0.5% of the neat VO₂ particles. The transmittance values tended to decrease with increasing concentration of VO₂ particles. A similar trend is also observed for the polymer composite films containing the modified VO₂ (VO₂@PSS : PEDOT) particles. The percentage visible light transmittance (Tvis, %) of each composite film decreased to the lowest values, ranging between 68% and 71%, when the polymer was loaded with 1.5 wt% of VO₂-based particles. These values became lower than those of some existing commercial products such as heat control window films [41]. Therefore, in this study, no further attempts were made to increase the concentration of VO₂ particles beyond 1.5 wt%.

Figure 14 shows the appearance of polymer composite films containing different types of VO₂ particles. The optical transparency of these films can hardly be differentiated by the naked eye, probably because the percentage loading of the particles is only 1.0 wt%. However, consideration of the percentage transmittance (Figure 12) reveals that a Tvis value above 75% of the composite films could be reached when the neat VO₂ particles were replaced with VO₂@PSS : PEDOT particles. Again, the improvement could be attributed to better dispersion of the particles after surface modification. However, as the concentration of VO₂@PSS : PEDOT was further increased to 1.5 wt%, the Tvis values of the composite film decreased again and became closer to the Tvis value of the acrylic/VO₂ film. This was due to more agglomeration of the modified VO₂ particles at higher loading (Figure 11). Interestingly, by using PSS and PEDOT (polymerized without the presence of VO₂ particles) as fillers, the transparency of the acrylic film also decreased. This was probably due to poor miscibility between the acrylic polymer and PSS/PEDOT. Moreover, the actual content of PSS/PEDOT chains loaded into the acrylic film was 1.0 wt%, which is much higher (about 10 times) than the actual weight of the PSS : PEDOT grafted onto the modified VO₂ particles. These factors contributed to the decrease in transparency. Nevertheless, the Tvis values of the acrylic polymer/VO₂@PSS : PEDOT composite films in this study are much greater than those of the EVA/VO₂@PE composites in our earlier report [12], provided that the same volume of VO₂ particles were loaded (1.0 wt%) (see Table 4). In our opinion, the discrepancy could be attributed to several factors, including the fact that different polymers and mixing processes were used. Hereafter, acrylic-based emulsion was used, and the mixing was carried out via a solution process. By contrast, EVA pellets were compounded with additives and VO₂ particles via an extrusion process under shear force and heat. In this regard, a different state of dispersion of the particles in the polymer matrices can be obtained. Besides this, the PSS and PEDOT grafting chains used in this study are intrinsically transparent. This feature contributed significantly to the greater Tvis of the acrylic film (Table 4). The above effect...
was not the case for the VO$_2$ coated with polyethylene, which is opaque.

Apart from the optical transparency, the percentage NIR transmittance ($T_{\text{NIR}}$) through the polymer films also decreased when the VO$_2$ particles were loaded. The higher the concentration of modified VO$_2$ particles, the lower the $T_{\text{NIR}}$ values. However, the percentage NIR reflectance ($R_{\text{NIR}}$) of these films did not increase, regardless of the type of concentration of VO$_2$-based particles. It is important to remember that the UV/Vis/NIR spectroscopy test was carried out at ambient temperature, which is below the $T_c$ of the VO$_2$ particles. Therefore, the metal oxide particles remained in a monoclinic phase, VO$_2$(M), which is incapable of reflecting the transmission of NIR radiation effectively. In this regard, the decrease in percentage NIR transmittance through the acrylic/VO$_2$@PSS : PEDOT composite film could be attributed uniquely to other factors including a light-scattering effect and the presence of PSS and PEDOT chains on the surface of the modified VO$_2$ particles. A similar effect was also observed in the PVC/VO$_2$ composites [42], and that influenced the thermal stability and durability of the composite films.

The heat shielding properties of the composite films containing VO$_2$ particles, however, began to appear and became remarkable when these samples were tested in a model house, installed with thermocouples and an infrared lamp. It is worth mentioning that when the lamp was turned on, the actual temperature in front of the model house was equal to 85°C, which is above the $T_c$ of the VO$_2$ particles. In this regard, it was possible that the monoclinic crystal structure

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**Table 4: Comparison of optical properties of various polymer composite films containing different types of VO$_2$ particles (1.0 wt% loading).**

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_{\text{Vis}}$ (%)</th>
<th>$T_{\text{NIR}}$ (%)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVA film (solution mixing)</td>
<td>89.95 ($\pm$0.54)</td>
<td>n/a</td>
<td>[1]</td>
</tr>
<tr>
<td>EVA film (melt mixing)</td>
<td>85.98 ($\pm$0.97)</td>
<td>n/a</td>
<td>[1]</td>
</tr>
<tr>
<td>EVA/VO$_2$ (solution mixing)</td>
<td>73.73 ($\pm$0.56)</td>
<td>n/a</td>
<td>[1]</td>
</tr>
<tr>
<td>EVA/VO$_2$ (melt mixing)</td>
<td>31.60 ($\pm$0.73)</td>
<td>n/a</td>
<td>[1]</td>
</tr>
<tr>
<td>EVA film (melt mixing)</td>
<td>90.20 ($\pm$0.83)</td>
<td>89.35 ($\pm$0.54)</td>
<td>[12]</td>
</tr>
<tr>
<td>EVA/VO$_2$ (melt mixing)</td>
<td>43.21 ($\pm$2.17)</td>
<td>42.48 ($\pm$2.12)</td>
<td>[12]</td>
</tr>
<tr>
<td>EVA/VO$_2$@PE (melt mixing)</td>
<td>41.91 ($\pm$1.28)</td>
<td>44.82 ($\pm$1.34)</td>
<td>[12]</td>
</tr>
<tr>
<td>Acrylic film</td>
<td>87.55 ($\pm$0.0049)</td>
<td>87.73 ($\pm$0.0030)</td>
<td>This study</td>
</tr>
<tr>
<td>Acrylic/VO$_2$</td>
<td>71.84 ($\pm$0.0027)</td>
<td>73.29 ($\pm$0.0049)</td>
<td>This study</td>
</tr>
<tr>
<td>Acrylic/VO$_2$@PSS : PEDOT-12</td>
<td>75.81 ($\pm$0.0020)</td>
<td>78.07 ($\pm$0.0025)</td>
<td>This study</td>
</tr>
</tbody>
</table>

**Figure 15: Change in temperature inside the model house installed with glass windows which were coated with various acrylic/VO$_2$ (1.0 wt%) composite films.**

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of the VO₂ particles changed to the rutile phase, which is thermochromic and capable of exhibiting NIR shielding properties. From Figure 15, the temperature of the normal acrylic polymer film (without VO₂ particles) increased steadily with time and reached a plateau at 85°C, after 30 min. However, when VO₂ particles were loaded into the acrylic polymer film, the temperature, after reaching equilibrium, decreased by 4.3°C.

Finally, when the neat VO₂ particles were replaced by the modified VO₂ particles, similar trends still existed. The final temperature after equilibrium of the system equipped with these films was also slightly lower than that installed with the neat VO₂/acrylic film. However, the differences were not obvious. Since the critical transition temperature of VO₂ increased slightly after the surface modification (see Table 3), it was possible that the phase transition of the modified VO₂ particles did not occur completely and so the NIR shielding efficacy of the materials was not fully exhibited. In addition, further work has yet to be carried out to optimize the grafting density and percentage loading of modified VO₂ particles in this system.

4. Conclusions

Vanadium dioxide particles grafted with polystyrene sulfonate/poly(3,4-ethylenedioxythiophene) (VO₂@PSS:PEDOT) were successfully prepared via surface functionalization and surface-initiated atom transfer radical polymerization. The thermochromic behaviors of the modified VO₂ particles were observed with phase transition temperatures ranging between 78 and 79°C. Window films made from the acrylic/VO₂@PSS:PEDOT (1.0 wt%) were capable of reducing the temperature inside a model house, of up to 5-6°C, compared with the control system (the acrylic coating without any particles). Overall, this study has demonstrated that it is possible to improve the dispersion of VO₂-based particles in acrylic polymer by grafting with PSS:PEDOT chains.

Data Availability

The data concerning the detailed synthesis procedure for preparation of various VO₂-based particles are described and reported within the supplementary information file. Additional data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Detailed synthesis procedures of the various vanadium dioxide-based particles. (Supplementary Materials)

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