

Hard Coating Materials Using Copolymers of 2,5-dichlorobenzophenone and 1,4-dichlorobenzene

Min Jae Shin[†]

Department of Cosmetics and Biotechnology, Semyung University, Jecheon 27136, Korea
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Abstract

In this study, 2,5-dichlorobenzophenone was synthesized as a monomer using 1,4-dichlorobenzene, and subsequently, copolymers of benzoyl-*p*-phenylene and *p*-phenylene were prepared. The average molecular weight was improved using the low-molecular-weight polymer cutting method. The average molecular weight and glass transition temperature of the synthesized polymers were estimated. The as-prepared polymer was used as a hard coating material, and the coating was conducted on a poly(methyl methacrylate) plate. Furthermore, physical properties of the coatings, such as pencil hardness, adhesive strength, and abrasion resistance, were estimated. As the amount of *p*-phenylene in the copolymer increased, pencil hardness and abrasion resistance improved. The amount of *p*-phenylene in the copolymer can be increased to 30 mol% in order to increase the hardness of the coating, and the adhesive strength was insufficient for the copolymers with *p*-phenylene ratio greater than 35 mol%.

Keywords: Hard coating, Poly(benzoyl-*p*-phenylene), Copolymer, Hardness, Adhesive strength

1. Introduction

Hard coating materials (HCMs) are used in many applications and are used to protect the surfaces of soft substrates. HCM play a crucial role in increasing the commercial value of a material. Both organic and inorganic polymers are used for preparing HCMs. One of the representative inorganic-polymer HCM is a material prepared via the sol-gel reaction[1-5]. A thin glass layer is formed on the surface through the sol-gel reaction, which is one of the optimal methods to form a hard surface. The sol-gel reaction is conducted at a relatively low temperature. Although the temperature required is not more than 1000 °C, it should be more than 200 °C. Therefore, it is difficult to apply this technique to substrates that cannot endure 200 °C.

Many organic polymeric materials can be used as HCM. Most of the organic coating materials do not show a harder surface than that obtained using the coating via the sol-gel reaction. One of the strongest organic polymer coatings is achieved using poly(*p*-phenylene)[6-13]. Poly(*p*-phenylene) exhibits good mechanical properties, and numerous research results regarding its applications have been reported. However, because the melting point of neat poly(*p*-phenylene) is very high and finding a suitable solvent is difficult, molding poly(*p*-phenylene) is challenging. Therefore, certain functional groups are added to the phenylene ring in poly(*p*-phenylene) to improve the solubility of the polymer[14-23].

The hard coating was conducted on the polycarbonate plate using poly(benzoylphenylene)[24]. This hard coating showed 2H pencil hardness. In this study, 2,5-dichlorobenzophenone (DCBP) was synthesized and used as a monomer with 1,4-dichlorobenzene to prepare the copolymer of benzoyl-*p*-phenylene and *p*-phenylene. The low-molecular-weight cutting process was conducted to increase the molecular weight of the copolymer. These copolymers were used as HCMs.

2. Experimental

2.1. Materials and equipment

1,4-Dichlorobenzene (DCB), benzoyl chloride, Zn powder, aluminum chloride anhydrous, nickel(II) chloride, 2,2'-bipyridine (BPY), triphenylphosphine, tetrahydrofuran (THF), toluene, anhydrous ethanol, acetone, methanol, and N,N'-dimethylformamide (DMF) were purchased from Aldrich. The poly(methyl methacrylate) (PMMA) plate used in this study was a hand-made commercial product, with dimensions of 10 cm × 10 cm × 5 mm. Zn powder was sequentially washed with acetic anhydride and dry ether and dried at 150 °C in a vacuum oven. Triphenylphosphine was recrystallized with dry diethyl ether. DMF was dried using 4 Å molecular sieves for 2 days.

An FTIR spectrophotometer (IRSpirit, Shimadzu), an NMR spectrometer (Bruker Avance III 400 MHz), and a UV spectrometer (UV-1800 UV spectrometer, Shimadzu) were used for analyses in this study. A Viscotek TDA302 gel permeation chromatography (GPC) system was employed, and the PL gel 10 μm MIXED-B was used as a column. TGA and DSC analyses were conducted using TGA SDT 2960 (TA Instruments) and DSC Q2000 (TA Instruments) systems, respectively. Scanning electron microscopy (SEM) was performed us-

[†] Corresponding Author: Semyung University
Department of Cosmetics and Biotechnology, Jecheon 27136, Korea
Tel: *** - **** - **** e-mail: newminj@gmail.com

ing a Hitachi S-5200 system. A Cannon-Fenske type viscometer was used to measure the solution viscosity. A Pencil hardness tester 221D was used to measure the pencil hardness, and a Mitsubishi pencil was used for the hardness tests. An NDH-2000 (Nippon Denshoku) instrument was used as a haze meter, and the adhesive strength was measured using 3M Scotch tape. The abrasion resistance was measured using a Taber abraser Model KPM-042 (CS-10 wheel) instrument.

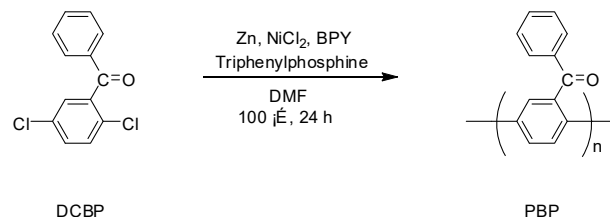
2.2. Synthesis of DCBP

First, 73.5 g (0.500 mol) of DCB and 70.3 g (0.500 mol) of benzoyl chloride were added to a 500 mL round-bottom flask with stirring. Thereafter, a calcium chloride drying tube was connected to the flask, and 133.3 g (1.00 mol) of anhydrous aluminum chloride was rapidly added to the flask. The temperature of the flask was increased to 100 °C, and the reaction was allowed to continue for 24 h. After the reaction, a small amount of water was added to quench the remaining anhydrous aluminum chloride. Sodium bicarbonate was used to remove the remaining benzoyl chloride. Extraction was conducted three times using toluene, and the solution was washed with water three times. Anhydrous sodium sulfate was used to dry the solution. The toluene solvent was removed using an evaporator. The product was recrystallized using ethanol and dried at 50 °C for 24 h in a vacuum oven. Very light pink colored 92.2 g (yield 73.4%) of DCBP was obtained. ¹H-NMR (DMSO-d₆): 7.56 (d, 1H), 7.60 (d, 1H), 7.67 (d, 2H), 7.71 (m, 1H), 7.73 (d, 2H), 7.76 (s, 1H).

2.3. Synthesis of poly(benzoyl-*p*-phenylene) (PBP)

DCBP (25.0 g; 0.0996 mol), Zn powder (19.5 g; 0.299 mol), nickel (II) chloride (1.29 g; 9.96 mmol), triphenylphosphine (10.4 g; 39.8 mmol), and BPY (1.56 g; 9.96 mmol) were added to a 100 mL of 3-neck flask. After a thermometer was connected, the nitrogen atmosphere was set up in the flask. Thereafter, 100 mL of anhydrous DMF was added to the flask, and the temperature of the flask was raised slowly with stirring. The solution turned deep orange at 40 °C, red at 60 °C, dark red at 80 °C, and radish black at 100 °C. The reaction was continued for 24 h. The product was gathered via precipitation in acetone. The product was washed with 5% HCl four times, with water three times, and finally with acetone. The product was vacuum-dried at 70 °C for 24 h, and 12.8 g (yield 71.3%) of PBP was obtained.

The removal of low-molecular-weight materials to increase the average molecular weight of the synthesized PBP was conducted. The synthesized PBP (9.02 g) was dissolved in 60 mL of THF, and every time, 5 mL of methanol was added consecutively until the precipitation was formed. The precipitate was gathered, and the process of dissolv-



Scheme 1. Synthesis of PBP.

ing PBP in THF and precipitating in methanol was conducted again. Finally, the obtained PBP was dried at 80 °C for 4 h under vacuum, and 5.87 g of PBP was obtained, and the yield of the low-molecular-weight cutting process was 65.1%.

2.4. Copolymerization of DCBP and DCB

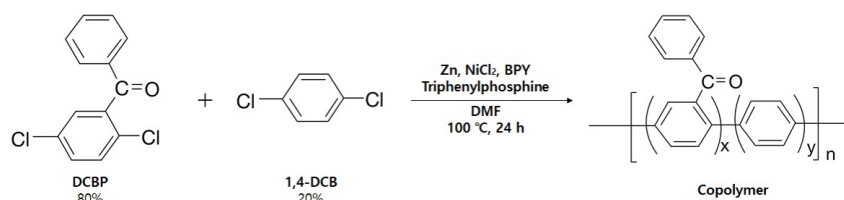
Several copolymers of DCBP and DCB were synthesized by varying the mole ratio in this study. A representative synthesis procedure of the copolymer with a mole ratio of 80:20 (DCBP: DCB) was described here. DCBP (10.0 g; 39.8 mmol) and DCB (1.46 g; 9.96 mmol) were added to a 100 mL 3-neck flask, and Zn powder (9.76 g; 149 mmol), nickel(II) chloride (0.645 g; 4.98 mmol), triphenylphosphine (5.22 g; 19.9 mmol), and BPY (0.778 g; 4.98 mmol) were also added. The copolymer was synthesized using a similar process that was used for synthesizing PBP, except that the washing process was different. The copolymer was washed with 5% HCl five times, and 5.49 g (yield 69.0%) of the copolymer was obtained. The process to increase the average molecular weight was the same as that used in the synthesis of PBP. The dissolution of copolymer in THF and precipitation in methanol were conducted twice. The process started with 5.27 g of the synthesized PBP, and 3.58 g was obtained with a yield of 67.9%.

2.5. Coating formation

The polymer solution was formed by dissolving polymeric material in THF. The coating was conducted via the solvent casting method. The solution was added dropwise on to the PMMA plate with dimensions of 10.0 cm × 10.0 cm × 5 mm. To remove the THF solvent, the coated plate was dried at room temperature (about 20 °C) for 10 h and then at 90 °C for 24 h. The drying process at room temperature for 10 h was essential to obtain a clean surface. When only drying was conducted at 90 °C for 24 h, the coating surface was very coarse.

2.6. Coating analysis

The hardness of the coating was measured using a pencil hardness tester. A Mitsubishi pencil, which was used to measure the hardness,



Scheme 2. Copolymerization of DCBP and DCB.

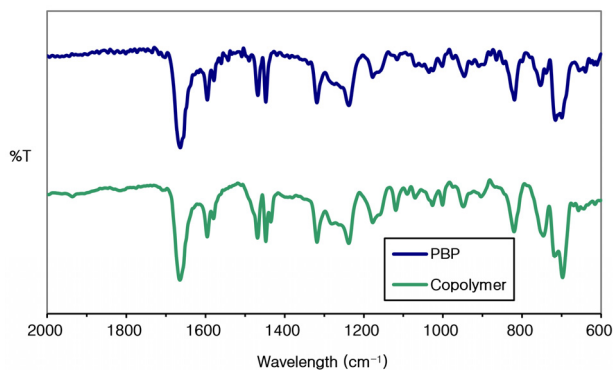


Figure 1. IR spectra of PBP and its copolymer (DCBP:1,4-DCB = 80:20).

was placed on the pencil hardness tester at a 45° angle with a 1 kg weight load.

The adhesive strength was measured using the cross-cut test method. First, 11 parallel cutting lines were made on the coating surface, and six parallel cutting lines perpendicular to the 11 cutting lines were also created. Finally, 50 squares were formed on the coating surface. Thereafter, 3M Scotch tape was attached to the 50 squares, and must be remained perpendicularly the excess tape. Using the remaining part of the tape, the tape on the coating was pulled perpendicularly. Afterward, the remaining coating-square number was counted.

Using the Taber abraser, the abrasion resistance was measured. Weight (500 g) was placed on the coating surface, and after turning for 500 rounds, the haze was analyzed for measuring the abrasion resistance.

3. Results and discussion

3.1. Synthesis of PBP and copolymer

DCBP was synthesized through the reaction of DCB with benzoyl chloride. Afterward, PBP was synthesized via the polymerization of DCBP. The copolymerization of DCBP with DCB yielded the copolymer of DCBP, and several copolymers were synthesized using different mole ratios. The IR spectra of PBP and copolymer with a mole ratio of 80:20 (DCBP:DCB) are shown in Figure 1.

The absorption of the carbonyl functional group was observed at 1650 cm^{-1} , and the absorption of para substitution in benzene ring was detected at 700-900 cm^{-1} in Figure 1.

The GPC was used to measure the weight average molecular weight (M_w) of PBP and copolymers. Polystyrene was used as the standard polymeric material, and an RI detector was used for detection. The viscosity was measured employing a Cannon-Fenske type viscometer using THF as a solvent. Glass transition temperature (T_g) was measured using DSC by increasing the temperature at a rate of 10 °C per minute. All the results are listed in Table 1.

From Table 1, the M_w of PBP was 57,600. The low-molecular-weight polymer cutting process, in which the synthesized polymeric material was dissolved in THF and then precipitated in meth-

Table 1. Physical Properties of PBP and Its Copolymers

Polymer	DCBP:DCB	M_w	T_g (°C)	η_{inh} (dL/g)
PBP		57,600	197	0.98
CPBP-10	90 : 10	52,100	189	0.95
CPBP-20	80 : 20	51,200	183	0.92
CPBP-30	70 : 30	51,800	178	0.90
CPBP-35	65 : 35	52,300	182	0.93

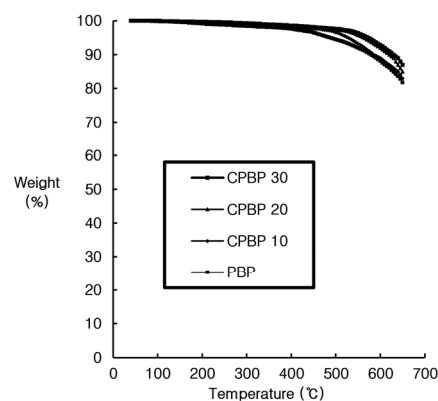


Figure 2. TGA data of PBP and its copolymers.

anol, was conducted twice in this study. The M_w of the PBP before this process was 51,400. Therefore, the M_w increased by 12.1% after the process. For CPBP-20, the M_w before the process was 43,700, and it increased to 51,200 after the process. Therefore, the M_w increased by 17.2% through the process. The M_w of the synthesized copolymers was in the range of 51,200-52,300, and this value was slightly lower than that of PBP. The viscosities of the synthesized copolymers were lower than that of PBP. The viscosity of PBP was 0.98, but the viscosities of copolymers were between 0.90 and 0.95. The lower viscosity might be because of the lower molecular weight.

The T_g of PBP was 193 °C, and T_g values of the copolymers were in the range of 178–189 °C. The lower T_g values of the copolymers were due to the increased flexibility while using two different monomers.

3.2. Thermal stability of PBP and its Copolymers

The thermal stabilities of PBP and its copolymers were measured using TGA. The thermal stability was measured under a nitrogen atmosphere at a ramp rate of 10 °C per minute from room temperature to 650 °C. The results are shown in Figure 2.

From Figure 2, all the polymers synthesized in this study showed excellent thermal stability, and negligible weight loss until 450 °C. For PBP, the weight loss started at 450 °C. For all the copolymers, the weight loss started at approximately 500 °C. Among the copolymers, CPBP-10 showed the fastest weight loss. Furthermore, CPBP-20 and CPBP-30 showed approximately similar weight loss curves, but the remaining weight at 600 °C of CPBP-30 was slightly higher than that of CPBP-20. Therefore, the order of thermal stability of the synthe-

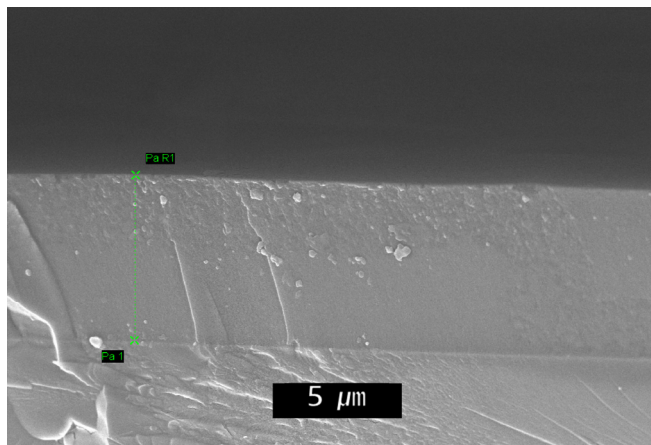


Figure 3. SEM image of the CPBP-20 coating.

sized polymers was CPBP-30 > CPBP-20 > CPBP-10 > PBP, implying that the phenylene part in the copolymer has more thermal stability than the part with the benzoyl side chain.

3.3. Solubility of PBP and its copolymers

The solubility of all synthesized polymers was tested in several solvents. It is challenging to find a suitable solvent for homo poly(*p*-phenylene), and therefore, poly(*p*-phenylene) is one of the most difficult polymers to process. However, because PBP possesses a benzoyl side chain, the solubility of PBP was improved significantly. PBP can be dissolved in THF, DCM, and chloroform. CPBP-20 can be dissolved in THF and chloroform. However, CPBP-20 suspended in DCM and cannot be dissolved completely.

3.4. Physical properties of the coatings

To examine the coating precisely, the SEM image of the coating was obtained. The coated plate was pre-treated by placed it in liquid nitrogen, and then, the plate was cut perpendicularly. SEM was used to observe the cut surface. An SEM image of the CPBP-20 coating is shown in Figure 3.

From Figure 3, the coating surface was very flat and uniform. The thickness of the coating was $6.30 \pm 0.2 \mu\text{m}$.

The hardness of the coating was measured using a pencil hardness tester. And the adhesive strength was estimated using the 3M Scotch tape. The results of the hardness and adhesive strength tests are listed in Table 2.

From Table 2, the pencil hardness of the coating was 1H for PBP, and it was improved to 2H in the case of CPBP-10. The hardness of CPBP-20 was slightly higher than that of CPBP-10, but the pencil hardness of CPBP-20 remained at 2H. For CPBP-30, the optimal pencil hardness has been shown in this paper. Therefore, as the mole ratio of *p*-phenylene in the copolymer increased, the pencil hardness increased. Attempts were made to measure the pencil hardness and adhesive strength of CPBP-40, but good results could not be obtained because it exhibited a low adhesive strength. Therefore, the result are not listed in Table 2. Moreover, the measured pencil hardness and adhesive

Table 2. Pencil Hardness and Adhesive Strength of the Coating with PBP and Its Copolymers

	Pencil hardness	Adhesive strength
PBP	1H	100
CPBP-10	2H	100
CPBP-20	2H	100
CPBP-30	3H	100
CPBP-35	3H	94

Table 3. Haze of Coating after the Abrasion Resistance Test

PBP	CPBP-10	CPBP-20	CPBP-30	CPBP-35
5.8	5.3	4.7	4.5	4.2

strength of CPBP-35 are listed in Table 2. The pencil hardness of CPBP-35 was 3H, and the adhesive strength was 94. CPBP-10, CPBP-20, and CPBP-30 exhibited sufficient adhesive strength values.

3.5. Abrasion resistance of the coating

The abrasion resistance was measured using a Taber abraser. After adding 500 g of weight and conducting 500 rotations, the degree of haze was measured using a haze meter. The results are listed in Table 3.

From Table 3, no significant increase in haze values is observed for all the cases, implying that all the coatings showed considerable abrasion resistance. In the case of PBP, the haze value was 5.8. In the case of all the copolymers, the haze values were smaller than that of PBP. Furthermore, as the mole ratio of phenylene increased, the haze value decreased, implying that the increasing phenylene ratio increases the abrasion resistance.

4. Conclusions

The copolymers of benzoyl-*p*-phenylene and *p*-phenylene were synthesized in this study. The average M_w values of the copolymers were in the range of 42,300–52,800, and the glass transition temperatures were 162–188 °C. Moreover, these copolymers were used as hard coating materials, and very good hard coatings were formed. As the mole ratio of *p*-phenylene in the copolymer increased from 0% to 30%, the pencil hardness increased from 1H to 3H. In addition, the abrasion resistance significantly increased. In the case of copolymers with >35% mole ratio of *p*-phenylene, the coating was not good because of the adhesive strength issue.

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Authors

Min Jae Shin; Ph.D., Professor, Department of Cosmetics and Biotechnology, Semyung University, Jecheon 27136, Korea; newminj@gmail.com