Asian Journal of Chemistry; Vol. 26, No. 11 (2014), 3191-3196

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15879

Preparation and Application of Novel Nanocomposite Coating Materials Based on Phenolic Resin

ONUR MÜKRIME BALCI and TÜLIN BANU IYIM*

Department of Chemical Engineering, Faculty of Engineering, Istanbul University, 34320-Avcilar, Istanbul, Turkey

*Corresponding author: Fax: +90 212 4737180; Tel: +90 212 4737070; E-mail: tulinb@istanbul.edu.tr

Received: 7 June 2013; *Accepted*: 28 September 2013; *Published online*: 25 May 2014; AJC-15211

The main aim of this work was to prepare resol type phenolic resin nanocomposite blends and was to investigate surface coating properties of their films. Firstly, phenolic resin nanocomposite blends were prepared by blending of bentonite (B) or silica (S) at different weight ratio (1, 2, 5 and 10 %) with resol resin. This nanocomposite blends were characterized by X-ray diffraction and SEM analysis. Thermal properties of these nanocomposite blends were also investigated using of thermogravimetric analysis technique. In order to investigate the usage of the nanocomposite blends as surface coatings materials, films were prepared from these products and applied standard test methods. The results showed that these products are thermally stable materials and all films are glossy or semiglossy and have excellent drying and adhesion properties.

Keywords: Resol type resin, Nanocomposite, Silica, clay, Surface coating material.

INTRODUCTION

Organic-inorganic nanocomposites have attracted the interest of materials scientists in recent decades because nanocomposites usually combine the advantages of the two components[1]. These nanocomposites exhibit improved tensile strength and moduli, decreased thermal expansion coefficient, decreased gas permeability, increased swelling resistance, enhanced ionic conductivity, flammability and other physical or mechanical properties[2-5]. These composite materials can be produced either by melt intercalation or by *in situ* polymerization. The latter approach involves monomer intercalation and polymerization in the gallery of the host to effect the exfoliation of the clay and the process is particularly convenient for thermoset-clay nanocomposites[6,7].

The phenolic resins may be considered to be the first polymeric products produced commercially from simple compounds of low molecular weight. Although they are now approaching their centenary, phenolic resins continue to be used for a wide variety of applications such as thermal insulation materials, molding powders, laminating resins, adhesives, binders, surface coatings, impregnants and composite material, because of its excellent ablative property, structural integrity, thermal stability and solvent resistance[2]. However, phenolic resin has been abandoned in the nanocomposite field even though it is the first synthesized resin and possesses many advantages. The reason is that general phenolic resins have a three-dimensional structure even if the resin is not crosslinked[2]. Although the lamella of the layered silicate can be easily intercalated by linear polymers, this three-dimensional structure of phenolic resin makes it very difficult to intercalate in the layered silicate gallery[2]. To overcome this difficulty, many experimental studies have been performed[2,8-12]. Researches on synthesized phenolic resin/layered silicate nanocomposites by melt intercalation or by intercalative polymerization of phenolic resin with phenol and formaldehyde in the presence of oxalic acid and montmorillonite modified with 4-aminophenol hydrochloride in these studies. These nanocomposites were determined mechanical properties or thermal stabilities. Up to now, only limited researches on resole-type phenolic resin/layered silicate nanocomposites *via in situ* polymerization of monomers have been published[1,2,6]. Manfredi *et al.*[13] synthesized resol/modified montmorillonites and resol/unmodified montmorillonites nanocomposites. They observed the influence of nanoreinforcement in the curing process and in the final properties of the cured nanocomposites. Kaynak and Tasan[14] have synthesized resol type phenolic resin/layered silicate nanocomposites by mixing of clay with liquid resol resin. In this research it was investigated that effects of production parameters on the structure of resol type phenolic resin/layered silicate nanocomposites.

In this work, the main aim was to prepare resol type phenolic resin nanocomposites blends and was to investigate surface coating properties of their films. At first, phenolic resin nanocomposite blends were prepared by blending of bentonite and silica with resol resin. This nanocomposite blends were characterized by X-ray diffraction (XRD) and SEM analysis. Thermal properties of these nanocomposite blends were also investigated. In order to investigate the usage of the nanocomposite blends as surface coatings materials, films were prepared from these products and applied standard test methods.

EXPERIMENTAL

All the chemicals were purchased from Merck AG (Darmstadt, Germany). All materials were synthesized or analytical grade and used as received.

Bentonite (natural clay) (B) and silica (silica fume) (S) were used as the reinforcement materials. The bentonite from Turkey was kindly provided by Dr. Gülten Atun from the Chemistry Department of Istanbul University. The silica was provided by Antalya Etibank Association. The chemical compositions of the reinforcement materials were presented in Table-1.

X-ray diffraction (XRD) patterns were obtained by using a Rigaku D/Max Ultima + X-ray diffractometer equipped with CuK_α radiation (λ = 0.15405 nm). SEM Micrographs were taken with The Quanta FEG 450 model scanning electron microscope. The micrographs were taken at a magnification 5000. Thermogravimetric analysis (TGA) was carried out with Linseis STA PT 1750 (German) thermal analyzer with a heating rate of 10 °C/min in air. The sample mass was 20 mg. Differential scanning calorimetry (DSC) analysis of the resins were carried out under nitrogen atmosphere, with approximately 10 mg samples by heating up to 300 °C, at a heating rate of 1 °C/min with Linseis DSC-PT10 model apparatus (German).

Preparation of resol resin: Polycondensation reaction of phenol (P) and formaldehyde (FA) (37 % aqueous solution stabilized with 10 % methanol) was carried out according to known procedure[15] using 1/3 mol ratio of phenol/formaldehyde. The reaction system was a 500 mL four-necked conventional glass reaction kettle equipped with a mechanical stirrer, heating mantle, reflux condenser, temperature control system. Phenol, formaldehyde and NaOH as catalyst (0.5 wt. % in the total reaction mixture) were added into reaction kettle at room temperature, mechanically stirred and the temperature was increased to 65 °C and kept there. The reaction was followed by the determination of the free formaldehyde amount according to the hydroxylamine hydrochloride method[16]. After the 4 h the amount of the free formaldehyde was constant and found to be 1 wt. %. At the end of the reaction, resol type resin (R) was purified using a rotary evaporator system and used for the preparation of the phenolic resin nanocomposite blends.

Preparation of nanocomposite blends: Resol type phenolic resin nanocomposite blends were obtained by the blending bentonite and silica with resol resin using 1, 2, 5 and 10 wt. %, based on weight of resol resin. Nanocomposite blends were prepared in a 250 mL glass reaction kettle. 50 g resol resin was added to the reaction kettle at room temperature, mechanically stirred (150 rpm) and the temperature was increased to 50 °C and kept there. Then the rate of mixing was increased to 900 rpm. The addition of reinforcement materials was completed in 2 h at same mixing speed and the blending process was continued for a 16 h. At the end of the reaction, homogenous nanocomposite blends (R1B, R2B, R5B, R10B, R1S, R2S, R5S and R10S) were obtained and storage using for the preparation of surface coatings films. The feeds compositions of nanocomposite blends are shown in Table-2.

TABLE-2
SYMBOLS AND THE FEEDING COMPOSITION
OF NANOCOMPOSITE BLENDS

Symbol of Product	Resin	Bentonite (%)	Silica (%)
R1B	100	1	–
R2B	100	2	–
R5B	100	5	–
R10B	100	10	–
R1S	100	–	1
R2S	100	–	2
R5S	100	–	5
R10S	100	–	10

Film preparation and determination of their properties: The films of nanocomposite blends were prepared from the 60 % solid content ethanol solutions by using 100 μ Erichsen applicator on the glass or metal plate according to the test methods. After the films were cured at 170 °C for 0.5 h in oven, in order to investigate the surface coatings properties of the films some main standard test methods such as drying time, hardness, adhesion, gloss, impact resistance, abrasion resistance, water, solvent and acid resistance were applied.

Drying degrees of the films were determined at 20 ± 2 °C, 60 ± 5 % relative humidity by Erichsen Type 415/E Tester which gave results according to DIN 53 150. As indicated in the DIN 53 150, there are 7 drying degree (or stage). Drying degree was determined at the 5, 10, and 15th min, at every 15 min up to 4 h, at every 30th minute up to 8 h and 24th after application of the films.

Hardness was determined by König pendulum, which gave results according to DIN 53 157, 72h after application of the films. The results were presented as König second compared with oscillation time of standard glass plate as 250 König second.

Adhesions of the films were tested by the cross-cut method according to ASTM D 3359-76.

Gloss of films was determined by Gardner Multi-Angle glossmeter according to ASTM D 523.

The impact resistance was determined on films according to ASTM D 2794-69, 72 h after application by FTMS 6226 Impact Flexibility Tester, which determines failure between 0.5 % and 60 % elongation of the film after impact.

TABLE-1
CHEMICAL COMPOSITION OF BENTONITE AND SILICA

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	Cr_2O_3 (%)	BaO (%)	SO_3 (%)	R* (%)
Bentonite	66.74	17.1	1.29	0.20	2.72	5.09	0.11	0.17	0.005	0.01	0.13	6.44
Silica	95.41	0.05	0.048	0.005	0.10	1.25	0.57	2.30	0.018	-	-	-

R* Residue

Abrasion resistance is usually performed with a falling sand abrasion tester. 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. Abrasion resistance was determined by Erichsen Sand Abrasion Tester, type 2511-11, which gave results according to ASTM 9685.

Water resistance of the films was determined according to ASTM D1647-59 by 18 h of immersion in water, 48 h after application of the films. The conditions of the films were determined immediately after wiping dry and after 20 min, 1, 2 and 24 h.

To evaluate the solvent resistance of films was performed as follows. A piece of absorbent gauze (2 cm × 2 cm) swollen in a solvent was set on a film coated a glass panel. The panel was covered with a laboratory dish and kept at 20 ± 2 °C for 0.5 h. The conditions of the films were observed[17].

Acid resistance tests were carried out according to ASTM D 1647. Films were prepared on glass test tubes by dipping and the tubes were inverted and supported on vertical pegs during the drying period (72 h). Then, the tubes immersed in acid solution. The tubes were removed from the solutions after immersion for 15 min, 0.5 h, 1, 2, 4, 8, 16 and 24 h and the appearances of films were observed.

RESULTS AND DISCUSSION

In this study, nanocomposite blends were obtained by blending a resol type phenolic resin as matrix and bentonite and silica as reinforcement. This nanocomposite blends were characterized by X-ray diffraction and SEM analysis. Thermal properties of nanocomposite blends were also determined. The films were prepared from these nanocomposite blends and surface coatings properties of these films were investigated.

Characterization of nanocomposite blends: The diffraction patterns of the pure bentonite and some nanocomposite blends (R5B and R10B) are shown in Fig. 1. The X-ray patterns of pure bentonite exhibit the intense diffraction peak at 2θ = 5.8°. However, this diffraction peak has disappeared in the nanocomposite blends containing 5 and 10 wt. % bentonite. This result indicates the exfoliation of clay sheets and uniformly dispersed in polymer matrix.

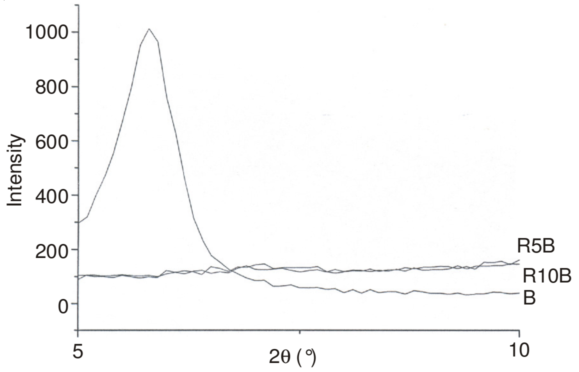

Fig. 1. XRD spectra of bentonite and some nanocomposite blends

SEM micrographs of silica containing nanocomposite (R5S) is given in Fig. 2. As shown in Fig. 2 silica particles were dispersed in phenolic resin matrix. Nanocomposite structure has a highly homogenous distribution.

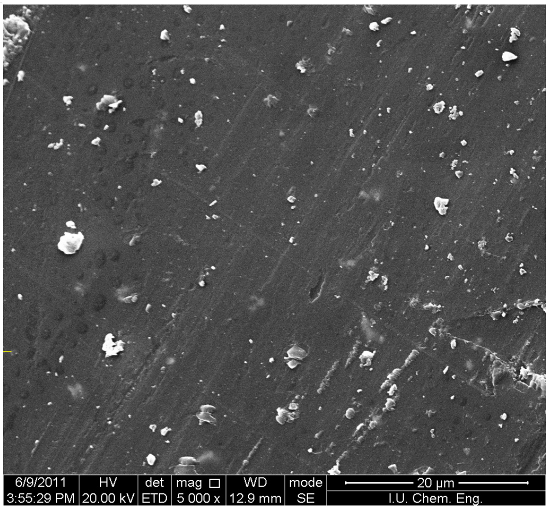

Fig. 2. SEM micrograph of R5S

Thermal properties of the nanocomposite films: Thermal oxidative degradations of the nanocomposite films were investigated by TGA technique under air atmosphere with a heating rate of 10 °C/min. Results were presented in Table-3 and Figs. 3 and 4. Thermogravimetric curves indicated that all nanocomposite films generally exhibit same degradation behaviors, so there are main three oxidative degradation steps. On the other hand, when the bentonite was used as 2 % wt. amount (R2B), thermal oxidative degradation stability and the final degradation temperature of the resol type phenolic resin obviously increased. Also, when the silica was used as 5 % wt. amount (R5S), thermal oxidative degradation stability and the final degradation temperature of the resol type phenolic resin obviously increased. It was known that the presence of silica compounds in medium would improve the thermal stability and provide a retarding effect on the thermal degradation of the component[2]. It was concluded that the thermal oxidative degradation stability and the final degradation temperature of the resol type phenolic resin can obviously be increased with the incorporation of the inorganic reinforcement such as bentonite or silica. It was confirmed that thermal decomposition temperatre of the R2B was slightly increased due to the formation of the organic-inorganic hybrid system (Fig. 5). This result is compatible with those given in literature[18].

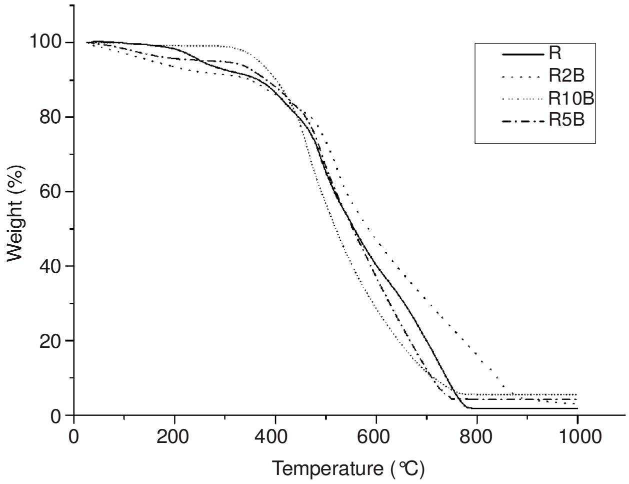

Fig. 3. TGA curves of resol type phenolic resin (R), R2B, R5B and R10B

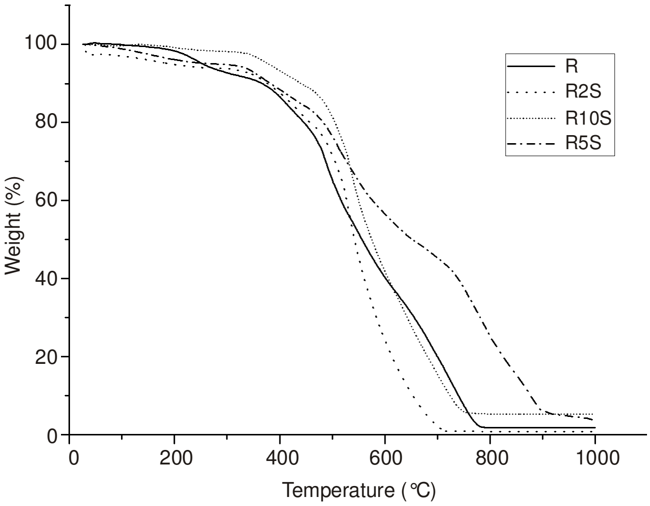

Fig. 4. TGA curves of resol type phenolic resin (R), R2S, R5S and R10S

Surface coatings properties of the products: Surface coatings properties of the films prepared from nanocomposite blends are given in Tables 4-7. Determination of drying time of the nanocomposite blends is performed by adherence or nonadherence of sand or paper to the film under various loadings. In this method there are seven drying stages and maximum drying stage are 7. Stage 1 is determined with silver sand (0.16 to 0.315 mm) or glass beads. The sand is allowed to remain on the film for 10 s. The remaining stages are determined with disks of typewriter paper (22 mm in diameter and weighing about 60 g/m^2). Loads range is from 5 to 5000 g/cm^2 and the loads on the disks remain for 60 second. As seen from Table-4, the drying stage of resol type phenolic resin is 7 and it was observed that all nanocomposite blends reach up to the 7th drying stage. So, all of the products have excellent drying properties. Furthermore, all films exhibit superior adhesion to the glass substrate.

As shown in Table-4, the hardness values of the nanocomposite blend films are higher than resol type phenolic resin. But an amount of 5 wt. % seems to be optimal. The higher hardness of nanocomposite blend films was also attributed to the cohered silica or clay particles on the film surface.

TABLE-3
THERMAL OXIDATIVE DEGRADATIONS OF THE NANOCOMPOSITE FILMS

Sample	$T_{10\%}$ (°C)[a]	$T_{30\%}$ (°C)[b]	$T_{50\%}$ (°C)[c]	Residue[d] (%)	Final Oxidative Degradation Temp. (°C)
R	367	488	557	1,84	791
R2B	351	511	585	3,89	925
R5B	382	492	554	4,39	767
R10B	401	467	520	5,7	785
R2S	377	505	542	0,98	725
R5S	383	527	653	5,33	918
R10S	441	532	575	5,44	785

[a]The temperature where 10 % weight loss was occurred, [b]The temperature where 30 % weight loss was occurred, [c]The temperature where 50 % weight loss was occurred, [d]Weight of residue at final oxidative degradation temperature

TABLE-4
DRYING DEGREE, HARDNESS, ADHESION, IMPACT RESISTANCE,
ABRASION RESISTANCE AND GLOSS OF THE NANOCOMPOSITE FILMS

Product	Drying Degree	Hardness (könig sec.)	Adhesion (%)	Impact resistance (%)	Abrasion resistance (mL sand)	Gloss
R	7	141	100	1	3500	80
R1B	7	170	100	1	2000	78
R2B	7	179	100	2	2200	78
R5B	7	187	100	2	1500	75
R10B	7	176	100	2	1500	69
R1S	7	180	100	1	1250	79
R2S	7	190	100	1	3200	79
R5S	7	198	100	1	4750	77
R10S	7	193	100	1	2000	74

TABLE-5
WATER RESISTANCE OF THE NANOCOMPOSITE FILMS

Product	Water resistance				
	0 min	20 min	1 h	2 h	24 h
R	C	C	C	C	C
R1B	C	C	C	C	C
R2B	C	C	C	C	C
R5B	C,SB	C,SB	C,SB	CSB	C,SB
R10B	C	C	C	C	C
R1S	C	C	C	C	C
R2S	SC	SC	SC	SC	C
R5S	C	C	C	C	C
R10S	C	C	C	C	C

Note: Appearance of the film after immersion in water for 18 h: C = clear, SB = slightly blistering, SC = semiclear

TABLE-6
SOLVENT RESISTANCE OF THE NANOCOMPOSITE FILMS

Product	Solvent			
	Toluene	Carbon tetrachloride	Methyl ethyl acetone	Ethyl alcohol
Resol type phenolic resin	NC	NC	NC	NC
R1B	NC	NC	NC	NC
R2B	NC	NC	NC	NC
R5B	NC	NC	NC	NC
R10B	NC	NC	NC	NC
R1S	NC	NC	NC	NC
R2S	NC	NC	NC	NC
R5S	NC	NC	NC	NC
R10S	NC	NC	NC	NC

NC: no change

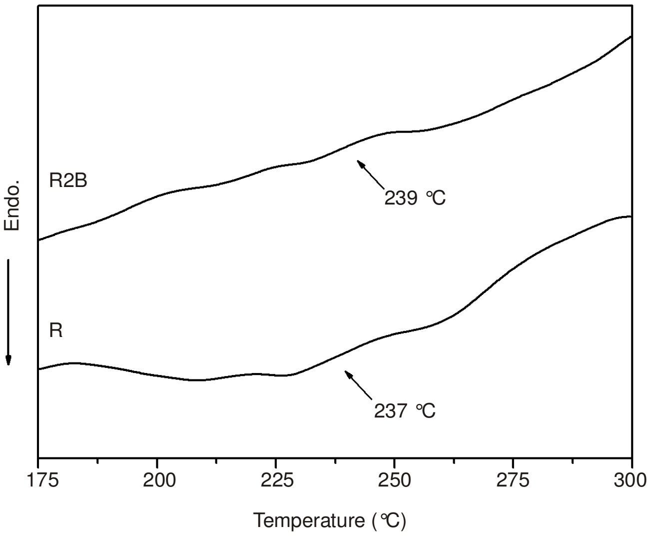

Fig. 5. DSC curve of resol type phenolic resin (R) and R2B

TABLE-7
ACID RESISTANCE OF NANOCOMPOSITE FILMS

Product	Acid resistance	
	16 h	24 h
R	R	-
R1B	W	-
R2B	W	-
R5B	W	-
R10B	NC	W
R1S	W	-
R2S	W	-
R5S	W	-
R10S	W	-

W: wrinkling, R: removal, NC: no change

On the other hand, the some films which prepared from R1B, R1S, R2S, R5S and R10S have same impact resistance values but the values R2B, R5B and R10B are slightly higher than these of resol type phenolic resin and other films.

The presence of bentonite and silica in nanocomposite blends did not cause to a significant decrease in abrasion resistance values of the films. In addition, the film prepared from R5S show better performance than the film prepared from resol type phenolic resin. Gloss properties of the nanocomposites are shown in Table-4. The addition of bentonite and silica reduced the gloss value of the nanocomposite blend films.

As seen from Table-5, water resistance of the nanocomposite blend films except prepared from R5B are excellent.

Table-6 indicates that all films show high solvent resistance.

As seen from Table-7, R10B film has the best acid resistance value, all films expect prepared from R10B have the same acid resistance.

Conclusions

In this work, resol type phenolic resin nanocomposites blends have been prepared by the blending of bentonite and silica with resol resin. This nanocomposite blends were characterized by X-ray diffraction and SEM analysis. Thermal properties of these nanocomposite blends were also investigated. In order to investigation of the surface coatings properties of the nanocomposite blends, some main standard test methods were applied to the films obtained from these nanocomposite blends.

The following conclusions can be drawn:

- Thermogravimetric curves were indicated that the R2B and R5S have the highest thermal stability in case of using bentonite and silica as reinforcement, respectively.
- Thermal oxidative degradation stability and the final degradation temperature of the resol type phenolic resin can obviously be increased with the incorporation of the inorganic reinforcement such as bentonite or silica.
- All of the nanocomposite blend films have excellent drying properties and adhesion properties.
- The hardness values of the nanocomposite blend films are higher than resol type phenolic resin. Increasing the bentonite and silica ratio up to 5 % causes an increment in hardness value of the films.
- Addition of bentonite and silica to nanocomposite blends did not have a negative effect on the water resistance (except R5B sample) and solvent resistance of the films.
- Addition of bentonite and silica to nanocomposite blends significantly improved to acid resistance of the films.

It was concluded that the resol type phenolic resin nanocomposite blends prepared in this study can be used as thermally resistant surface coating materials.

REFERENCES

1. Z. Wu, C. Zhou and R. Qi, *Polym. Compos.*, **23**, 634 (2002).
2. W. Jiang, S.H. Chen and Y. Chen, *J. Appl. Polym. Sci.*, **102**, 5336 (2006).
3. J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris, E. Manias, E.P. Giannelis, M. Wuthenow, D. Hilton and S.H. Phillips, *Chem. Mater.*, **12**, 1866 (2000).

4. G.M. Kim, D.H. Lee, B. Hoffmann, J. Kressler and G. Stöppelmann, *Polymer*, **42**, 1095 (2001).
5. T.K. Chen, Y.I. Tien and K.H. Wei, *Polymer*, **41**, 1345 (2000).
6. H. Wang, T. Zhao, Y. Yan and Y. Yu, *J. Appl. Polym. Sci*., **92**, 791 (2004).
7. X. Kornmann, H. Lindberg and L.A. Berglund, *Polymer*, **42**, 1303 (2001).
8. A. Usuki, T. Mizutani, Y. Fukushima, M. Fujimoto, K. Fukomori, Y. Kojima and Q. Kurauchi, US Patent 4,889,885 (1989).
9. M.H. Choi and I.J. Chung, *J. Appl. Polym. Sci*., **90**, 2316 (2003).
10. H. Wang, T. Zhao, L. Zhi, Y. Yan and Y. Yu, *Macromol. Rapid Commun*., **23**, 44 (2002).
11. J. Gao, C. Jiang and X. Su, *Int. J. Polym. Mater*., **59**, 544 (2010).
12. J.- Gao and M. Zhao, *J. Polym. Mat*., **57**, 101 (2007).
13. L.B. Manfredi, D. Puglia, J.M. Kenny and A. Vazquez, *J. Appl. Polym. Sci*., **104**, 3082 (2007).
14. C. Kaynak and C.C. Tasan, *Eur. Polym. J*., **42**, 1908 (2006).
15. G. Eastmond, A. Ledwith, S. Russo and P. Sigwalt, Phenol-Formaldehyde Polymers, Comprehensive Polymer Science, Pergamon Press, New York (1989).
16. G.F. D'Alelio, Experimental Plastics and Synthetic Resins, Wiley, New York (1955).
17. T. Mizutani, K. Arai, M. Miyamoto and Y. Kimura, *Prog. Org. Coat*., **55**, 276 (2006).
18. J.M. Lin, C.C.M. Ma, F.Y. Wang, H.D. Wu and S.C. Kuang, *J. Polym. Sci. B, Polym. Phys*., **38**, 1699 (2000).