

SYNTHESIS, PHYSICO-CHEMICAL PROPERTIES, AND SPECTROSCOPIC CHARACTERIZATION OF PHENOLIC MODIFIED CASTOR OIL BASED POLYOL

A. VAZID¹, V. URVASHI¹, K. JYOTSNA², S. A. ALHADI FAROUN³, I. MOHD³

¹Chaudhary Devi Lal University, Department of Chemistry, Polymers and Advanced Materials Research Lab
Sirsa-125 055, Haryana, INDIA

✉E-mail: kanikavashist2007@gmail.com

²Chitkara University, Department of Applied Sciences, Rajpura, Chandigarh 160014, INDIA

✉E-mail: jyotsna.kaushal@chitkara.edu.in

³Jamia Millia Islamia University, Department of Mechanical Engineering, New Delhi, INDIA

Physico-chemical properties and optical characterization of synthesized polyol explores the possibility to understand the mechanism and controlling the reaction parameters in a suitable manner during the production of polyurethane products. Castor (*Ricinus Communis*) is generally grown for its oil yielding seeds, which contains ricinoleic acid and only the oil with hydroxyl group in molecular structure due to this castor oil can be exploited as modified polyol. In the present study, castor oil has been modified with blending phenolic resin and reacted with diethanolamine (DEA) and diethyleneglycol (DEG) to synthesize the polyol. Various physico-chemical properties of synthesized polyol such as acid value, OH value, and moisture content have been measured. UV-VIS, FTIR and NMR spectroscopic studies of the synthesized castor oil based polyol are carried out. Optical properties such as absorption coefficient (α), extinction coefficient (k) and optical band gap (E_g) of polyols were determined. FTIR studies show the information of changes in the functional group with changing concentration of diethanolamine (DEA), diethyleneglycol (DEG), and phenolic resin (Ph. resin). Infrared spectroscopy (IR) is used to understand the characterization worth with suitable standards in view of chemical and structural characterization of synthesized polyol.

Key Words: Phenolic resin, physico-chemical properties of polyol, optical properties and spectroscopic studies

Introduction

Studies based on experimental and spectroscopic characterization of polymeric materials may provide the information for versatile engineering applications. Although many research works have been directed to petrochemicals based polyurethanes (PUs), just a few studies have been reported on agro based products with formation and their spectroscopic characterization. Polyurethanes are rapidly developing products especially in coating industry. Thus, the important area of present day research in the surface protective coatings is to explore the potential utility of renewable and non-conventional raw materials for preparation of resins. The most common among these materials are starch, cellulose, and various oils such as castor oil, soyabean oil etc. Phenolic resins are one of the most important thermosetting polymers because of their good temperature and electrical resistance properties [1]. The traditional phenolic resins have various advantages [2] such as heat resistance, good electronic properties, and flame retardance. Phenolic (resole) resins are used as cross-linkers for adjusting flexibility and improving surface contact in various types of coatings [3]. Resole type phenolic resins have the capability to cure either by

use of a curing agent or by heating only [4]. Although the importance of phenolic resins has dwindled, they still have significant uses. Their importance is likely to remain considerable because the used raw materials can be obtained at a reasonable cost. The individual development of phenolic resins is still continuing despite their long history [1]. In many industrial applications, amino resins are used as thermosetting polymers. Despite possessing many attractive features, the acceptance of many engineering areas especially in the coating industry as paint binders is obstructed by some of its inherent qualities such as brittleness and poor water resistance (Osemmeahon and Barminas, 2006a; Conner, 1996; 1990).

The importance of synthesizing polymers containing moieties capable of participating in polymerization reactions continue to increase in today's coating industry [5]. Alkyd resins are complex network polyesters widely used in the paint and coatings industries [6]. Polyols are alkyd resins with a specified high hydroxyl content that can react with compounds containing epoxy, isocyanate groups to produce hybrid coatings with superior performance [7]. A literature survey reveals that mostly petrochemicals-based polyurethanes have covered the polymer industries, which are costly raw materials as compared to vegetable oil based PUs.

In the present investigation, attempt has been made to synthesize polyols for polyurethane system by using castor oil, diethanolamine (DEA) and diethyleneglycol (DEG); modified oil based polyol with phenolic resin. Physicochemical properties such as acid value, OH value, moisture content; and also spectroscopic techniques such as UV-VIS, FTIR and NMR have been used for the characterization of prepared phenolic modified polyol.

Experimental

Raw materials

Castor oil and phenolic resin supplied by Shivathene Ltd. Parwanoo (HP) were used. Diethanolamine and diethyleneglycol obtained from (Qualigens Fine Chemicals, Mumbai) were used. Acetone (Sisco Research Laboratory, AR grade) and KOH solution were prepared for analysis (Himedia Laboratories Pvt. Ltd. Mumbai).

Synthesis of modified Polyol

The reaction for the preparation of modified polyol from castor oil was carried out in a three-necked round bottom flask (equipped with nitrogen inlet, thermometer, stirrer, and reflux condenser). Three sets of polyols were synthesized with repeated sets of conditions. In the first set, castor oil was taken into the three necked flask after heating it with added phenolic resin at varying concentrations keeping the quantity of castor oil constant. In the second and third set, castor oil and phenolic resin concentration were kept constant in all the three prepared polyol samples with varying concentrations of diethylene glycol and diethanolamine as shown in *Table 1*. The mechanism of esterification was carried out via controlling the temperature of reaction. Dehydration occurred from 150–200°C. The progress of condensation reactions were confirmed by checking hydroxyl and acid values. The time required to complete the reaction was 6 h, after this it was cooled and taken to the sample bottles. Further, resulted synthesized polyols are characterized by measuring physico-chemical properties such as acid value, OH value, and moisture content. Optical properties and spectroscopic studies of synthesized polyol samples were also carried out by using various spectroscopic techniques such as UV-VIS, FTIR, and NMR. Proposed possible structures for all the three kinds of polyols as confirmed by FTIR are given below in *Figure 1–3* respectively.

- *C. O. = Castor oil,
- *Ph. resin = Phenolic resin,
- *DEG = Diethyleneglycol,
- *DEA = Diethanolamine

Table 1: Physico-chemical properties of synthesized Phenolic modified polyol (PhMP).

Polyol Samples	Acid value (mg KOH/g)	OH value (mg KOH/g)	Moisture Content (% moisture)
1. C.O. + Ph. resin			
a. 180 + 15 g	66.37 ± 10	201.02 ± 10	0.05
b. 180 + 10 g	58.11 ± 10	195.93 ± 10	0.06
c. 180 + 7 g	41.44 ± 10	172.19 ± 10	0.02
2. C. O.+ Ph. resin + DEG			
a. 180 + 10 g	50.12 ± 10	218.90 ± 10	0.02
b. 180 + 7 g	41.41 ± 10	181.78 ± 10	0.02
c. 180 + 5 g	28.40 ± 10	179.94 ± 10	0.04
3. C.O. + Ph. resin + DEA			
a. 180 + 10 g	28.05 ± 10	186.93 ± 10	0.017
b. 180 + 5 g	30.80 ± 10	221.80 ± 10	0.074
c. 180 + 3 g	36.46 ± 10	252.88 ± 10	0.132

Results and Discussion

Optical Characterization

In the present study, castor oil and phenolic resin modified polyol have been prepared. Physico-chemical properties such as acid value, OH value, moisture content, optical and structural modifications using various spectroscopic techniques of the prepared polyol have been taken into consideration. Physico-chemical properties of modified polyol shown in *Table 1* and UV-VISNIR (Schimatzu Spectrophotometer UV 1601) are used for the optical characterization of prepared modified polyol samples. The optical properties such as absorption coefficient (α), extinction coefficient (K), and energy band gap (E_g) have been studied for all the castor oil based polyol samples. The relationship between optical band gap (E_g), absorption coefficient (α), and the energy ($h\nu$) were estimated using the Tauc relation [8]:

$$(\alpha h\nu) \propto (h\nu - E_g)^n \quad (1)$$

Table 2: Optical properties of Phenolic modified polyol (PhMP). Where n = 1, 2, 3 for Indirect transitions

Polyol Samples	Band Gap (E_g)	Abs. Coefficient (α)	Ext. Coefficient (K)
1. C. O. + Ph. resin			
a. 180 + 15 g	2.655	3.913	100.84
b. 180 + 10 g	2.594	4	102.45
c. 180 + 7 g	2.227	3.039	94.278

Polyol Samples	Band Gap (E_g)	Abs. Coefficient (α)	Ext. Coefficient (K)
2. C. O.+ Ph. resin + DEG			
a. 180 + 10 g	2.921	0.88	19.6
b. 180 + 7 g	2.732	0.575	12.532
c. 180 + 5 g	2.556	0.628	13.687
3. C.O. + Ph. resin + DEA			
a. 180 + 7 g	2.542	0.871	19.399
b. 180 + 5 g	2.682	1.315	30.962
c. 180 + 3 g	2.862	4	98

It has been observed by using the UV-visible spectra that all the polyol samples show indirect transitions. Band gap for the indirect transitions has been determined by plotting $(\alpha h\nu)$ vs. $h\nu$ as shown in Figure 4. By plotting the graph it has been observed that the polyols prepared using phenolic resin show decrease in band gap with decreasing concentration.

Similar trend has been observed with diethylene glycol (DEG) modified polyols. Interestingly, in the case of diethanolamine (DEA) modified polyol increase in the band gap with decreasing concentration of DEA has been observed. The extinction coefficient (K) and absorption coefficient (α) which are determined by using equation given below

$$K = \alpha\lambda/4\pi \quad (2)$$

show almost similar trend as shown for the energy band gaps. Optical parameters such as band gap, absorption coefficient (α) and extinction coefficient (K) have been given in Table 2 respectively. Similar to that of band gap, extinction coefficient (K) and absorption coefficient (α) show decreasing trend with decreasing concentration in both the phenolic resin made polyol and DEG modified polyol, while in case of DEA modified polyol increase in extinction coefficient (K) and absorption coefficient (α) with decreasing concentration has been observed.

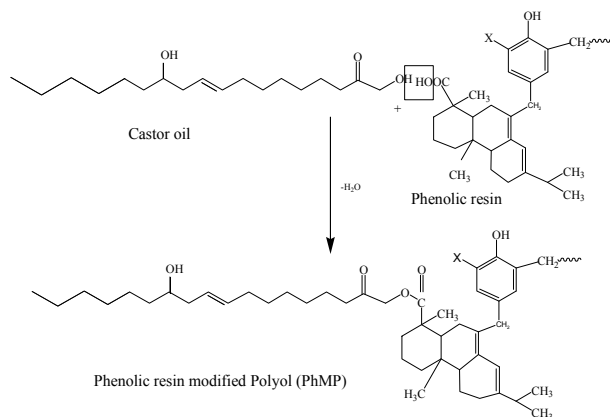


Figure 1: Proposed possible structure of phenolic resin modified polyol (PhMP)

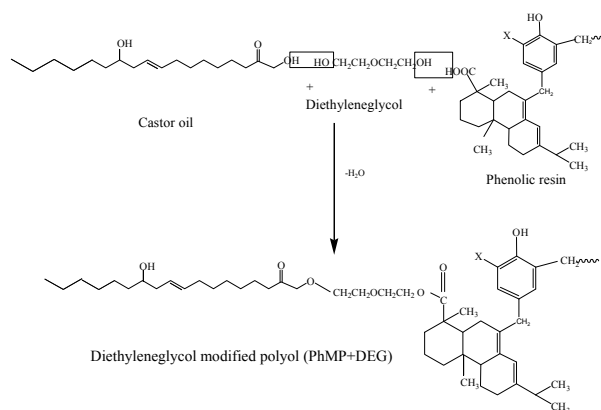


Figure 2: Proposed possible structure of DEG modified polyol (PhMP + DEG)

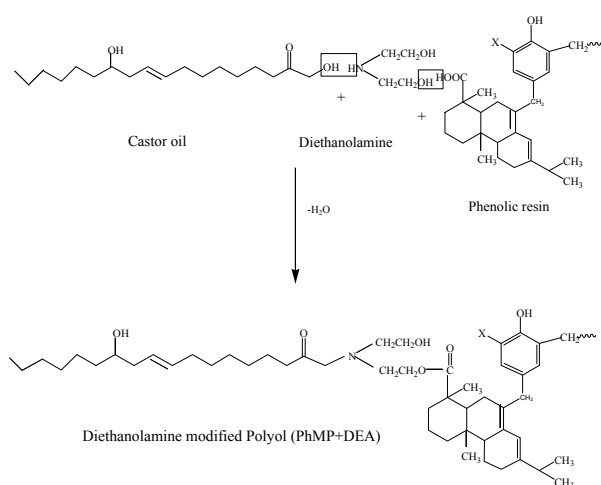


Figure 3: Proposed possible structure of DEA modified polyol (PhMP + DEA)

FTIR Study

Absorption bands that are characteristic of organic molecular vibrations are seen throughout the spectrum of the sample, many occurring within relatively narrow wavenumber ranges that are associated with particular molecular groupings [9]. FTIR spectra of the synthesized polyols were obtained using a Perkin Elmer 2000 Spectrophotometer to see the effect of phenolic resin with DEG and DEA. The spectra show a broad peak at 3433 cm^{-1} indicating the hydroxyl group of polyols. At 2928 cm^{-1} and 2856 cm^{-1} peaks have been obtained for all the C-H stretching of CH_2 group present in the compound. The peak at 1741 cm^{-1} gives strong evidence for ester formation. 1460 cm^{-1} shows peak for CH_2 bending vibrations within the compound. At 1160 cm^{-1} peak obtained shows symmetric stretching of C-O-C group present in the compound. Peak at 3007 cm^{-1} is due to C-H stretching vibration of aromatic ring. While the peak at 726 cm^{-1} is due to aromatic ring. In all the samples of synthesized polyol almost similar pattern has been observed as shown in Figure 4–6 respectively.

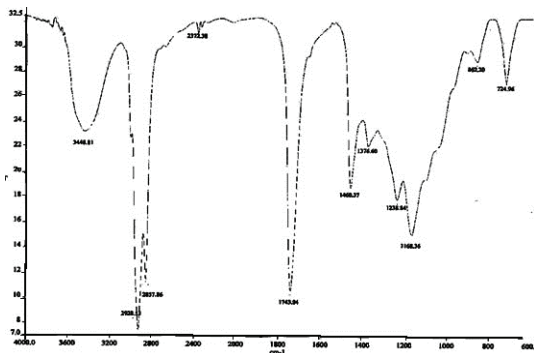


Figure 4: FTIR spectra of PhMP

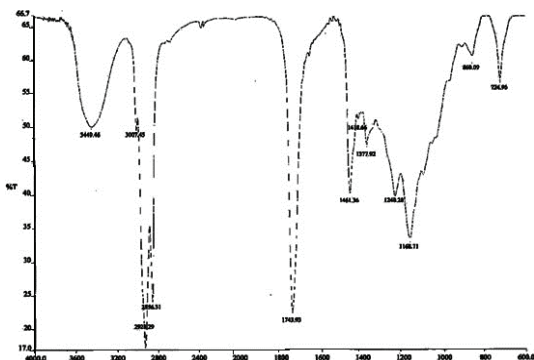


Figure 5: FTIR spectra of PhMP + DEG

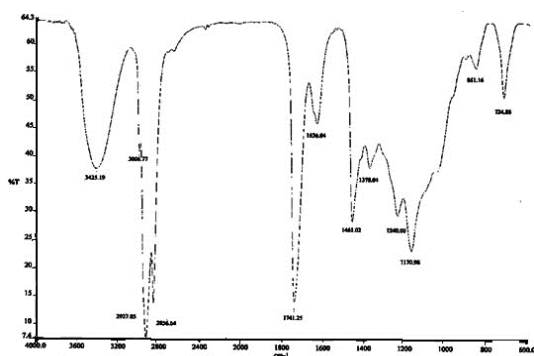


Figure 6: FTIR spectra of PhMP + DEA

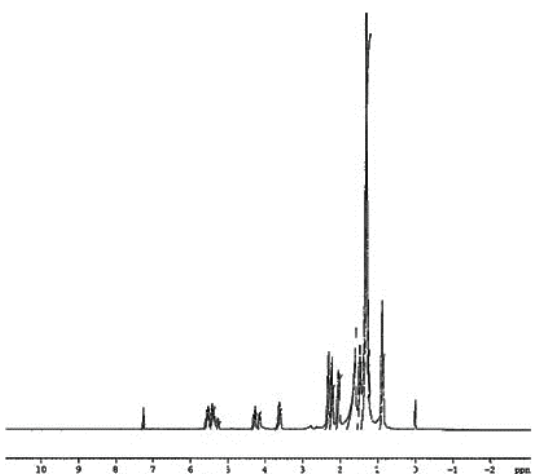


Figure 7.: NMR spectra of PhMP with highest concentration of phenolic resin

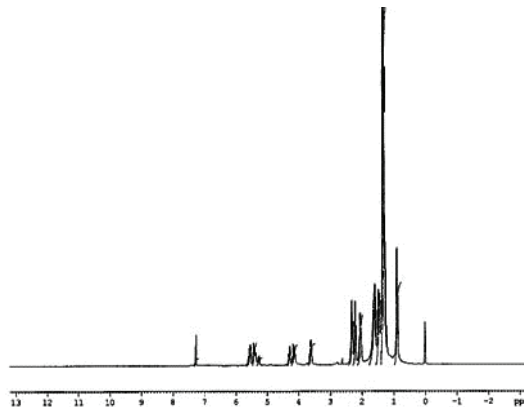


Figure 8: NMR spectra of PhMP + DEG with highest concentration of DEG

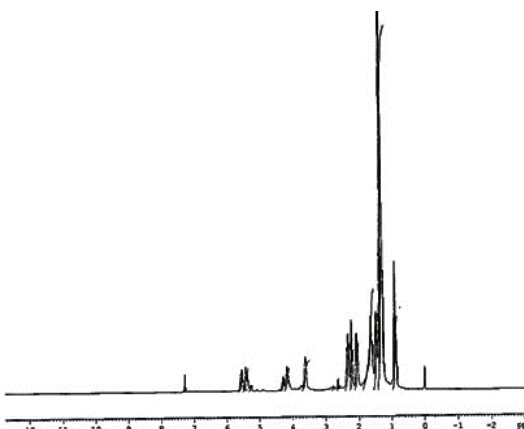


Figure 9: NMR spectra of PhMP + DEA with highest concentration of DEA

NMR Study

NMR spectra of synthesized polyol and its characterization have been done using (Bruker Spectrospin DPX-300). ¹H-NMR spectroscopy gives indirect information about the carbon skeleton of an organic molecule because most of carbon atoms have at least one attached hydrogen. After analyzing the synthesized polyols the chemical shift (δ) shown within the range of 0.88–2.3 ppm indicates long aliphatic protons present in castor oil. Peak at 3.6 ppm indicates for CH₂OH. Chemical shift at 4.2 ppm for acetate protons is shown in *Fig. 4–6* respectively. Peak at 5.2 ppm is for C=CH and chemical shift of 7.2 ppm indicates phenolic protons. On interpreting the prepared polyol samples using NMR spectra obtained, it has been observed that as the amount of phenolic resin increases intensity of peak of aromatic protons increases. This has been observed in similar fashion in both the cases of phenolic resin and diethyleneglycol (DEG) modified polyols. While in dithanolamine (DEA) (i.e. 3% w/w) modified polyol this minimum amount of DEA favours the enhancement of phenolic protons as the amount of DEA increases from 3 to 5 and 10% w/w the intensity of absorption signal decreases.

Conclusively, it has been shown by prepared polyol samples that optimum amount of resin and DEG favours the polyol formation in first two cases of diethyleneglycol modified polyol and phenolic modified polyol. While minimum amount of DEA favours the polyol formation in the third case of diethanolamine modified polyol. It has also been observed in NMR spectra that the aromatic peak at 7.2 ppm of aromatic protons of phenolic resin in *Fig. 7* is showing significant change by retarding the peak intensity which appeared in DEG and DEA modified polyols *Fig. 8, 9*. The NMR spectra of the synthesized polyol have been given in the *Fig. 7–9* respectively.

Conclusions

In the present study modification of castor oil based polyol has been carried out by blending castor oil with phenolic resin, diethyleneglycol (DEG) and diethanolamine (DEA). They were then investigated for physico-chemical properties and spectroscopic studies. On interpreting the physico-chemical properties such as acid value, hydroxyl value and moisture content it has been observed that acid value and hydroxyl value show almost similar trend. In case of phenolic modified polyol (PhMP) and diethyleneglycol modified polyol (PhMP + DEG) acid value as well as the hydroxyl value (OH value) goes on decreasing with decreasing concentration of resin and DEG. While diethanolamine modified polyol is showing contrary results to as those of resin and DEG modified polyols i.e. with decreasing concentration of DEA (diethanolamine) acid and OH value are increasing. Moisture content in all the three cases of PhMP, PhMP + DEG and PhMP + DEA are increasing with decrease in concentration of blending moieties.

By studying UV-VIS spectra's of the modified polyol samples energy band gap, extinction coefficient and absorption coefficient, energy band gap of all the polyols show indirect kind of transitions. For confirming the results of band gaps all the samples were taken twice and then also almost similar band gap has been observed. In case of phenolic and DEG modified polyols, band gap shows decreasing trend with decreasing concentration of phenolic resin and DEG whereas, in case of diethanolamine modified polyol (PhMP + DEA) increase in band gap with decreasing concentration of DEA has also been observed. Extinction and absorption coefficient show similar trends as that of energy band gap in all the three synthesized polyols. FTIR spectra of prepared polyol samples do not show any significant changes in the prepared polyol with changing concentrations of blending moieties. On studying the NMR spectra of polyol samples informative results have been obtained. In the first two cases of phenolic resin modified and DEG modified polyols optimum amount of resin and DEG favours the formation of polyols showing increase in the peak of aromatic protons of phenolic resin with increasing concentration while minimum amount of DEA favours the formation

of polyols, showing increase in the resonance intensity with decreasing concentration of diethanolamine (DEA).

REFERENCES

1. S. ATTAJARIYAKUL, S. VANICHSENI: Development of a kinetic model for resole type phenolic resin formation, *Thammasat Int. J. Sc. Tech*, (6) (2001) 3, pp. 13–18
2. A. M. MOTAWIE, E. M. SADEK: Adhesives and coatings based on poly(vinyl acetal)s, *Journal of Applied Polymer Science*, (70) (1998) pp. 1769–1777
3. S. A. OSEMEAHON, J. T. BARMINAS: Development of amino resin for paint formulation: Copolymerization of methylol urea with polyester, *African Journal of Biotechnology*, (6) (2007) 12, pp. 1432–1440
4. A. SPYROS: Quantitative determination of distribution of free hydroxyl and carboxylic groups in unsaturated polyester and alkyd resins by ³¹P-NMR spectroscopy, *Journal of Applied Polymer Science*, (83) (2002) pp. 1635–1642
5. T. P. SHARMA, D. PATIDAR, N. S. SAXENA, K. SHARMA: Measurement of structural and optical band gaps of Cd_{1-x}Zn_xS (x = 4 and 6) nanomaterials, *Indian J Pure & Appl Physics*, (44) (2006) pp. 125–128
6. V. ALI, Z. HAQUE NEELKAMAL, M. ZULFEQ-UAR, M. HUSAIN: Preparation and characterization of polyether based polyurethane dolomite composite, *Journal of Applied Polymer Science*, (103) (2006) pp. 2337–2342
7. H. S. PARK, J. P. WU, H. K. KIM: Synthesis and physical properties of two component polyurethane coatings using bromine-containing aromatic modified polyesters, *Journal of Ind. & Eng. Chemistry*, (3) (1997) 4, pp. 282–287
8. J. V. PATEL, S. D. DESAI, V. K. SINHA: Bioacrylic polyols for two pack polyurethane coating, *Journal of Scientific & Industrial Research*, (63) (2004) pp. 259–264
9. M. A. ESPINOSA, M. GALIA, V. CA'DIZ: Novel phosphorilated flame-retardant thermosets: Epoxy benzoxazine-novolac systems, *Polymer*, (45) (2004) pp. 6103–6109
10. A. M. MOTWIE, M. M. BADR, M. S. AMER, H. Y. MOUSTAFA, I. M. ALI: Some coating studies on phenolic epoxy/poly(vinyl acetal) resins, *Journal of Applied Sciences Research*, (4) (2008) 9, pp. 1043–1051
11. V. ISABELLE, L. TIGHZERT: Biodegradable Polymers, *Materials*, (2) (2009) 2, pp. 307–344
12. S. N. SURESH, Y. JIN, K. XIAOHUA: Production of polyols from canola oil and their chemical identification and physical properties, *J Amer Oil Chem Soc*, (84) (2007) pp. 173–179

13. J. Z. LIN, Y. T. JIN, Z. TONG, Z. Y. YUN: Preparation of phenolic resin/silver nanocomposites via in situ reduction, *Chinese Chemical Letters*, (14) (2003) 4, pp. 426–428
14. Y. ZHONGREN, E. JAMES, B. GARY: Preparation and characterization of NaOH activated carbons from phenolic resin, *J. Mater. Chem.*, (16) (2006) pp. 1456–1461
15. C. L. CHIANG, MA M. CHEN-CHI: Synthesis, Characterization, thermal Properties and flame retardance of novel Phenolic resin/silica nanocomposites, *Polymer Degradation and Stability*, (83) (2004) pp. 207–214
16. LINDA, F. LORENZ, W. CHRISTIANSEN ALFRED: Interactions of Phenolic Resin Alkalinity, Moisture Content and Cure Behavior, *Ind. Eng. Chem. Res.*, (34) (1995) pp. 4520–4523
17. Z. FAHMINA, S. ERAM, M. S. ASHRAF, A. SHARIF: Studies on poly(styrene-co-maleic anhydride)-modified polyesteramide based anticorrosive coatings synthesized from a sustainable Resource, *Journal of Applied Polymer Science*, (92) (2004) 4, pp. 2538–2544
18. J. B. CALVIN: Chemistry and Physics of foam formation Vol. I, (Eds) Plastic Foam, John Wiley and Sons Inc., New York, (1969)
19. J. H. SAUNDERS, K. C. FRISCH: Polyurethane Chemistry and Technology, Part II, Interscience Publishers, New York, (1964)
20. J. H. SAUNDERS, K. C. FRISCH: Polyurethane Chemistry and Technology, Part I, Interscience Publishers Inc., New York, (1962)