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Nano Composite of Clay and Modified Ketonic Resin as Fire Retardant Polyol for Polyurethane

D. Önen, N. Kızılcan, B. Yıldız, A. Akar

Abstract**—**In situ modified cyclohexanone-formaldehyde resins were prepared by addition of alendronic acid during resin preparation. Clay nanocomposites in ketonic resins were achieved by adding clay into the flask at the beginning of the resin preparation. The prepared resins were used for the synthesis of fire resistant polyurethanes foam. Both phosphorous containing modifier compound alendronic acid and nanoclay increases fire resistance of the cyclohexanone-formaldehyde resin thus polyurethane produced from these resins. The effect of the concentrations of alendronic acid and clay on the fire resistance and physical properties of polyurethanes was studied.

Keywords**—**Alendronic acid, clay, ketonic resin, polyurethane.

I. Introduction

KETONIC resins are generally used as additives in many applications including surface coating industry. By modifying the resin, it may have better physical properties thus the number of application of the resin could be increased.

Modification of ketonic resin could be achieved *in situ* by adding reactive compounds to the polymerization flask during resin preparation [1]-[10]. The modifier should react with either formaldehyde or cyclohexanone under the polymerization conditions. The modifier may be added to the polymerization system either at the beginning or later stage of polymerization depending on its reactivity. Ketonic resin could also be modified by the reaction its functional hydroxyl and carbonyl groups with appropriate reagents [10]-[14]. Properties such as solubility, melting point of modified resin are affected by the degree of modification.

Besides, ketonic resin and modified ketonic resin have been used for production of copolymer [15]-[23] and as polyol in polyurethane preparation [24].

Nano composite of clay and ketonic was produced earlier. The composites have improved thermal properties [25].

In this work cyclohexanone resin is in situ modified with alendronic acid in the presence of nanoclay such as montmorillonite and sepiolite in order to produce alendronic acid modified ketonic resin-clay nanocomposites. These modified resins are used to produce fire retardant polyurethanes.

D. Önen is with the Polymer Science and Technology Department, Istanbul Technical University, Istanbul, 34469 Turkey (phone: +90-555-691-54-74; e-mail: derya.onen@hotmail.com).

N. Kızılcan is with Chemistry Department, Istanbul Technical University, Istanbul, 34469, Turkey (phone: +90-212-285-32-42; e-mail: kizilcan@itu.edu.tr).

B. Yıldız is with the Polymer Science and Technology Department, Istanbul Technical University, Istanbul, 34469 Turkey (phone: +90-212-866-49-00; e-mail: Basar.Yildiz@poliser.com.tr).

A. Akar is with Chemistry Department, Istanbul Technical University, Istanbul, 34469, Turkey (phone: +90-212-285-32-47; e-mail: akara@itu.edu.tr).

II. Experimental

A. Materials

Cyclohexanone, formaldehyde, alendronic acid and sodium hydroxide were all reagent grade chemicals of the highest purity and used without further purification. Clays that are used in this work are montmorillonite and sepiolite. Sepiolite samples both Sivrihisar region of Turkey and Pangel S9 (commercial name) was kindly supplied by Tolsa Group, Turkey. The chemical analysis of the Sivrihisar sample was accomplished with ICP (Inductively Coupled Plasma Spectrometer) in ACME Analytical Lab., Canada. The main constituents of chemical analysis and relative amounts of weight % are as follows: SiO_2 49.85, Al_2O_3 2.38, Fe_2O_3 0.87, MgO 20.15, CaO 2.65. This sample consists of 85 ± 3% sepiolite, according to mineralogical analysis of the Sivrihisar performed using Shimadzu XRD-6000 equipped with Cu X-ray tube (λ= 1.5405Å) with Dolomite, Calcite, Albite and Quartz. The nanofiller, sodium-montmorillonite (MMT) (Nanofil 757) was used from Süd-Chemie (Switzerland). It is a highly purified natural sodium montmorillonite with cation-exchange capacity of 80 meq/100 g m medium particle size as < 10 μm, and bulk density of approximately 2.6 g cm^{-3}.

B. Instruments and Analysis

Fourier transform infrared (FTIR) spectra were obtained with a recording model PerkinElmer Spectrum One FTIR spectrophotometer with an attenuated total reflectance sampling accessory; they were obtained directly from the sample without KBr discs.

^{1}H- NMR spectra was obtained from $CDCl_3$ solution on an Agilent VNMRS (Varian 500 MHz) spectrometer. Chemical shifts (δ in ppm) were reported down field from tetramethylsilane.

C. Synthesis of Cyclohexanone-Formaldehyde Resin (CF-Resin)

98 g (1 mole) of cyclohexanone, 30 ml of 37% formalin and 25 ml cyclohexane were mixed into a three-necked flask and heated to 60^0C while stirring and then 0.05 ml of 20% NaOH solution added in three equal portions. When the temperature of mixture rose to 75-80^{o}C, refluxing began and a mixture of 3,7 ml NaOH solution and 100 ml 37% formalin was added in equal potions in 30 minutes. Stirring was increased while keeping reaction pH of about 11. Reaction is completed after 5

hours and water phase was decanted. Residue was washed with hot water 5-6 times. White colored resin was held in vacuum oven at 80^oC for 5-6 hours. Light yellow resin was obtained.

D. Synthesis of Alendronic Acid Modified of Cyclohexanone-Formaldehyde Resin (CFR-AA)

Alendronic acid is used for modification of cyclohexanone-Formaldehyde resin. Three different percentages of alendronic acid are used such that 5%, 10% and 20% of cyclohexanone by weight. Into a three-necked flask, 20.7 ml of cyclohexanone, 7.5 ml of 37% formalin, and 6.4 ml of cyclohexane are mixed with 4.9 g of alendronic acid, which results in 20% alendronic acid modified resin (CFR-AA20). Similar resins such as CFR-AA10 and CFR-AA5, 2.5 g and 1.25 g of alendronic acid are used respectively. The mixture was heated to 60^0C while stirring and 0.05 ml of 20% NaOH solution added in three equal portions. When the temperature of the mixture rose to 75-80^oC, refluxing began and a mixture of 3,7 ml NaOH solution and 25 ml 37% formalin was added in equal potions in 30 minutes. Stirring was increased while keeping reaction pH of about 11. Reaction was completed after 5 hours, then water phase was decanted. Residue was washed with water 5-6 times. Light colored resin was dried in vacuum oven at 80^oC for 5-6 hours. Light yellow resin was obtained.

E. Preparation of Ketonic Resin- Clay Nanocomposites

Sepiolite and montmorillonite are used as nanoclay for nanocomposite of cyclohexanone-Formaldehyde resin.

Sepiolite was used as 1%, 3% and 5% of cyclohexanone by weight. Into a three-necked flask, 52 ml of cyclohexanone, 12.5 ml of cyclohexane, and 15 ml of 37% formalin are mixed with sepiolite powder. The mixture was heated to 60^0C while stirring and 20% NaOH solution was added during reaction to stabilize pH about 11. When the temperature of mixture rose to 75-80^oC, refluxing began and 50 ml of 37% formalin was added in three equal potions in 30 minutes. Stirring was increased while keeping reaction pH 0f about 11. Reaction was completed after 5 hours, then water phase was decanted. Residue was washed with water 5-6 times. Resin was held in vacuum oven at 80^oC for 5-6 hours. Light yellow resin was obtained.

Nanocomposites of Montmorillonite and cyclohexanone-formaldehyde resin were similarly prepared by using Montmorillonite as 1% and 5% of cyclohexanone by weight. Light yellow resins were obtained.

F. Preparation of Nano Composites of Montmorillonite-Alendronic Acid Modified Ketonic Resin (CFR-M5-AA5)

5% alendronic acid and 5% montmorillonite are mixed for modification of Cyclohexanone-Formaldehyde resin (CF-Resin). Percentages are calculated in the base of cyclohexanone weight. Into a three-necked flask, 52 ml of cyclohexanone, 12.5 ml of cyclohexane, and 15 ml of 37% formalin were mixed with 2.6 g of alendronic acid and 2.6 g montmorillonite. The mixture was heated to 60^0C while stirring and 20% NaOH solution was added during reaction to stabilize pH about 11. When the temperature of mixture rose to 75-80^oC, refluxing began and 50 ml of 37% formalin was added in equal potions in 30 minutes. Stirring was increased while keeping pH about 11. Reaction was completed after 5 hours, then water phase was decanted. Residue was washed with water 5-6 times. White colored resin was held in vacuum oven at 80^oC for 5-6 hours. Light yellow resin was obtained.

G. Preparation of Rigid Polyurethane Foam

15 g of polyol and certain amount of nancomposites and modified cyclohexanone-formaldehyde resin were mixed with a high speed mechanical stirrer for about 10 minutes to produce homogenous mixture. Sometimes resin was dissolved in CH_2Cl_2 then mixed with polyol. To this mixture, 20 g of isocyanate component was added and stirred with a high speed for about 10 second and let to form the foam.

III. RESULTS AND CONCLUSIONS

A. Structure of Modified Ketonic Resins-Nanoclay

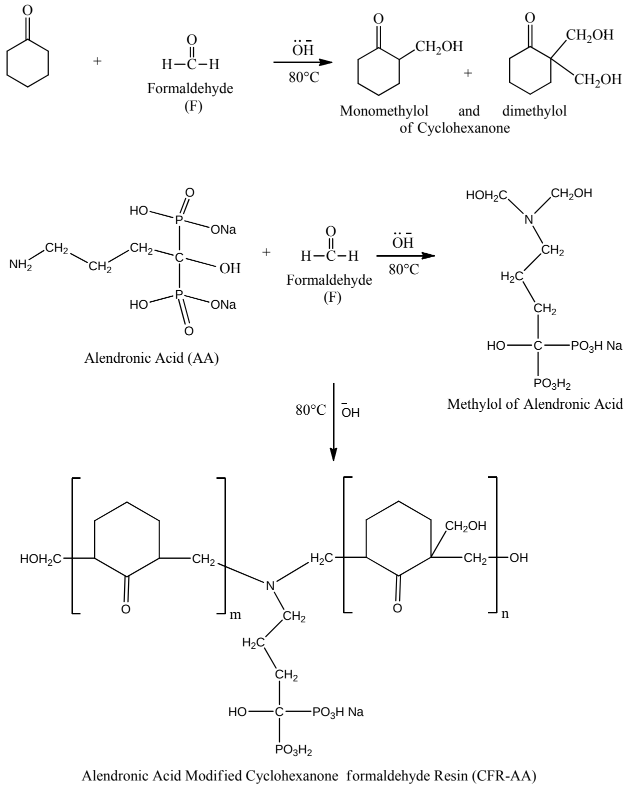

Fig. 1 Possible formation of alendronic acid modified cyclohexanone-formaldehyde resin (CFR-AA)

The physical properties of Cyclohexanone–Formaldehyde resin (CF-R), Alendronic acid modified Cyclohexanone–formaldehyde resin (CF-R-AA), Clay-Cyclohexanone–formaldehyde resin nanocomposite (CFR-CLAY), Alendronic acid modified Cyclohexanone–formaldehyde resin-Montmorillonite nanocomposites (CF-R-M-AA) are shown in Table I.

The formation of alendronic acid modified cyclohexanone-formaldehyde resin is shown in the Fig. 1. At the beginning of polymerization, both cyclohexanone and alendronic acid probably react with formaldehyde in the presence of NaOH solution to form their methylol derivatives such as Monomethylols and dimethylols. Condensation reaction between cyclohexanone, alendronic acid, monomethylols and dimethylols present in the reaction media results modified cyclohexanone-formaldehyde resin.

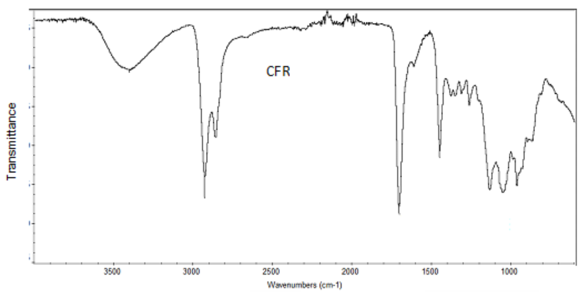

Fig. 2 ATR- FTIR of CF-Resin

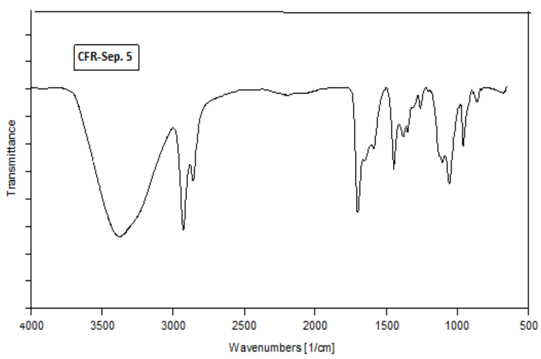

Fig. 3 ATR-FTIR of Sepiolite-CF-Resin nanocomposite containing 5% sepiolite (CFR-S5)

The structures of modified resins are examined with TLC, FTIR and NMR techniques. TLC examination showed that the Rf of alendronic acid modified CF-resin was completely different than CF- resin and the product contained only modified resin molecules as shown in Fig. 1.

ATR-FTIR of Nano composite containing about 5% of sepiolite (CFR-S5) showed higher peak intensities compared CF-Resin at about 3500 cm-1 and 1630 cm-1 due to bound H2O and about 1000 cm-1 due to sepiolite Si-O-Si bond stretching (Figs. 1 and 2).

Alendronic acid modified CF-Resins showed peaks at about 2700cm-1 and 900cm-1 due to P-OH of phosphonic acid groups as well as peaks due to CF-Resin (compare Fig. 3).

As expected CF-Resin containing 5% alendronic acid and 5% Montmorillonite (CFR-M5-AA5) showed peaks due to P-OH and adsorbed water and Si-O-Si bonds.

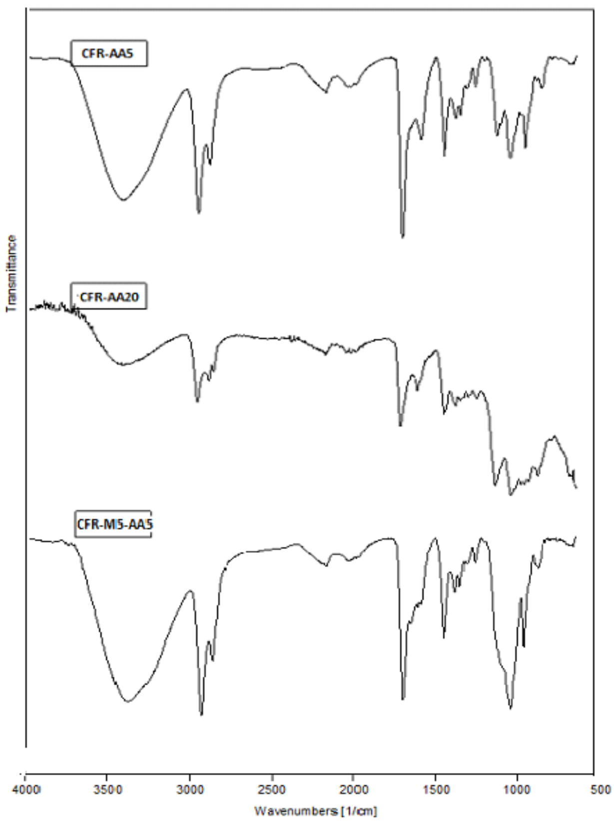

Fig. 4 ATR-FTIR of nanocomposites of montmorillonite-resins. CFR-AA5: 5% montmorillonite containing CF-Resin, CFR-AA20: 20% montmorillonite containing CF-Resin, CFR-M5-AA5:%5 montmorillonite and 5% alendronic acid containing CF-Resin

B. Polyurethane Foam

Commercial polyol and hardener system for medium density foam production was used for modified foam production. Polyol component and Modified resins were mixed with a mechanical stirrer to produce homogeneous mixture. Resin may sometimes be dissolved in CH_2Cl_2 and then mixed with polyols.

The mixture of polyol-nano composites of CF-Resin was then mixed with isocyanate hardener to produce foam. LOI values of these polyurethane foam samples were increased as the content of alendronic acid and clay increased.

TABLE I
PHYSICAL PROPERTIES OF NANOCOMPOSITES AND MODIFIED CYCLOHEXANONE-FORMALDEHYDE RESIN

Resins	Ketone modifier % w/w	Melting point (^0C)	$(CH_2)_4O$	C_2H_6OS	$CHCl_3$	CH_3OH	C_3H_7NO	CH_2Cl_2	$CH_3OC_2H_5$
CF-Resin	1/0	110	soluble	Soluble	soluble	slightly soluble	soluble	soluble	soluble
CFR-Montmorillonite	100/1	114	slightly soluble	hot soluble	soluble	soluble	soluble	soluble	soluble
CFR–Montmorillonite	100/5	120	insoluble	insoluble	hot soluble	slightly soluble	slightly soluble	soluble	soluble
CFR–Sepiolite	100/1	97	insoluble	soluble	slightly soluble	hot soluble	soluble	soluble	soluble
CFR–Sepiolite	100/3	125	slightly soluble	hot soluble	slightly soluble	insoluble	slightly soluble	soluble	soluble
CFR–Sepiolite	100/5	150	slightly soluble	insoluble	hot soluble	insoluble	soluble	soluble	soluble
CF-Alendronic acid	100/5	107	slightly soluble	insoluble	insoluble	insoluble	slightly soluble	insoluble	insoluble
CF-Alendronic acid	100/10	110	soluble	soluble	soluble	insoluble	soluble	soluble	soluble
CF-Alendronic acid	100/20	120	soluble	slightly soluble	soluble	insoluble	soluble	soluble	soluble
CFR- Montmorillonite and Alendronic acid	100/(5+5)	98	insoluble	insoluble	soluble	insoluble	insoluble	soluble	insoluble

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Derya Önen was born in 1990 in İstanbul. She is a chemical engineer and graduated from Middle East Technical University in 2013. She is a MSc student in the department of Polymer Science and Technology in İstanbul Technical University. Önen is a research and development engineer in Karbosan, which is a private firm working on abrasives.

Nilgün Kızılcan was born in İstanbul,Turkey, in 1965.She is currently a Lecturer and Researcher in the Organic Chemistry group in Chemistry Department and Polymer Science and Technology Programmers at Istanbul Technical University. She obtained her BSc in Chemical Engineering Department in 1986, her MSc and PhD degrees in chemistry at the same university in 1990 and 1995, respectively

She has published 44 research papers and 48 national and 47 international presentations. She was 16 completed research project coordinators, 5 PhD thesis supervisors, 18 MSc thesis supervisors. She wrote book chapters in 2 books. She is on the Editorial Advisory Board of ISRN Polymer Science. She specializes in resins, conducting polymer and copolymers. Professor N. Kizilcan is a member of Turkish Chamber of Chemical Engineers.