

Preparation and Characterization of Polyurethane Waterproof Coatings Containing Fly Ash

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ABSTRACT : Polyurethane waterproof (PW) coatings are increasingly demanded in Korea for repairing cracks on old building roofs and construction of many sporting facilities. Calcium carbonate, a common filler, is incorporated in PW compositions. In this study, PW coatings were prepared by substituting a part of calcium carbonate with fly ash. The maximum amounts of calcium carbonate which can be substituted by fly ash obtained in the cyclone and bag filter dust collectors were 20 and 10%, respectively. It was found that the curing rate of PWs can be controlled by varying the amount of Pb-octoate catalyst. The elongations at break as well as tensile strength and tear strength of PW coatings containing fly ash could also be adjusted such that their values were comparable to those of a standard PW coating by varying relative amounts of some components. However, the amount of cadmium, mercury, and lead leached from PW coatings containing fly ash obtained from the bag filter collector exceeded the respective allowed upper limits, mainly due to the initial high contents of them in the fly ash. On the other hand, PW coatings containing fly ash obtained from the cyclone collector exhibited better mechanical properties and did not release any significant amounts of the heavy metals. Thus, it was concluded that PW coatings containing fly ash can be utilized for practical applications as long as an appropriate fly ash is used.

요약 : 국내에서 폴리우레탄 방수 코팅은 노후된 건축물의 지붕 수리와 다양한 스포츠시설의 시공으로 인하여 수요가 증가되고 있다. 본 연구에서는 일반적으로 많이 사용되고 있는 탄산칼슘 충전제의 일부를 비산재로 대체하여 폴리우레탄 코팅을 제조하였다. Cyclone과 Bag filter에서 수집된 비산재가 대체할 수 있는 탄산칼슘의 최대량은 각각 20%와 10%로 결정되었다. 폴리우레탄의 경화속도는 Pb-octoate 촉매를 사용하여 조절할 수 있었다. 코팅의 제조에 사용되는 성분들의 상대적인 양을 조절하면, 비산재를 함유하는 폴리우레탄 코팅의 인장강도, 인열강도 및 신장율 등이 폴리우레탄 코팅의 표준 값들과 유사하게 되었다. 그러나 bag filter에서 수집된 비산재를 사용할 경우에는, 제조된 폴리우레탄 코팅으로부터 카드뮴(Cd), 수은(Hg) 및 납(Pb)이 허용 수치보다 높게 용출되었다. 한편, cyclone으로부터 수집된 비산재를 사용해서 제조한 폴리우레탄 코팅은 더 우수한 기계적 특성을 보였으며 중금속의 용출양도 심각하지 않았다. 결론적으로, 적당한 비산재를 선정하여 사용한다면, 비산재 함유 폴리우레탄 코팅도 현장에서 활용될 수 있을 것이다.

Keywords : fly ash, polyurethane waterproof, coating, calcium carbonate, filler

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I. Introduction

Ashes produced in burning facilities are classified into bottom ash and fly ash. In general, levels of heavy metals in bottom ashes are lower than the allowed limits, but those in fly ashes are higher than the limits.¹ Especially, cadmium (Cd), copper (Cu) and lead (Pb) were reported to have a high mobility for a relatively long period of time, which can lead to contamination of soil and ground water.² Various efforts have been made for the use of fly ash during the last decade.³⁻⁵ However, most of fly ashes produced in Korea are still buried in lands although a part of them is occasionally incorporated into concrete and brick compositions. Thus, the fly ash should be properly treated in order to avoid problems associated with secondary contamination and increasing landfill burden.⁶

Polyurethane waterproof (PW) agents are usually applied on a concrete surface to form coating films with a thickness of about 3 mm, followed by the protective mortar (non-exposed PW) or the transparent coating layer (exposed PW) on the top. The PW coatings are increasingly demanded in Korea due to several advantages over other coatings such as excellent elastic property, water-resistance, weather-resistance, and mechanical property, etc. For example, PW coatings are commonly used for repairing cracks on roofs of many old concrete buildings. Also, many sporting facilities such as tennis courts and basket ball courts are constructed using PW coatings.⁷

Although fillers are usually inorganic inert materials added to plastic resins primarily in order to reduce cost, they may also improve surface appearance, moldability, ultraviolet resistance, heat deflection temperature, electrical properties, blocking resistance, and control opacity and gloss. Calcium carbonate, CaCO_3 , is a common filler and incorporated in PW compositions. It is a mined material that requires the crushing and grinding of mined limestone to be used as a filler material. The mining, and subsequent crushing and grinding of

calcium carbonate add to the cost of the calcium carbonate filler. Calcium carbonate has limited regional availability and may require extensive shipping which also adds to its cost. In contrast, fly ash is a byproduct that is produced by trash or coal burning facilities, and more readily available. Thus, the use of fly ash as a filler offers various advantages over the use of other mineral fillers because fly ash has lower cost than other widely used mineral fillers. Fly ash also has a lower specific gravity (2.1-2.4) compared to calcium carbonate (~2.7).

The purpose of this research is to develop new PW coatings containing fly ash produced in the process of burning municipal waste, which meet commercial standards. Thus in this study, new PW coatings were prepared by substituting a part of calcium carbonate with fly ash. This paper describes the preparation and some general characterization of the PW coatings.

II. Experimental

1. Materials

Poly(oxypropylene triol) (KONIX GP-3000) and poly(oxypropylene glycol) (KONIX PP-3000) were obtained from Korea polyol Co. 4,4'-Methy lenebis (2-chloroaniline) (MOCA) and dioctylphthalate (DOP) were obtained from Kingyorker (China) and Aekyung petrochemical Co., respectively. The paint tar (PT-1500) and calcium carbonate (NAC-400, 10.5 μm) were obtained from Dongso Chemical Industry and Ujin Chemical, respectively. Xylene, Pb-octoate (24%), dispersing agent (Nuosperse 657), and defoamer (Airex-931) were obtained from SK, Jinyanghwasing, CONDEA Servo LLC, and Tego Chemical, respectively. An anti-settling agent (Tediset 410-20) and a hardener (NCO% = 5.4%) were obtained from TEDI and Jungwoo Fine Chemical, respectively. The hardener ingredients are listed in Table 1.

The burning temperatures for municipal waste are

Table 1. Hardener Ingredients Which Were Commonly Used for the Preparation of Various PW Coatings

Ingredient	Content (wt%)
GP-3000	37.5
PP-2000	30.4
DOP	10.2
1,4-butanediol	1.5
Toluene diisocyanate	20.4

800 and 1300 °C, depending on the type of waste. Fly ashes are separated via centrifugation and relatively heavier particles are collected in the cyclone cylinder. The remaining lighter particles are channelled to a bag filter dust collector and trapped with the help of calcium hydroxide.⁸ Thus four different fly ashes are generated from the burning process. The fly ashes collected in the cyclone when the burning temperatures were 800 and 1300 °C are designated as C/L and C/H, respectively. Similarly, the fly ashes collected in the bag filter when the burning temperatures were 800 or 1300 °C are designated as B/L and B/H, respectively.

2. Preparation of PW coatings

PW coatings are usually prepared by mixing a base part with a hardener part. The content of calcium carbonate filler in the base part is usually in the range of 50-60 wt%. According to our preliminary experimental results, the burning temperature (800 or 1300 °C) of municipal waste did not make much difference in the properties of the resulting PW coatings containing fly ashes as long as the ashes were obtained from the same dust collector.⁹ Thus, we focussed on the PW coatings prepared from B/L and C/L. According to the viscosity of the base part, the B/L could substitute about 10% of the initial amount of calcium carbonate while the C/L could substitute about 20% of it. The base part ingredients employed in this experiment along with their designations are shown in Table 2. B-0 was prepared without fly ash. B-1 and B-2 were prepared using 10% B/L and 20% C/L,

Table 2. Compositions in the Base Parts for Preparation of PW Coatings

Ingredient	B-0	B-1	B-2	B-3	B-4
MOCA	2.14	2.26	2.35	3.06	3.11
PP-3000	9.01	16.7	17.4	19.3	19.7
GP-3000	6.83	-	-	-	-
DOP	3.40	3.59	3.73	3.33	3.40
PT-1500	13.1	13.9	14.4	12.9	13.1
CaCO ₃	58.7	44.2	40.8	44.3	40.2
B/L	-	4.91	-	5.00	-
C/L	-	-	10.2	-	10.0
Xylene	3.47	6.04	4.42	3.96	4.24
Nuosperse 657	0.44	0.47	0.49	0.44	0.45
Airex 931	0.22	0.23	0.24	0.22	0.22
Tediset 410-20	2.02	2.14	2.22	1.89	1.92
Pb-octoate	0.67	5.56	3.71	5.65	3.71

respectively. B-3 and B-4 were also prepared from 10% B/L and 20% C/L, respectively, but their ingredient ratios are different from those of B-1 and B-2.

The base part for PW coatings usually contains both PP-3000 and GP-3000 which are polydiol and polytriol, respectively. However, when GP-3000 was present with fly ash in the base part, the tensile properties such as elongation and tensile strength of the resulting PW coatings were not satisfactory. Thus, all of the base parts containing fly ashes were prepared without GP-3000, but the contents of PP-3000 and MOCA were increased instead. It should be noted that all of the hardeners employed in this experiment were the same and contained GP-3000, as listed in Table 1, even though the base parts of B-1~B-4 did not contain GP-3000. The base part (B-0~B-4) was mixed with the hardener part for 5 min. The resulting mixture was cast on a flat substrate and dried at room temperature for 7 days. PW-S is a non-exposed PW coating commercially obtained (KU-1700, Kangnahmhwang) and used as a standard for comparison with PW coatings containing fly ash.

3. Measurements

The viscosity of PW formulations was measured with a Brookfield Digital Viscometer (Model: DV-1, Brookfield Engineering Laboratories, Inc.) at 25 °C. The time required for the viscosity of a mixture of base part and hardener part to attain 100,000 cps was considered to be the pot life. The tensile strength, tear strength, and elongation at break of the PW coatings were determined with a UTM (Model: AG-1, Shimadzu) at an elongation rate of 500 mm/min. Five different measurements were made for each film specimen (10 mm×10 mm, thickness 1.0 mm), and the average of at least three individual determinations was taken. The hardness was measured on an A-type spring hardness tester.

4. Leaching of Heavy Metals

The experiment on the leaching of heavy metals was performed by following the KSLT (Korean Standard Leaching Test). The prepared samples (5 mm×5 mm×5 mm, 100 g) were transferred into a 2.0 L-Erlenmeyer flask, followed by addition of deionized water (pH 5.8-6.3, sample/deionized water = 1/10). The mixture was shaken at room temperature and atmospheric pressure (200 rpm, amplitude of 4-5 cm) for 6 h. The resulting mixture was filtered through a glass filter, and the filtrate was taken for analysis with ion-coupled plasma (ICP, Model: ICPS-7500, Shimadzu).

III. Results and Discussion

1. Fly Ash

The fly ashes used in this experiment were provided twice with six months interval. They were dried at 60 °C for 24 h and analyzed semi-quantitatively with X-ray fluorescence (XRF, Model: PW-2400, Philips). The results are listed in Table 3. The numbers of 1 and 2 indicate the first (provided early) and second fly ash samples (provided later), respectively. The compositions of the samples

Table 3. Major Components of Fly Ashes (Number of 1 or 2 in each column represents the fly ashes provided by a company early and later, with a six month-interval)

Component	B/L		B/H		C/L		C/H	
	1	2	1	2	1	2	1	2
MgO	0.72	0.55	1.21	1.21	2.37	2.48	3.07	1.68
Al ₂ O ₃	1.40	0.87	2.40	2.40	9.33	6.26	8.33	5.10
SiO ₂	12.8	7.62	16.1	6.90	25.6	14.3	23.4	14.1
P ₂ O ₅	1.23	1.29	1.16	1.27	0.61	0.91	0.66	0.83
Cl	17.4	25.2	13.6	25.7	2.00	8.60	5.83	1.92
K ₂ O	7.05	6.98	6.06	6.16	3.02	2.13	3.13	1.84
CaO	11.3	8.78	9.72	9.27	20.3	17.6	19.5	19.9
PbO	8.41	6.27	6.72	6.45	0.45	1.60	0.97	0.95
Fe ₂ O ₃	4.34	4.41	5.96	3.63	19.7	23.6	15.8	26.8
Cr ₂ O ₃	-	-	-	-	0.20	0.25	0.18	0.39
CuO	1.84	0.53	2.99	1.24	0.58	0.64	0.97	0.81
CdO	1.48	0.86	0.26	-	-	-	-	-
HgO	0.34	-	-	-	-	-	-	-

obtained from the same collector under the same conditions were similar to each other with very few minor exceptions. In most cases, major elements are silicon (Si), chlorine (Cl), calcium (Ca), and iron (Fe), but depending on the sample and the type of dust collector, their relative amounts are slightly different.¹⁰ Significant amounts of heavy metals such as chromium (Cr), copper (Cu), and cadmium (Cd) were present in most of the fly ashes tested. Significant amount of lead (Pb) was detected from only B/L and B/H.

The size and morphology of the second fly ashes were analyzed with scanning electron microscopy (SEM, Model: S-4700, Hitachi). Figure 1 shows SEM micrographs for B/L and C/L. The size and morphology of B/L and B/H were very similar to each other. The same things happened to C/L and C/H. The fly ashes are not homogeneous in size and shape. Most of C/L particles have approximately spherical shapes, but B/L shows irregular aggregates of smaller particles. The differences in the size and shape of the fly ashes are mainly due to the different structural features of the dust collectors. The cyclone dust collector was designed to collect particles

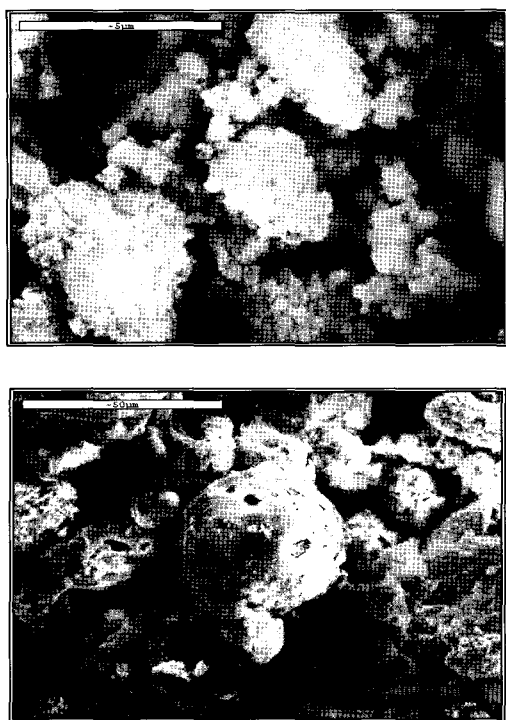


Figure 1. SEM micrographs of fly ashes: B/L (upper) and C/L (bottom).

with relatively high gravities via centrifugation while the bag filter dust collector was designed to trap relatively smaller and lighter particles which were passed through the cyclone collector. The size and morphology of the fly ashes are very important factors because they can significantly influence the viscosity of the base part as well as the physical and mechanical properties of the resulting PW coatings.

2. Physical and Mechanical Properties of PW coatings

The fly ashes used in the preparation of PW coatings were the second batch supplied by the company after six months, i.e., fly ashes of column 2 in Table 3. As mentioned in the experimental section, the maximum amount of calcium carbonate to be substituted by B/L and C/L was about 10 and 20%, respectively. At significantly higher contents

of fly ash, the resulting base parts were too viscous to be stirred. The difference in the substitution degree of calcium carbonate with fly ashes is mainly due to the different gravity and surface morphology of the fly ashes. In other words, the difference in the viscosity of the base parts containing B/L and C/L is the consequence that B/L contains lighter and more porous particles compared to C/L.

The physical properties of PW coatings containing fly ashes were compared with those of a PW-S standard. The results are listed in Table 4. The flowing and settling properties of PWs containing 10% B/L or 20% C/L were comparable to those of PW-S and PW-0. However, some non-dispersed particles appeared on the surface of the coatings. The interaction of a filler surface with a polymer is a highly complex physicochemical phenomenon. In order to maximize performance, the individual filler particle must be deagglomerated, dispersed uniformly throughout the polymer matrix and wetted by the polymer. The method of improving the interaction of the filler surface with the polymer includes treating the surface of the filler particles with stearates, resinates, silanes, etc. However, these

Table 4. Physical and Mechanical Properties of PW Coatings (PW-0, PW-1, PW-2, PW-3, and PW-4 coatings were prepared from base parts of B-0, B-1, B-2, B-3, and B-4, respectively)

Property	PW-S	PW-0	PW-1	PW-2	PW-3	PW-4
Levelling	○	○	◎	◎	◎	◎
Appearance	○	○	○	◎	◎	◎
Mixing viscosity (cps)	5500	5000	3300	4700	3300	4700
Pot life (min)	45	75	64	75	64	75
Tensile strength (kgf/cm ²)	25.3	28.4	16.2	20.3	25.3	42.1
Tear strength (kgf/cm)	11.3	12.7	9.3	9.3	10.6	13.5
Elongations at break (%)	470	290	480	430	530	600
Hardness (Shore A)	60	65	45	45	55	61

◎: Excellent ○: Good

surface treatments add to the cost of fillers. In this experiment, the base parts containing the fly ashes in xylene were treated with a ball mill before the hardener was added. The resulting particles have a mean diameter of $60 \mu\text{m}$ while the mean diameter of calcium carbonate used was $10.5 \mu\text{m}$. And, PW-1 and PW-2 coatings looked smooth and no aggregates were observed on their surfaces. The mixing viscosity of PW-1 and PW-2 was somewhat lower than that of PW-S, but such a viscosity is not problematic for practical application.

Even though the levelling and surface appearance of PW-1 and PW-2 coatings were satisfactory, their mechanical properties such as tensile strength, tear strength, elongation at break, and hardness were occasionally inferior to those of PW-S coating. The main reason for this inferiority may be due to the fact that the particles are larger and their hardness are lower than those of calcium carbonate. However, it may be difficult to treat further the fly ashes for reduction of the particle size and surface modification because the treatments add to the cost of the fly ashes. Increase in the MOCA content can enhance the strength and hardness of the resulting PW coatings. The elongation property can also be enhanced by increasing the soft segment (PP-3000) content. In this work, the MOCA content was increased from 2.26 and 2.35% (PW-1 and PW-2) to 3.06 and 3.11% (PW-3 and PW-4), respectively, as shown in Table 2. The PP-3000 content was also increased from 16.7 and 17.4% (PW-1 and PW-2) to 19.3 and 19.7% (PW-3 and PW-4), respectively. And then, the resulting coatings of PW-3 and PW-4 exhibited mechanical properties comparable to those of PW-S coating.

In addition, the curing rate of PW-0 was slower than that of PW-S, based on the measured pot life. When the component ratios were varied in order to enhance the mechanical properties, the amount of Pb-octoate catalyst was also adjusted. Initially, the amount of Pb-octoate was increased from 0.67% (PW-0) to 1.62%, but the curing rate of PW containing B/L or C/L was still too slow as compared

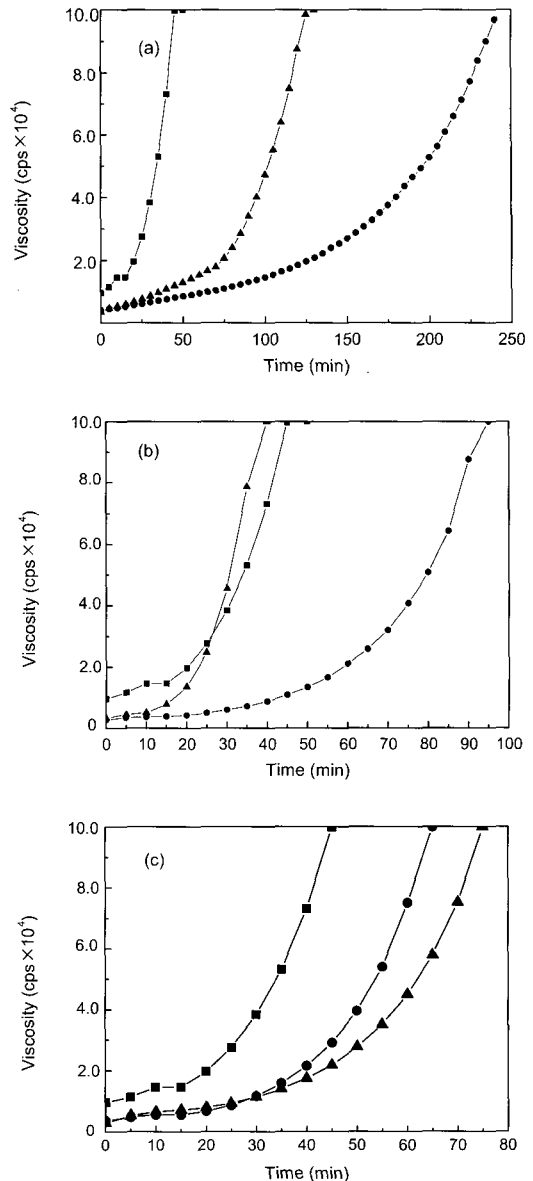


Figure 2. Viscosity change of PW formulations prepared using various contents of Pb-octoate as a function of time. The symbols of \blacksquare , \bullet , and \blacktriangle represent PW-S, PW containing 10% B/L, and PW containing 20% C/L, respectively. The amounts of Pb-octoate employed were (a) 1.62% for both \bullet and \blacktriangle , (b) 4.33% for both \bullet and \blacktriangle , and (c) 5.65 for \bullet and 3.71% for \blacktriangle .

to PW-S (Figure 2a). Consequently, the amount of the catalyst was increased to 4.33%. Then the curing

rate of PW containing B/H still remained slower, but that of PW containing C/L was slightly faster than that of PW-S (Figure 2b). Finally, the amount of Pb-octoate added to PW-3 and PW-4 was adjusted to be 5.65 and 3.71%, respectively. And then their curing rates were slightly slower than that of PW-S, but acceptable because their curing behaviors are similar to that of PW-S, as shown in Figure 2c.

3. Leaching Behavior of Heavy Metals

The leaching of heavy metals out of the PW-3 and PW-4 coatings was tested in deionized water (pH 5.8-6.3, sample/deionized water = 1/10) at room temperature as described in the experimental section. The leached metals were detected with ICP and the result is listed in Table 5. The amounts of chromium, copper and arsenic leached out of the samples are smaller than their respective allowed levels. However, the amounts of cadmium, mercury, and lead leached from the PW-3 coating exceeded the allowed levels. Significant amounts of cadmium and lead were initially detected in the B/L by XRF. Furthermore, a large amount of Pb-octoate was added as a catalyst in order to increase the curing rate. Presently, it is thought that the relatively high amount of lead leached from the PW-3 coating is due to the initial high content of lead in the fly ash and the large amount of Pb-octoate used for the efficient curing process. Mercury was also probably present initially in the B/L, thus it was detected only

Table 5. Heavy Metals Leached out of PW-3 and PW-4 Coatings

Leached Metal	PW-3	PW-4	Allowed Level (mg/L)
Cr	^a 0.0018-0.0045	0.0014-0.0058	1.5
Cu	0.44-0.86	0.022-0.028	3
As	0.029-0.055	0.030-0.051	1.5
Cd	0.18-0.31	0.036-0.066	0.3
Hg	0.0088-0.0123	-	0.005
Pb	0.74-10.23	0.29-0.30	3

^aConcentration of leached metal is given with a range based on two different measurements

in the PW-3 coating by XRF because its amount was relatively small.

IV. Conclusions

New PW coatings were prepared by substituting a part of calcium carbonate filler with fly ash. The base parts containing fly ash were treated with a ball mill for reduction of the particle size and better homogeneity of the fly ashes. The maximum amounts of calcium carbonate to be substituted by the fly ashes obtained in the cyclone and bag filter dust collectors were 20 and 10%, respectively. The curing rate of PW formulations was in the acceptable range as compared to that of PW-S standard when appropriate amounts of Pb-octoate were added to their base parts. The elongation at break as well as tensile strength and tear strength of PW coatings containing fly ash were also comparable to those of PW-S coating when the relative amounts of MOCA and PP-3000 were adjusted. The amounts of cadmium, mercury, and lead leached from PW-3 coating exceeded the allowed levels mainly because they were present in significant amounts in the B/L. On the other hand, the leached heavy metals out of PW-4 coating were much less than their allowed limits. Thus, PW coatings containing fly ashes (C/L and C/H) obtained in the cyclone collector are expected to be utilized for practical applications.

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