

Study on Polypropylene - Acrylic Block Copolymers as Additives in UV Curable Coatings

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Abstract

Polypropylene - acrylic block copolymers have been developed for additives in UV curable coatings which give excellent adhesion to polypropylene substrates. In this study the factors affecting the coating performance properties have been investigated. The results show that the balance of the compatibility and the adhesion to polypropylene substrates is achieved through controlling the melting temperature, the molecular weight and the chemical structure of the block copolymers.

Introduction

Due to their high chemical stability, low price, excellent balance of physical properties and excellent recyclability, the amount of polypropylene (PP) used in automobiles, household electrical appliances and other molded articles has been increasing. However, coating properties of PP is generally poor because of its low surface energy, hence chlorinated polyolefins (CPOs) or acid modified polyolefins (APOs) have been widely used as adhesion promoters.¹⁻³

UV curable coatings have been intensively studied due to the high productivity, lower energy consumption and greatly reduced volatile organic compounds emission.⁴ PP is one of major target substrates for UV curable coating. UV curable coatings are mainly composed of acrylic monomers and oligomers which have too high polarity to obtain good adhesion to PP substrates. Hence, surface treatments on PP substrates are generally necessary such as physical treatments (corona treatment, plasma treatment)⁵⁻⁷ and chemical treatments (primer containing CPOs or APOs)⁸⁻¹⁰. These treatments require additional process steps. Many trials have also been done using CPOs or APOs as an additive for UV curable coatings, but it has been difficult for traditional CPOs or APOs to keep good balance between the adhesion to PP substrates and the compatibility with acrylic UV curable monomers and oligomers.

The goal of this study is developing a novel modified polyolefin as an additive for UV curable coatings which exhibit good adhesion to PP substrates without any surface treatments. This study investigates PP - acrylic block copolymers (PP-*b*-PAcs) composed of the PP block with different

molecular weight and crystallinity. Discussed is the relationship between the physical properties of the PP block and the resulting UV curable coatings performance such as the compatibility and the adhesive strength to PP substrates.

Experimental Section

Synthesis of PP-*b*-PAcs

Two type of propylene-based polyolefins with relatively low crystallinity and melting temperature (T_m) were used as the starting materials of PP-*b*-PAcs to give good adhesion to PP substrates even at no or low baking temperature which is a typical condition for UV curable coating system. After the propylene-based polyolefins were decreased in molecular weight by thermal chain scission to adjust the molecular weight, the double bonds residing chain ends of the polyolefins were thiolated with a thiol agent.¹¹ Acrylic monomers were polymerized radically under the presence of the thiolated polyolefins, and the propagating acrylic polymer radicals were transferred to the thiol groups to produce PP-*b*-PAcs.¹² Ethyl acrylate (EA) and acrylic acid (AA) were used as acrylic monomers to obtain the acrylics block with enough low T_g , flexibility, wetting and melting under the condition of this study.

Weight average molecular weights (M_w) were measured with gel permeation chromatography (GPC, Tosoh, HLC8120GPC) against narrow molecular weight polystyrene standards.

The heat of fusion (ΔH_f) and melting temperature (T_m) properties were measured with differential scanning calorimetry (DSC, Seiko Instruments, DSC6200, method: first cooling; 30 to -50 °C at -20 °C/min., first heating; -50 to 200 °C at 10 °C/min., second cooling; 200 to -50 at -20 °C/min., second heating; -50 to 200 °C at 10 °C/min.). The ΔH_f was determined during the first heating scan, and T_m was determined during the second heating scan.

Heat seal strength test

15% PP block (PP decreased in molecular weight prior to thiolation) toluene solution was coated onto a PP film (Futamura Chemical, OPP FOS #80) without corona treatment using No. 10 Mayer bar, which was dried for 24 hours at room temperature. The coated surfaces were superposed between themselves and heat sealed under the condition of 2 kgf/cm, 80 and 90 °C, and 10 seconds using No.526 Heat Seal Tester (from MYS Tester). Each specimen was cut to a width of 15 mm and peeled off under the condition of 5 kg weight and 100mm/min using RTG-1210 tensile tester (from A & D) to measure the peel strength. Tests were made three times and the result was expressed by the average value.

Formulation of UV curable coatings

The commercially available UV curable monomers used in the experiment were

1,6-Hexanediol diacrylate (HDDA), 1,9-Nonanediol diacrylate (NDDA), Tripropyleneglycol diacrylate (TPGDA), Pentaerythritol triacrylate (PETA), Trimethylolpropane triacrylate (TMPTA) and Dipentaerythritol hexaacrylate (DPHA). A polyester acrylate (Aronix M-8030, TOAGOSEI Japan) was used as a UV curable oligomer. 1-Hydroxycyclohexyl Phenyl Ketone (Irgacure 184, BASF) was used as a photoinitiator. The procedure of formulating the UV curable coatings is as follows:

- 1) PP-*b*-PACs was blended with the same amount of a monomer at 80 to 90 °C for 1 to 2 hours.
- 2) Other monomers (or oligomers) were added and mixed at 70 °C for 1 hour.
- 3) Compatibility of the coatings was checked after 24 hours at room temperature.
- 4) 5 wt% of photoinitiator was added to the coatings.

Adherence test of UV cured coatings on PP substrate

After the addition of photoinitiator into each coating, each mixture was coated on PP substrates (high modulus TPO, NY-10, TOPLA, Japan) with #30 Meyer bar, and then UV was irradiated with a mercury lamp (120 w/cm, ESC-1511U, EYE GRAPHICS, Japan) after or without heat treatment at 80 °C for 5 minutes. Slits reaching the substrate were scribed with cutter to make 100 crosscuts at intervals of 2 mm. Then, cellophane adhesive tape was applied and peeled off 5 times in the direction of 180 degrees to count the number of remaining crosscuts.

Results and Discussion

Physical properties of PP-*b*-PACs

Three PP-*b*-PACs, PBA-1, PBA-2 and PBA-3 were used in this study as shown in Table 1. The molecular weights of PBA-1 and PBA-2 and each PP block are almost the same, respectively, and there is a difference in the T_m and ΔH_f between the PP blocks. The PP blocks showed almost the same level of heat seal strength to PP films at 80 °C heat seal, but the PP block of PBA-1 showed higher heat seal strength than that of PBA-2 at 90 °C heat seal. On the other hand, the PP blocks of PBA-2 and PBA-3 have almost the same T_m and ΔH_f and have different molecular weight. The PP block of PBA-3 showed higher heat seal strength than that of PBA-2 both at 80 and 90 °C.

It is assumed that the adhesion property of PP-*b*-PAC will be dependent on the physical properties of the PP block. Next studies confirm that the relationship between the physical properties of the PP block and the adhesion property and the compatibility with acrylic monomers and oligomers of the resulting PP-*b*-PAC.

Table 1. Physical properties of PP-*b*-PAcs samples and the corresponding PP blocks

PP- <i>b</i> -PAcs	PP block				Heat seal strength (gf / 15 mm)		PP- <i>b</i> -PAC M_w ($\times 10^4$)
	M_w ($\times 10^4$)	T_m ($^{\circ}\text{C}$)	ΔH_f (J/g)				
				80 $^{\circ}\text{C}$	90 $^{\circ}\text{C}$		
PBA-1	2	70	54	45	120	3	
PBA-2	2	65	33	46	50	3	
PBA-3	3	65	32	110	130	4	

Compatibility of PP-*b*-PAC with UV curable acrylic monomers

Compatibility of PBA-1, PBA-2 and PBA-3 with UV curable acrylic monomers was investigated and the results are shown in Table 2. Each PP-*b*-PAC was dissolved in the acrylic monomers at 10 % PP-*b*-PAC content, the compatibility was observed after one day at room temperature.

Table 2. Compatibility of PP-*b*-PAcs with UV curable monomers

PP- <i>b</i> -PAcs	UV curable monomers			
	TPGDA	HDDA	TMPTA	PETA
PBA-1	Hazy	Hazy	Clear	Clear
PBA-2	Hazy	Clear	Clear	Clear
PBA-3	Hazy	Hazy	Insoluble	Insoluble

PBA-1 and PBA-2 were soluble in all of four acrylic monomers used in this study. PBA-3 showed poor compatibility and was insoluble in TMPTA and PETA. It seems that TMPTA and PETA are acrylic monomers with relatively higher viscosity and then the higher molecular weight of PBA-3 results in a more inhomogeneous mixing. From the comparison of PBA-1 and PBA-2, it is also confirmed that PP block with lower crystallinity related to T_m and ΔH_f gives slightly better compatibility of the resulting PP-*b*-PAC with UV curable acrylic monomers.

Chlorinated polyolefins and acid modified polyolefins available in the market are not soluble in acrylic monomers without help of a solvent. It is very interesting that PP-*b*-PAC is soluble in acrylic monomers without addition of any solvents. Probably the acrylic polarity and the block type chemical structure contribute to this effect.

Adhesion properties to PP substrate of UV cured coatings containing PP-*b*-PAcs

A series of UV curable coatings containing PP-*b*-PAC were formulated and the adhesion properties after UV curing was examined.

The effect of ΔH_f s of PP blocks on the adhesion to PP substrate

To make a comparison between PBA-1 and PBA-2, UV curable coating formulations were chosen as shown in Table 3 to obtain clear solutions containing either PBA-1 or PBA-2. The UV cured coating

film containing PBA-1 showed excellent adhesion to PP substrates, but the adhesion obtained from the film containing PBA-2 was poor. The difference between PBA-1 and PBA-2 is the ΔH_f of the PP block. The difference probably relates to the heat seal strength at 90 °C as shown in table 1, although the temperature is obviously higher than the UV curing condition in this study. It is assumed that higher crystallinity of PP block helps adhesion to PP substrate of UV cured coating film by some sort of mechanism, but further studies will be needed.

Table 3. Adhesion of UV cured coatings containing PP-*b*-PAcs onto PP substrate

UV curable coating formulation (wt%)				Solution Appearance	Cellophane adhesive tape test (remained / 100)
PP- <i>b</i> -PAcs		NDDA	PETA		
PBA-1	15	56.7	28.3	Clear	100 / 100
PBA-2	15	56.7	28.3	Clear	33 / 100

The effect of molecular weight of PP blocks and the PP-*b*-PAcs on the adhesion to PP substrate?

To investigate an effect of molecular weight of PP blocks and the resulting PP-*b*-PAC, we chose PBA-2 and PBA-3 and we formulated UV curable coatings containing either PBA-2 or PBA-3 as shown in Table 4. The result shows that higher molecular weight of PP block gives better adhesion to PP substrate. Although higher molecular weight of the resulting PP-*b*-PAC also be beneficial for adhesion in terms of stronger cohesive strength, the effect is assumed to be small in this case.

Table 4. Adhesion of UV cured coatings containing PP-*b*-PAcs onto PP substrate

UV curable coating formulation (wt%)				Solution Appearance	Cellophane adhesive tape test (remained / 100)
PP- <i>b</i> -PAcs		HDDA	PETA		
PBA-2	15	65-	20	Clear	0 / 100
PBA-3	15	72.5	12.5	Clear	86 / 100

The adhesion of UV cured coatings with PBA-1 and PBA-3

The adhesion of the UV cured coatings containing either PBA-1 or PBA-3 was compared and the results are shown in Table 5 and 6. In the coating formulation of Table 5, the UV cured coating containing PBA-3 showed slightly better adhesion, but the coating containing PBA-3 showed poorer adhesion than that of PBA-1 in the formulation of Table 6. The appearance of the coating solution containing PBA-3 in Table 6 is hazy, which suggests that good compatibility of the UV curable coating containing PP-*b*-PAC also play a key role to obtain good adhesion to PP substrates.

Table 5. Adhesion of UV cured coatings containing PP-*b*-PACs onto PP substrate

UV curable coating formulation (wt%)				Solution Appearance	Cellophane adhesive tape test (remained / 100)
PP- <i>b</i> -PACs		HDDA	M-8030		
PBA-1	15	65	20	Clear	90 / 100
PBA-3	14.4	41.1	44.5	Clear	100 / 100

Table 6. Adhesion of UV cured coatings containing PP-*b*-PACs onto PP substrate

UV curable coating formulation (wt%)				Solution Appearance	Cellophane adhesive tape test (remained / 100)
PP- <i>b</i> -PACs		HDDA	DPHA		
PBA-1	15	65	20	Clear	97 / 100
PBA-3	15	65	20-	Hazy	6 / 100

Effect of heat treatment prior to UV curing on adhesion to PP substrate

Chlorinated polyolefins and acid modified polyolefins are adhesion promoters which normally need heat treatment to obtain the maximum adhesion. In the case, the heat helps melting and wetting of the polyolefins based polymers. Therefore, the UV coating containing PP-*b*-PAC was coated on PP substrate and heated prior to UV curing at 80 °C for five minutes, and the effect on the adhesion to PP substrate was examined. The result is shown in Figure 1.

The adhesion is poor with no heat treatment prior to UV curing, the process which is usual for current UV curing coating system. There was also a tendency that use of an acrylic monomer with more functionality like DPHA deteriorated adhesion without heat treatment. The fast curing of the monomer with more functionality may result in negatively impacting adhesion to PP substrate. On the other hand, regardless the functionality of the acrylic monomer, adhesion of the UV cured coating to PP substrate improved dramatically. We estimate that PP block of PP-*b*-PAC melts and wets the surface of the PP substrate enough to render proper adhesion.

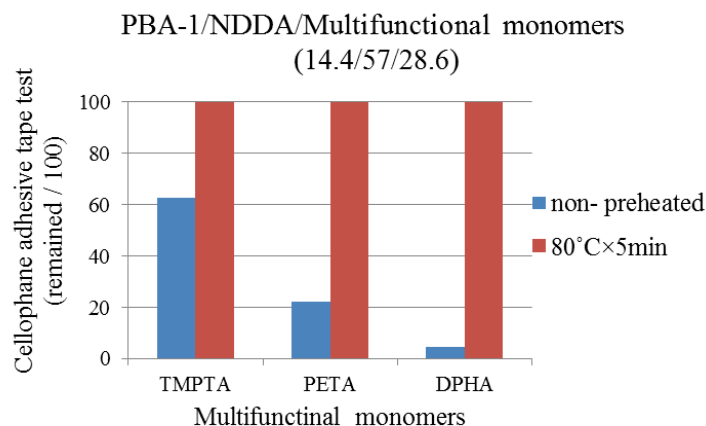


Figure 1. Effect of pre-heat treatment on adhesion to PP substrate

Mechanism of adhesion

In this study, we observed that adhesion strength of PP-*b*-PAcs to PP substrates is significantly affected by compatibility to UV coatings, M_w , T_m and crystallinity of PP block. We suppose that excellent adhesion can be obtained according to the steps described below:

- 1) PP-*b*-PAcs of good compatibility distributes uniformly in a UV curable coating.
- 2) PP block of the PP-*b*-PAcs adjacent to substrates makes ordered array on the surface of the substrates.
- 3) The PP block is melted and its wetting to the substrates is enhanced by pre-heat treatments.
- 4) The coating film with excellent adhesion is obtained after UV cure.

The coatings containing PBA-1 give better adhesion as compared to PBA-2 and PBA-3, indicating better compatibility and higher crystallinity (higher ΔH_f value) are favorable.

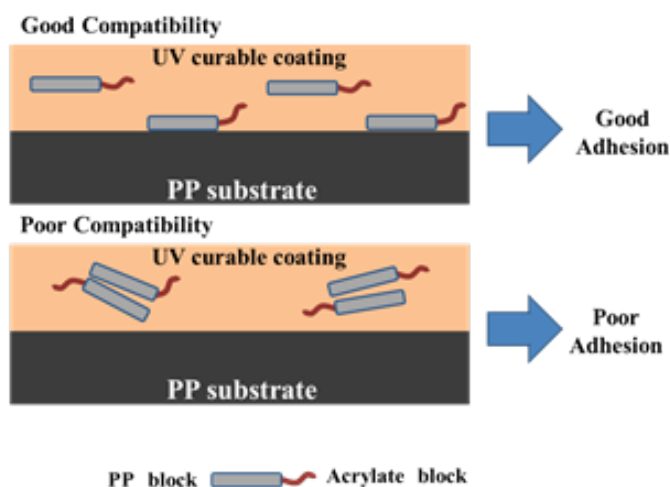


Figure 2. Mechanism of adhesion of the PP-*b*-PAcs

Conclusions

PP-*b*-PAcs were incorporated in UV curable coating system and exhibited good compatibility with UV curable monomers, which result indicates these block copolymers can be reasonably used in UV curable coatings. The UV curable coatings containing PP-*b*-PAcs exhibited excellent adhesion to PP substrates. This result is significant, since it has been difficult to achieve adhesion for UV curable coatings without primers or special substrate treatment.

M_w , T_m and crystallinity of PP block in PP-*b*-PAcs significantly influenced compatibility with UV curable monomers and adhesion to PP substrates, thus those properties should be taken into account when designing PP-*b*-PAcs.

By usage of the PP-*b*-PAcs, development of new UV curable coatings and inks for PP substrates is expected.

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