Development of Mechanically Reliable and Transparent Photochromic Film Using Solution Blowing Spinning Technology for Anti-Counterfeiting Applications

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ABSTRACT: Photochromic materials have attracted broad interest to enhance the anti-counterfeiting of commercial products. In order to develop anti-counterfeiting mechanically reliable composite materials, it is urgent to improve the engineering process of both the material and matrix. Herein, we report on the development of anti-counterfeiting mechanically reliable nanocomposites composed of rare-earth doped aluminate strontium oxide phosphor (RESA) nanoparticles (NPs) immobilized into the thermoplastic polyurethane-based nanofibrous film successfully fabricated via the simple solution blowing spinning technology. The generated photochromic film exhibits an ultraviolet-stimulated anti-counterfeiting property. Different films of different emissive properties were generated using different total contents of RESA. Transmission electron microscopy was utilized to investigate the morphological properties of RESA NPs to display a particle diameter of 3–17 nm. The morphologies, compositions, optical transmittance, and mechanical performance of the produced photochromic nanofibrous films were investigated. Several analytical methods were employed, including energy-dispersive X-ray spectroscopy, scanning electron microscopy, and Fourier-transform infrared spectrometry. The fibrous diameter of RESA-TPU was in the range of 200–250 nm. In order to ensure the development of transparent RESA-TPU film, RESA must be prepared in the nanosized form to allow better dispersion without agglomeration in the TPU matrix. The luminescent RESA-TPU film displayed an absorbance intensity at 367 nm and two emission intensities at 431 and 517 nm. The generated RESA-TPU films showed an enhanced hydrophobicity without negatively influencing their original appearance and mechanical properties. Upon irradiation with ultraviolet light, the transparent nanofibrous films displayed rapid and reversible photochromism to greenish-yellow without fatigue. The produced anti-counterfeiting films demonstrated stretchable, flexible, and translucent properties. As a simple sort of anti-counterfeiting substrates, the current novel photochromic film provides excellent anti-counterfeiting strength at low-cost as an efficient method to develop versatile materials with high mechanical strength to create an excellent market as well as adding economic and social values.

1. INTRODUCTION

With the fast progress in the fields of market and information technology, fake and poor products have been shown in many fields of modern commodities, presenting a huge threat to community. Thus, there have been urgent and increasing demands for the development of new anti-counterfeiting materials with exclusive production procedures, making it difficult to copy and easy to identify.1–3 There are different conventional anti-counterfeiting techniques, such as ink, paper, and digital technologies. The current models of smart anti-counterfeiting technologies include radio frequency identification (RFID) tags, holographic labels, and quick response (QR) codes. However, the preparation and recognition of those models depend on sophisticated and costly apparatus, which restricts their further usage.4,5 Photochromic anti-counterfeiting films have recently employed in various commodities. Photochromic compounds can be recognized as stimuli-responsive photo-switchable materials with the capability to vary their color upon exposure to a light source. There are two different types of photochromic materials, including compounds that can alter their color under ultraviolet light and those with the ability to change their color under visible daylight.6 This colorimetric change process...
has received high attention owing to its capability to present a variety of commodities, such as displays, sunglasses and ophthalmic lenses, packaging, memories, security prints, colored advertisements, sensors, and optical data storage. The utility of photochromic materials in composites can provide creative prospects to create smart commodities to function as brand protection, security barcodes, camouflage for military purposes, ultraviolet protective agents, and electronic image displays. An ultraviolet-induced photochromic film exhibits a colorless transparent appearance under ordinary visible daylight; nonetheless, it displays a previously determined anti-counterfeiting model under an ultraviolet light source. According to these properties, an ultraviolet-induced photochromic film possesses unique and new visual effects as well as the ability to achieve the anti-counterfeiting function. For packaging purposes of various commodities, such anti-counterfeiting photochromic film, they must simultaneously exhibit an optical performance, original water vapor barrier, and fast packaging. To explore mechanically effective photochromic composite films, the manufacturing processes at the material/matrix levels have been broadly studied.

The use of lanthanide-doped photoluminescent materials for anti-counterfeiting purposes has been recently increased due to their characteristic antenna effect with ligands, high luminous efficiency, long stokes displacement, and sharp emission spectra. Rare-earth strontium aluminate phosphor (RESA; SrAl2O4: Eu2+, Dy3+) has been broadly reported for various photoluminescence applications. RESA has been employed in a variety of commodities, such as switches, safety marks, luminous ornamental articles, decorations, and directional signs. This can be attributed to its photostability, durability, and long-persistent luminescence. There is a variety of known rare-earth doped phosphors with the ability to emit the different primary colors, such as Y2O3:Eu3+, Mg2+, Ti4+, and CaS:Eu2+, Ce3+, Tb3+, and SrAl2O4: Eu2+, Dy3+ for red emissions, MgAl2O4:Mn2+, Ce3+ for green emissions, and CaMgSi2O6:Eu2+, Dy3+ and CaAl2O4:Eu2+, Nd3+ for blue emissions. However, it proved to be one of the best long-lasting phosphors due to its distinctive brightness, nontoxicity, non-radioactivity, thermal and photostability, long-persistence time (>10 h), recyclability, and resistance to chemicals. Thus, the development of ultraviolet-induced photochromic RESA-immobilized TPU nanofibrous films is an interesting innovative technique with high durability, photostability, low-cost, excellent handle, and improved superhydrophobic activity, which opens new horizons to develop more stable and efficient anti-counterfeiting smart commodities. However, the chemical and physical features and particulate molding of RESA are usually unideal, which limits their applications. Thus, RESA complexes have been immobilized into various organic and inorganic compounds to overwhelm their low mechanical stability. Thermoplastic polyurethane (TPU) have been known as a category of elastomeric rubbers with excellent characteristics lying among rubber and plastics. Thermoplastic polyurethanes are incomparable by other plastic substrates due to their superior toughness, heat preservation, waterproof property, high transparency, and high strength, as well as resistance to weather, wear, and aging. Moreover, TPU can maintain outstanding flexibility at low temperatures. TPU is renewable and environmentally friendly, facilitating its use in a broad range of applications. Nonetheless, it has been significant to incorporate RESA into polymeric substrates to develop anti-counterfeiting products.

Smart nanofibers are highly significant due to their potential applications, such as displays and wearable sensors for healthcare purposes. Electrospinning has been used to integrate RESA complexes into polymers to afford nanofibrous films with high photoluminescence efficiency as well as good mechanical stability and processability. For instance, the large-scale production of perovskite/TPU-based multicolor photoluminescent core–shell nanofibrous film was reported for stretchable and wearable electronics. Nonetheless, nanofibers produced by electrospinning are costly, requires high voltage, and usually generate fibers in a very low yield. Moreover, electrospinning is restricted to visco-elastic substrates. Compared to the electrospinning technique, the recently innovated solution blowing spinning technology demonstrated simplicity, low cost, high yield, excellent production rate, and is safer as there is no need to apply a high voltage. The incorporation of RESA into the matrix of TPU by the solution blowing spinning technology is still unreported yet. Herein, we develop a simple technique to prepare RESA-TPU nanofibrous photochromic film for anti-counterfeiting applications. The morphological properties, chemical contents, mechanical properties, photostability, optical transmittance, and photoluminescence properties were studied. The hydrophobic performance was investigated by recording both slide and contacting angle to indicate an enhanced hydrophobic activity without negatively influencing the original physico-mechanical performance of the prepared samples. The results showed that RESA nanoparticles were immobilized homogeneously into TPU. The produced samples demonstrated flexibility, stretchability, and transparency. The stretching-resilient capability was distinguished with stability underneath diverse tensile strains. The produced homogeneous luminescent translucent films belong to a class of ultraviolet-induced photochromic materials, which is appropriate as an anti-counterfeit mark. Such anti-counterfeiting pattern shows greenish-yellow pattern underneath UV light without trace underneath visible daylight as illustrated by CIE Lab colorimetric parameters.

2. RESULTS AND DISCUSSION

2.1. Fabrication of Photochromic Nanofibrous Film.

The produced microsized particles of RESA were then subjected to the top-down technology to afford RESA NPs. The average particle size of RESA was discovered by TEM to show nanoparticle diameters of 3–17 nm as illustrated in Figure 1. To prepare RESA-TPU nanofibrous films (Figure 2), TPU and RESA nanoparticles were dispersed in a mixture of DMF and THF. The produced viscous solutions of RESA-TPU nanocomposites were subjected SBS under ambient conditions to afford nanofibrous films.

![Figure 1. TEM images of RESA NPs.](https://doi.org/10.1021/acsomega.1c04127)
2.2. Photoluminescence Properties. All RESA-TPU films demonstrated a colorless background to accomplish a better optical detection of the ultraviolet-induced color shift to green. All RESA-TPU films displayed an instant and reversible ultraviolet-induced photochromism. However, only RESA-TPU films with a low ratio of RESA of less than 0.4 wt % were capable to develop rapid reversibility demonstrating fluorescence emission. The other samples with higher ratios of RESA more than 0.4 wt % showed a long-persistent emission due to their slower reversibility. After irradiation with ultraviolet, the UV device was turned off and the decreased absorbance and emission intensities were reported versus time from 0 to 25 s (Figure 3). An absorbance curve was observed at 367 nm, which quickly decreased as a function of time. Two emission bands were detected at 431 and 517 nm. The curve of the absorption band at 367 nm declined, whereas the intensity of the emission bands at 431 and 517 nm simultaneously increased. The TPU organic matrix held RESA NPs, which enhanced the bonding between the inter-polymeric strands throughout physical trapping of RESA in the TPU matrix and/or via coordinative bonding between the positive cations of RESA and the partial negative charges on TPU polymeric strands.

The photoluminescence spectra gained from the prepared nanofibrous RESA-TPU-4 film are displayed in Figure 3. A strong greenish emission peak (517 nm) and a weaker blue emission peak (431 nm) can be seen in Figure 3. Those peaks originate from the 4f to 5d transition of the divalent europium ions. Those two peaks are attributed to two strontium sites in the crystal structure of SrAl2O4. Nonetheless, the blue emission peak has the characteristic of thermal quenching under ambient conditions, making the bluish peak extremely weaker. Thus, only the stronger greenish emission could be visually monitored. The emission induced by the trivalent europium was not observed in the luminescence spectra. Hence, the photoluminescence only arise from the divalent europium ions. There is a major reason for the decreased intensity of photoluminescence, which can be attributed to the declined concentration of RESA. The luminescence quantum yields (QY) of the prepared RESA-TPU films were determined by the integration sphere approach to present results of 15 to 40%, with increasing RESA. However, the cause for the decreased QY of RESA-TPU compared to the solid RESA nanopowder (85%) can be attributed to the excited light that could be blocked by the polyurethane bulk leading to decreasing the quantity of photons. The decaying times of RESA-TPU nanofibrous films were measured (Figure 4). All decay curves were found to follow an exponential second-order decay as demonstrated by eq 1.

\[
I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)
\]

where \(A_1\) and \(A_2\) are constants, \(I\) is the initial photo-luminescence intensity, \(\tau_1\) and \(\tau_2\) are the decaying time, and \(t\) represents the decaying time. The average lifetime (\(\tau_{ave}\)) can be determined using eq 2.

\[
\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 (\tau_2)^2}{A_1 \tau_1 + A_2 \tau_2}
\]

According to eq 2, the \(\tau_{ave}\) of RESA NPs is 880.7 \(\mu\)s, while \(\tau_{ave}\) values of RESA-TPU nanofibrous films are increasing in the range of 245.3–282.3 \(\mu\)s with increasing RESA NPs. This implies that the inclusion of polyurethane results in shorter...
Table 1. Colorimetric Measurements of RESA-TPU Films under Vis and UV Light; the Films from RESA-TPU-0 to RESA-TPU-8 Were Denoted by Symbols from R1 to R8

| RESA (wt %) | R1 | R2 | R3 | R4 | R5 | R6 | R7 | R8 |
|-----------|----|----|----|----|----|----|----|----|
| L* (vis)  | 87.95 | 86.53 | 84.64 | 83.74 | 83.09 | 81.31 | 80.98 | 80.23 | 79.28 |
| UV        | 87.03 | 79.60 | 78.52 | 75.28 | 75.39 | 73.65 | 71.97 | 70.42 | 68.99 |
| a* (vis)  | -1.75 | -1.27 | -1.19 | -1.17 | -1.22 | -1.12 | -1.06 | -0.89 | -0.75 |
| UV        | -1.82 | -4.25 | -4.87 | -5.01 | -5.86 | -6.31 | -7.29 | -7.88 | -8.35 |
| b* (vis)  | 1.37  | 1.40  | 1.62  | 1.55  | 1.45  | 1.32  | 1.26  | 1.02  | 0.96  |
| UV        | 1.24  | 9.77  | 9.09  | 8.45  | 7.85  | 7.63  | 5.86  | 5.21  | 4.81  |
| K/S (vis) | 0.38  | 0.40  | 0.48  | 0.56  | 0.80  | 0.92  | 1.23  | 1.76  | 1.85  |
| UV        | 0.44  | 1.46  | 1.61  | 1.76  | 1.58  | 1.96  | 2.18  | 2.53  | 2.77  |

Figure 5. Photos of translucent photochromic RESA-TPU-4 and long-persistent phosphorescent RESA-TPU-5 films under ultraviolet light demonstrating a butterfly pattern with green and intense white colors, respectively, depending on the ratio of RESA; for potential prototype package of RESA-TPU film.

RESA lifetime. The equivalent decrement of QY for the RESA-TPU films also accounts for the decreased lifetime depending on eq 3.

\[
QY = \left[ 1/r_1 \right] / \left[ \left( 1/r_1 + 1/r_{nr} \right) \right] = \frac{\tau_{ave}}{\tau_r}
\]

(3)

where \( r \) and \( r_{nr} \) represents radiation and non-radiation decays, respectively; \( r \) is constant. QY is proportional to \( \tau_{ave} \). The correlation between QY and \( \tau_{ave} \) of RESA NPs and RESA-TPU nanofibrous films can be converted according to eq 4.

\[
QY(\text{RESA NPs}) / QY(\text{RESA} - \text{TPU}) = \frac{\tau_{ave}(\text{RESA NPs})}{\tau_{ave}(\text{RESA} - \text{TPU})}
\]

(4)

Thus, QY of RESA NPs was almost three folds that of RESA-TPU nanofibrous films. This was nearly compatible with our testing results generated by the integration sphere approach. The long-persistent luminescence lifetime of RESA NPs and RESA-TPU films (under ultraviolet irradiation for 10 min at 365 nm; decaying in the dark) were almost similar. The long-persistent luminescence lifetime of RESA NPs can last for 10 s, while the long-persistent luminescence lifetime of RESA-TPU nanofibrous films are increasing in the range of 0–5 s with increasing RESA NPs after stopping UV irradiation.

2.3. Coloration Measurements. The photochromic coloration properties are summarized in Table 1. All TPU samples immobilized with RESA possessed translucent look. To ensure the assembly of a translucent RESA-TPU film, the RESA NPs phosphor must be immobilized via homogenous physical dispersion to avoid agglomeration. Nanomaterials have been important due to their excellent ability to maintain transparency of different products. The films developed a green color at lower ratios of RESA less than RESA-TPU-4 as detected by CIE Lab results. Nonetheless, a long-persistence bright white was detected underneath UV light for RESA ratios between RESA-TPU-5 and RESA-TPU-8. Under visible daylight, negligible differences were detected in K/S with raising the ratio of RESA from RESA-TPU-0 to RESA-TPU-8 confirming transparency of those films owing to the low concentrations of nanosized RESA. Upon incorporating RESA into TPU, a small increase in K/S was detected under ultraviolet light, indicating a change from colorless for RESA-TPU-0 to greenish-yellow for RESA-TPU-1. However, only insignificant differences were observed in K/S with increasing RESA from RESA-TPU-1 to RESA-TPU-8. The K/S of RESA-TPU underneath UV light was more than the equivalent unirradiated film owing to greener and bright white colors depending on the ratio of RESA. Irradiating RESA-TPU with UV resulted in substantial increment in the absorption maxima from 367 nm under visible daylight to indicate transparent appearance to 517 nm underneath UV to indicate greenish or intense white. The RESA-TPU-0 film demonstrated negligible differences in CIE Lab between visible and UV irradiation. Underneath visible daylight, the RESA-TPU films showed substantial variations in L*, a*, and b* with increasing RESA. Under visible daylight, L* decreased between RESA-TPU-1 and RESA-TPU-8 to indicate lower transparency imparting the samples an off-white shade. Underneath UV, L* decreased from RESA-TPU-1 to RESA-TPU-8 due to the greener shade monitored with increasing RESA. Under ultraviolet light, the -a* increased, and +b* decreased to indicate colorimetric shift from transparent to green. Immediately after turning off the ultraviolet device, the films (RESA-TPU-1 to RESA-TPU-4) retrieved instantaneously their original translucent appearance demonstrating fluorescence. On the other hand, the films with higher RESA ratios (from RESA-TPU-5 and RESA-TPU-8)
8) demonstrated long-persistent phosphorescence associated with a considerable decrement in $b^*$ and considerable increment in $a^*$. These results illustrate that the best fitting photochromism was detected for RESA-TPU-4.

2.4. Photochromic Measurements. Ultraviolet-induced photoluminescent materials have been widely utilized in the fields of anti-counterfeiting applications. Nonetheless, there have been restricted studies on the usage of photochromic plastic-based films. Herein, we merge RESA NPs and translucent TPU to gain a chromic plastic-based film. No traces were monitored by the naked eye under visible daylight; however, it emits a bright greenish-yellow color under ultraviolet irradiation. Currently, the anti-counterfeiting techniques utilized in cosmetic products are based on conventional techniques, in which different anti-counterfeiting marks were applied as prints. Therefore, high-end brand cosmetics can be exposed to fake and shoddy problems. Hence, we developed a gasket from the produced RESA-TPU film to be applied. The model can be developed with a rectangular shape impregnated in the film. The middle gasket applied on the product is translucent beneath visible daylight; however, it is emissive with a greenish-yellow color under UV irradiation providing an anti-counterfeiting function, which cannot be imitated. To afford a more packaging prototype, the RESA-TPU film was subjected to gluing onto a plastic bottle sign. The sign is visible to the naked eye; however, it also emits greenish color upon exposure to UV, demonstrating the concept of UV induced anti-counterfeiting. Figure 5 shows a schematic diagram of preparing UV-induced anti-counterfeiting prototype package.

2.5. Photostability and Reversibility. The emission curves of RESA were derived from the $4f^5D^1\leftrightarrow4f^6$ transition of Eu$^{3+}$. No characteristic emission was monitored for neither Eu$^{3+}$ nor Dy$^{3+}$ to verify a full exchange of Eu(III) to Eu(II). The function of Dy$^{3+}$ is to induce the formation of trapping entities to be released later in the dark and then transferred to Eu$^{3+}$ to go back to the ground state. Anti-counterfeiting commodities should be fatigue-resistant to prove photostability and durability. Therefore, the coloration–decoloration process was explored under ultraviolet and visible daylight over several cycles to indicate fast and complete reversibility without deterioration as illustrated in Figure 6.

2.6. Morphologies and Elemental Composition. Figure 7 displays the morphological properties and chemical composition of TPU nanofibers immobilized with RESA nanoparticles. No considerable differences were observed between blank TPU (RESA-TPU-0) and TPU immobilized with RESA (RESA-TPU-1 to RESA-TPU-8). The produced RESA-TPU nanofibrous substrates demonstrated a smooth surface. The nanofibers demonstrated average diameters in the range of 200–250 nm. The RESA was fully impregnated inside the nanofibrous film as no nanoparticles were observed on the surface of nanofibers. The existence of RESA within the matrix of TPU was verified by exploring the elemental compositions employing EDX spectra (Figure 8a). To identify the chemical compositions of the generated nanofibers, the elemental distribution was studied by EDX analysis to indicate a homogenous distribution of strontium aluminum oxide with trace doping of Eu$^{3+}$ and Eu$^{3+}$ ions. The EDX mapping of RESA-TPU film indicated the presence of carbon, nitrogen, oxygen, strontium, aluminum, europium, and dysprosium. The chemical compositions were studied at triple selected locations, as shown in Table 2. The results indicated quite similar elemental compositions at the triple inspected locations to prove the consistent distribution of RESA. The mapping was also applied to verify the consistent dispersion of RESA on the film surface as illustrated in Figure 8b.

FTIR curves were utilized to verify the substituents on the generated RESA-TPU-4 nanofibers as demonstrated in Figure 9. The RESA-TPU nanofibrous films showed an absorbance intensity at 2911 cm$^{-1}$ owing to the aliphatic CH tensile vibrations. The intensity at 3355 cm$^{-1}$ is attributed to the N–H tensile vibrations. The characteristic bands at 712 and 866 cm$^{-1}$ are attributed to the vibrations of the Al–O tetrahedron with a symmetrical lattice arrangement. The absorption bands of SrAl$_2$O$_4$ are nearly submerged to indicate overlapping of TPU bands with the main characteristic bands of SrAl$_2$O$_4$. The absorption bands at 432, 496, and 3470 cm$^{-1}$ were only noticeable in RESA-TPU, indicating that TPU could be utilized as a protection film.

2.7. Transparency and Mechanical Properties. The produced RESA-TPU nanofibrous films were rubbery. The film thickness could be controlled by adjusting the parameters of the solution blowing technique. The RESA-TPU layer with a 25–28 μm thickness was mechanically reliable. The RESA-TPU nanofibrous films emit a greenish-yellow color. Thermoplastic polyurethane is a sort of elastomeric rubber exhibiting features lying among rubber and plastics. TPU is not comparable with plastics due to its high strength. Thus, both elasticity and flexibility of RESA-TPU films were testified. Another significant feature of RESA-TPU films is obviously their transparency. The transmittance was performed to confirm the film transparency. The different total contents of RESA NPs in TPU would result in changes in optical transmission. It could be monitored that the transmission of films decreases with increasing RESA. The RESA-TPU-4 film displayed a transmittance of 55%, which is lower than that of RESA-TPU-0. It emits a greenish-yellow color under an ultraviolet light of 365 nm to demonstrate both high transparent and obvious greenish fluorescence. The characteristic of simple invisibility allows for the preparation of anti-counterfeit substrates. The stretching ability of the generated RESA-TPU films was examined to assess the mechanical performance. A film rectangle stretchable underneath various tensile strains was reported in the range of 0–
The elongation at break (e) could be subjected to calibration employing eq 5.43

\[
e = \frac{L_o - L_s}{L_o}
\]

where \( L_o \) is the film length and \( L_s \) is the length of tensile.

Generally, the higher values of elongation at break result in higher elasticity and softness. The magnitude of 415% indicated that RESA-TPU exhibits a very high flexibility. The luminescence spectral curves were examined underneath tension, in which a strong emission band was obviously monitored at 517 nm. The luminescence intensity of 517 nm was found to decrease with increasing the stretch elongation. This could be attributed to the decreased ratio of RESA in the

415%. The elongation at break (e) could be subjected to calibration employing eq 5.43

**Table 2. Elemental Compositions (wt%) of RESA-TPU-4 at Three Selected Spots (A, B, and C)**

| film | C   | O   | N   | Al  | Sr  | Eu  | Dy  |
|------|-----|-----|-----|-----|-----|-----|-----|
| spot A | 48.03 | 40.71 | 5.10 | 2.88 | 2.18 | 0.66 | 0.44 |
| spot B | 48.22 | 40.72 | 5.05 | 2.83 | 2.24 | 0.49 | 0.45 |
| spot C | 48.13 | 40.03 | 5.69 | 2.97 | 2.05 | 0.63 | 0.51 |

Figure 7. SEM images of RESA-TPU-4 film.

Figure 8. EDX diagram (a) and elemental mapping (b) of RESA-TPU-4 film.
luminescence spectra range underneath large strains. The band position at 517 nm did not change with increasing the stretch elongation between 0 and 415%, conﬁrming stable photoluminescence chromatic activities. Moreover, the ﬁlms can regain its origin shape after stretching reﬂecting a good rubbery and reusability for various practical anti-counterfeiting applications, such as smart packaging. The inclusion of RESA NPs (RESA-TPU-1) demonstrated a lesser tensile strength in comparison to RESA-TPU-0 (Figure 10). Young’s modulus was found to depend on strain and tensile. Hence, it decreased from RESA-TPU-0 to RESA-TPU-1. After that, it increased with increasing the ratio of RESA NPs from RESA-TPU-1 to RESA-TPU-4 and then continued stable from RESA-TPU-4 to RESA-TPU-8. Both of the tensile strength and Young’s modulus increased with increasing the ratio of RESA from RESA-TPU-1 to RESA-TPU-4 and then remained constant with increasing the ratio to RESA from RESA-TPU-4 to RESA-TPU-6. Negligible differences were observed in the strain percent at break due to the complete incorporation of the RESA NPs within the matrix of the TPU nanofibrous ﬁlm. The inclusion of RESA improved the bonding process of the inter-polymeric strands throughout physical and/or coordinative bonding between the RESA positive cations and the partial negative charges on the TPU polymeric strands. The tensile enhancement was observed upon raising the ratio of RESA till reaching a certain concentration, RESA-TPU-4. Then, the tensile strength decreased due to increasing the spaces between the inter-polymer chains as a result of the coagulation of the RESA NPs between polymer chains. Hence, the tensile strength was monitored to decrease at the high ratios of RESA.

### 2.8. Hydrophobic Measurements

The contact angle of the produced RESA-TPU-0 nanofibrous ﬁlm was detected at 147.1°, which was found to increase to 155.3° after embedding RESA NPs into the matrix of TPU (RESA-TPU-1) as shown in Table 3. The contacting angles were then improved from 155.3° to 163.7° with raising the ratio of RESA NPs in the TPU matrix from RESA-TPU-1 to RESA-TPU-5. However, the contact angle slightly decreased back to 162.8° with the increasing ratio of RESA NPs from RESA-TPU-5 to RESA-TPU-8. This can be attributed to improving the surface roughness at the higher ratios of RESA NPs. However, the very high ratios of RESA NPs within the TPU bulk can extremely decrease the spaces amid NPs, which decrease the roughness of the surface, leading to the reduction of the contacting angles. The slide angle was also applied to evaluate the hydrophobic activity of the RESA-TPU ﬁlms. When the RESA NPs embedded in the TPU nanofibers, the wetting activity was found to change as the slide angle increases with the increasing ratio of RESA. The sample photochromic emission in water was also proved as shown in Figure 11.

**Table 3. Hydrophobic Properties of RESA-TPU Nanofibrous Films**

| ﬁlm       | contact angle (°) | slide angle (°) |
|------------|-------------------|-----------------|
| RESA-TPU-0 | 147.1             | 6               |
| RESA-TPU-1 | 155.3             | 7               |
| RESA-TPU-2 | 157.6             | 9               |
| RESA-TPU-3 | 159.8             | 10              |
| RESA-TPU-4 | 162.2             | 12              |
| RESA-TPU-5 | 163.7             | 12              |
| RESA-TPU-6 | 163.5             | 13              |
| RESA-TPU-7 | 163.1             | 12              |
| RESA-TPU-8 | 162.8             | 12              |

**Figure 10.** Effect of increasing RESA NPs on the mechanical performance of the TPU ﬁlms from RESA-TPU-0 to RESA-TPU-8 represented by the symbols from R₁ to R₈.
3. CONCLUSIONS

Ultraviolet-induced RESA-TPU anti-counterfeiting film was prepared via a solution blowing spinning technology. The preparation process of the photochromic films was simple, fast, and inexpensive. The best photoclinometric results were monitored at the RESA ratio of 0.4 wt %. The morphologies and chemical composition demonstrated that RESA NPs are dispersed homogeneously in the thermoplastic polyurethane film. The produced films displayed elasticity, flexibility, and transparency. The presence of RESA NPs was found to increase the contacting angles of RESA-TPU films enhancing hydrophobic properties. The stretching/rubbery capability demonstrated stability with increasing the tensile elongation values. RESA NPs displayed a particle diameter of 3–17 nm, while the fibrous diameter of RESA-TPU was in the range of 200–250 nm. The photoluminescent RESA-TPU films displayed an absorbance intensity at 367 nm and two emission bands at 431 and 517 nm. The produced RESA-TPU nanofibrous films demonstrated an improved hydrophobic activity associated with increased contact angle values in the range of 147.1–163.7°. The RESA-TPU films are appropriate for anti-counterfeit marks to function as a greenish-yellow pattern under UV irradiation without any traces underneath the visible daylight as indicated by the photoluminescence spectra and CIE Lab colorimetric measurements. Thus, we designed a gasket applied onto a cosmetic spray sample to demonstrate excellent anti-counterfeiting ability. The prepared films demonstrated high photostability and reversibility, making them promising smart materials for many applications, such as brand protection, military camouflage, optical electronics, antireflective coatings, and security printing.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. TPU (1.2 g cm\(^{-3}\)) was supplied from Sigma-Aldrich. All solvents including \(\text{N,N-dimethylformamide (DMF, \(\geq\)99\%)}\) and tetrahydrofuran (THF, 99%) were supplied from Sigma-Aldrich and used as received without further purification. The starting materials employed in the synthesis of RESA, including \(\text{Dy}_2\text{O}_3\), \(\text{Al}_2\text{O}_3\), \(\text{H}_2\text{BO}_3\), \(\text{Eu}_2\text{O}_3\), and \(\text{SrCO}_3\) were supplied from Aldrich.

4.2. Preparation of RESA NPs. RESA \((\text{SrAl}_2\text{O}_4\text{Eu}^{3+}, \text{Dy}^{3+})\) was fabricated utilizing the solid-state high-temperature method. \(^{15}\) A mixture of dysprosium oxide (0.03 mol), \(\text{Al}_2\text{O}_3\) (2.0 mol), \(\text{Eu}_2\text{O}_3\) (0.02 mol), \(\text{H}_2\text{BO}_3\) (0.2 mol), and strontium carbonate (1.0 mol) was stirred in ethanol (100 mL), homogenized (25 kHz) for 60 min, dried at 90 °C, and then subjected to grinding for 2 h in a laboratory planetary ball-milling system. The admixture was subjected to sintering at 1300 °C over 3 h in an ambiance of reduced carbon. The provided fine particles were subjected to sieving to give RESA micr.osized particles. The nanosized particles of RESA were synthesized utilizing the top-down technology. \(^{36}\) RESA micr.osized fine particles (10.0 g) were charged to a ball-mill (stainless-steel vial; 20 cm) on a vibrating tablet. The SiC-based ball (0.1 cm) was pushed to collide continually with RESA powder in the vial and the tablet for 24 h to give RESA NPs.

4.3. Preparation of RESA-TPU Nanofibrous Films. TPU (12% wt-v) was added to a mixed solution of DMF and THF (1:1) to afford a solution of TPU. RESA nanoparticles were then added to the prepared TPU solution at different ratios, including 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 wt % relative to the weight of TPU. The samples were marked as RESA-TPU-0, RESA-TPU-1, RESA-TPU-2, RESA-TPU-3, RESA-TPU-4, RESA-TPU-5, RESA-TPU-6, RESA-TPU-7, and RESA-TPU-8. Each RESA-TPU solution was stirred for 2 h on a magnetic stirrer until the mixture became homogenous. The produced viscous solutions were then charged into the SBS device to generate the corresponding RESA-TPU nanofibrous films. The SBS consists of an air compressor, injection pump, fiber collector, and spin nozzle as illustrated in Figure 12. The viscous solution of RESA-TPU was injected, at a flow rate of 8 mL h\(^{-1}\) and air pressure of 0.5 bar, throughout a spinning needle (19 gauge). The spinning needle was adjusted at the center of the concentric nozzle, whereas the protruding needle was carried out at 1 mm from the concentric nozzle. The collector was placed at a distance of 10 cm from the spin nozzle.

4.4. Analytical Methods. The morphological properties of the produced nanofibers were evaluated by SEM (Quanta FEG250; Czech) coupled with EDX. The diameters of the generated RESA-TPU nanofibers were measured by Image J software. Transmission electron microscopy (TEM, JEOL-1230; Japan) was utilized to study the surface morphology and size of RESA nanoparticles. FT-IR spectra were measured by a Nicolet Nexus 670 spectrometer (United States). The contact angle measurements were examined by Dataphysics OCA15EC (GmbH, Germany). The optical transmission of the prepared RESA-TPU films was monitored by a UV–visible U-3010 HITACHI spectrophotometer. The luminescence spectral profiles were measured using an FP-8300 JASCO spectrofluorometer (Japan) associated. An ultraviolet device (6 W) was employed as an UV source at 365 nm. The photoluminescence quantum yields were determined using an Edinburgh FSS fluorescence spectrophotometer. The photoluminescence decay time was studied using a photoluminescence accessory connected to an FP-8300 (JASCO, Japan) spectrophotometer, while the afterglow lifetime was determined by a persistent luminescence material optical testing system as the sample is first pre-irradiated at 365 nm for 10 min. The mechanical measurements were determined by a Shimadzu AGX (Japan) with a loading Cell of 100 N.

4.5. Colorimetric Properties. The coloration measurements of the RESA-TPU films, including CIE Lab and tintorial strength (K/S), were determined by a Hunter Lab Ultra-Scan-PRO (United States). The three-dimensional colorimetric space parameters (CIE Lab) were measured employing L* as the lightness from white (100) to black (0), a* is the ratio from red (−) to green (+), and b* is the ratio from blue (−) to yellow (+). The RESA-TPU nanofibrous films were subjected to irradiation at 365 nm using an ultraviolet lamp. The colorimetric results were recorded before and after irradiation with the ultraviolet lamp. The K/S values were measured utilizing the reflectance method. The photo-
graphs of the photochromic fibers were reported by the digital camera A710-IS.

4.6. Photostability and Resistance to Fatigue. The photostability and reversibility were tested by determining the emission spectra prior to and following exposure to a UV device (365 nm) placed at 5 cm above the sample. The sample was placed underneath UV for 5 min, and after that, it is left for an hour to release the emission energy in the dark and returns to its origin state. The emission spectra (517 nm) were reported before and after each cycle.

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Notes
The authors declare no competing financial interest.
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