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ARTICLE TYPE

Mutual Protection UV Aging of EVA Composites Using Highly Active Optical Conversion Additives

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The mutual ultraviolet (UV) degradation protection mechanism and optical conversion of ethylene-vinyl acetate copolymer (EVA) rare earth organic complex (REOC) composite were investigated. The uniform Sm(TTA)₃Phen (MSTP) particles have been successfully synthesized via microwave ultrasonic technique, and uniformly embedded into the EVA long chain crosslinked structure and have excellent dispersion. The MSTP doped EVA film provides an excellent active optical conversion and highly visible transmission performance, which the properties are strongly dependent on size and concentration of doped particle, absorption and emission properties. The MSTP was effective as a resistance UV light agent and highly active optical conversion additive for EVA rare earth organic complex composites with perfect network structure and excellent adhesion properties, which can timely transform the heat energy of destroy the structure into the form of light energy.

Introduction

Owing to outstanding sunlight transmission, flexibility, adhesion to organic/inorganic materials¹, ethylene-vinyl acetate copolymer (EVA) is widely applied in many fields, such as Solar PV cell²⁻⁵, food packaging⁶, mortar and concrete modifier⁷, shoes and so on. However, the EVA exposed to ultraviolet (UV) irradiation of sunlight for a long term, will accelerate its aging rate. And vinyl acetate (VAc) units of EVA are more vulnerable to heat, oxygen, and UV light radiation, which can easily form reactive radical or unstable hydroperoxide, and facilitate further irreversible chemical reactions.² In order to ensure optical transparency, many traditional solutions were added to UV aging agent, most of which released energy in the form of heat leading to thermal aging. One way to achieve improved the light utilization and decreased UV degradation rate is to perform composite rare earth organic complex (REOC). The REOC species absorb the UV wavelength photons and re-emit them at visible wavelength before they reach the solar cells⁸.

REOC conventional synthetic methods are coprecipitation and hydrothermal, which have large size distribution and amorphous

particles. Nowadays, particles with uniform size and controlled morphology is successfully synthesized by a novel microwave ultrasonic technique, which focused on inorganic particles⁹⁻¹². After a long time of exploration, the researchers found that microwave ultrasonic Synergy method is also applicable to rare earth organic complex in order to obtain uniform size and controlled morphology particle.

Based on our long term research in morphology investigation of rare earth organic complex, the objective of this work was to make further detailed studies of compound REOC and EVA. Through mutual protection mechanism, EVA long chain and Sm(TTA)₃Phen particle slowed down the rate of ultraviolet degradation. Meanwhile, island Sm(TTA)₃Phen can convert light to available energy range. Photoluminescence (PL) and infrared spectroscopy (FT-IR) were used to discuss the degradation mechanism, the intensity of light conversion and relationship between Sm(TTA)₃Phen and EVA chain. Island microstructural characterization was observed by field emission scanning electron microscopy (FSEM).

Experiment

Materials

The raw of complex Sm(TTA)₃Phen (MSTP) is a-thenoyltrifluoroacetone (HTTA, 99.00%), 1,10-phenanthroline (Phen, 99.00%), NaOH (99.00%), ethanol (99.70%), benzoyl peroxid (BPO, 98.0%), tetrahydrofuran (THF, 99.0%) were obtained from Sinopharm Chemical Reagent Company Ltd. (China). The ethylene vinyl acetate (EVA) copolymer was provided by Mitsui EVA 150 (33 wt%, Vac, Japan). SmCl₃·6H₂O (99.99%) were purchased from Funing Rare Earth Industrial Company Ltd. (China). All the chemicals were analytical grade

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and used as received without further purification.

Synthesis $\text{Sm}(\text{TTA})_3\text{Phen}$ powder (MSTP)

Uniform small rectangular MSTP powder was prepared by using microwave ultrasonic method. As for the synthesis of MSTP stoichiometric $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$, HTTA, Phen with molar ratio of 1:3:1 were thoroughly dissolved with an appropriate amount of ethanol. HTTA solution was previously added to the microwave ultrasonic reactor at 60 °C for microwave power 500 W and ultrasonic power 500 W in the four flat bottom flask. Then, the $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ and Phen solution slowly dropped into the reactor by using a peristaltic pump. The pH value of the mixture was adjusted to between 5 and 6 by adding sodium hydroxide solution (1 mol/L). After reaction time 4 h the samples were washed with ethanol and water three times and dried powder at 60 °C for 48 h.

Synthesis MSTP doped EVA film (EMSTP)

The MSTP complex and ethylene vinyl acetate (EVA) were mixed with different weight ratio (0, 0.2, 0.4, 0.6, 0.8 % MSTP doped) and dissolved in THF (5% weight percentage concentration). The solution was dispersed in ultrasonic power 500 W at 30 min. Then, adding 1% benzoyl peroxide (BPO) to the mixed solution for 2 h stirring. The recycling of whole mixture solvent was distilled at 60 °C under vacuum for approximately 24 h, which can be obtained the film. After evaporating the EVA film, samples were heated to 145 °C for 10 min at 10 MPa pressure by flat-panel vulcanizer, which EVA film with the thickness in the range of $150 \pm 10 \mu\text{m}$ were sandwiched between two PET films, then taken out and cooled down in air.

Characterization

Photoluminescence (PL) excitation and emission spectra were recorded on a Horiba Jobinyvon FL3-221 fluorescence spectrophotometer equipped with a 450W Xe light source as an excitation wavelength of 380 nm. Field emission scanning electron microscopy (FESEM) was performed with an S-4800 scanning electron analyzer with an accelerating voltage of 15 kV. Absorption and transmission spectra were measured on Shimadzu UV3101PC spectrophotometer (Shimadzu Corporation, Japan). FT-IR was performed by an ATR technique on a PerkinElmer, model Frontier FT-IR, USA. Spectra were obtained using 32 scans and a 4 cm^{-1} resolution from 400 to 4000 cm^{-1} . The artificial accelerated UV aging was applied using a Q-SUN1000 xenon lamp test chamber (Q-Panel, USA). The distance between the light source and the samples kept at 20 cm constantly. The irradiation intensity was maintained at 0.51 W/m^2 at $\lambda = 340 \text{ nm}$, with a constant temperature at 65 °C (ISO 4892-2:2006). The aging time ranged from 0 h to 800 h. The heat effect of the EVA films were recorded on a professional infrared thermal imaging camera (FLIR A615) and the light source was provided by ShangHai GuCun Optic Instrument Factory (model ZF-7A hand UL traviolet ray examining lamp, 16W 365/254 nm).

Results and discussion

FT-IR

Fig. 1 shows FT-IR spectra for the MSTP doped different concentrations of EVA film. It is observed that an increase in concentrations increases the intensity of the C-H bending bands

in $-\text{CH}_3$ and $-(\text{CH}_2)_n$ groups, i.e. the peaks at 1466 cm^{-1} and 1372 cm^{-1} , and C-H stretching bands at $2800\text{--}3000 \text{ cm}^{-1}$ ¹³. The appearance of peaks at 1736 cm^{-1} is correspond to the stretching vibration of $\text{C}=\text{O}$. The bending vibration of C-H at 719 cm^{-1} belongs to the $-\text{CH}_2$ groups of EVA as enlargement at right in Fig. 2. As doping the MSTP concentrations from 0 wt% to 0.8 wt%, the new bending vibration of C-H at 730 cm^{-1} appeared and increased. The bending vibration of C-H splits into two peaks, owing to the MSTP molecules into the EVA crosslinking network structure. And the more MSTP doped EVA, the more obviously peak in 730 cm^{-1} and the crystalline regions rearrangement. This indicates the MSTP molecules embedded into crosslinking network, which affect the structure of the degree of crystallinity and protect and avoid UV damage.

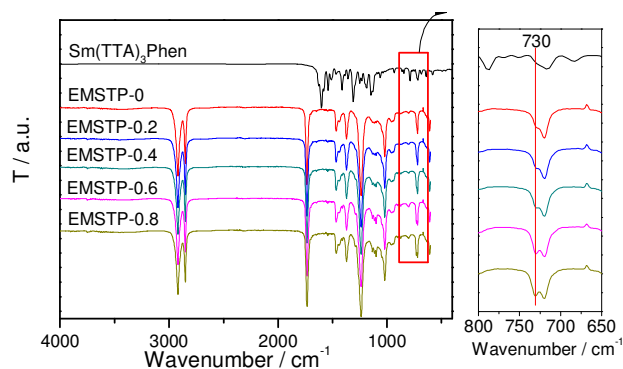


Fig. 1 FTIR spectra of MSTP powder and MSTP doped EVA films in different concentration from 0-0.8 wt% (left: $400\text{--}4000 \text{ cm}^{-1}$ full spectrum, right: $650\text{--}800 \text{ cm}^{-1}$ enlargement).

PL

The absorbance and emission of EMSTP films characteristic are shown in Figure 2. It can be seen in the Figure 2(a) that the pure EMSTP-0 only can weakly absorb UV before 270 nm. However, the MSTP doped EVA film have a broad and strengthen ultraviolet absorption from 250 nm to 400 nm, because the organic of the MSTP powder has a strong absorption in UV light. And the more increased doped concentrations from 0.2 wt% to 0.8 wt%, the stronger absorption UV light. After the doped concentration of 0.2 wt%, the growth of absorption rate slowed that because of optical transmission impact in film. Owing to the effect of residual solvent tetrahydrofuran (THF), the pure EVA (EMSTP-0) has a strong absorption peak in 270 nm. As doping the MSTP concentrations from 0.2 wt% to 0.8 wt%, the 345 nm UV absorption peak is wider and stronger. The emission spectra (Fig 2(b)) are similar to the excitation spectra regular. The luminescence spectra are similar in which there are three main peaks: 564, 600 and 645 nm, corresponding to $^4\text{G}_{5/2} \rightarrow ^4\text{H}_{5/2}$ ($j=5/7/9$) transition of Sm^{3+} ion. With the increase of doped concentration, the emission peak intensity has also enhanced. And the rate of increase leveled off with increasing concentration.

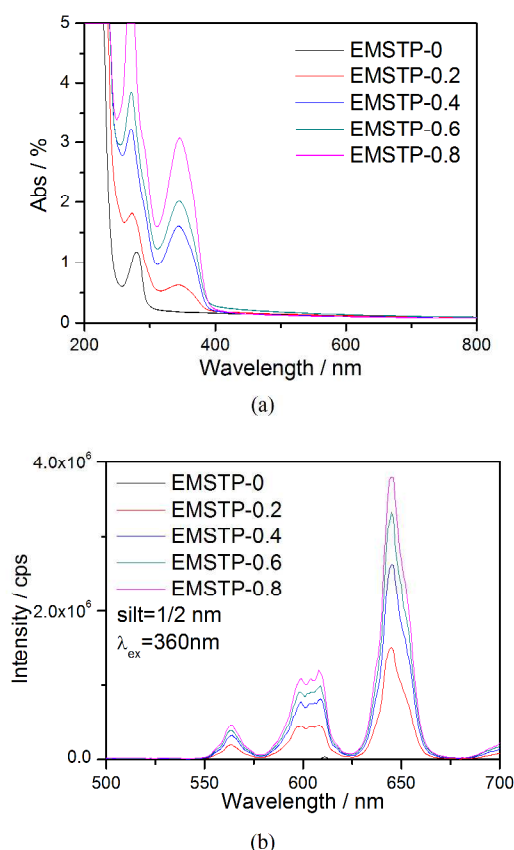


Fig. 2 Room-temperature (25 °C) absorbance (a) and emission (b) spectra of MSTP doped EVA films in different concentration from 0-0.8 wt%, all samples were excited with a 360 nm.

FSEM

Using microwave ultrasonic assisted synthesis MSTP powder diagram is shown in Fig 3(a). The size of small rectangular particle is nearly about 3-5 μm , which uniform more than using previous coprecipitation synthesis powder (Supplementary Fig. S1). This reveals that the controllable particle rare earth organic complex size can be obtained by ultrasonic microwave synergistic effect that effect can changed the surface properties of the particles of powder. Fig 3(b) exhibits the 0.8 wt% MSTP particle distribution in EVA film by scanning electron micrograph. Since the growth mechanism of MSTP, the MSTP dissolved in THF and re-growth so that the presence in the EVA film particle is slightly smaller than the size of the powder. Other differences distribution of content is similar, except that the concentration and aggregation of the dispersed. The MSTP particles have excellent dispersibility in EVA film that can ensure transparent the sunlight and improve optical conversion efficiency. The MSTP particle connected with long-chain of polymer EVA, which can reduce MSTP ultraviolet degradation.

Transmission

Transmission measurements are performed through several points of each of the MSTP doped different concentrations of EVA film in order to confirm that no additional scattering of light is introduced by the molecules. The results are plotted in Figure 4(a). It is found that the transmittance of EMSTP descends rapidly from wavelength 400 nm and that of pure EVA film only

descends from 300 nm, which shows the MSTP doped EVA film has also a strong absorption in ultraviolet light. At gradual increased concentrations from 0.2 wt% to 0.8 wt%, the visible of transmission part has a slight decrease and ultraviolet absorption has increased. Especially, the 0.6 wt% transmission is higher than others MSTP doped EVA samples, because the antireflection effect. The Fig 4(b) photograph is the physical map transmission of EVA films doped with MSTP in different concentration from 0-0.8 wt%. The EVA film appeared slightly yellow with increasing MSTP weight.

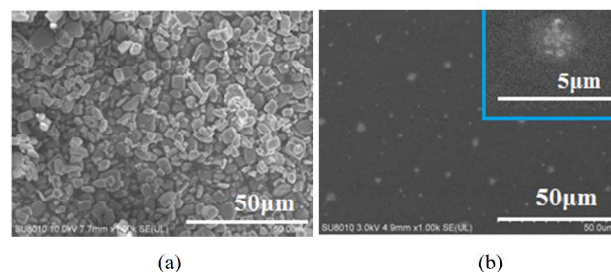


Fig. 3 FSEM images of MSTP powder via microwave ultrasonic method (a), the surface of a representative 0.8 wt% film of MSTP on EVA (b).

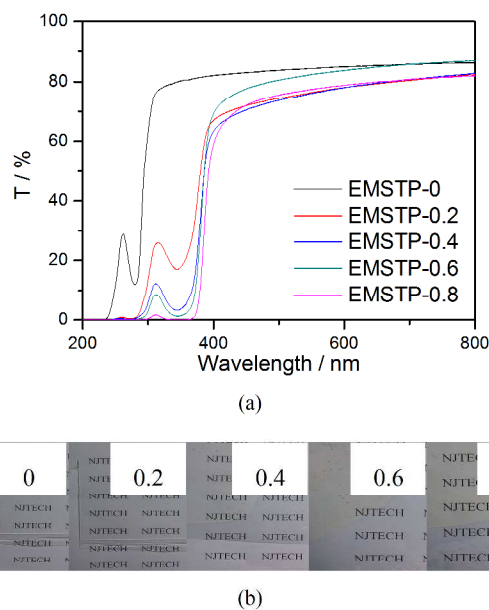


Fig. 4 Transmission (a) UV-vis spectra and optical images (b) of MSTP doped EVA films in different concentration from 0-0.8 wt%.

Aging ATR-FTIR

Influences from photo-oxidation on the surface of pure EVA (EMSTP-0) and doped 0.8 wt% MSTP EVA films (EMSTP-0.8) are first characterized through ATR-FTIR. As presented in supplementary Fig. S2 of spectra, notable formation of functional groups in EMSTP-0 and EMSTP-0.8 appear during UV irradiation. According to supplementary Fig. S2 calculation, the carbonyl index (CI) values ($CI = A_{1718}/A_{2850}$)^{14,15} of specific functional groups are listed in Table 1. The EMSTP-0 and EMSTP-0.8 are appeared corresponding degradation infrared peaks. On one side stand for the new generation carbonyl $\nu_{C=O}$ stretching in the slowly forming that close to zero ketone structure, which growth at the absorption shoulder at 1718 cm^{-1}

and another broad band with an absorption maximum at 1176 cm^{-1} . It might be obtained during the acetaldehyde evolution process in Norrish III photolysis reaction. On the other side of the absorption band around 1735 cm^{-1} and the emergence of new carbonyl vibration at 1778 cm^{-1} is mostly due to the lactone formation reported by Allen. Variations in A_{1718}/A_{2850} , A_{1176}/A_{2850} and A_{1778}/A_{2850} all indicate that ketone forms more intensively during the first 400 h exposure than the latter irradiation.

Combining the obvious O-H bands at $3600\text{--}3200\text{ cm}^{-1}$ (supplementary Fig. S2(f)) is higher 1.06 times than pure EVA (supplementary Fig. S2(f)) without irradiation. This data can infer that hydrogen bonding¹⁶⁻¹⁹ forms between the MSTP and EVA chain. Then, the A_{3500}/A_{2850} decreased tendency at irradiation, because the hydrogen bonding is crack and rearrange with the

temperature increase at irradiation.

As the elongation of time, A_{730}/A_{2850} refers to the methylene crystallization peak a first growing and then dropping tendency. The EMSTP-0.8 methylene crystallization first growth 0 h is bigger than that of EMSTP-0, which indicates that the MSTP into the EVA crosslinking network make the methylene crystalline region more closely aligned. Then, methylene crystalline regions thermal motion increased, the degree of orderly arrangement reduced with the UV irradiation time. At last, owing to the heat energy, the methylene group activities improve to increase the ability of rearrangement of crystalline. The data analysis reveals that MSTP added in crosslinking structure enhance EVA resistance to UV light radiation.

Table 1 CI of pure EVA and MSTP doped EVA films in 0.8 wt% concentration irradiated for various time from ATR-FTIR spectra.

Sample	Aging time (h)	$V_{\text{crystalC-C}}$	$V_{\text{O-C=O}}$	$V_{\text{C=O}}$	$V_{\text{lactoneC=O}}$	$V_{\text{O-H}}$
		A_{730}/A_{2850}	A_{1735}/A_{2850}	A_{1718}/A_{2850}	$A_{1176}\times 10^{-4}/A_{2850}$	$A_{1778}\times 10^{-4}/A_{2850}$
EMSTP-0	0	0.017	2.111	--	0.532	1.349
	100	0.021	2.063	--	0.525	0.206
	400	0.009	1.865	--	--	0.196
	800	0.008	1.777	--	--	0.782
EMSTP-0.8	0	0.039	2.423	0.009	1.759	1.593
	100	0.014	2.202	0.003	1.114	0.645
	400	0.007	2.015	--	0.471	0.851
	800	0.008	1.913	--	0.737	0.885

Aging PL

Comparing with the previous the data published of SiO_2 coated and uncoated MSTP samples²⁰, the aging behavior of fluorescence highest intensity of EVA films doped with MSTP in 0.8 wt% (EMSTP-0.8) is shown in Fig. 5 at 400 h UV radiation. And, the calculation of decay percentage is characterized by photoluminescence at room temperature (25°C). The intensity of curve of EMSTP-0.8 is higher and flatter than others, especially, before 100 h irradiation. After exposure for 400 h, the decay percentage of EMATP-0.8 is 1.79 times (75 %) of that in SiO_2 coated (42 %) and 3.41 times uncoated MSTP (22 %). The phenomenon might be the MSTP particles are bound by a crosslinked structure that restrictions bond movement and reduce the non-radiative energy loss. Thus, fluorescence decay intensity slowly decreased at UV light radiation. The EVA long chain and MSTP particle decreased the rate of ultraviolet degradation through mutual protection mechanism.

FLTR

The temperature of pure EVA (EMSTP-0)(left) and MSTP doped EVA films in 0.8 wt% concentration (EMSTP-0.8)(right) at 365 nm and 254 nm UV irradiation (16W) for 120 h are shown in Fig. 6 via thermal imaging and visual imaging. First, the temperature of EMSTP-0 is close to EMSTP-0.8 without irradiation. Then, as prolonged UV radiation, the EMSTP-0.8 is lower temperature than EMSTP-0, and the temperature difference increased. Because of the UV lamp irradiated from top to bottom, the heat temperature transport heat from top to downward. Due to the MSTP low high effect and high efficiency of the down-shift conversion luminescence, the heat energy conversion to light energy is achieved. As it is proved at the end, the MSTP particle can absorbed UV light and converted into visible energy, which can transfer heat energy to light energy. Hence, the MSTP doped

EVA film has lower temperature than pure EVA film and simultaneously reduce the UV degradation.

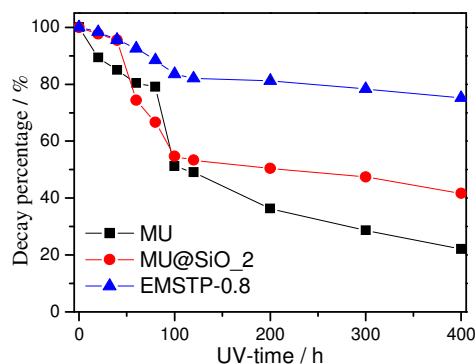


Fig. 5 Aging behavior of fluorescence highest intensity of MSTP doped EVA films in 0.8 wt% (EMSTP-0.8) and previous the data published of SiO_2 coated and uncoated MSTP samples (Ni et al.²⁰ ©2013 J Mater Sci) at room temperature (25°C).

Mechanism

The proposed mechanism molecular chain structure and three-dimensional network structure for MSTP doped EVA polymer are shown in Fig. 7. When the EVA crosslinking process between some long-chain, MSTP particles are embedded in the crosslinking structure. EVA crosslinking structure could absorb ultraviolet energy and transfer energy to MSTP through hydrogen bonding (Fig. 7(b)(right)), which can continuous converted UV energy to visible light. The proposed mechanism ensured that the heat energy of destroy the structure timely dissipate in the form of light energy. The EVA network structure is not susceptible to UV degradation and long-term stability turn light energy.

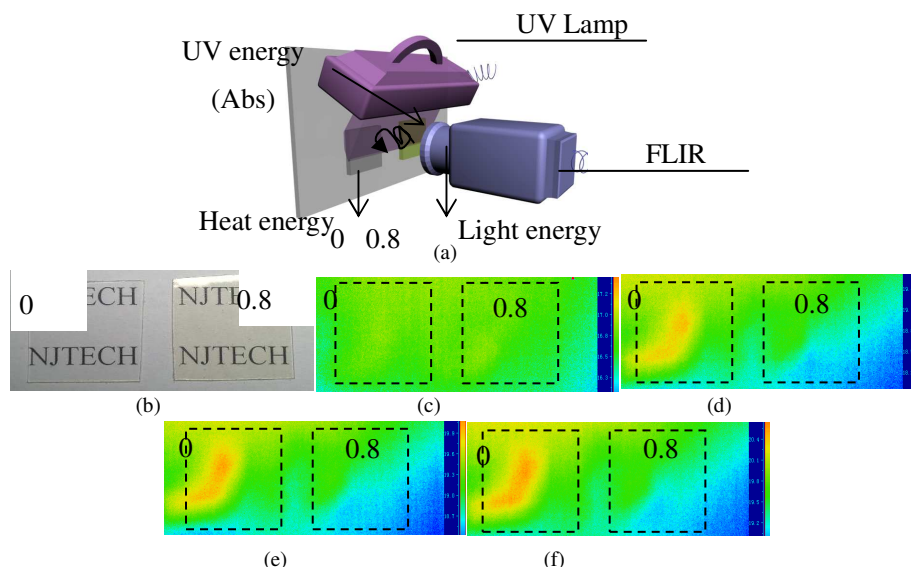


Fig. 6 Thermographic images of pure EVA (0)(left) and MSTP doped EVA films in 0.8 wt% concentration (0.8)(right) at UV irradiation (16W@365/254nm) for various time tests simulate picture, (b) optical image, (c) UV radiation 0 min, (d) UV radiation 30 min, (e) UV radiation 90 min, (f) UV radiation 120 min.

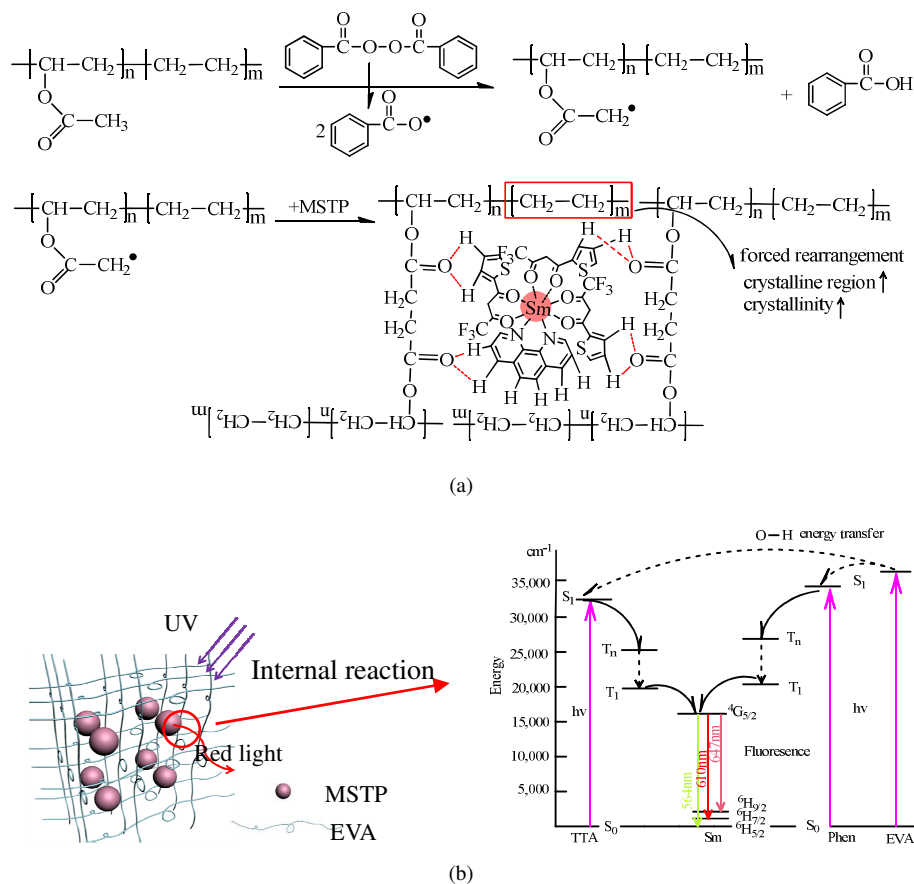


Fig. 7 Proposed mechanism for MSTP doped EVA polymer and energy transfer. (a) molecular chain structure of hydrogen bonding, (b) three-dimensional network structure (left) and energy lever (right).

Conclusion

The Work presented in this paper has shown that EVA rare earth organic complex composites can provide effective mutual protection on both UV degradation and light conversion properties. The proposal mechanism might be that the MSTP particles are bound by a crosslinked structure via hydrogen bonding that restricts bond movement and reduces the non-radiative energy loss. Then, EVA chain transfer energy to the MSTP, which the MSTP convert light energy, which can obviously decrease heat energy. The adjustable and uniform REOC MSTP materials have been successfully synthesized via microwave ultrasonic technique. The absorption UV light of doped EVA descends rapidly from wavelength 400 nm and that of pure EVA film only descends from 300 nm and the visible transmission has decreased slightly, especially, the 0.6 wt% exhibits the best visible transmission. The higher MSTP doped concentration, the higher excitation, emission and absorption intensity in light. After exposure for 400 h UV radiation, the emission intensity decay percentage of EMATP-0.8 (75%) is the best of previous research (22%, 42%). The work demonstrated that EVA rare earth organic complex composites with perfect network structure and excellent adhesion properties are effective mutual protection for avoiding ultraviolet degradation.

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