A Novel Type Nanocomposite Coating Based on Alkyd-Melamine Formaldehyde Resin Containing Modified Silica: Preparation and Film Properties

Ayça Bal, Işıl Acar, Gamze Güçlü

Department of Chemical Engineering, Faculty of Engineering, Istanbul University, 34320 Avcılar, Istanbul, Turkey

Received 4 February 2011; accepted 1 June 2011
DOI 10.1002/app.35029
Published online 27 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, the surface of the silica particles was modified with glycidoxypropyl trimethoxysilane and then silica nanoparticle modified alkyd-melamine resins were synthesized by two methods, namely *in situ* (IS) polymerization and blending (BL) methods. After alkyd resins containing 40% oil were prepared; these resins were blended with 30% of a commercial melamine-formaldehyde. The films of the alkyd-melamine formaldehyde resins were prepared from 60% solid content in xylene solutions. These films were cured at 170°C and properties of the films were determined. The effect of modified silica on the film properties and thermal behaviors of the resins was investigated. The scanning electron micrographs of the nanocomposite resin showed that modified silica particles have been dispersed into polymer resins substantially for IS polymerization. According to results of surface coating tests, we can say that, film properties of the resins prepared by IS method were better than that of prepared by BL method. In addition, using modified silica did not have a negative effect on the thermal behaviors of the resins with respect to thermogravimetric analysis. Furthermore, adding the modified silica in the resin structure caused increasing the thermal stability especially for resins prepared by IS method. As a result, alkyd-melamine resins containing modified silica nanoparticle are suitable for manufacturing of industrial baking enamels. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: E85–E92, 2012

Key words: alkyd resin; melamine–formaldehyde resin; coating; silica; nanotechnology

INTRODUCTION

Alkyd resins have been defined as the reaction product of polyhydric alcohols and polybasic acids. Alkyds are most common synthetics resins used in the paint industry because of their versatility and good coating properties. Alkyd-based coatings are well known for good corrosion protection, high gloss, and the ease of application.[1] The wide spectrum of properties of alkyd resins is broadened by modification with a variety of reactive chemicals and other polymeric materials.[2] Alkyd amino resins are used as matrix resins in the lacquer and paint industry. The short oil alkyd resins including nearly 35–45% phthalic anhydride (PA) contain a higher proportion of hydroxyl groups which provide compatibility and reactive sites with alkylated urea-formaldehyde and melamine-formaldehyde resins. This combination is widely used in industrial baking enamels for metal cabinets, appliances, window blinds, toys etc.[2]

The well-dispersed inorganic particles into a polymer matrix have been demonstrated to be immensely effective to improve the performance of the nanocomposites.[3] Inorganic–organic composite materials are increasingly important due to their superior properties. Polymer nanocomposites are normal composites with the difference that they have at least one phase in the nanometer range. Nanocomposites are a promising new class of materials containing filler due to the remarkable change in properties such as mechanical, thermal, electrical, and magnetic compared with pure organic polymers.[4–6] Nanomaterials greatly improve properties of the polymers such as thermal, mechanical, barrier, and flame retardant.[7] Nowadays, nanoparticle additives such as silica, layered clay are used to improve the properties of conventional coatings. The nanosize silica has a high surface area due to their silanol groups. Hydrophilic surface of silica does not process good compatibility with the polymer resin, and therefore the silica cannot be wetted very well by the resin.[3] The main disadvantages of silica are agglomeration and incompatibilities of these particles with the organic matrix, which limit their use.[8] The surface modification of silica nanoparticles with coupling agents is an effective way to improve inorganic–organic interfacial compatibility and miscibility with the polymeric matrix.[8] A literature survey

Correspondence to: G. Güçlü (gguclu@istanbul.edu.tr).
Contract grant sponsor: Research Fund of the Istanbul University; contract grant number: 3253

TABLE I
Properties of Silica Fume

Physical properties		Chemical composition (wt %)					
Spesific weight (mg/m^3)	Spesific surface (m^2/kg)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
2.21	26000 (BET)	93.00	1.00	2.00	1.50	0.70	0.40

has not yielded any research on alkyd-amino resin containing chemically modified silica. But, there are several papers about modified alkyd resins with nano particles such as zinc oxide, iron oxide titanium dioxide, and silica.[9–13]

In this study, the surface of the silica particles was modified with glycidoxypropyl trimethoxysilane (GPTMS) and then silica nanoparticle-modified alkyd-melamine resins were prepared by two methods, namely *in situ* (IS) polymerization and blending (BL) methods, for the first time. Then the effect of silica nanoparticle addition on the surface coating properties and thermal behaviors of alkyd-melamine resins was investigated.

EXPERIMENTAL

Materials

Coconut oil fatty acid (COFA) was used in the preparation of alkyd resins (A). COFA was prepared from synthetic fatty acids (5.5% caprylic acid, 8.5% capric acid, 46% lauric acid, 18.5% myristic acid, 11% palmitic acid, 2.5% stearic acid, and 8% oleic acid). These fatty acids and the other materials were obtained from Merck. Melamine-formaldehyde (MF) resin and silica fume were kindly provided by *MSc. Chem. Eng. Mehmet Emre* from *ÇKS Kimya Inc. Co*. and *Prof. Dr. Fahriye Kılınçkale* from *Istanbul University Civil Engineering Department*, respectively. Properties of silica fume are given in Table I. The silane-coupling agent GPTMS and rest of the materials were Merck (Germany) synthesis or analytical grade.

Preparation of alkyd resins

Alkyds formulated to have oil content 40% were prepared with PA, glycerine (G), COFA, dipropylene glycol (DPG). "K alkyd constant system" was used for the formulation calculations of the alkyd resins.[14] The K constant was 1.1 and the ratio of basic equivalents to acid equivalents (R) was 1.15. The reaction was carried out in a round bottom flask equipping with a Dean-Stark piece, gas bubbler, contact thermometer, and mechanical stirrer system. The temperature of the reaction was kept constant at 210–220°C. The reactions were followed with acid value (AV). Condensation reaction was allowed to continue until the AV of the resin was approximately 30–45 mgKOH/g. The AVs were determined by titration of samples dissolved in ethanol–toluene with 0.1*N* KOH solution. After the reaction, the resins were dissolved in xylene (60 wt % solution).

Surface modification of silica particles

First, stabilized fumed silica dispersion was prepared in toluene (about 7 wt %) using Tween 60 (1 wt % of silica). Then this silica dispersion were charged into a three necked round bottom flask equipping with a mechanical stirrer, a dropping funnel, condenser, contact thermometer, and a gas bubbler and heated to 80°C. And *p*-toluene sulfonic acid (0.1 wt % of total mixture) was added as a catalyst. GPTMS (8 wt % of total mixture) in 10 g toluene was then slowly added from a dropping funnel for half an hour. After the addition was complete, the reaction mixture was further stirred for 1 day at 80°C. Then, the nonbonded GPTMS was removed by toluene extraction.[15] For the structural analysis of the silica and modified silica samples, the infrared spectra were taken with Digilab Excalibur-FTS 3000MX model FTIR spectrophotometer using KBr pellets.

Preparation of alkyd-melamine formaldehyde resins

Alkyd resins were blended with 30% (wt) of a commercial melamine-formaldehyde resin for preparing of A-MF resins. Then A-MF resins were dissolved in

TABLE II
The Combinations of Alkyd-Melamine Formaldehyde Resins

Alkyd-amino resins	Modified silica (wt %)	Alkyd (wt %)	MF (wt %)
A0-MF	0	70	30
A0.5-MF-BL	0.5	70	30
A1-MF-BL	1	70	30
A2-MF-BL	2	70	30
A3-MF-BL	3	70	30
A0.5-MF-IS	0.5	70	30
A1-MF-IS	1	70	30
A2-MF-IS	2	70	30
A3-MF-IS	3	70	30

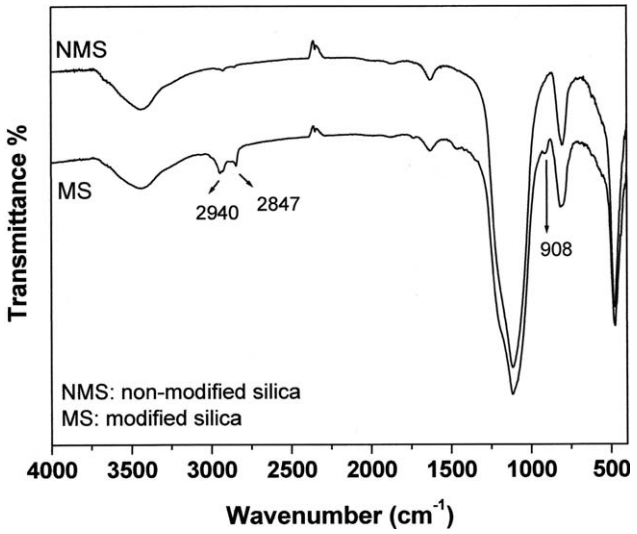

Figure 1 FTIR spectra of silica and modified silica samples.

xylene (60 wt % solution) and the films cast by 50 μm applicators from the solutions were heated at 170°C for 3 h in an oven and their surface coating properties were determined. The combinations of A-MF resins and the symbols of these resins are shown in Table II.

Preparation of silica nanoparticle-modified alkyd-melamine formaldehyde resins

Silica nanoparticle-modified alkyd-melamine resins were prepared by two methods, namely IS polymerization and BL methods. Silica nanoparticles were added to the reaction mixture at the beginning of the reaction for IS method. Another method called as BL, silica nanoparticles were directly mixed with alkyd-melamine resins with vigorous stirring. The amounts of nanoparticles were selected as 0, 5, 1, 2, and 3 wt % according to the total alkyd amount.

Testing of alkyd-melamine formaldehyde resins

Films cast by 50 μm applicators from the solutions were heated at 170°C for 3 h in an oven and their properties were determined. Drying time was determined by an Ericsen 415/E apparatus, which gave results according to DIN 53150. For hardness, a Konig Pendulum, which gave results according DIN 53157 was used. Adhesion strength of the films was determined by the crosscut method according to DIN 55 350-18. Abrasion resistance was determined by an Ericsen Send Abrasion Tester, type 2511-11, which gave results according to ASTM 9685. Abrasion resistance is usually performed with a falling sand abrasion test. Sand is dropped down a vertical tube onto the panel that is mounted at a 45° angle. The results are given as the amount of sand required removing a certain thickness of coating.

TABLE III
Physical Film Properties Alkyd-Melamine Formaldehyde Resins

Alkyd-amino resins	Hardness (könig sec)	Drying degree	Adhesion strength (%)
A0-MF	61	7	100
A0.5-MF-BL	61	7	100
A1-MF-BL	63	7	100
A2-MF-BL	63	7	100
A3-MF-BL	66	7	100
A0.5-MF-IS	70	7	100
A1-MF-IS	71	7	100
A2-MF-IS	72	7	100
A3-MF-IS	74	7	100

The effect of water immersion was determined according to ASTMD1647-59 by immersion in water for 18 h. The alkaline and acid resistance determinations were carried out according to ASTM D 1647. Films were prepared on glass test tubes and these films were heated at 170°C for 3 h in an oven. Then, the tubes were immersed in alkaline or acid solutions (3 wt %). The tubes were removed from the solutions after immersion for 1, 2, 3, 5, 7, and 24 h and the appearances of films were observed.

The wet–dry and heat cycle test consisted of three steps: (1) a test panel was immersed in a water bath kept at 23 ± 2°C for 18 h, then (2) the panel was took out and cooled to −20 ± 2°C in a refrigerator

TABLE IV
Acid Resistance of Alkyd-Melamine Formaldehyde Resins

Alkyd-MF resins	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h	24 h	48 h	72 h
A0-MF	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD	D
A0.5-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A1-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A2-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A3-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A0.5-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A1-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A2-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A3-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD	PD

NC, no change; PD, partial detachment from the surface; D, dissolved.

TABLE V
Alkali Resistance of Alkyd-Melamine Formaldehyde Resins

Alkyd-MF resins	1 h	2 h	3 h	4 h	5 h	6 h	7 h	8 h	24 h	48 h	72 h
A0-MF	NC	NC	NC	NC	PD	PD	PD	PD	PD	PD	PD
A0.5-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A1-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A2-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A3-MF-BL	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A0.5-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A1-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
A2-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD
A3-MF-SI	NC	NC	NC	NC	NC	NC	NC	NC	PD	PD	PD

NC, no change; PD, partial detachment from the surface; D, dissolved.

for 3 h, and (3) it was heated to 50 ± 2°C in an oven for 3 h. This cycle was repeated 10 times. After the test, the change of the sample surface in appearance such as cracking, blistering, or peeling was inspected visually.[16] All tests were repeated three times to confirm the repeatability of the tests.

Thermogravimetric analysis (TGA)

TGA was carried out by Linsesis STA PT 1750 model under air at a rate of 10°C/min with about 20 mg of cured alkyd-melamine formaldehyde resins.

Scanning electron microscopy (SEM)

SEM micrographs were taken with The Quanta FEG 450 model scanning electron microscope. The micrographs were taken at a magnification 40,000.

RESULTS AND DISCUSSION

Characterization of GPTMS-modified silica

Fourier transform infrared (FTIR) spectra of silica and GPTMS-modified silica particles were given in Figure 1. Epoxy functional silica particles has characteristic peaks at 2843 and 2941 cm^{-1} (C—H stretching band) and at 908 cm^{-1} (the epoxy band).[15] As seen in Figure 1, aforementioned peaks were observed at the spectrum of the GPTMS-modified silica.

TABLE VI
The Results of the Wet–Dry and Heat Cycle Test

Alkyd-amino resins	The appearance of sample surface
A0-MF	P
A0.5-MF-BL	NC
A1-MF-BL	NC
A2-MF-BL	NC
A3-MF-BL	NC
A0.5-MF-SI	NC
A1-MF-SI	NC

P, peeling; NC, no change.

Briefly, we can say that, FTIR spectra of samples prove that the reaction occurred between of the GPTMS with silica structure.

Physical properties of the films

The films of the alkyd-melamine formaldehyde resins were prepared from 60% solid content xylene solutions by using 50 μm applicators. After the films

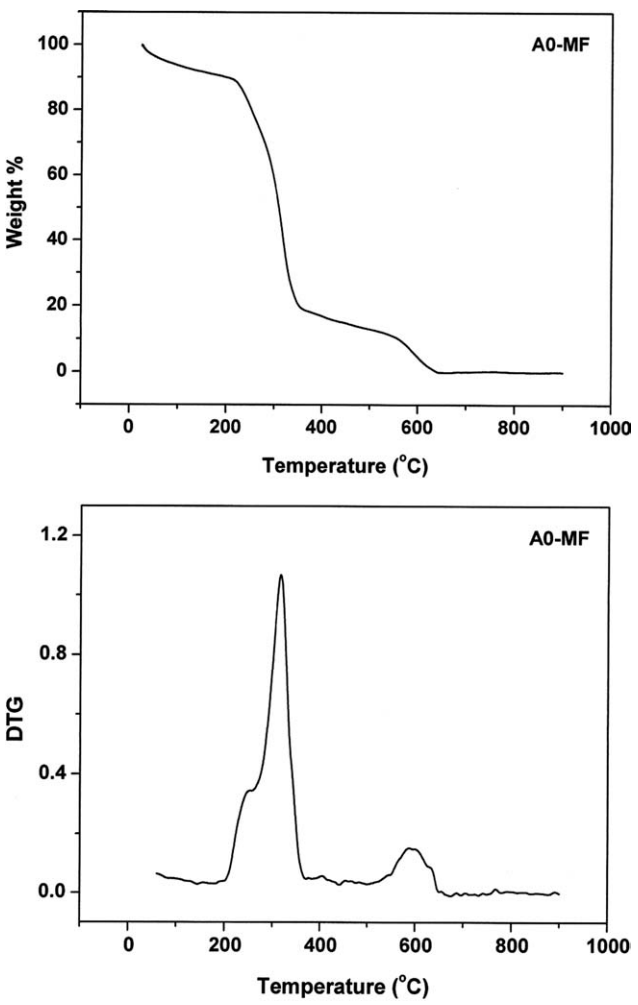

Figure 2 TGA and DTG curves of A0-MF resin.

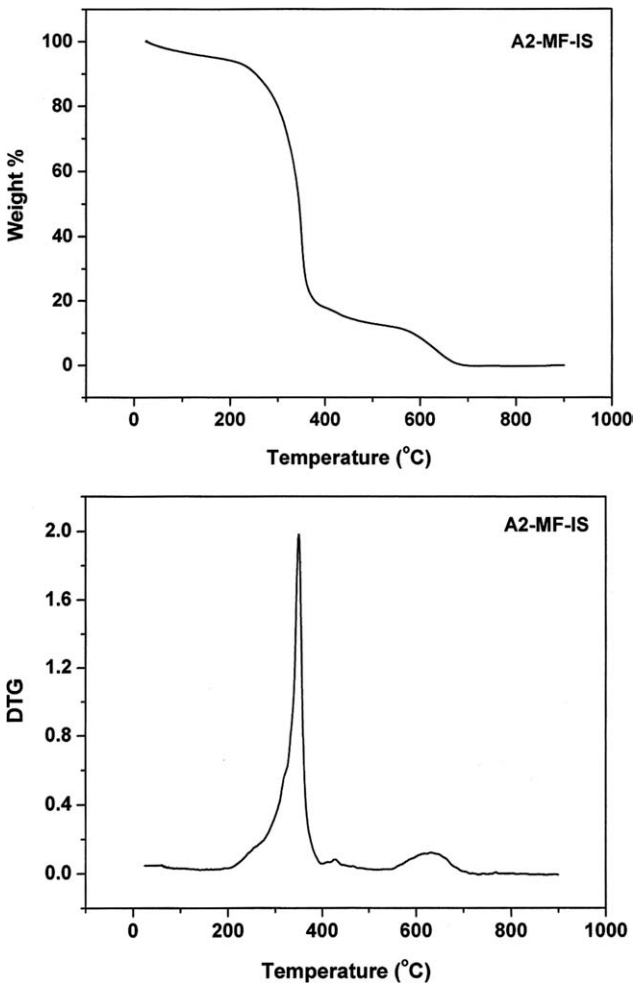

Figure 3 TGA and DTG curves of A2-MF-IS resin.

were cured at 170°C for 3 h in an oven, properties of the films were determined.

Physical properties of the resins were given in Table III. Determination of drying time of the resins is estimated by adherence or nonadherence of paper or glass beads. There are seven drying stages of this method, and the maximum drying degree is 7. Stage 1 is determined with glass beads and the remaining stages are determined with disks of typewriter paper (loads range from 5 to 5000 g/cm^2). The glass beads are allowed to remain on the film for 10 s, and the loads on the disks remain for 60 s.[17,18] As shown in Table III, all of the resins have excellent drying properties. Hardness values of the resins prepared by IS method higher than that of resins prepared by BL method. When the BL method was used, increment of hardness values of the resins was about interval of 0–8%. On the other hand, this increment interval was about 15–21%, for the IS method (Table III). Adhesion strength values of films were also given in Table III. As seen in table, all of the resins are excellent adhesion properties (adhesion strength 100%). Abrasion resistances values of A-MF-BL, A-MF-IS, and reference resin films determined as 1000, 1300, and 1200 mL sand, respectively.

Chemical properties of the films

The major disadvantage of the alkyd resins is poor alkaline resistance. In addition, other chemical resistance properties are also not desirable level. As seen in Table IV and V, addition of modified silica to resin significantly improved to alkaline and acid resistance especially A-MF-IS resins. In addition, all of the resins have excellent water resistance.

The results of wet–dry and heat cycle test show that the addition of the modified silica has positive effect on the resistance to environmental conditions of all resins (Table VI).

Thermogravimetric analysis

Thermal oxidative degradation experiments of alkyd-amino resins were carried out in Linsesis STA PT 1750 Thermogravimetric analyzer (Germany). The samples weighing about 20 mg in an alumina crucible were heated from room temperature to

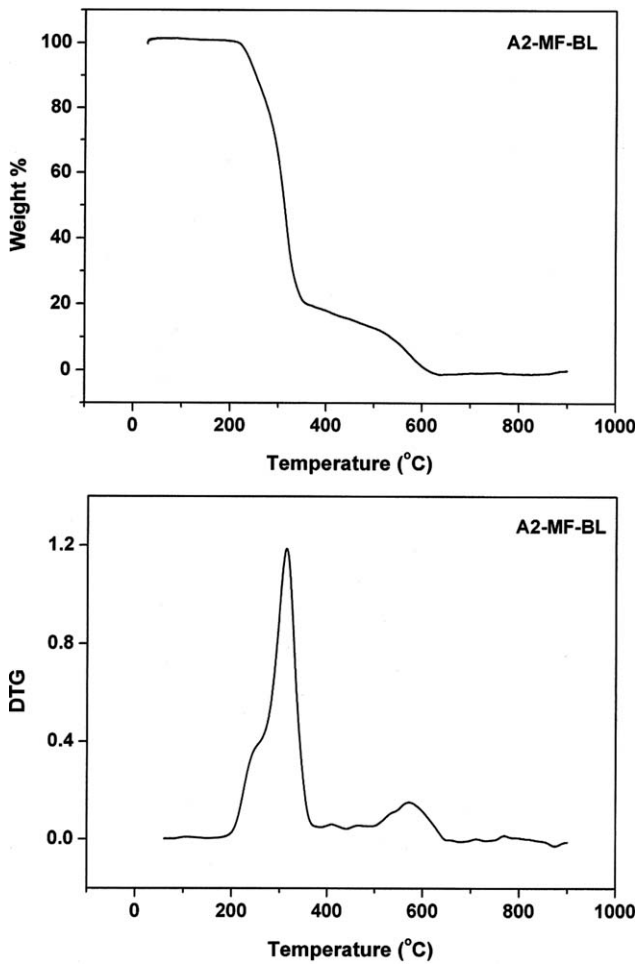

Figure 4 TGA and DTG curves of A2-MF-BL resin.

TABLE VII
DTG Peak Temperatures of the Samples

Sample	First weight loss step			Second weight loss step		
	On-set point (°C)	Maximum point (°C)	Off-set point (°C)	On-set point (°C)	Maximum point (°C)	Off-set point (°C)
A0-MF	200	314	375	500	576	654
A2-MF-BL	201	316	382	501	588	657
A2-MF-IS	204	350	401	551	636	725

900°C at a heating rate of 10°C min^{-1} in air atmosphere. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the A0-MF, A2-MF-BL, and A2-MF-IS samples were shown in Figures 2–4, respectively. As it is seen in Figures 2–4, degradation behaviors of all resins are similar. Modified silica containing alkyd-melamine formaldehyde resins have two main weight loss steps. The first weight loss step of resin occurred between about 200 and 400°C was due to the degradation of alkyd resin. Weight losses during thermal oxidative degradation of alkyd resins are due to decomposition of both the fatty acid chain and the polyester backbone.[19] The second weight loss step also occurred between about 500 and 725°C. This weight loss step may be caused by the decomposition of melamine-formaldehyde resins. Previous research about thermal oxidative degradation of alkyd resins has shown that; maximum degradation temperature of alkyd resin based on soybean oil fatty acid, PA, and glycerin has been observed at 400°C.[19] Generally, the incorporation of melamine-formaldehyde to the alkyd structure affects the degradation behavior of alkyd resins. In this study, thermal oxidative degradation rates of these alkyd-melamine formaldehyde resins substantially decreased with the incorporation of modified silica into the alkyd structure (Fig. 2–4, Table VII). However, change of silica nanoparticles addition method also affects the degradation behavior of alkyd resin. As it is seen in Table VII, in case of same feeding compositions, use of IS method increased the maximum degradation peak temperature. For example, the comparison of A2-MF-BL and A2-MF-IS, the first step degradation peak was observed at 316°C for A2-MF-BL and 350°C for A2-MF-IS. In addition, the second step degradation peak was observed at 588°C for A2-MF-BL and 636°C for A2-MF-IS (Table VII). That is, using of IS method instead of BL method for the adding of silica nanoparticles to the reaction mixture, caused increasing the degradation peak maxima approximately 40°C and 60°C for first degradation step and second degradation step, respectively.

As a result, incorporation of melamine formaldehyde to the resin structure increases the thermal stability of alkyd resin significantly. Alkyd-melamine formaldehyde resin degrades in a two step and this degradation behavior varies according to the silica nanoparticles addition method. Furthermore, the initial step of second degradation of A2-MF-IS starts at higher temperature than those of A0-MF and A2-MF-BL.

The temperature values required for reaching to certain weight losses (25, 55, 75, and 100%) were obtained from TGA curves are listed in Table VIII. According to these values, we can say that, thermal oxidative stability of A2-MF-IS has better than the other resins. In addition, as it is seen in Table IX, increasing the amount of modified silica from 0 to 2% caused increasing the degradation peak temperature at 80% weight loss from 424 to 514°C, for resins prepared by IS method. That is, increasing the modified silica ratio in the resin structure caused increasing the thermal stability. Nevertheless, the thermal resistance of the BL resins did not show any significant difference depending on the increase in the amount of modified silica. In other words, the thermal resistance of resins prepared by BL method,

TABLE VIII
The Temperatures Required for Reaching to Certain Weight Losses (%) for A2-MF Resins

Sample	Temperatures (°C)			
	25%	55%	75%	100%
A0-MF	250	309	338	654
A2-MF-BL	278	315	340	657
A2-MF-IS	301	345	360	725

TABLE IX
The Effect of Silica Content and Adding Method to 80% Weight Loss

Sample	Silica nanoparticles content (%)	Adding method of silica nanoparticles	Temperature required for reaching to 80% weight loss (°C)
A0-MF	0	-	424
A0.5-MF-BL	0.5	BL	454
A0.5-MF-IS	0.5	IS	442
A1-MF-BL	1	BL	450
A1-MF-IS	1	IS	462
A2-MF-BL	2	BL	452
A2-MF-IS	2	IS	514

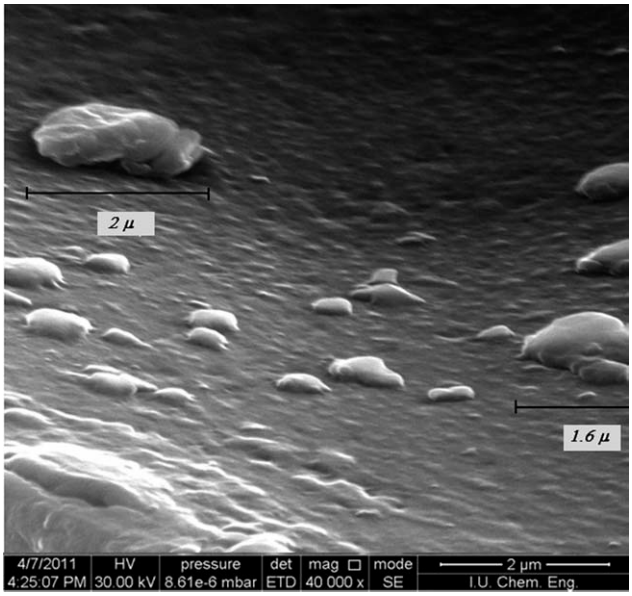

Figure 5 SEM micrographs of alkyd-melamine formaldehyde resins containing modified silica (BL method).

compared with the reference resin, a slight increase was observed. According to experimental data of TG analysis, we can say that, IS method is suitable method for preparing of silica modified alkyd-melamine resins and 2% is optimum silica content for IS method.

SEM analysis

The scanning electron micrographs of the nanocomposite resins for surface morphology analyses of the resins were illustrated in Figures 5 and 6.

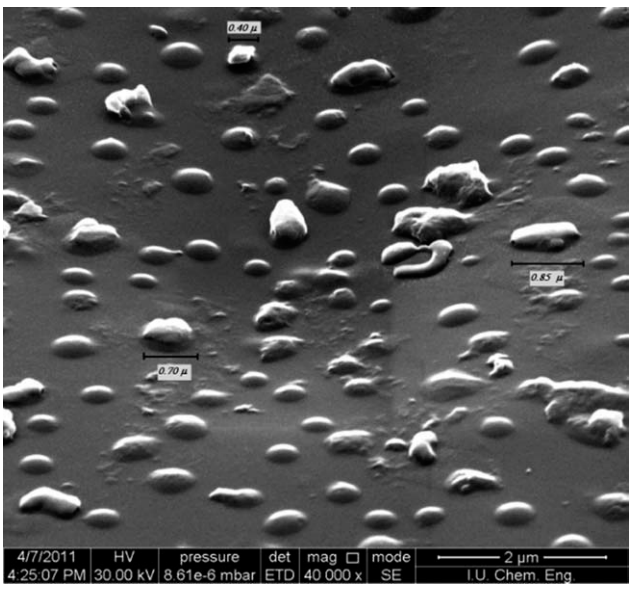

Figure 6 SEM micrographs of alkyd-melamine formaldehyde resins containing modified silica (IS method).

The micrographs of the nanocomposite resins prepared by IS and BL method showed that modified silica particles has been dispersed into polymer resins substantially for IS polymerization. On the other hand, homogeneous distribution of modified silica into the polymer resin was not observed depending on aggregation for BL method.

CONCLUSIONS

In this study, alkyd resins containing GPTMS-modified silica were synthesized and these modified alkyd resins were cured with different ratios of melamine-formaldehyde resin, for the first time. Surface modification of silica using GPTMS was achieved successfully. After the films were cured at 170°C for 3 h in an oven, physical, chemical, thermal, and morphologic properties of the films were investigated. The following conclusions can be drawn from the obtained results;

- Hardness values of the resins prepared by IS method higher than that of resins prepared by BL method. All of the resins are excellent adhesion properties (adhesion strength 100%).
- Addition of modified silica to resin significantly improved to alkaline and acid resistance especially A-MF-IS resins. All of the resins have also excellent water resistance. The results of wet–dry and heat cycle test show that the addition of the modified silica has positive effect on the resistance to environmental conditions of all resins.
- The SEM micrographs of the nanocomposite resins show that modified silica particles have been dispersed into polymer matrix substantially for IS polymerization.
- Thermal oxidative degradation rates of these alkyd-melamine formaldehyde resins substantially decreased with the incorporation of modified silica into the alkyd structure. According to experimental data of TG analysis, IS method is suitable method for preparing of silica modified alkyd-melamine resins and 2% is optimum silica content for IS method.

References

1. Gan, S. N.; Tan, B. Y. J Appl Polym Sci 2001, 80, 2309.
2. Mark, H. F.; McKetta, J. R.; Othmer, D. F. Encyclopedia of Chemical Technology; John Wiley & Sons: New York, 1978; Vol.2.
3. Sun, Y.; Zhang, Z.; Wong, C. P. J Colloid Interface Sci 2005, 292, 436.
4. Zhang, R.; Hu, Y.; Xu, J.; Fan, W.; Chen, Z. Polym Degrad Stab 2004, 85, 583.
5. Essawy, H.; Badran, A.; Youssef, A.; El-Hakim, A. E. A. Polym Bull 2009, 53, 9.

6. Kickelbick, G. Prog Polym Sci 2003, 28, 83.
7. Zhang, F.; Yu, C. Eur Polym Mater 2007, 43, 1105.
8. Rahman, I. A.; Jafarzadeh, M.; Sipaut, C. S. Ceramics Int 2009, 35, 1883.
9. Dhoke, S. K.; Bhandari, R.; Khanna, A. S. Prog Org Coat 2009, 64, 39.
10. Dhoke, S. K.; Khanna, A. S. Corrosion Sci 2009, 51, 6.
11. Allen, N. S.; Edge, M.; Ortega, A.; Sandoval, G.; Liauw, C. M.; Verran, J.; Stratton, J.; McIntyre, R. B. Polym Degrad Stab 2004, 85, 927.
12. Youssef, E. A. M.; Ahmed, N. M.; Abd El-Ghaffar, M. A. Pigm Resin Technol 1998, 27, 88.
13. Abu-Ayana, Y. M.; Yossef, E. A. M.; El-Sawy, S. M. Anti-Corros Methods Mater 2005, 52, 345.
14. Patton, T. C. Alkyd Resin Technology; John Wiley and Sons: NewYork, 1962.
15. Işın, D.; Kayaman, N.; Güngör, A. Prog Org Coat 2009, 65, 477.
16. Mizutani, T.; Arai, K.; Miyamoto, M.; Kimura, Y. Prog Org Coat 2006, 55, 276.
17. Güçlü, G.; Orbay, M. Prog Org Coat 2009, 65, 362.
18. Küçükoğlu, E.; Acar, I.; İyim, T. B.; Özgümüş, S. J Appl Polym Sci 2007, 104, 3324.
19. Güçlü, G.; Gürdağ, G.; İbiş, C.; Orbay, M. Chim Acta Turc 1996, 24, 219.