

EFFECTS OF ADDITIVES, PIGMENT AND FILLER ON PHYSICO-MECHANICAL PROPERTIES AND WEATHER RESISTANCE OF POLYUREA COATINGS

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ABSTRACT

Polyurea coatings are known to provide high hardness, stable color, excellent weather durability and good scratch resistance. Being cured, the coatings can also express heat resistance up to 150 °C, good resistance to acids, oils, as well as other chemicals, high flexibility and strain, excellent adhesion to various substrate materials such as concrete, steel, ceramic, glass and others. In this paper, a polyurea coating has been developed on basis of polyaspartic acid esters and polyisocyanate curing agent, using 3 % nanoclay additive. The physical, mechanical, and chemical properties of the coatings were examined by current technical specifications. The results for developed coating were recorded as follow: 76 in.lb impact strength, 7.5 mm elongation, and 0.7 relative hardness; no blistering was observed after 30 days of immersion in 5 % HCl and 5 % NaOH solutions. Weather resistance of the coatings was also evaluated with full absence of peeling, blistering and high gloss retention after 500 h accelerated UV testing.

Keywords: polyurea, polyaspartic acid esters, nanoclay, weather resistance

1. INTRODUCTION

Polyurea combines a number of valuable properties such as good scratch and abrasion resistance, high chemical and corrosion stability, excellent weather and solar radiation durability, completely non-toxic and environmental friendly impact. The polyurea possesses considerably fair adhesion to various substrate materials, including concrete, steel, wood and others. Thank to these values, polyurea has been extensively applied in recent years as protective coatings for different materials used in industry, construction, transportation, etc. [1 - 4].

Compared to the other coating materials, the polyurea coating is advantaged by its rapid curing time, conveniently used to apply onto concave and vertical surfaces without flowing down, moderate waterproofing ability, long-term insensitivity to humidity and temperature, high

mechanical properties, chemical and weather resistance. Furthermore, this type of material can also be manufactured in whole solid paint composition and coated by multiple layer consistency.

However, besides the specific role of polyurea binder, the good technological characteristics of the coating are dependent on used additives, pigments, and fillers. There are reported data on specific effect of nano materials in enhancing polyurea coating performances. For example, Cai D. showed in [5] that the intercalation of C20 could be easily achieved by simple mixing to form polyurea/organoclay nanocomposite with improved mechanical properties; nano-reinforcing effect and energy dissipation turned out to be much more significant for the polyurea with higher crosslinking degree. Other results were informed in [6], where both nanoclay and multiwalled carbon nanotubes (MWCNs) can enhance mechanical properties of polyurea like conventional fillers, but at much lower levels than for carbon black, silica, etc.

In this study, a novel formulation of polyurea coating was proposed, investigating the effects of additives, pigments, nanoclay fillers on the coating properties.

2. MATERIALS AND METHODS

2.1. Materials

Polyaspartic ester resin (PACM 20 cycloaliphatic amine) with acid value: 190 mg KOH/g, viscosity (25 °C): 1000 mPa.s, equivalent weight: 290 g/mol, volumetric density (20 °C): 1.06 g/mL and polyisocyanate curing agent (Desmodur VPLS 2371) were supplied by Bayer Co. Texaphor dispersing agent and Raybo 3 Antisilk flow resistance additives were provided from BASF Cognis. I.30E nanoclay additive modified with 25 – 30 % octadecylamine was purchased from Sigma-Aldrich. Other chemicals such as dioctyl phthalate plasticizers (DOP), talc, BaSO₄, TiO₂ powders, acetone, xylene, butanol, toluene, butyl cellosolve were products of China.

2.2. Procedure of polyurea synthesis

Procedure of polyurea synthesis is described as block scheme in Figure 1.

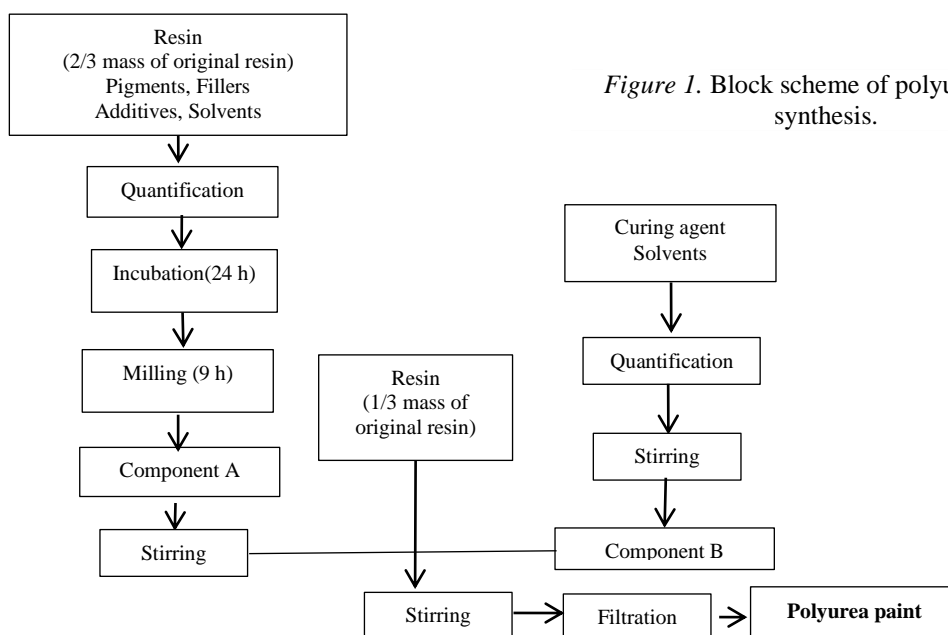


Figure 1. Block scheme of polyurea paint synthesis.

2.3 Test methods

Following methods were used for testing samples: ASTM D 2794 - 93(2004) for impact strength, ISO 1519:2002 for bend strength, ISO 1522:2006 for relative hardness, ISO 2409:2007 for adhesion (points), ISO 1518-1:2011 for scratch resistance, ISO 1520:2006 for elongation. Meanwhile, weathering and salt spray resistance were evaluated according to ISO 11507:2007 (TCVN 9277:2012) and ASTM B 117-11. Sheen chamber was used for accelerated testing. Gloss was measured following TCVN 8789:2011 by BYK-Gardner Glossmeter under angle 60°.

The polyurea samples were also characterized using scanning electron microscopy (SEM) and Bruker D8 Advance Diffractometer (Germany).

3. RESULTS AND DISCUSSION

3.1. Effect of additives on mechanical properties of coating

Experiment was conducted independently with three types of additives: Raybo 3 Antisilk flow resistance, Texaphor dispersing agent and DOP plasticizer. Coatings including binder and curing agent were investigated using single additive with different contents (wt% to coating weight). Mechanical properties of coating examined by above standards were presented in Table 1. Content of each additive was calculated comparing to resin weight.

Table 1. Influence of additives on physico-mechanical properties of coating (thickness: 50 ± 5 µm).

Type of additive	Additive content (wt%)	Impact strength (in.lb)	Elongation (mm)	Bend strength (mm)	Adhesion (points)	Scratch resistance (N)	Relative hardness
Raybo 3 Antisilk	0	50	5.0	3	2	6	0.305
	0.1	60	5.8	3	2	9	0.501
	0.2	70	6.8	2	1	14	0.608
	0.3	64	6.0	2	1	13	0.568
	0.35	58	5.8	3	2	9	0.487
Texaphor	0	48	4.7	3	2	7	0.368
	0.8	68	6.5	2	1	13	0.576
	1.0	70	6.8	2	1	14	0.608
	1.2	56	5.7	3	2	9	0.465
DOP	0	52	5.1	4	3	6	0.755
	2.4	60	5.8	3	2	9	0.528
	2.8	70	6.8	2	1	14	0.608
	3.2	66	6.2	2	1	11	0.565

The results in Table 1 show undesirable appearance and mechanical properties of coatings in case of additives absence. Without Raybo 3 Antisilk, the coating surface underwent flow. Similarly, pigment sedimentation was observed after mixing for the sample without Texaphor. Non-DOP coating was found to be exceptionally hard with relative hardness of 0.755 leading to low bend strength and low film adhesion. However, with additives using, all technological properties of coatings were improved, shown by clearly uniform appearance and significantly higher mechanical properties. Especially, with increase in additive contents, the mechanical properties of the coatings noticeably rose up to a certain limit, and took a gradual fall afterward. From Table 1, the optimum contents of Raybo 3 Antisilk, Texaphor and DOP additives were selected at 0.2, 1.0 and 2.8 wt%, respectively, for further coating formulation to gain the best mechanical properties.

3.2. Effect of pigments and fillers on mechanical properties

Five coating compositions prepared from polyaspartic ester resin and polyisocyanate curing agent with varying BaSO₄ and TiO₂ contents (wt%) were selected for further evaluation of mechanical properties. Summarized data are presented in Table 2.

Table 2. Influence of pigments and filler contents on coating properties (thickness: 50 ± 5 μm).

Type of pigment/filler	Pigment/Filler (wt%)	Impact strength (in.lb)	Elongation (mm)	Bend strength (mm)	Adhesion (points)	Scratch resistance (N)	Relative hardness	Gel content (%)
BaSO ₄	0	60	6.0	3	2	9	0.370	96.18
	26	70	6.8	2	1	11	0.405	97.98
	32	76	7.2	2	1	14	0.435	98.97
	38	72	7.0	2	1	13	0.415	98.25
	44	64	6.4	3	2	10	0.590	98.31
TiO ₂	0	60	5.7	3	2	8	0.385	95.18
	40	74	6.9	2	1	14	0.425	96.98
	50	76	7.2	2	1	14	0.435	97.97
	60	68	6.3	3	2	13	0.410	97.25
	70	58	5.5	4	3	8	0.376	96.31

According to data of Table 2, mechanical properties were considerably changed after applying BaSO₄ and TiO₂ into coating. Elongation and impact strength rose with increasing BaSO₄ content, reaching 20 and 27 %, respectively, while relative hardness and scratch resistance were slightly increased. The mechanical properties reached their maximum values at 32 wt% BaSO₄ and began to decrease with further filler addition.

In a range of TiO₂ content varying from 0 to 70 wt%, the mechanical properties of coating were also examined and similar effect was revealed for this pigment with fixed maximum values at 50 wt% TiO₂ weight content. Therefore, 32 wt% BaSO₄ and 50 wt% TiO₂ were the optimum contents to be selected for further investigations.

3.3. Effect of nanoclay on mechanical properties of coating

As recently informed in [5, 6], nanomaterials can substantially enhance working performances of polyurea coating. A detailed investigation of nanoclay effect on coating was performed with results presented in Table 3.

It is clearly noticeable from Table 3, an increase of nanoclay content to 3 wt% resulted in superior mechanical properties of the coating, significantly exceeding the values determined for nanoclay-free sample. At 3 wt% I.30E content, the elongation and impact strength increased on 17.65 and 11 %, respectively, while abrasion reduced sharply to 62.07 %. Other properties such as bend strength and, adhesion were not change. However, when the nanoclay contents increased further to 4 and 5 wt%, the mechanical properties of the coating decreased greatly, significantly lower than those of the initial sample. Thereby, the optimal condition was found at 3 wt% nanoclay content to formulate the polyurea/nanoclay composite coating and was selected for final composition to perform further tests, including XRD and SEM examinations.

Table 3. Influence of nanoclay on properties of polyurea coating (thickness: $50 \pm 5 \mu\text{m}$).

I.30E content (%)	Bend strength (mm)	Impact strength (in.lb)	Elongation (mm)	Scratch resistance (N)	Adhesion (points)	Relative hardness	Abrasion mg/1000 cycles
0	2	72	6.8	14	1	0.725	29
1	2	78	7.2	15	1	0.742	19
2	2	80	7.7	15	1	0.757	13
3	2	80	8.0	16	1	0.808	11
4	3	68	6.1	12	2	0.705	15
5	3	62	5.6	9	2	0.700	20

The polyurea/nanoclay composite sample that used for structure characterization via XRD technique was prepared from polyaspartic ester resin and 3 wt% I.30E nanoclay by mechanically stirring (1500 rpm, at 70 °C for 7 h.) and additional ultrasonic stirring. After this step, polyisocyanate curing agent was added to the mixture to form a composition, followed by pressing into thin film and keeping to stabilize at room temperature. The film was transferred for XRD characterization with comparative patterns presented in Figure 2 to Figure 4.

XRD pattern of original nanoclay in Figure 3 show a base-layer spacing of $d = 23.12 \text{ \AA}$. After nanoclay dispersion into polyurea for 7 h mechanical mixing, a wider interlayer spacing occurred with $d = 40.51 \text{ \AA}$ (compare Figure 2 to Figure 4). Therefore, nanoclay dispersion into polyurea favored the complete interlayer “flaking” status. These results define optimum conditions for composite formulation: 7 h of stirring (1500 rpm) at 70 °C.

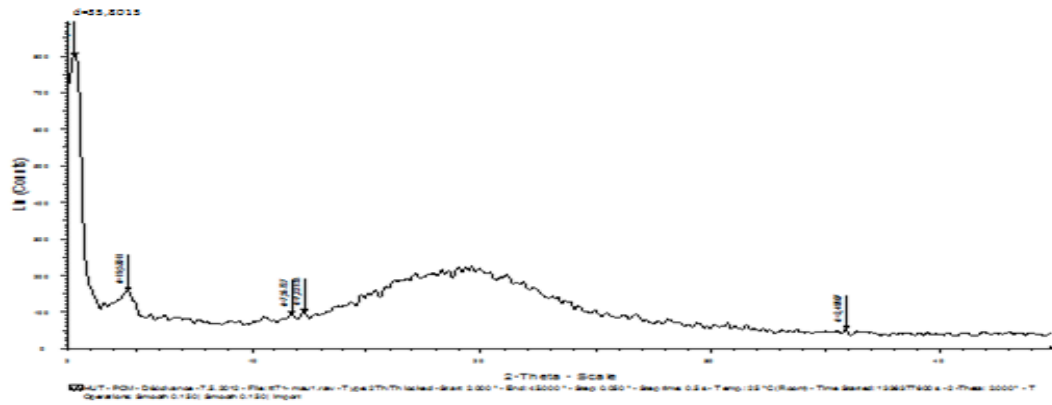


Figure 2. XRD pattern of polyurea sample.

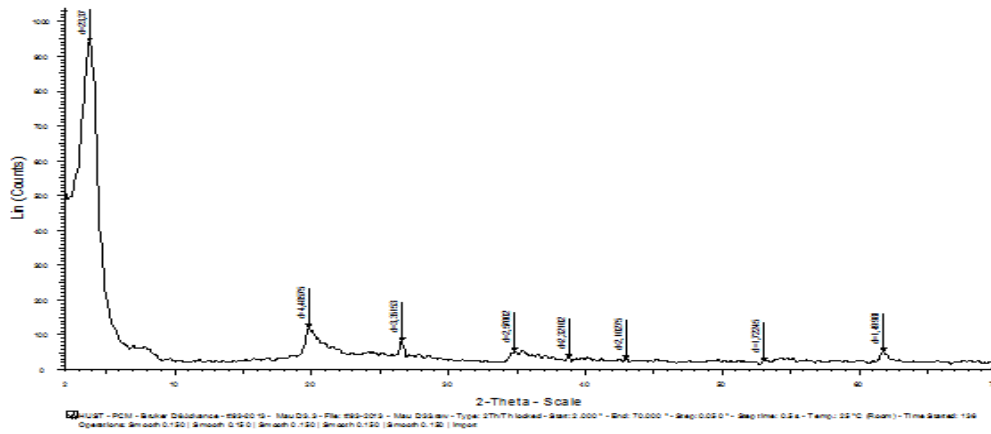


Figure 3. XRD pattern of original nanoclay sample.

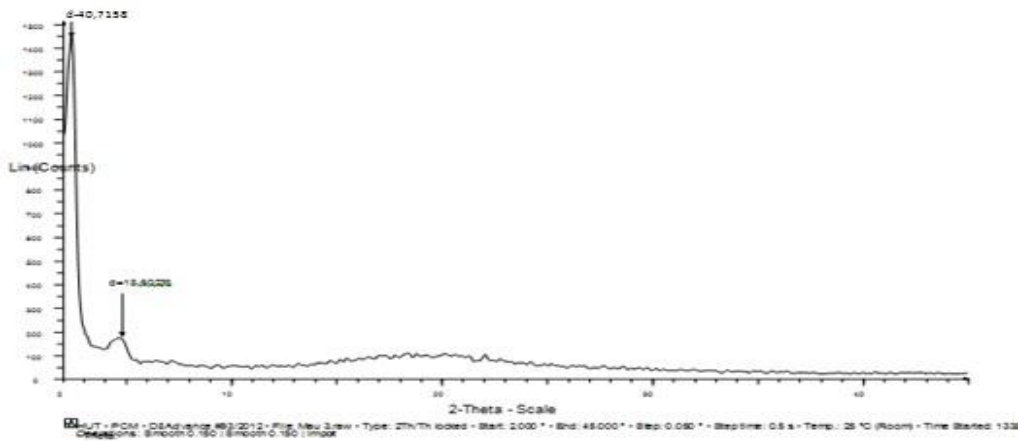


Figure 4. XRD diagram of polyurea/nanoclay composite with 3 wt% nanoclay content.

SEM image in Figure 5 shows uniform distribution of 3 wt% nanoclay content in polyurea/nanoclay composite coating thanks to appearance of defects completely filled in on the polyurea surface.

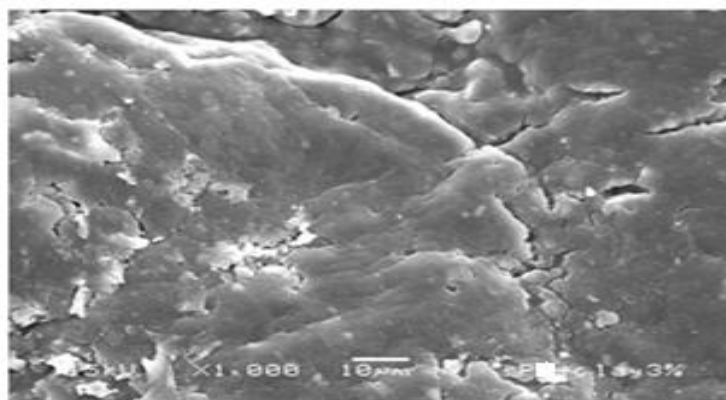


Figure 5. SEM image of 3 wt% polyurea /nanoclay composite coating.

3.4. Weather durability and chemical resistance of polyurea composite coating

3.4.1. Accelerated test under UV radiation

Based on above described results, two series of coating samples were prepared with (E series) and without (M series) UV resistant additives. The samples were exposed for 500 h of UV testing and surface gloss was evaluated. According to TCVN 8789:2011, the coating after UV testing is required less than 30 % of gloss loss. Results of the sample gloss (E2, M2) compared to the back-up gloss (E1, M1) were recorded in Table 4.

Table 4. Gloss loss of polyurea coatings after 500 h exposure testing.

Sample	Average gloss after 500 h testing (%)	Average gloss before testing (%)	Gloss loss (%)
M1	85.0	94.12	9.7
M2	77.8	90.72	14.3
E1	80.4	82.64	2.7
E2	87.2	93.17	5.4

Results in Table 4 show insignificant differences in initial gloss for the samples prepared with and without UV resistance additives. However, these values substantially changed after 500 h testing with gloss loss 14.3 for M2 and 5.4 for E2. Nevertheless, these loss values were in an acceptable range of < 30 % required by standard and affirmed an important role of UV resistance additive in polyurea composite coating.

3.4.2. Chemical resistance of polyurea coating

The prepared coatings were tested in 5 % NaOH and 5 % HCl solutions for 30 days. After testing, weight of coating was determined and appearance of coating was checked. No blistering

occurred on surface for both coatings tested in acid and alkali media. Chemical penetration data were collected and demonstrated in Figure 6.

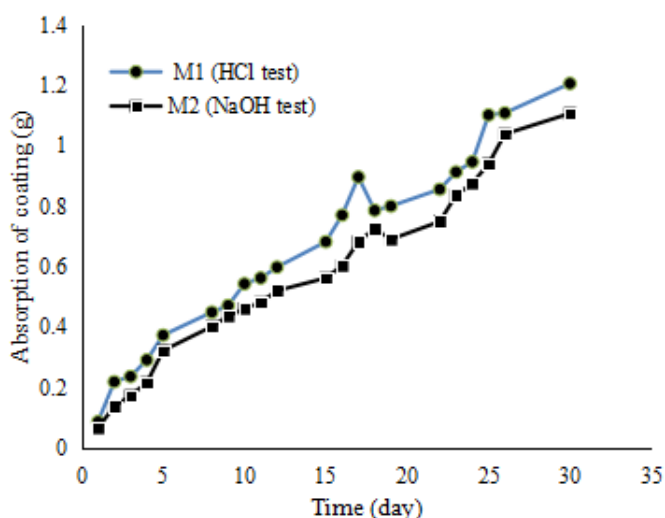


Figure 6. Weight change of polyurea coatings after testing in NaOH and HCl solution.

3.4.3 Technical specifications of polyurea coatings

Polyurea coating was prepared based on investigated formulation with 0.2 wt% Raybo 3 Antisilk, 1 wt% Texaphor, 2.8 wt% DOP additives, 32 wt% BaSO₄ filler, 50 wt% TiO₂ pigment, and 3 wt% nanoclay. Its technical specification was evaluated according to TCVN 8789:2011 with results summarized in Table 5. Clearly, data listed as technical specifications for polyurea coatings reached higher values than those required by TCVN 8789:2011.

Table 5. Technical specifications of polyurea composite coatings.

No	Property	Results	TCVN 8789:2011 Standard	Method Test
1	Bend strength (mm)	2	2	TCVN 2099:2007
2	Impact strength (in.lb)	76	≥ 45 (kg.cm)	TCVN 2100:2007
3	Adhesion (points)	1	1	TCVN 2097:1993
4	Scratch resistance (N)	14	-	ISO 1518-2006
5	Relative hardness	> 0.70	≥ 0.20	TCVN 2098:2007
6	500 h UV test	Absence of peeling, blistering, color fading. Gloss loss < 15% (compared to initial gloss)	Absence of peeling, blistering, color fading. Gloss loss < 30% (compared to initial gloss)	TCVN 9277:2012
7	Elongation (mm)	7.5	-	ISO 1520:2006.
8	Gloss (60° angle)	86	>70	TCVN 2101:2008

3.5. Polyurea in coating system

3.5.1. Design of durable coating system

A protective coating system on basis of developed polyurea was proposed to meet requirement of high durable to severe humid tropical conditions. Life expectancy of the system was designed for more than 15 years of service. The designed system is consisted of four coats with total thickness: 250 ÷ 285 µm, including:

- Primer coat: Solvent free epoxy primer, thickness: 60 ÷ 65 µm;
- First middle coat: MIO epoxy, thickness: 90 ÷ 110 µm;
- Second middle coat: Polyurea, thickness 50 ÷ 55 µm;
- Top coat: Polyurea, thickness: 50 ÷ 55 µm.

The system was applied to steel substrates, following common procedure of surface preparation to Sa2 – Sa2.5 sand blasting grades and the selective samples were undergone accelerated weathering and salt spray tests.

3.5.2. Accelerated salt spray test

Corrosion resistance of the polyurea coated system was tested and compared to the Interpaint reference with proved service life >15 years. Tested results are recorded in Table 6.

Table 6. Evaluation of sample conditions during salt spray testing.

Criteria	Duration of testing (h)		
	0	360	720
Rusting (ASTM D 610), degree	10	10	10
Blistering (ASTM D714)	No	No	No
Cracking (ASTM D661)	No	No	No
Flaking (ASTM D772)	No	No	No
Resistance to corrosive environment (ASTM D1654), degree	10	10	10
Cross cut adhesion, point	1	1	1
Pull-off adhesion, MPa	2	2	2

Results show high quality of the tested system with non evidence of blistering, cracking, flaking and other criteria after 720 h of salt spraying. The samples remained at high adhesion, meeting requirements of TCVN 8789-2011. All checked criteria were similar to the Interpaint reference [7].

3.5.3. QUV Weathering Test

The parallel samples were undergone QUV weathering test with gloss loss and color degradation results presented in Figure 7. It is clear from the data in Figure 7a, the coating gloss

was remained highly after 500 h of QUV testing with 91.66 % retention, what proves excellent durability of the system to ultraviolet aging.

Furthermore, alongside the corrosion protection, top coat is still required to express beautiful appearance during application for which the color durability is also served as a criterium to be tested. Then, the color differences of polyurea coatings were calculated from the color measured change data compared to back-up sample. Time dependence of color difference (ΔE) is presented in Figure 7b. Insignificant color change was observed during 500 h of testing, what demonstrates high protective and fair decorative properties of polyurea coating.

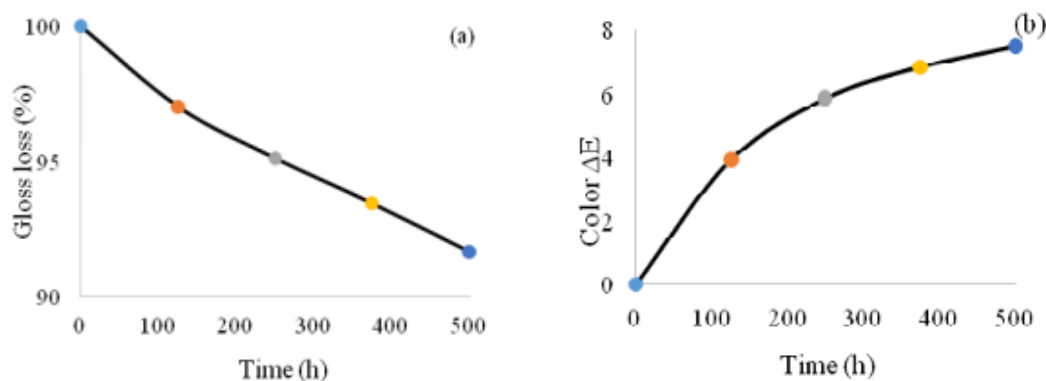


Figure 7. Time dependence of gloss loss (a) and color difference (b) for polyurea coating.

Other criteria of coating performance were also checked after QUV testing and all data were summarized in Table 7. Insignificant chalking was noticed for polyurea coating after 500 h testing while all other criteria were recorded with high stability.

Table 7. Technical performance criteria of polyurea coating.

Test criterium	Duration of testing (h)		
	0	250	500
Chalking (ASTMD 4214), degree	10	10	8
Blistering (ASTM D714)	No	No	No
Cracking (ASTM D661)	No	No	No
Flaking (ASTM D772)	No	No	No
Resistance to corrosion environment (ASTM D1654), degree	10	10	10
Color difference ΔE	0	5.85	7.49
Pull-off adhesion, MPa	2	2	2

4. CONCLUSIONS

A novel polyurea coating composition with 0.2 wt% Raybo 3 antisilk flow resistance agent (of total paint composition), 1 wt% Texaphor dispersing agent (of total filler and pigment), 2.8 wt% DOP (of total paint composition), 32 wt% BaSO₄, 50 wt% TiO₂, and 3 wt% nanoclay was proposed and the best physico-mechanical characteristics were achieved at this formulation.

An optimum 3 wt% nanoclay content dispersed into polyurea resin was reached by mechanical stirring with 1500 rpm at 70 °C during 7 h with ultrasonic assistance. Nanoclay showed significant influence on physico-mechanical properties of the polyurea composite coating with enhanced results reached at 3 wt%.

Polyurea composite coating expressed high chemical resistance and weather durability. Its technical specifications were evaluated and the obtained values proved that the coating fully meets requirement of current national standard TCVN 8789:2011. Polyurea in combined system with epoxy primer can be served as high durable protective and decorative coating.

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