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ORIGINAL PAPER

Preparation of PP-g-PEG by using partial pre-irradiated polypropylene as initiator and its properties

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Abstract Polypropylene (PP) grafted with poly(ethylene glycol) acrylate (PEG acrylate) was prepared through melting reaction with partial pre-irradiated PP (rPP) as initiator and its properties were investigated. Along with the increase of the PEG acrylate content, the grafting degree of functionalized PP increased, while the degradation of PP was accordingly alleviated. The PEG grafts on the PP backbones may act as nucleating agent of the crystallization of PP. The crystallization temperature of PP-g-PEG gradually increased from 111.8° of PP to 118.9°, and the size of spherulites gradually decreased with increasing the amount of PEG acrylate grafts. Comparing to that of pure PP, the contact angles of functionalized PP film decreased from 112.2° to 88.2° and the surface energies increased from 15.85 to 30.34 mJ/m^2 when the PEG grafting degree was 5.62%. And the number of blood platelet adhesion was also obviously decreased onto the functionalized PP film compared to that of pure PP.

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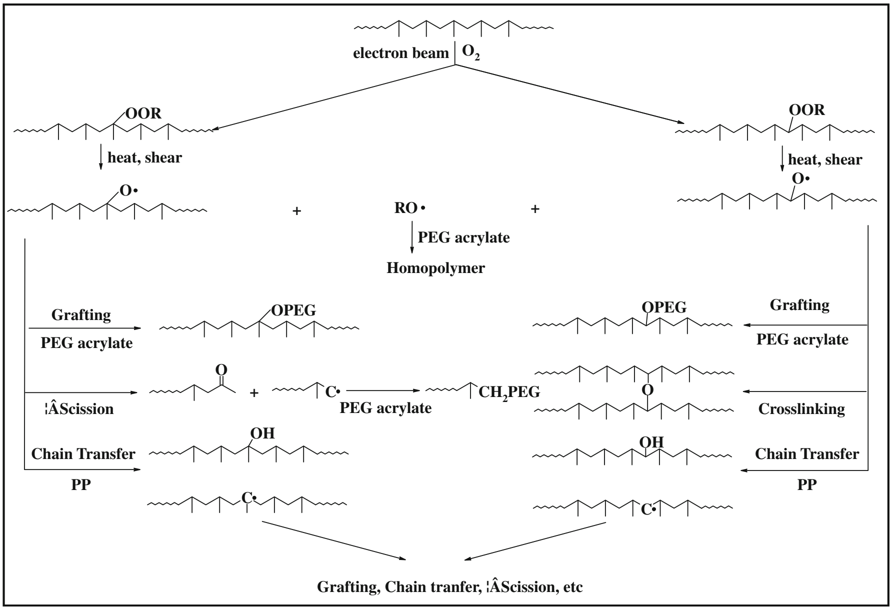
Introduction

Because of its good mechanical properties and relatively low cost, polypropylene (PP) is a polymer widely used in our daily life. However, its application field has been largely limited due to its hydrophobic properties. For instance, compatibilizers must be added when it is blended with some other polar polymers [1]. Recently, in order to enhance the surface polarity or hydrophilicity of PP films [2, 3], post-irradiation treatment of the film in the presence of some polar monomers [4–7] were often carried out. Nevertheless, this method is costly and complicated in processing. Another compromising technique to make up this disadvantage consists in using a functionalized polymer instead of the neat polymer to prepare the film [8, 9]. In this case, the chain scission occurring to PP during the functionalization process cannot be avoided, which will result in the poor processing and mechanical properties of the final products. A lot of efforts have been taken to solve this problem during the last few decades [1, 10, 11]. The pre-irradiation technique is a clean and effective method for modification of polymers. This technique has been widely used due to its relatively simple operative conditions, long storage periods of the intermediate products, and low content of formed acrylic homopolymer formation compared with conventional adding initiator technique [12]. Recently, in our lab Cai et al. [13] have successfully reduced PP chain scission with partial pre-irradiated PP as initiator in the preparation of acrylic acid grafted PP (PP-g-AA).

Poly(ethylene glycol) (PEG) has been widely used in materials science and biotechnology [14, 15] due to its low toxicity and good biocompatibility. It has also been commonly applied to functionalize [16, 17] or be blended [18, 19] with some other polymers in order to improve their biocompatibility. In this article, PP grafted with PEG acrylate (PP-g-PEG) was prepared by melting process with partial pre-irradiated PP as initiator to improve the biocompatibility of PP. Compared to those conventional grafting processes involving peroxides such as Benzoyl peroxide (BPO) and Dicumyl peroxide (DCP) as initiators, this method should not only cause less chain scission side reactions but also avoid the release of toxic debris in the final products. This non-toxic functionalized PP has much potential application in biomedical area.

In this article, PP-g-PEG was prepared by using partial pre-irradiated polypropylene as initiator and its properties were investigated. The detailed grafting mechanism has been added in Scheme 1 according to Cai's study [13] in our research group. When PP was pre-irradiated by electron beam in the air, the macromolecular peroxide and (or) hydroperoxide were formed [20, 21]. At high temperature, these peroxides decompose and directly form the polymeric free radicals. Then, these macromolecular free radicals initiated the grafting reaction, chain transfer reaction and β-Scission, and so on. Due to the good dispersion of macromolecular free radicals, the "cage effect" could be largely avoided in the grafting reaction.



Scheme 1 Schematic presentation of grafting PEG acrylate onto the pre-irradiated polypropylene

Experimental

Materials

Polypropylene homopolymer powder with Melt flow rate (MFR) of 13 g/10 min (2.16 kg, 230 °C) used in this study was manufactured by Jinlin Petrochemical Company of China. Poly(ethylene glycol) acrylate ($\overline{M}_n = 375$, $\mathrm{CH_2{=}CH\overset{\overset{O}{\|}}{C}(OCH_2CH_2)_nOH}$) was purchased from Aldrich Company. Pre-irradiated PP ($M_n = 1.03 \times 10^4$, $M_w/M_n = 2.30$) was prepared by PP irradiation under electron accelerator with a radiation dose of 15 kGy and a dose rate of ca. 1.1 kGy/s in Jifu New Material Company of China. Xylene and acetone were purchased from Beijing Chemical Factory of China. Human platelet-rich plasma (PRP) was kindly provided by Changchun Blood Center of China.

Preparation of PP-g-PEG

The grafting of PEG acrylate onto PP was carried out in a Haake internal batch mixer. The PP, rPP, and PEG acrylate (Table 1) were premixed in a high speed mixing machine and then added into the internal mixer at 190 °C with the rotor speed of 50 rpm. The graft reaction was continued for 5 min.

Table 1 Experimental recipe and grafting degree

Samples	PP (g)	rPP (g)	PEG acrylate (%)[a]	Oxygen content/%	Grafting degree/%	Grafting efficiency/%
1#	40	–	–	–	–	–
2#	32	8	0	–	–	–
3#	32	8	2	0.49	0.77	39.4
4#	32	8	4	0.94	1.96	51.0
5#	32	8	6	1.43	3.24	57.2
6#	32	8	8	2.33	5.62	75.9
7#	0	40	0	1.03	–	–

[a] PEG acrylate (%) was calculated by the addition mass of PP and rPP

Purification of PP-g-PEG

Crude PP-g-PEG (3 g) was dissolved in 100 mL xylene at 130 °C for 1 h and the hot xylene solution of PP-g-PEG was added into about 500 mL acetone to remove nonreacted PEG acrylate. The precipitated PP-g-PEG was filtered, washed with acetone for three times, and then dried in vacuum oven at 80 °C for 48 h.

FTIR analysis of PP-g-PEG

The purified PP-g-PEG films with the thickness of 10–100 μm were prepared by hot compression at 190 °C. The films were characterized using a Bruker Vertex 70 FTIR spectrometer operating from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} for 32 scans.

Elemental analysis (EA)

The content of elemental oxygen was determined by A Vario EL CHNOS Elemental Analyzer (elementar Analysensysteme GmbH). The samples were digested by using oxidative combustion. The quantitative digestion is based on the principle of explosive combustion in a highly oxygenated helium atmosphere and carried out in a combustion tube filled with CuO at a temperature of 950–1000 °C. A thermal conductivity detector (TCD) with a wide dynamic range and improved sensitivity to the carrier gas helium, served as the detector module.

GPC measurements

The molecular weight measurements of the virgin PP and the modified PP were performed on a high-temperature GPC (PL-GPC220). 1,2,4-Trichlorobenzene was used as the eluent. The samples were dissolved in trichlorobenzene at 150 °C, and the concentrations of the solutions were in the range of 2–3 mg/mL. The injected volume was 200 μL, and the eluent flow rate was 1.0 mL/min. The measuring system was maintained at 150 °C during the experiment.

DSC tests

The thermal properties of the grafted materials were investigated with a Perkin Elmer DSC-7 system. About 5–10 mg samples were sealed in Al crucibles. The samples were first heated from room temperature to 210 °C with the rate of 10 °C/min and kept at this temperature for 5 min to erase the thermal history, then cooled down to ambient temperature and heated again to 210 °C again with the rate 10 °C/min.

Polarized light microscopy (PLM)

The spherulites growth rates of pure and functionalized PP were observed via Leica optical microscopy with a hot stage. All the samples were preheated up to 200 °C, kept at this temperature for 3 min to eliminate the thermal history, then cooled down to 130 °C with the rate of 100 °C/min, and held at 130 °C for 10 min to follow the spherulite growth in isothermal conditions.

Contact angle tests

The determination of contact angle was conducted on a Drop Shape Analyzer DSA100 (KRÜSS company). A droplet of water (2 µL) was put on the surface of a film and the contact angle was measured. Five measurements for each sample were carried out for a single sample and the obtained values were averaged.

Platelet adhesion measurements

20 µL of fresh PRP was dropped on the center of PP and modified PP films, and the films were allowed to remain at 37 °C for 30 min. The films were rinsed with phosphate-buffered solution (PBS) and then treated with 2.5% glutaraldehyde in PBS for 30 min at room temperature. The samples were washed with PBS again and dehydrated by systemic immersion in a series of ethanol/water solutions (50, 60, 70, 80, 90, 100%, v/v) for 30 min and finally allowed to evaporate at room temperature. The platelet-attached surfaces were coated with gold prior to being observed by SEM.

Results and discussion

Table 1 shows the elemental analysis results of ungrafted and grafted samples. Based on the oxygen content in pure PEG acrylate molecule, the grafting degree that refers to the weight of PEG grafted with respect to the total weight of graft copolymer can be calculated accordingly ($\mathrm{GD} = \frac{\mathrm{O}_{\mathrm{sample}}\% - \mathrm{O}_{\mathrm{rPP}}\% \times 20\%}{37.92\%} \times 100\%$). It was found that the oxygen element content in the samples and the grafting degree increased gradually with increasing the dosage of PEG acrylate added in the grafting systems. The grafting efficiencies that refer to the weight of PEG graft with respect to the amount fed into the mixer in these PP-g-PEG systems are quite higher than those in the PP-g-MAH system initiated by peroxides [1, 10, 20]. This increasing trend of graft degree can also be reflected as the intensity increase of the carbonyl absorption band at 1734 cm^{-1} in FTIR spectrum of the grafted products, as shown in Fig. 1. The absorption band of carbonyl vibration in pure PEG acrylate was at 1725 cm^{-1}. The observed shift can be ascribed to the disappearance of the α C=C bond in PEG acrylate molecule after it was grafted onto PP chain.

Figure 2 shows the relationship between grafting degree calculated and the ratio of the areas of the absorption bands at 1734 and 841 cm^{-1} (the absorption band at 841 cm^{-1} is the characteristic of the helix band of propylene unit in isotactic polypropylene). This linear relationship is quite similar to those obtained in PE-g-AA- and PE-g-GMA-grafted systems [22].

The molecular weights of the grafting products determined by GPC are shown in Table 2. It is quite clear that if PP and rPP are just simply mixed in proportion without melt blend, the molecular weights of PP/rPP mixture could be calculated from that of pure and radiated PP accordingly. In this system, the value should be $M_n = 2.64 \times 10^4$, which is much larger than that of Sample $2^\#$. This result indicates that PP should also be largely degraded during the melt-mixing process initiated by the radicals raised from rPP. As the graft degrees of PEG are relatively low in all our samples (See Table 1), the molecular weight increased from sample $3^\#$ to sample $6^\#$ should not be ascribed to the increase of PEG side chains, but owing to the less degradation of PP backbones. And the amount of rPP was the same, so macromolecular radical concentration should be equal in each sample. As there was no so called "cage effect" in our grafting system, PEG acrylate would be easily initiated by the macromolecular radicals produced by rPP, which will largely enhance the grafting reaction and alleviate the degradation of PP [1, 10].

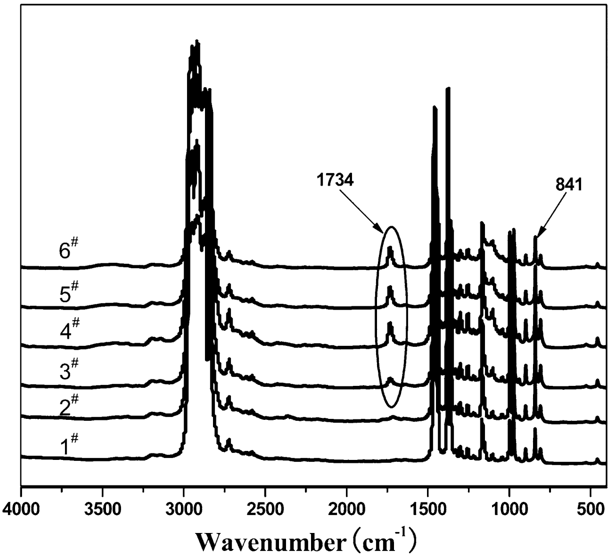


Fig. 1 FTIR spectra of PP and functionalized PP

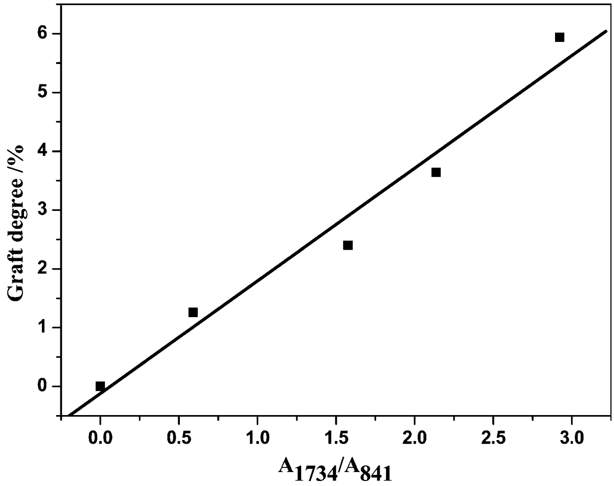


Fig. 2 Quantitative relationship between grafting degree and IR for PP-g-PEG

Table 2 Molecular weight of the samples

Samples	M_n × 10^4(g/mol)	M_w × 10^4 (g/mol)	M_w/M_n
$1^{\#}$	3.04	14.7	4.84
$2^{\#}$	1.64	5.80	3.56
$3^{\#}$	2.48	7.95	3.20
$4^{\#}$	2.66	9.23	3.46
$5^{\#}$	2.69	8.97	3.34
$6^{\#}$	2.83	11.7	4.14
$7^{\#}$	1.04	2.39	2.30

DSC curves of PP and functionalized PP samples are shown in Fig. 3. From Fig. 3 and Table 3, the crystallization peak) temperature (T_c) of functionalized PP shifted to higher temperatures along with the increase of PEG dosage in the product, ranging from 111.8° of PP to 118.9°. This result indicated that the PEG grafts on PP backbones could act as a nucleating agent in the crystallization of PP. The crystallization temperature of sample $2^{\#}$ that is higher than that of pure PP should be ascribed to the shorter PP molecules in sample $2^{\#}$. However, as the molecular weight increased rather than decreased from graft copolymer sample $3^{\#}$ to $6^{\#}$, the crystallization temperature increased should not be ascribed to the molecule degradation, but the nucleating effects of PEG grafts. Figure 3b shows the melting curves of neat PP and functionalized PP. The shoulder peak at high-temperature side decreased gradually with the increase of graft degree in the functionalized samples, which inferred that addition of PEG acrylate affected the perfection extent of crystalline spherulites.

It was also verified from PLM micrographs reported in Fig. 4 that the size of crystalline spherulites decreases when the PEG grafts are present on the PP backbones and acts as nucleating agent; it can also be observed that the spherulite dimensions further decrease with the increase of grafting degree.

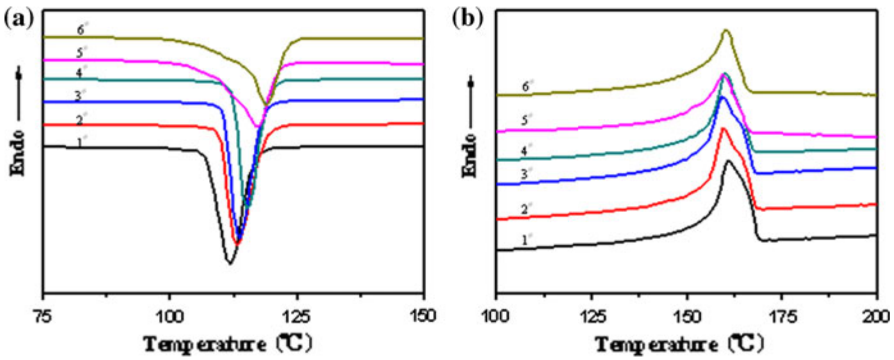


Fig. 3 Crystallization and melt curves of PP and functionalized PP (**a** crystallization curves; **b** melt curves)

Table 3 Crystallization temperature of PP and functionalized PP

Samples	$1^{\#}$	$2^{\#}$	$3^{\#}$	$4^{\#}$	$5^{\#}$	$6^{\#}$
T_c/°C	111.8	113.2	113.6	115.2	117. 2	118.9

In general, contact angle measurements are the most convenient way to evaluate the hydrophilicity characteristics of the films. From Fig. 5, the contact angle value decreased with the increase of PEG acrylate content, reaching a minimum of 88.21° for sample $6^{\#}$, compared to a value of 112.17° for neat PP. The solid surface free energy was obtained by Neumann's equation as follows [23, 24]:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}}\, e^{-\beta(\gamma_s-\gamma_l)^2}$$

where γ_s represents the surface free energy of PP and functionalized PP, and γ_l represents water surface energy which is 72.80 mJ/m^2. β is the constant coefficient which is equal to 0.0001247 [25]. According to the results of surface energy, it increased from 15.85 for PP to 30.34 mJ/m^2. It could be explained that polyethylene glycol is a hydrophilic molecule, and, as expected, when it grafted onto PP, the polarity of PP increased.

The morphology change and number of the adhered platelets are considered to be an early indicator of thrombogenicity when blood contact foreign materials. Figure 6 shows the SEM pictures of the PP and Sample $6^{\#}$ films exposed to PRP for 30 min. It was found that numerous adherent platelets were aggregated and deformed on the non-functionalized PP film. On the other hand, platelet adhesion was effectively suppressed on PP-g-PEG film. This phenomenon could not be simply explained by the hydrophilic surface properties of PP-g-PEG film, which was usually thought to result in more platelets adhesion. However, owing to the good solubility of PEG in water [26], the PEG grafts on the surface of functionalized PP film should have relatively good mobility and mostly extend when the film was soaked into the aqueous solution. These highly stretched PEG

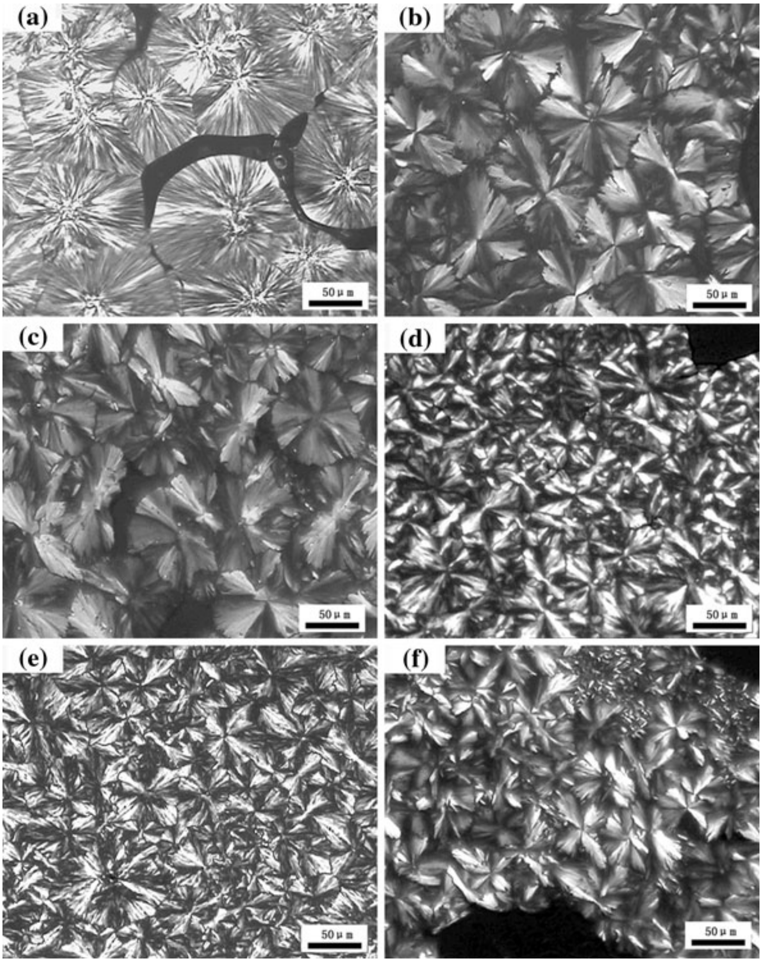


Fig. 4 PLM pictures of PP and functionalized PP (**a**—1#, **b**—2#, **c**—3#, **d**—4#, **e**—5#, **f**—6#)

molecule chains would prevent platelet molecules from approaching the film surface with strong steric exclusion force [27–30]. This steric repulsive force between PEG molecule chains and platelet molecules not only comes from the loss of conformation entropy of PEG molecule chains but also relates to the osmotic interaction between them when the platelet molecules were approaching to the PEG grafts onto the PP-g-PEG film [29, 31, 32].

Conclusions

Pre-irradiated PP could be used as an initiator to graft poly(ethylene glycol) acrylate onto PP. According to the results of FTIR, PEG acrylate indeed grafted onto PP

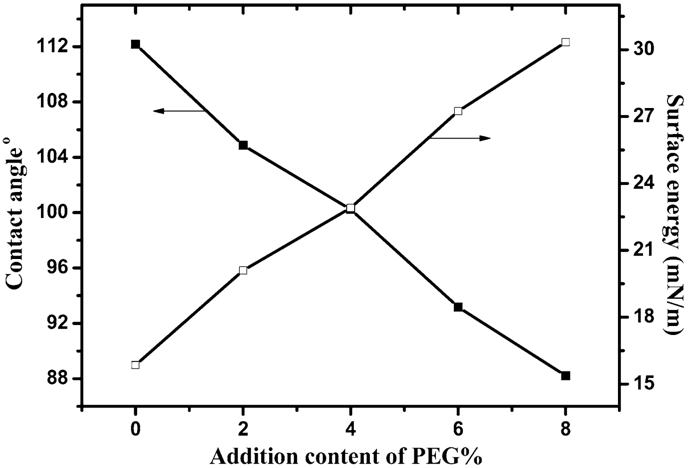


Fig. 5 Contact angle and surface energies of PP and PP-g-PEG films

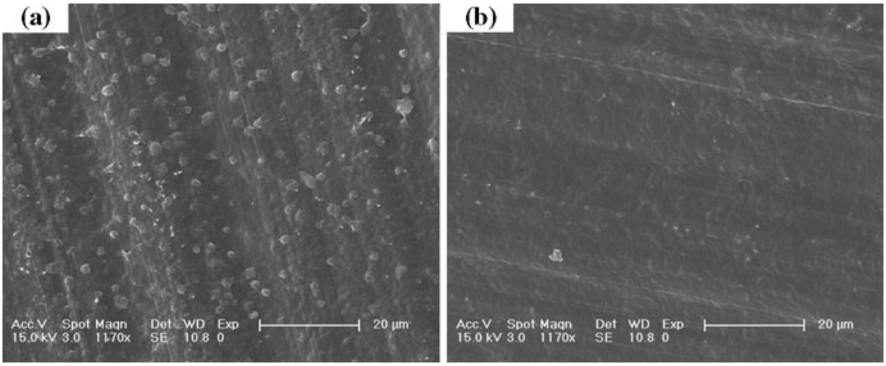


Fig. 6 SEM pictures of adhesion of platelets on the films (**a**—PP, **b**—PP-g-PEG (6#))

molecules. Compared to the conventional grafting process, higher grafting degree that can reach 5.62% and lower degradation of PP from GPC results could be obtained. DSC and PLM results showed that the crystallization temperature of PP-g-PEG gradually increased from 111.8° of PP to 118.9° of functionalized PP with grafting degree of 5.62%, and the size of the crystalline spherulites gradually decreased with increasing the dosage of PEG acrylate grafts. It demonstrated that the grafted PEG acrylate could act as nucleating agent of the crystallization of PP. After PP modified with PEG, the hydrophilicity of PP film increased, exhibiting that the contact angles decreased gradually with increased dosage of PEG acrylate addition, namely from 112.2° to 88.2°and the surface energies increased from 15.85 to 30.34 mJ/m^2. Platelet adhesion test results showed that the number of platelet adhesion onto PP film obviously decreased compared with pure PP.

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