INFLUENCE OF ACRYLIC/ MELAMINE RATIO ON SOME PROPERTIES OF ACRYLIC- MELAMINE COATING

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ABSTRACT

This article introduces effects of acrylic/melamine ratio on mechanical properties, chemical stability, thermal resistance,… of baking acrylic- melamine varnish. Infrared spectroscopy (FT-IR), Thermal gravimetric analysis (TGA), FESEM,... were used to examine the investigation's results. Through testing mechanical properties and through- drying temprature of coating, acrylic / melamine ratio is 35/15 and drying temperature of 140ºC, in 60 minutes are determined. Infrared spectroscopy (IR) shows curing reaction between acrylic and melamine resin. In addition, article also introduces testing results in lubricant, HCl acid 5%, A95 gasoline for 240 hours and thermal stability of acrylic- melamine varnish. Results of TGA have shown that thermal decomposition of varnish coatings depend on ratios of acrylic/melamine resin. Acrylic- melamine coating is capable of being used to protect metal parts in some chemical conditions and the coating can be used for cars' fuel tank or motors' fuel tank,...

ẢNH HƯỞNG CỦA TỶ LỆ ACRYLIC/ MELAMINE ĐẾN MỘT SỐ TÍNH CHẤT CỦA MÀNG PHỦ ACRYLIC- MELAMIN

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THÔNG TIN BÀI BÁO

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TỪ KHÓA

Vecny acrylic- melamin
Sơn acrylic- melamin
Màng phủ acrylic- melamin
Độ bền hóa chất
Độ bền nhiệt

TÓM TẮT

Bài báo trình bày kết quả nghiên cứu ảnh hưởng tỷ lệ nhựa acrylic/ melamin đến tính chất cơ lý, độ bền hóa chất, độ bền nhiệt,… của vecny acrylic- melamin khô sấy. Các kết quả nghiên cứu được kiểm tra bằng cách chụp phổ hồng ngoại (FT-IR), phân tích nhiệt TGA, chụp ảnh FE-SEM,… Thông qua việc khảo sát tính chất cơ lý và thời gian khô hoàn toàn của màng vecny xác định được tỷ lê nhựa acrylic/ melamin là 35/15 ở nhiệt độ sấy 140ºC, thời gian khô hoàn toàn của màng vecny 60 phút. Kết quả chụp phổ hồng ngoại (IR) cho thấy đã xảy ra phản ứng đóng rắn giữa nhựa acrylic và nhựa melamin. Bên cạnh đó, bài báo cũng giới thiệu kết quả thử nghiệm trong môi trường dầu nhờn, axit HCl 5%, xăng A95 trong thời gian 240 giờ và độ bền nhiệt của mẫu vecny acrylic/ melamin. Kết quả cho thấy sự phân hủy nhiệt của vecny acrylic- melamin phụ thuộc vào tỷ lệ nhựa acrylic/melamin.. Lớp phủ acrylic- melamin có thể được sử dụng để bảo vệ các chi tiết kim loại làm việc trong môi trường hóa chất và lớp phủ này có thể sử dụng cho thùng chứa nhiên liệu của ô tô hoặc xe máy,...

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1. Introduction

Melamine formaldehyde resin is a product of condensation between melamine and formaldehyde. For applying for paints or coating, this resin is often denatured with alcohol, usually butanol (butylated melamin formaldehyde). In fact, butanol modified melamine formaldehyde resin is still called melamine resin, this resin is high compatible with other resins such as: alkyd, acrylic, epoxy, polyester, urea,... to make baking paint [1]-[3]. Studies on alkyd-melamine coating used as insulating coatings and automotive coatings have been studied and published many [4], [5]. Acrylic- melamine (AC-ML) coating has high relative hardness, polish, and chemical resistance in coparision with alkyd- melamine coating while its cost is lower than that of epoxy- melamine coating. Acrylic- melamine coating widely used for electrical details and many household items [6]-[11]. Some authors have studied on water-based paints and UV-cured paints based on acrylic- melamine [12], [13]. Even baking acrylic- melamine coating is used in many fields but investigations on it hardly have been published. This article presents effects of acrylic/melamine ratios, baking temperature,... on mechanical properties, thermal resistance, chemical restance,… so as to determine the best ratio and processing temperature for acrylic-melamine coating.

2. Materials and methods

2.1. Chemicals

- Acrylic resin, Eterac 7108-X-54 (Taiwan), solid content: 54%.
- Melamine resin, MF268 (India), solid content: 60%.
- Xylene, acetone, butyl acetate: Industrial products made in China.
- Castrol Activ lubricant, A95, HCl: Industrial products.

2.2. Sample preparation

Table 1. *Compositions of Acrylic- melamine coating*

No.	Components	Content (%)
1	Acrylic, Eterac 7108-X-54	25- 45
2	Melamine, MF268	5- 25
3	Xylene	30
4	Butyl acetate	15
5	Acetone	5

- Preparing raw materials as in table 1.
- Dissolving acrylic resin and melamine resin in xylene, acetone, butyl acetate. Stirring varnish mixture well and making samples (according to TCVN 2090:2007) on steel sheets according to TCVN 5670:2007 for testing mechanical properties.

2.3. Analysis methods

- Infrared spectroscopy (FT-IR) on the Fourier FTIR-8700 series converter (Japan).
- Adhesion, flexural strength, impact resistance, relative hardness and through-drying time of coating are determined according to TCVN 2097:2015, TCVN 2099:2013, TCVN 2100-1:2013, TCVN 2098:2007 and TCVN 2096-6:2015.
- Thermal resistance: Thermal gravimetric analysis (TGA) was analyzed by NETZSCH TG 209F1 LIBRA in argon with temperature step of 10 ^{o}C/minute from room temperature to 600 ^{o}C.
- Morphology of coating film was observed by FESEM Hitachi S4800 machine (Japan) with a magnification of 2,000 times and voltage of 5 KV.
- Resistance to chemical conditions of coatings are determined according to TCVN 10517-1:2014 at temperature (23 ± 2) ^{o}C and relative humidity (50 ± 5) %.

3. Results and discussion

3.1. Effect of acrylic/ melamine ratios on mechanical properties coating

To study effect of acrylic/ melamine ratios (weight percent- Wt. %) on mechanical properties varnish coating, samples were made with compositions as in table 2. Samples were processed on standard steel sheets with a thickness of 30 µm. Samples were baked at 130 ^oC for 80 mins. Results were shown in table 2.

Table 2. *Effect of acrylic/ melamine ratio on coating mechanical properties*

Samples	Acrylic/ melamine (Wt. %)		Mechanical properties of coating			
	AC	ML	Adhesion (Points)	Flexural strength (mm)	Impact resistance (Kg.cm)	Relative hardness
M1	45	5	1	2	200	0.46
M2	40	10	1	2	200	0.51
M3	35	15	1	2	200	0.56
M4	30	20	1	4	160	0.65
M5	25	25	3	5	120	0.73

Table 2 showed that, when ratio of melamine increases adhesion, flexural strength, impact resistance of coating decreases but relative hardness increases. It can be explained that, three dimesional network creation is to make coating through the reactions between hydroxyl group of acrylic resin and alkoxy group in melamine resin as:

$=N-H + HO-R \rightarrow =N-R + H_2O$

$-CH_2-OH + HO-R \rightarrow -CH_2-O-R + H_2O$

$-CH_2-OC_4H_9 + HO-R \rightarrow -CH_2-O-R + C_4H_9OH$

So more melamine resin means more actions for creating three-dimensional network. Besides that, melamine resin is more brittle than acryllic resin so melamine increases the coating becomes harder and more brittle [13].

3.2. Effect of drying temprature on through- drying time of coating

Investigating effect of drying temprature on through drying time of coatings with a thickness of 30 µm at 110 ^oC, 120 ^oC, 130 ^oC, 140 ^oC, 150 ^oC and M3 of Table 2 was chosen. Results were shown in table 3.

Table 3. *Effect of drying temprature on through- drying time of coating*

Drying temprature (^oC)	Through drying time (Mins.)	Coating Surface
110	103	Transparent, homogeneous
120	88	Transparent, homogeneous
130	72	Transparent, homogeneous
140	60	Transparent, homogeneous
150	48	Yellow with air bubbles

Table 3 showed that, in the range of 110- 150^oC, through drying time of coating decrease rapidly. However, when temprature reaches 150^oC, coating surface becomes yellow with air bubbles. This can be explained that, curing reaction of acrylic resin with melamine resin mainly occurs between hydrogen atom in amine group or hydroxyl group of melamine resin with active functional group (eg. hydroxyl group) of acrylic resin. In addition, curing reaction also occurs between alkyl group in acrylic resin and other active functional groups and releases alcohol. Melamine resin itself also occurs curing, but in case of low temperature (110 ^oC, 120 ^oC), it does not happen significantly, so through drying time of vecny takes place slowly. When the drying temperature is high (above 130 ^oC), reaction between functional groups of acrylic resin and

melamine resin as well as reaction of melamine resin itself. Besides, we also see that, when increasing curing reaction temperature, it will increase movement speed of molecules involved in the reaction, so reaction speed increases. A very small increase in temperature can greatly increase reaction rate [13].

3.3. Infrared spectroscopy (IR) of compositions and coating

To study curing reaction of acylic- melamine coating, infrared spectroscopy (IR) of acrylic resin, melamine resin, uncured acrylic- melamine, cured acrylic- melamine coating were conducted by FTIR-8700 (Japan). Results were shown in table 4 and figures 1a, 1b, 1c. 1d.

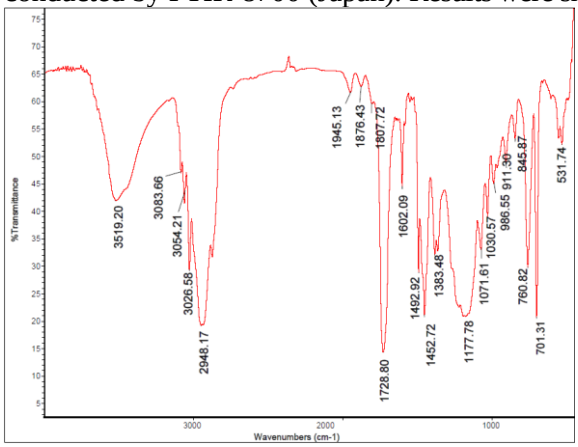

Figure 1a. *IR of acrylic resin*

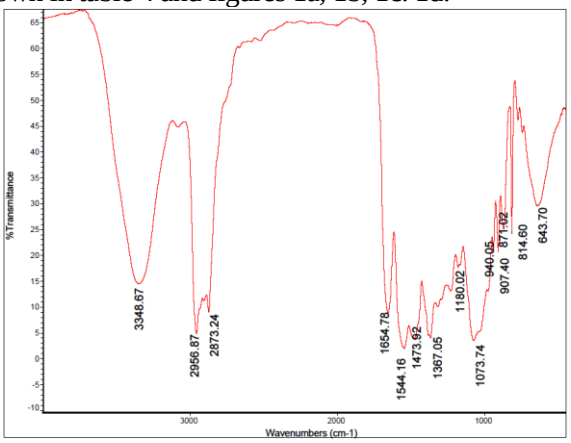

Figure 1b. *IR of melamine resin*

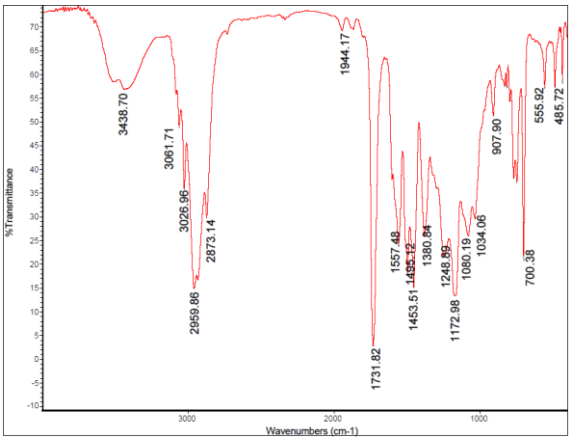

Figure 1c. *IR of uncured acrylic/melamine*

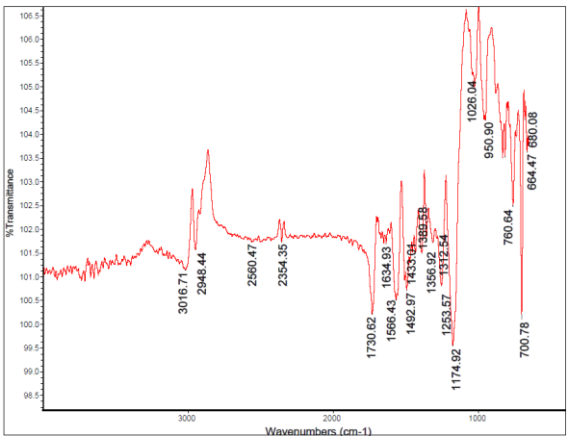

Figure 1d. *IR of cured acrylic/melamine coating*

Essence of coating forming is the reaction between functional groups of acrylic resin and melamine resin as mentioned above. -NH_2 group with peak 3519 on figure 2a, and peaks 3083, 3054, 3026, 2948, 3348, 2956, 2873, 3061, 2959,… of assymatry of CH_2 in carbon chain in figures 2a, 2b, 2c but lost on figure 2d. Peaks of C=C in vinyl group (1654), C=C in aromatic ring (1544, 1473) of figure 2b had moved to new peaks on figure 2d. Figure 2d with peaks 1728- oscilation of CO group in fat acid of figure 2a (acrylic resin) has changed to peak 1730 on figure 2d and peak 1654- oscillation of C=C in vinyl group of figure 2b has changed to peak 1634 of figure 2d. Therefore, curing reaction between acrylic and melamine resin has occurred.

Table 4. *Fluctuations in infrared cured acrylic/melamine coating*

No.	Typical spectrum	Wavenumbers (cm^{-1})
1	$\nu_{as}(CH_2=)$, asymmetry in vinyl group	3016
2	$\nu_{as}(CH_2=)$, asymmetry in carbon chain	2948
3	νOH, in COOH group	2560
4		2354
5	ν (CO) of fat acid	1730
6	ν (C=C) in vinyl group	1634
7	νC=C (epoxy aromatic ring)	1566
8	$\omega(CH_2)$, oscillation of CH_2 near vinyl group	950
9	□(CH), oscillation deformation of CH in aromatic ring	760

3.4. Effect of acrylic/melamine ratios on thermal resistance of coating

To study effect of acrylic/melamine ratios on thermal resistance of varnish coating, Thermogravimetric analysis (TGA) was used. Samples were M1, M2, M3, M4 with compositions as in table 2 and baked as in 3.1. Results were shown in table 5 and figure 2a, 2b, 2c, 2d.

Table 5. *Effect of AC/ML ratios on thermal resistance of coating*

Samples	Weight loss (%)	
	200°C	500°C
M1	4.58	94.19
M2	5.77	89.19
M3	8.09	86.41
M4	3.90	84.64

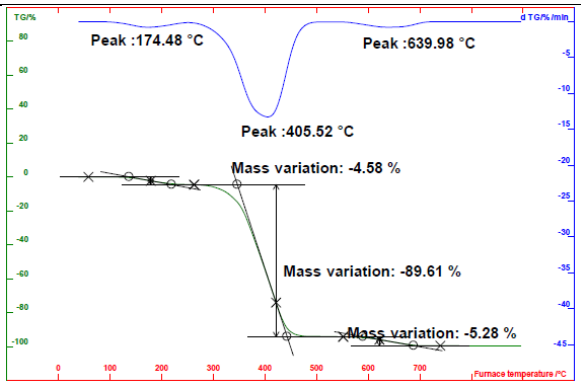

Figure 2a. *TGA of M1*

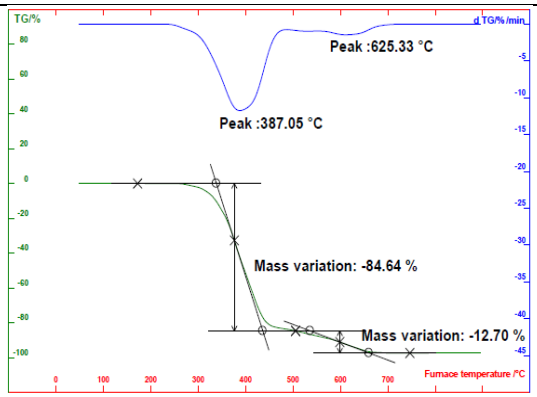

Figure 2b. *TGA of M2*

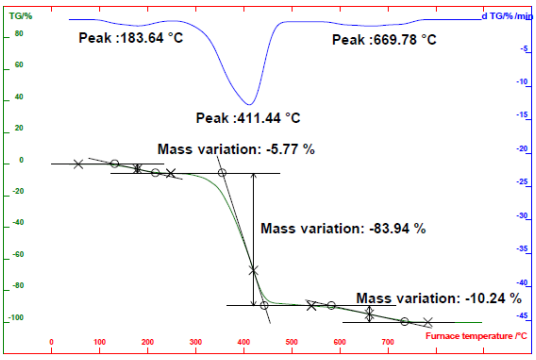

Figure 2c. *TGA of M3*

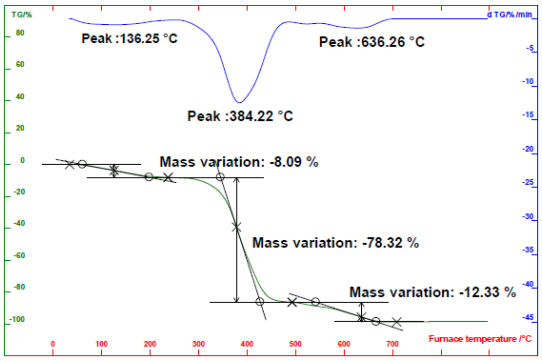

Figure 2d. *TGA of M4*

Table 5 and figures 2a, 2b, 2c, 2d showed that when temperature is below 200 °C: Decomposition of low molecular substances and residual solvents. Decomposition volume is

about 4- 8 %. In range from room temperature to 350 ºC: Decomposition of residual functional groups in polymer circuits, low molecular substances,.... For the total decomposition volume from room temperature to 500 ºC, M1 has the highest decomposition of 94.19 %. M4 has the lowest decomposition of 84.64 %. M2 and M3 have equivalent decomposition, about 86.41 and 89.19.

3.5. Investigation on usability of coating in some chemicals

To investigate usability of acrylic- melamine varnish in some chemical conditions, samples M1, M2, M3, M4 as mentioned above were baked at 140 ºC for 60 mins. Coatings were immersed in Castrol Activ lubricant, A95, HCl acid 5% for 240 hours. SEMs were also taken with magnification of 2,000 times to observe surfaces of coating before and after testing. Results were shown in table 6 and figures 3a, 3b, 3c, 3d.

Table 6. *Effect of chemical conditions on coating*

Samples	Coating surface (240 hours of immersion)		
	Castrol Activ	**5% HCl**	**A95**
M1	Unchanged	Unchanged	Unchanged
M2	Unchanged	Unchanged	Unchanged
M3	Unchanged	Unchanged	Unchanged
M4	Unchanged	Unchanged	Unchanged

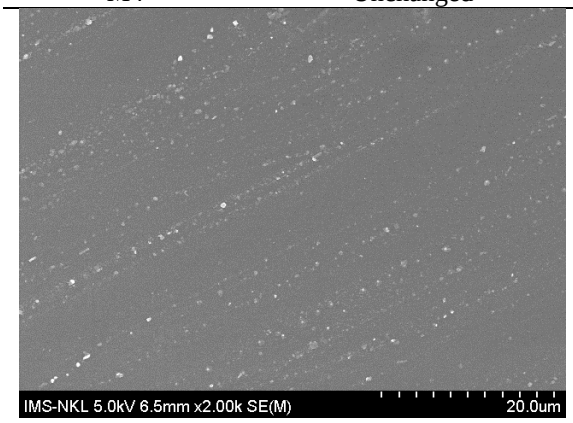

Figure 3a. *SEM of M1 before immersing in A95*

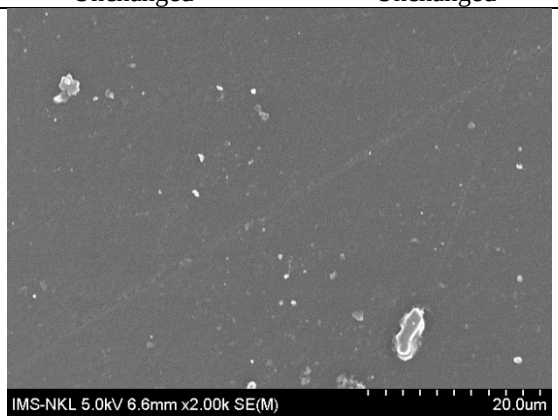

Figure 3b. *SEM of M1 after immersing in A95*

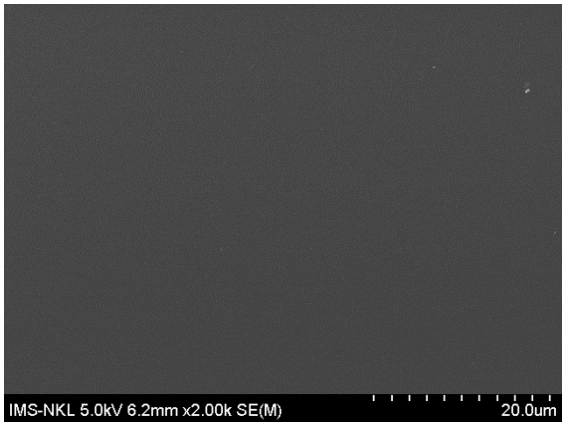

Figure 3c. *SEM of M4 before immersing in A95*

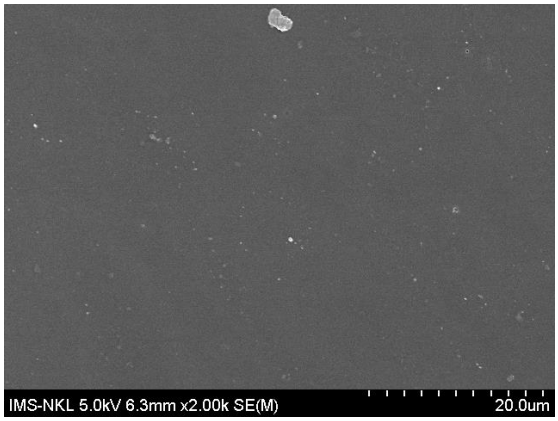

Figure 3d. *SEM of M4 after immersing in A95*

Results in table 6 and figures 3a, 3b, 3c, 3d showed that, all samples have high durability in Castrol Activ, HCl acid 5%, A95. This means that, acrylic- melamine coatings are capable of being used to protect metal parts in some chemical conditions and the coating can be used for cars' fuel tank or motors' fuel tank,...

4. Conclusions

1. When melamine content increases, relative hardness of coating increases, while adhesion, flexural strength, impact resistance decreases. The best ratio of acrylic/melamine is 35/15.

2. Drying temprature significantly effects to through-drying time of acrylic/melamine coating. At 140 ^{o}C, through- drying time of coating is 60 mins.

3. Thermal decomposition of varnish coatings depends on ratios of acrylic/ melamine resin. From room temprature to 500 ^{o}C, with ratio of acrylic/ melamine: 40/10, decomposition is 94.19 and the value is 84.64 when ratio of acrylic/ melamine resin is 20/30.

4. Baked acrylic- melamine coating can be used for metal details in chemical conditions such as Castrol Activ lubricant, A95, HCl 5% acid.

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