Preparation of High Polarity Polypropylene Packaging Films

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Abstract: To improve the polarity of polypropylene (PP) packaging materials, Glycidyl methacrylate and Styrene were applied as co-monomer and grafted onto polypropylene molecules by radiation method. The properties of grafted PP films were characterized by differential scanning calorimeter (DSC), contact angle instrument and mechanical measurement. The results showed that the polarity, printability, lamination performance and thermal stability of PP film increased after grafting which demonstrates that grafting by radiation is an effective way to broaden the application of ordinary PP materials.

Keywords: polypropylene; pre-radiation; grafting; polarity; flexible packaging

1. Introduction

Polypropylene (PP) is one of the most promising thermoplastic polymer materials nowadays. It is widely used in automobile, household appliance, packaging and other industries.

As flexible packaging materials, the consumption amount of polypropylene film ranks second and accounted for 30% in plastic films. According to the processing methods of polypropylene film, PP can be divided into IPP (blow film), CPP (cast film), and BOPP (biaxial oriented polypropylene).

PP is mainly used as the outer or the inner layer material of the flexible packaging. The outer layer (printing layer) is generally formed by BOPP. CPP with the heat-sealing is mainly used as the inner layer of the retort pouch.

According to different requirements, multilayer laminated films are mainly selected as packaging pouches, such as two-laminated and three-laminated layers. For most simple pouch materials like PET/VMCPP, ,the adhesion strength of general adhesive with aluminum foil of VMCPP is higher than the adhesion strength between aluminum foil and CPP, which lead to peeling between aluminum foil and CPP[1,2].So, to improve the polarity of PP could avoid the peeling between aluminum foil and CPP. In the same way, the phenomenon of layer separation in high temperature will reduce if the retort pouch was prepared by high polarity PP.

In addition, the organic solvents in ink or adhesive, especially toluene, can be easily absorbed by the low polarity PP materials and difficult to desorbed, it will result in the exceeding standard of toluene residual in final packaging products, while residue level of benzene are low in high polarity film.

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All the above features show that increase the polarity of PP is a way to improve its printing and composite performance. A technology that anhydride was grafted onto PP molecules by peroxide initiating method was reported by Li Jingze [3], and the modified PP was used in the production of the automobile bumper. Another technology that the polar monomer was grafted onto PP molecules by radiation method was studied by Yin Jinghua [4]. The modified PP has high adhesion strength with metals; it can be used as adhesive and compatilizer of polymer alloy.

In order to increase the polarity of PP film and improve its printing and laminating performance, the polar glycidylmethacrylate (GMA) monomer was grafted onto PP molecules by radiation method in this work. Styrene was added to the system as the second monomer so as to improve the ratio of grafting. The experiment results showed that increase the polarity of PP is helpful to improve the printing and packaging effect of PP films through grafting polar monomers by radiation method.

2. Experimental

2.1. Materials and analytical methods

PP powder, GMA and antioxidant raw materials were purchased from domestic chemical corporations. Water contact angles were measured by using a JY-82 contact angle analyzer. The DSC analysis was measured by DSC-200PC differential scanning calorimeter from Netzsch Co.Ltd, Germany. The temperature range varies from -50 to 230 centigrade temperature with rate of 10 centigrade temperature /min.

The mechanical properties of PP films were tested by an Instron 5565A electronic tensile testing machine manufactured by Illinois Tool Works Inc. The Ultimate Strength and Tensile Strength were measured under the standard of ASTM D638-03. The Bending Strength and

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Bent Modulus were measured under the standard of ASTM D790-03. The Strike Strength of Cantilever Grider Gap was measured under the standard of ASTM D256-06a. The Heat Distortion Temperature was measured under the standard of ASTM D648.Adhesion Strength of PP was tested under the standard of ISO 813. The modified PP was pressed into sheets of 150*150*2mm on a Plate Vulcanizing Press Machine. Then the sheets were laminated with standard 3M gummed tape to test a force required to separate two objects of standard bonded area.

The ink absorbability was test under the standard ASTM D3359-97. It was evaluated of through detecting the amount of ink peeled off the pre-coated membrane on PP sheets.

2.2. Modification by radiation grafting

Take some PP powder into a sealed plastic button, puffed under pure nitrogen atmosphere at a rate of 10 L/min for 60 minutes to eliminate the rudimental oxygen. Then the PP powder material was radiated under Co60. After standing for 24 hours, the radiated PP material was co-mixed in a special proportion with un-irradiated PP powder, GMA, styrene and antioxidant in a high speed mix machine for 5mins. During the process of melt blending in the twin screw extruder, the graft reaction between GMA, styrene and PP took place. Some of the experimental data were shown in table.1.

Table.1 Melting blend conditions of modified PP

Sample No.	Melt Pressure /MPa	Current of mainframes /A	Feeding frequency /rpm	Host speed /rpm
0	1.51	16.2	9	300
1	1.50	14.4	9	300
2	1.40	16.2	9	299
3	1.52	16.2	9	299

3. Results and Discussion

3.1. Effects on Mechanical Properties

According to some references, the mechanical properties of PP is reduced dramatically because of degradation effect [5,6] while mechanical shear especially under conditions of oxygen or peroxide. So the free radicals on PP induced by Co60 radiation [7,8]. In this work, the PP sample was sealed under protection of nitrogen. The graft reaction was carried out in a twin screw extruder. Furthermore, styrene was added as co-monomer to increase the graft efficiency of GMA. The result in table 2 indicates that compared with the untreated PP sample(0#), the ultimate strength (tensile yield stress), tensile (break) stress, bending strength, bending modulus and strike strength of cantilever girder gap of the grafted PP reduced in different degrees because of the decomposition of PP macromolecule in the process of radiation and melt grafting.

Table.2 Physical properties of modified PP films

Sample No.	Ultimate Strength /Mpa	Tensile Strength /MPa	Strike Strength /kj·m^{-2}	Heat Distortion Temp./℃
0	35.4	24.5	9.3	102
1	32.1	10.1	2.4	103
2	34.0	18.4	6.0	104
3	35.0	18.7	5.4	105

The sample 1# prepared fully by irradiated PP as the raw materials, its mechanical properties were sharply decreased. This indicates that irradiation process could induce the decomposition of PP macromolecular. The structure and properties of irradiated PP is thus changed dramatically. Compared with untreated sample of 0#, the ultimate strength, tensile strength, bending strength and strike strength of cantilever girder gap of sample 1# were reduced by 9.3 percent, 59 percent, 11 percent and 74 percent respectively.

If adding some PP without irradiation used material into Formula of the grafted PP, the results show that mechanical properties were greatly improved. Compared with sample 0#, the ultimate strength, tensile strength, bending strength and strike strength of sample 2# were reduced by 4 percent, 25 percent, 4.5 percent and 35 percent respectively. This means that adding some PP without irradiation is helpful to enhance the mechanical properties.

3.2. Effect on Thermodynamics Properties

The recrystallization and melting temperature of samples were measured by DSC instrument. The results obtained from table 3 show the recrystallization temperature of grafted PP slightly increased, while the melting temperature reduced. The recrystallization temperature enhancement is attributed to the pp macromolecules which tend to be crystallization by GMA polarity chain segments at high temperature. The recrystallization temperature could be elevated to prolong the crystallization time of PP. This made the crystallization state tend to thermodynamic equilibrium state. So the thermal stability of grated PP could be improved further. This explanation of thermal distortion temperature is consistent with the variation of recrystallization temperature result.

Table.3 Recrystallization and melting temperature results

Sample	Recrystallization temperature/ ℃	Melting temperature / ℃
0	111	162
1	114	156
2	113	158
3	113	158

Whereas the order of PP molecular was destroyed by the introduction of polar monomer, which declined the ability of crystallization of PP. Along with the reduction of PP molecular mass induced by radiation, the melting temperature was decreased. The decrease of temperature during manufacturing process means upper production efficiency and lower energy consumption. However, because of heterogeneous nucleation of polar chains, the physical interconnections of PP molecular increased, thus improved the thermal stability of PP.

The two facts above are in accordance with the conclusion of reference [10]. When acrylic monomers were incorporated into the PP molecules, the nucleating point of samples increased and the crystals grew faster which caused spherulite formed by recrystallization to become small and intensive. It indicates that the grafting chains played a role as heterogeneous nucleation agent in the process of isothermal crystallization. Because of the final crystal habit is controlled by crystallization kinetics, the generated crystals caused by rapid crystallization had some changes. For example, the bulk density increased, the size decreased and the number of crystal defects also increased.

3.3 Effects on Polarity, Composite Performances

Contact angle value can indirectly demonstrates the polarity of PP resins. The test results of contact angle are shown in fig.1. It can be seen that the contact angle of sample 0# was 108.7°, which indicated that unmodified PP reject highly polar materials such as ink and binder etc. So the printing and composite properties of unmodified PP were poor. The contact angles of modified PP samples have a obvious declination compared with unmodified PP, especially in case of sample 3# of 90.9°. This means it could be wet with polar ink and binder materials much more easily, so the printing and composite properties of modified PP are good.

According to the standard of GB 8808-88, the modified PP slices were pressed with transparent adhesive tape of 15mm's width under a certain pressure. Then the peeling tests were taken. The values of average peeling forces were measured carefully, which were shown in fig.2. We can learn that the peeling force was only 2.5N for unmodified PP composite membrane. Whereas the average peeling forces for the samples with irradiation treatments have a 16～68% improvement.

The adhesion force of modified PP was tested under the standard of GB/T 13217.7-91. The samples of 0～3# were coated with ink carefully and let it dry completely. Then the numerical values of peeled off areas were measured, the adhesion forces of PP were shown in fig.2. It is obvious that the adhesion force of the modified PP have an apparent increase (1.1 to 3.8 times). The values were increased in a order from sample 1# to 3#. This indicated that the polarity of modified PP has a dramatic improvement and the polarity of modified PP makes a great contribution to the printing properties of PP membranes.

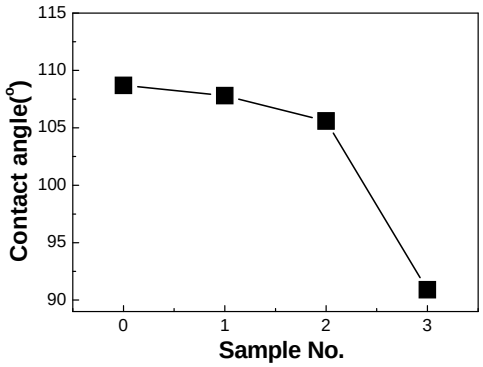

Fig.1 contact angle test result

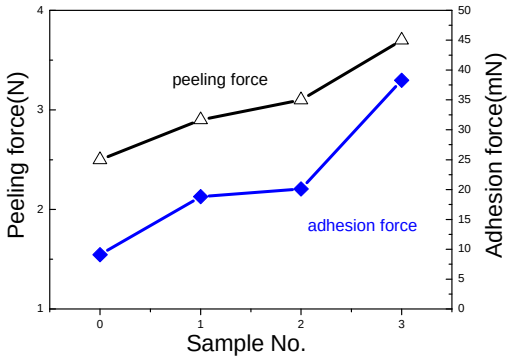

Fig.2 peeling force and adhesion test results

4. Conclusions

After grafting GMA polar monomer, properties of the resulting modified PP changed greatly. For example, the heat distortion temperature increased 3 centidegree, the processing temperature decreased 4 centidegree, the combined strength had increased 50%, and the ink adhesion increased 4 times. These results indicated that the printing property and composite performance of PP packaging materials were improved in this way. The decrease of processing temperature means higher production efficiency and lower energy consumption.

5. Acknowledgment

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