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Preparation and Characterization of Polypropylene Grafted with ULP containing Europium as Photoluminescence Films

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Summary

The films generating photoluminescence have unique properties for various applications. In this work, the chemical or covalent bonding between unsaturated linear polyester (ULP) containing rare earth Europium (Eu) complex (Eu-ULP) and polypropylene (PP) was introduced through a melt-grafting polymerization, which led to an improved approach for the preparation of photoluminescent films. Eu-ULP was synthesized, and then grafted onto PP in melt phase to render the resin fluorescence-active. The grafted PP was systematically characterized using various analytic tools including TG, IR, DSC, WAXS and fluorescence. The results indicated that Eu-ULP was covalently grafted onto polypropylene backbones. The findings from DSC and WAXS measurements revealed that Eu-ULP acted as a nucleating agent, increasing the crystallization rate effectively and destroying the integrity of crystalline as well.

Introduction

Rare earth (RE) polymers generally refer to polymers with rare earth ions doped in or bonded on. Woff[1] pioneered the research on RE polymers and studied fluorescence and laser properties of $Eu(TAA)_3$ (TAA: thenoyltrifluoroacetone) in PMMA in 1963. Since then, a number of functional RE polymers have been synthesized; and RE polymers have been employed as various functional materials including fluorescent, laserable, protective and optic ones [2]. There are two type of RE polymers: one is doping-type in which RE chemical compound is uniformly dispersed in polymer matrix as a doping; the other is bonding-type in which RE ions are bonded onto macromolecular chains directly [3]. Compared with the bonding-type, doping-type RE polymers have disadvantages in application due to the poor dispersion of RE complexes in polymer matrix. The doping-type RE polymers also create concentration quenching effect among fluorescence molecules, lowering the proportion of effective fluorescence molecules and weakening fluorescence intensity [4]. In contrast, bonding-type RE polymers allow the high RE concentration and strong light transmittance. At present, there are two approaches to synthesize bonding-type RE polymers: 1) RE ions coordinate with polymers containing coordination groups; 2) low molecular RE complexes take part in polymerization as monomers [5].

Polypropylene (PP) is a widely used material because of its outstanding mechanical properties and cost-effectiveness. Adding RE complexes to PP matrix further extends its applications, rendering PP photoluminescence. The previous research [6-7] has been mainly focused on polymers doped with RE complexes. This type of RE polymers, however, had limited applications due to the poor compatibility of RE complexes with polymers. Whereas RE complexes combining with polymers by chemical bonds can address such a problem. Li et al [8] grafted RE complex containing acrylic acid onto polyethylene films by UV-induced polymerization and conferred the RE complex having incorporate with polymer materials with chemical bonds. Zhang et al [9] improved the thermal stability and hardness of PVC by grafting RE acrylate in tetrahydrofuran solution. However, PP modification using bonding-RE complex approach has seldom been reported. This has stimulated stimulates our interest in developing an effective approach to utilize this method for PP modification. Nevertheless, rare earth complexes with excellent luminescence generally possess large steric hindrance of space, not allowing complexes grafting onto polymer backbone easily. Therefore, the key objectives of the research presented in this paper were to synthesize Eu-ULP containing unsaturated double bonds and then to melt-graft it onto PP backbone to produce the plastic resin emitting red fluorescence under UV. The modified PP was well characterized in order to establish the structure-property relation for the bonding-type RE polymers.

Experimental

Materials

Eu_2O_3 (99.9wt%) was purchased from Shanghai Yuelong Non-ferrous Metals Co. Ltd. and used without further purification. Polypropylene Y1600, was provided by Shanghai Petrochemical Co., Ltd. (Shanghai, China), with the melt flow index (MFI) of 16g/10min at 230°C, the weight-average molecular weight ($\overline{M}_w$) about 664000, and the number-average molecular weight ($\overline{M}_n$) about 81000. The unsaturated linear polyester containing rare earth (Eu-ULP) as grafting macromonomer was self-prepared. Chemical grade Diisopropylbenzene hydroperoxide (DCP), purchased from Shanghai Gaoqiao Petrochemical Co., Ltd., was used as an initiator. Other organic solvents were analytical grade and purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd..

Characterization

The content of Eu^{3+} in the polymer was determined by EDTA titration. IR-spectra were recorded on a Nicolet Magna 550 FTIR spectrophotometer; Fluorescence spectra were obtained using a Hitachi F-4 spectrophotometer. Thermal gravimetric analysis (TGA) was carried out with TGA-SDTA851E thermal analyzer and the heating rate was 10°C/min, the measurement was performed in the N_2 atmosphere. DSC measurements were conducted with a PerkinElmer (DSC7) thermal analyzer (Foster City, CA). The samples were heated up to 220°C at a rate of 20°C/min under a nitrogen atmosphere and maintained at 220°C for 5 min. Afterward, the samples were cooled to room temperature (20°C) at a rate of 10°C /min and held on room temperature for 5 min to destroy anisotropy. The samples were measured from room temperature to 220°C at a rate of 20°C/min, held for 5 min, and then cooled to room temperature at the same rate. Both melting and crystallization parameters were obtained from the heating and cooling scans. WAXS was performed using a Rigaku WAXS diffractometer (Janpan) set at 40 kV and 30 mA with Cu Kα radiation (λ=1.54056 Å).

Modification procedure

A Haake mixer (Rheocord System40) was used to prepare the grafted modified PP. The pre-determined amounts of PP pellets, Eu-ULP, initiator Diisopropylbenzene hydroperoxide (DCP), styrene and antioxidant agent 1010 were premixed manually in a small container prior to being charged into the mixing chamber. The mixing temperature, time, and rotor speed were maintained constant at 180°C, 5min, and 60 rpm, respectively for all runs. The grafted product was removed from the mixing chamber and added to liquid nitrogen to terminate any further reaction. Approximately 3g of the crude polymer was collected and completely dissolved in xylene at 140°C for 5 min, and then precipitated by the dropwise addition of the xylene solution into a 10-fold excess of acetone. The purification was repeated twice using acetone. Unreacted Eu-ULP and styrene, along with DCP and antioxidant agent, remained in the solution. The precipitated sample was filtrated out and dried to a constant weight at 110°C in a vacuum oven.

Results and discussion

Film discs of various samples were prepared by the compression-molding at 180°C for 5 min, producing the films with the thickness of 0.05 mm and 0.2 mm. Such films were used for FT-IR and fluorescence measurements. To determine the grafting efficiency, the same film samples were heated at 800°C for 2h and the remainder was dissolved in a diluted chlorhydric acid solution before EDTA titration. Grafting efficiency was calculated as follow:

$$G\% = \frac{m_{Eu-ULP}}{m_{PP}} \times 100\% \tag{1}$$

where G is the grafting efficiency. M_{Eu-ULP} and M_{PP} are the weights of Eu-ULP and PP for the processed product, respectively.

Structure of grafted PP

As Eu-UPL macromonomer is crucial for rendering the modified PP fluorescent, it is important to identify whether the Eu-UPL has been bonded on the PP backbond chemically. Figure 1 shows the FT-IR spectra of Eu-ULP, the original PP and the grafted PP. The typical absorption peak of methylene occurs at 1455 cm^{-1}, whereas the methyl absorption peak for grafting PP is shifted to 1372 cm^{-1} with the intensity higher than that of methylene. This suggests that backbone of PP had been incorporated with Eu-ULP. Meanwhile, compared to original PP, the C=O stretch vibration peak of carboxylate in the grafted PP appears at 1561 cm^{-1}, which originates from rare earth complex; the absorption peak at $1732cm^{-1}$ represents the carbonyl group which originates from the unsaturated linear polyester. Moreover, the absorption peak at $459cm^{-1}$ represents Eu-O, which originates from the Eu-ULP. The results above provide the evidence of the PP being grafted with the Eu-ULP.

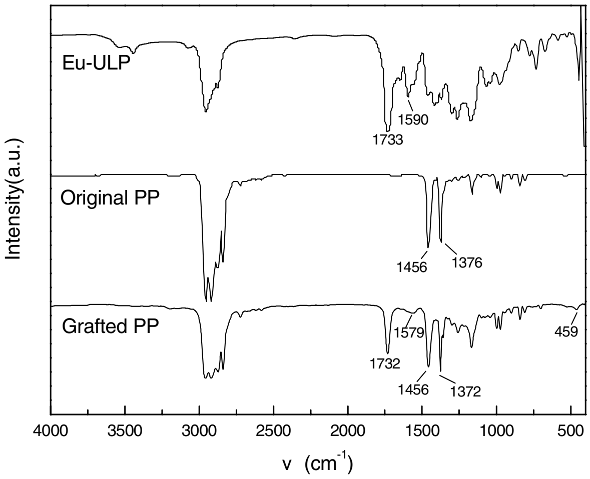

Figure 1. The IR spectrum of original PP and grafted PP

Table 1. Gel Content (wt) of the Grafted PP

No.	Original PP (g)	Eu-ULP (g)	Styrene (mL)	Grafting Efficiency (wt %)	Gel content (wt %)
1	100	10	2	8.90	0
2	100	12	2	10.54	0
3	100	15	2	12.23	0
4	100	20	2	16.94	0

In addition, the gel contents of the grafted PP at various unsaturated linear polyester /styrene levels were measured. Results are shown in Table 1. Clearly, zero gel content simply indicated that PP was only grafted by the unsaturated linear polyester containing rare earth and styrene, and did not form crosslinked or network structure. This implies that the grafted PP can be softened or melted for the follow-up application and cast into thin films readily, which is important in optical application.

Fluorescence of the grafted PP

If the original PP has been grafted with Eu-UPL successfully, the modified PP will possess strong fluorescence at the corresponding wavelengths. This can be found from fluorescence tests. Figure 2 shows the fluorescence spectra (excited at 270 nm) of the grafted PP with grafting efficiency ranging from 8.90 to 16.94%. At this excitation wavelength, the grafted PP emits visible and intense red fluorescence whereas the original PP cannot emit any color fluorescence. The modified PP with different grafting efficiency all exhibits typical fluorescence of Eu^{3+} that corresponds to $^5D_0 \rightarrow ^7F_j$ (j=0, 1, 2, 3, 4) transitions of Eu^{3+} 4f electron; and their emission peaks at 580, 592, 617, 650 and 699 nm successively in which $^5D_0 \rightarrow ^7F_2$ emission (about at 617 nm) is the most intense and emits typical red fluorescence of Eu^{3+} [10].

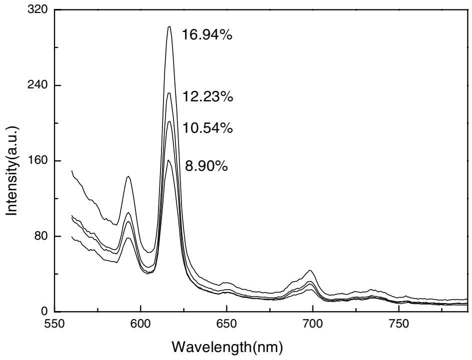

Figure 2. The emission (λ_{ex}=270nm) spectrum of grafted PP with different grafting efficiency

Figure 2 also shows that fluorescence intensity of grafted PP improves as grafting rate increases and reaches a maximum at 16.94% without typical emission concentration quenching. The possible explanation is Eu-ULP is distributed along PP chains uniformly and the distance between Eu^{3+} is relatively large, leading to the weak concentration quenching.

Table 2. Fluorescence Spectrum Data of Eu-ULP and Grafted PP Film

	λ_{ex}/nm (λ_{em}=617.0nm)	λ_{em}/nm (λ_{ex}=270.0nm)				
		$^5D_0 \rightarrow ^7F_0$	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_3$	$^5D_0 \rightarrow ^7F_4$
Eu-ULP	330.0	580.0	594.0	617.0	651.0	696.0
Grafted PP	270.0	580.0	592.9	617.0	650.0	699.0

To confirm that a chemical bond combination, instead of physical adsorption, occurred between the fluorescent Eu-ULP and the macromolecular film, their fluorescence spectra were recorded and the data are listed in Table 2. To facilitate the comparison, the spectra of Eu-ULP and the fluorescent film, their excitation spectra were measured with the same emission wavelength (i.e. 617.0 nm), and their emission spectra were measured with the same excitation wavelength (i.e. 270.0 nm). It can be seen that both the excitation and emission wavelengths of the fluorescent film, compared with their corresponding grafting macromonomer, show remarkable differences. It has long been known that the fluorescence of rare earth complexes results from the intramolecular energy transfer from organic ligands to rare earth ions — that is, the ligands absorb excitation energy, and the rare earth ions exhibit fluorescence when they are excited with the ultraviolet light absorbed by ligands [8]. The differences show that the coordination environment of the rare earth ions has been changed in the fluorescent films compared with the corresponding Eu-ULP. The finding above clarifies the fact that chemical bond combination, instead of simple physical adsorption, has occurred between the fluorescent Eu-ULP and the grafted films.

Thermal analysis of the grafted PP

The Eu-UPL may not only create the fluorescence for the modified PP, but also potentially influence the crystallization behavior of PP. To further identify the role of Eu-UPL in the crystallization of PP, thermal measurements based on TGA and DSC were conducted.

TGA results for both original PP and grafted PP are illustrated in Figure3. The results showed the grafted PP had a higher decomposition temperature, 311.6°C, while that of the original PP was 252.5°C. This indicated that the grafting improved the heat resistance of PP.

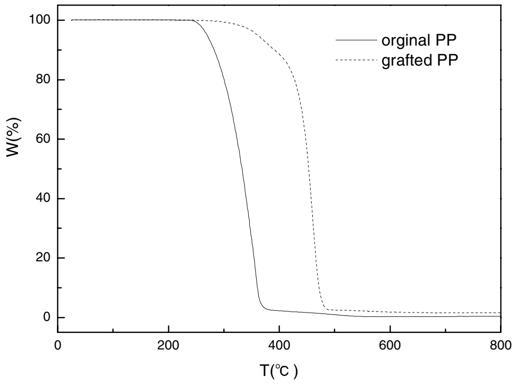

Figure 3. TAG curve of original PP and grafted PP

The crystallization parameters of the original PP and grafted PP obtained from the heating and cooling scans are given in Table 3. The $\triangle H_f$ and $\triangle H_c$ are the melting and crystallization enthalpies of the samples, respectively. The crystallization peak temperature (T_c) represents the temperature at the maximum crystallization rate. T_c of grafted PP is about 8°C higher than that of the original PP. The observed crystallization behavior of grafted PP can be explained in terms of heterogeneous nucleation. In a certain range of grafting process, Eu-ULP functions as a heterogeneous nucleating agent for PP homopolymer, which accelerated the nucleation rate and allowed the nucleation to occur at a higher temperature. As a result, the shortening of half crystallization and the crystallization induction period of the grafted product were observed (see Table 3). Change in the crystallization peak width ($\triangle T_c$) represents the variation in the homogeneity of the crystallization; and a narrower value of $\triangle T_c$ means a faster nucleation rate. The $\triangle T_c$ value for grafted PP is about 6°C narrower than that of the PP homopolymer (46.2°C) that further proves that Eu-ULP acts as a nucleating agent in crystallization process and improves the crystallization effectively. $\triangle H_c$ of grafted PP (87.7 J/g) is lower than that of original PP (97.3 J/g), suggesting that the crystallinity of PP reduces for the nucleation of Eu-ULP decreasing the crystal size and enlarging its defect after PP being grafted with Eu-ULP.

The melting temperature (T_m) of PP-g-Eu(AA)$_3$(phen) is lower than that of PP (167.6°C), resulting from the detoraited regularity of PP crystal caused by melt-grafting as well as PP chain degradation occurred in the process of melt grafting. Moreover, $\triangle H_f$ and the melting peak width ($\triangle T_m$) of grafted PP are lower than those of PP homopolymer, which is attributed to the heterogeneous nucleation of Eu-ULP for PP crystallization decreasing the crystallinity of PP. These results indicate that the crystallites in the grafted PP are less perfect than those in the original PP.

Table 3. Values of Original PP and Grafted PP from DSC

Content of Eu-ULP(%)	T_c(°C)	$\triangle T_c$(°C)	$\triangle H_c$(J/g)	T_m(°C)	$\triangle T_m$(°C)	$\triangle H_f$(J/g)
0	108.7	46.2	97.3	167.6	69.0	92.3
16.94	116.5	40.1	89.7	161.9	62.8	85.4

WAXS analysis of grafted PP

To reveal the impact of the grafting modification on the crystal structure or crystallite size of PP, WAXS measurements were performed. The crystallite size (*D*) vertical to the lattice plane (*hkl*) can be obtained according to the Scherrer's equation [11]:

$$D = k\lambda/\beta\cos\theta \tag{2}$$

where k is the factor of the crystal figure, taking k=0.89. λ is the wavelength of the X-ray (λ=1.54056 Å, taking Å=0.1 nm), and θ is the diffraction angle. β is equal to $(B^2 - b_0^2)^{1/2}$, where B is the width at half-tallness of the diffraction peak and b_0 is the broadening factor of the instrument. If we take no account of the lattice distortion, the equation can be simplified as follows:

$$D = K\lambda/\beta\cos\theta = 0.89\times1.54056\times57.3 / B\cos\theta \tag{3}$$

Table 4. Crystal Parameters of Original PP and Grafted PP from WAXS

Content of Eu-ULP(%)	Hk1	2θ	d_{hk1}(Å)	I(%)	B(o)	D(Å)
0	110	14.10	6.28	100	0.43	181.7
	040	16.90	5.24	44.1	0.37	209.0
	130	18.56	4.78	31.9	0.39	203.7
16.94	110	14.00	6.32	100.0	0.52	152.0
	040	16.72	5.30	99.3	0.42	188.2
	130	18.46	4.80	35.1	0.42	190.9

The results of WAXS for original PP and grafted PP are shown in Table 4. In Table 4 *I* is the relative intensity of the crystalline peaks and *B* is the peak width at half height, d_{hkl} is the space between lattice planes (*hkl*). As shown in Table 4, both curves exhibit scattering angles at 2θ=13.92, 16.66, and 18.40, indicating a α-phase monoclinic structure [12]. *The d* spacing of grafted PP has slightly changed while *D* decreases. The results can be explained by the heterogeneous nucleation induced by Eu-ULP. The nucleation accelerates the crystallization in which the growth of grains is restricted for their crushing each other in the course of their growing. As mentioned previously, the over-dosing of Eu-ULP onto the backbones of PP tends to decrease the crystallinity as well as the perfectibility of spherulites.

Conclusions

The unsaturated linear polyester containing rare earth (Eu-ULP) has been successfully grafted onto the backbones of PP in the presence of a free-radical initiator DCP through a melt-grafting polymerization. As a result, a novel bonding-type RE polymer material with favorable workability, emitting red fluorescence under UV, has been created. This material possesses desirable fluorescence intensity and color purity. The preparation of the materials is also relatively easy and cost-effective. The resulting RE-grafted PP is of great potential as antiforgery film, photoluminescent display materials, lighting transformation agricultural film and so on. The results of DSC and WAXS characterizations demonstrated that the functional groups introduced in PP also acted as nucleating agents which promoted the crystallization of PP and destroyed the integrity of crystalline simultaneously.

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