

Preparation of nano alumina via resin synthesis

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ABSTRACT

The effect of type of precursor on the characteristics of alumina powders prepared via urea formaldehyde resin formation is demonstrated through the introduction of three different Al³⁺ precursors. An Al ester (aluminum acetate), and two inorganic salts aluminum sulphate and aluminum phosphate hydrate, were added during resin formation. The resins and the powders after burning out of the organic part were studied by FTIR, TG and XRD. The results obtained showed that the precursors behaved differently.

The Al ester did not participate in the cross linking reaction of the resin. The alumina powder obtained was the result of the combustion of the ester. While the Al³⁺ from the other two precursors participated in the structure of the resin. The sulphate precursor gave alumina powder with crystallite size 26.96 and 29.78 nm at 1200 and 1400 °C, respectively. The Al³⁺ and the PO₄³⁻ participated in the resin structure, but reunite after burning out of the organic part to give AlPO₄ as main product plus α-alumina.

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1. Introduction

The utilization of sol–gel technique for over three decades gave rise to the production of ultra fine powders, highly homogeneous, with controlled chemical purity and crystallinity [1].

Sol–gel process involves the hydrolysis and condensation of various metal alkoxide molecules under controlled conditions to form metal–oxygen–metal bridging units. Generally, the aluminum alkoxides, such as aluminum secondary butoxide and aluminum iso-propoxide are used to prepare alumina fine powder as well as alumina membranes [2–7]. However, these metal alkoxide precursors have some disadvantages such as costs, flammability and toxicity [8]. Moreover, they are very sensitive to water, and need stringent conditions to control their hydrolysis reaction [9,10].

An alternative method for the production of fine powder is the Pechini's method. It is based on a chelation process between metal cations in the form of chlorides, nitrates, carbonates, or hydroxides with a hydroxyl carboxylic acid e.g. citric acid. It is believed that the crosslinked resin may provide more homogeneous mixing of the cations and less tendency for segregation during charring and calcination [11,12].

Urea formaldehyde as a precursor for the preparation of metal oxide was introduced by Ibrahim et al. [13]. A polymerization reaction to form the resin was used to incorporate the different cations added as metal salts or alkoxides. The cations are distributed throughout the active sites of the polymer structure. Heating of the resin in air causes break-down of the polymer and “charring” at about 400 °C to produce the submicron oxide powders.

In a previous work, Ibrahim et al. [14] used aluminum chloride as a precursor to introduce Al³⁺ in the urea formaldehyde resin during synthesis, where uniform substitution of the added cations took place in the active sites. α-alumina was produced after calcination at 1000 °C with submicron grain size (≈8 nm). Another attempt to prepare α-alumina through the reaction of urea formaldehyde in presence of aluminum soap (aluminum stearate) [15] instead of the inorganic chloride salt was carried out. In this case α-alumina was obtained as spherical particle with uniform grains in the form of clusters with average size between (22.02 and 30.5 nm).

Other aluminum precursors are added during resin formation of urea formaldehyde in the present study; aluminum acetate as organic ester, aluminum phosphate and aluminum sulphate as other inorganic salts to study the effect of type of precursor on the characteristics of the powder obtained.

2. Materials and methods

Chemically pure reagent grades were used as precursor materials including:

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Urea,¹ formaldehyde solution (37% conc.),¹ ethylene glycol,² basic aluminum acetate [(CH₃COO)₄·OAl₂·4H₂O],³ aluminum orthophosphate [Al (PO₄) + H₂O],⁴ and aluminum sulphate [Al₂ (SO₄)₃·16H₂O]⁴.

2.1. Preparation of urea formaldehyde resin

Urea and formaldehyde in the proportion 1: 2 mol, respectively, were used to prepare the resin. The respective aluminum salt or ester was introduced in the ratio of 1.0 mol per 1 mol resin. The polymerization reaction between urea and formaldehyde started at pH ≈ 8–9 and proceeded under a reflux at 70 ± 5 °C for about 20 min. The inorganic salt or organic ester was added simultaneously with ethylene glycol after the end of the first step of resin synthesis (addition step). The second step which is a condensation reaction proceeded in an acid media at pH ≈ 4–4.5 under reflux and a temperature of 70 °C, for another 60 min. Water and other by products were pumped out by vacuum.

Four resins were prepared:

- R: urea formaldehyde resin modified with ethylene glycol as a blank resin.
- RS2: urea formaldehyde resin modified with ethylene glycol in presence of aluminum acetate ester.
- RS3: urea formaldehyde resin modified with ethylene glycol in presence of aluminum orthophosphate salt.
- RS4: urea formaldehyde resin modified with ethylene glycol in presence of aluminum sulphate salt.

2.2. Characterization of the obtained resins and calcined powders

The thermal behavior of the different prepared resins was determined quantitatively by thermal gravimetric analysis (TG) and differential thermogravimetric analysis (DTG). Samples were diluted 1: 1 with α-alumina standard powder. A known weight was scanned utilizing a Shimadzu Thermal Analyzer at a rate of heating of 10 °C min⁻¹ up to 700 °C.

The different absorption bands corresponding to the resin and additives were determined by Fourier Transform Infrared Spectral Analysis (FTIR) using FTIR JASCO Spectrophotometer, Model FT/IR-6100 type A. Resolution 4 cm⁻¹, with a scanning speed 2 mm s⁻¹.

The resins were first dried at 100 °C for 24 h, then calcined following the results of TG up to 600 °C. The obtained powders were fired at 700, 1000, 1100 and 1400 °C. XRD analysis was carried out using Philips XRD equipment Type PH 9920/05 (Cu – Target and Ni – filter) operating at 30 kV, 25 A, to determine the different crystalline phases developed after calcination. Scanning was carried at a rate of 2 °C min⁻¹ between 2θ = 4° and 60°. Crystallite size was calculated from the measurements of XRD broadening of patterns scanned at a slow rate of 1/4° min⁻¹. Broadening of peaks for alumina powder occurring at 2θ = 43.4°, *d* spacing = 2.0832 Å, *hkl* = 113. Powders calcined at different temperatures were scanned and the respective crystallite sizes [16] were calculated from the following Sherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where: *D* = crystallite size, λ = the wavelength, β = peak width at half height, and θ = the diffraction angle.

Microstructure of the calcined powders was determined by Transmission Electron Microscope (TEM) using an equipment by Philips model XL – 30 attached with EDS unit working at an accelerate voltage of 30 kV.

3. Results and discussion

3.1. Thermal analysis

- TG and DTG of resin (RS2) are shown in Fig. 1. A dissociation reaction of the organic resin occurs in two steps. The first step started from 25 °C and ended at 260 °C, and is due to the evolution of water and other byproducts. The second step took place between 260 and 340 °C and corresponds to the combustion of the resin, and continues till it ends with its complete destruction at 600 °C. The main dissociation peak appeared at 300 °C.
- TG and DTG of the resin (RS3) are illustrated in Fig. 2. Two main endothermic reactions were recorded. The first started from room

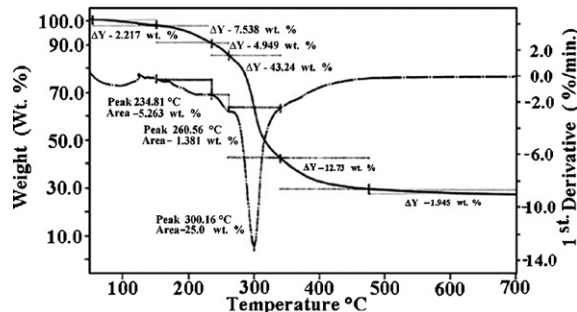


Fig. 1. Thermal gravimetric analysis (TG) and differential thermogravimetric analysis (DTG) Curves of Resin (RS2).

temperature; 25 °C, and ended at 130 °C, attributed to water evaporation. The second reaction occurred between (130 and 350 °C) corresponding to the resin destruction, with the main peak occurring at 264 °C.

- TG and DTG [17] curves of the resin (RS4) incorporating aluminum sulphate salt as precursor showed two main endothermic troughs, the first extended between room temperature and 140 °C, and corresponds to the loss of reaction products. The second trough started from 150 °C and ended at 400 °C, with the main peak corresponding to the combustion process at 380 °C.

Resins (RS2, RS3 and RS4) were calcined according to TG and DTG curves up to 600 °C to obtain the respective alumina powders.

3.2. FTIR analysis

IR spectra of urea formaldehyde blank resin (R), aluminum acetate ester (S2) and the urea formaldehyde resin incorporating aluminum acetate ester (RS2) are displayed in Fig. 3. It is clear that the spectrum of (S2) is similar to that of the resin (RS2). This indicates that the ester (S2) did not participate in the network of the resin (RS2).

Fig. 4 shows IR spectra of the urea formaldehyde blank resin (R), aluminum orthophosphate salt (S3) and urea formaldehyde resin incorporating aluminum orthophosphate salt (RS3).

Fig. 5 shows the IR spectra of urea formaldehyde resin blank (R), aluminum sulphate salt, and urea formaldehyde resin incorporating aluminum sulphate (RS4). Table 1 summarizes the results of both Figs. 4 and 5.

All the IR bands corresponding to the blank (R), (RS3) and (RS4) resins are found but were shifted, reduced in size or absent as displayed in Table 1.

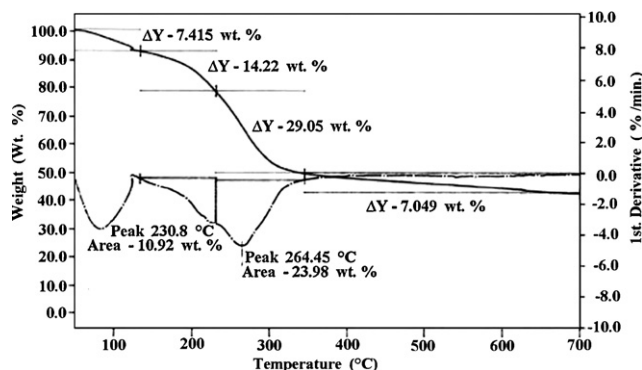


Fig. 2. Thermal gravimetric analysis (TG) and differential thermogravimetric analysis (DTG) curves of resin (RS3).

¹ EL-NASR Pharmaceutical Chemicals, Egypt.

² VEB Labo – Rchemie APOLDA, Germany.

³ ADWIC, El-Nasr Pharmaceutical Chemicals Co.

⁴ BDH Laboratory Reagent, BDH Chemicals Ltd., Poole, England.

Table 1
IR bands of (R), (RS3) and (RS4)

Blank resin bands		RS3 bands (cm ⁻¹)	RS4 bands (cm ⁻¹)
Type of bond	cm ⁻¹		
CH aliphatic (symmetric)	2946	2953(decreased in size)	Absent
CH (asymmetric)	2883	2880(decreased in size)	Absent
OH and NH	3366	3382(decreased in size and shifted to higher wavelength)	3386(decreased in size and shifted)
Amidel and Amidell	1643	1647(decreased in size)	1645(decreased in size)
	1561	1551(decreased in size and shifted to lower wavelength)	Absent
Carbonyl (C=O)	1643	1647(decreased in size and broadened)	1645(decreased in size and broadened)
CN	1298, 1262	1247(decreased in size and appeared as one very small band)	Absent
CH ₂ OH	1460, 1880	Absent	Absent
NH bending (out of plane)	645	Absent	679(decreased in size and shifted to higher wavelength)
CO	1085, 1043	1085, 1042 (decreased in size and broadened)	1091(decreased in size and appeared as one broad band at higher wavelength)

Also, it is clear that PO₄⁴⁻ bands appeared in (S3) spectra at 1026 and 1156 cm⁻¹ but have disappeared in (RS3) spectrum. Also, the band at 605 cm⁻¹ belongs to SO₄ group in (S4) spectra have disappeared in (RS4) spectrum.

These results indicate that Al³⁺ from aluminum sulphate and Al³⁺ and PO₄³⁻ of aluminum orthophosphate salt were introduced to the active sites in the main chain of the polymer such as NH, OH, CO, CH₂OH, and CN groups.

3.3. XRD analysis

XRD patterns of the urea formaldehyde blank resin (R) in Fig. 6, shows an amorphous nature. XRD diffraction patterns of the S2,

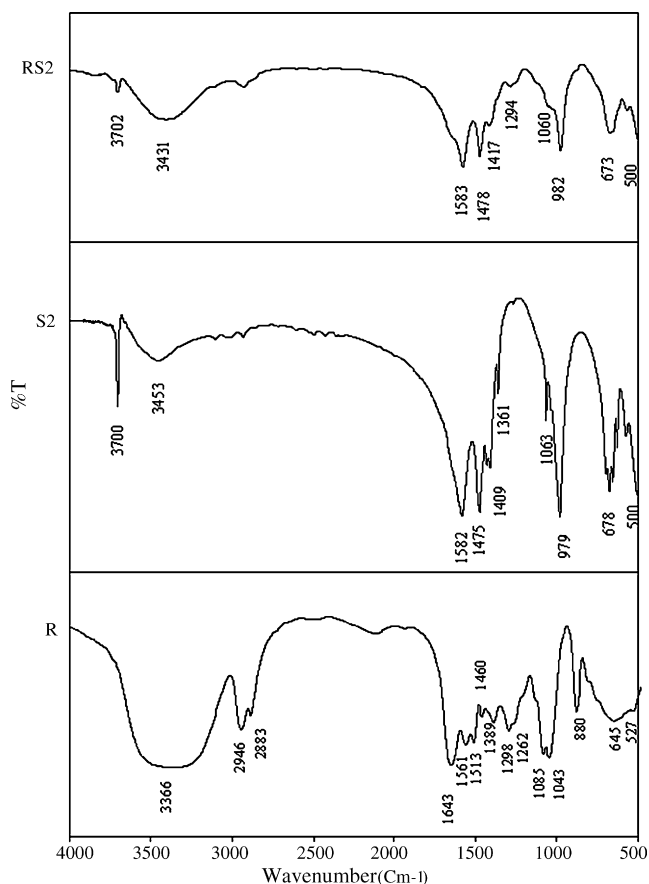


Fig. 3. IR Spectra of: R: urea formaldehyde blank resin. S2: aluminum acetate ester. RS2: urea formaldehyde incorporating aluminum acetate ester.

RS2 resin and calcined RS2 powder at 1000 and 1400 °C are shown in Fig. 7. The (S2) curve shows the lines of the acetate phase. This finding confirms the above IR view that the acetate phase did not participate in the network structure of the urea formaldehyde resin during preparation. Patterns of the powders after calcining the resin (RS2) at 1000 °C, showed nearly amorphous structure, with ill-crystallized θ and γ alumina. These phases are the result of the calcination of aluminum acetate ester alone. Firing at 1400 °C, gave rise to α -alumina as shown in Fig. 7. Results of peak broadening of (RS2) resin calcined at 1000, 1100, 1200 and 1300 °C are displayed in Fig. 8. The calculated crystallite sizes were found to be 25.8 and 29.2 nm, at 1200 and 1300 °C, respectively.

XRD diffraction patterns of (S3), (RS3) and calcined (RS3) resins at both 1000 and 1400 °C are shown in Fig. 9. XRD curves of aluminum orthophosphate salt (S3) showed Veriscite (aluminum orthophosphate hydrate 2AlPO₄·4H₂O, JCPDF card no. 8-157), while the pattern of the resin showed no characteristic peaks of the added precursor. This indicates that the Al³⁺ and PO₄³⁻ participated in the

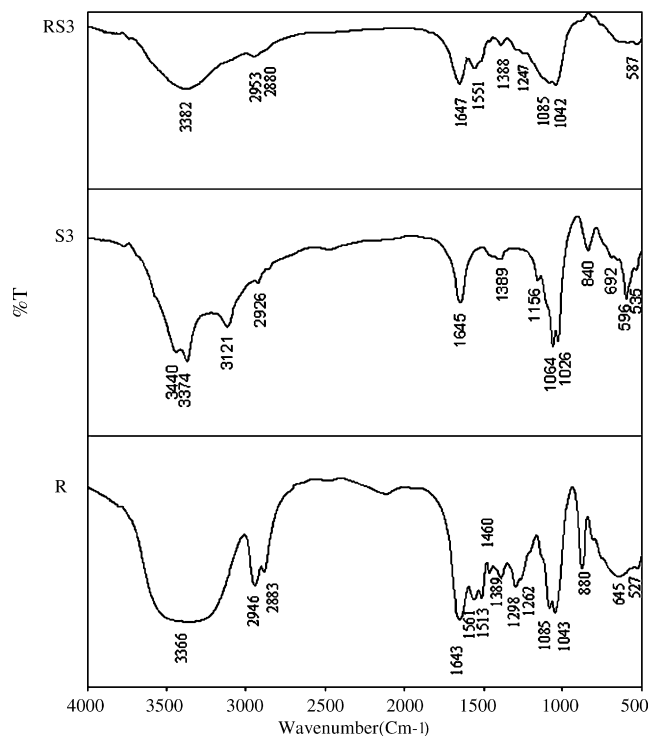


Fig. 4. IR Spectra of: R: urea formaldehyde blank resin. S3: aluminum orthophosphate salt. RS3: urea formaldehyde resin incorporating aluminum orthophosphate salt.

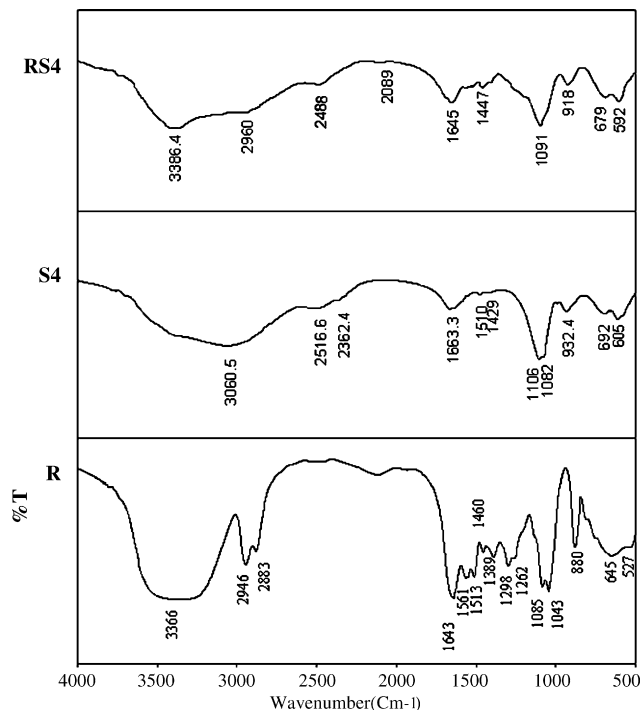


Fig. 5. IR Spectra of: R: urea formaldehyde blank resin. S4: aluminum sulphate salt. RS4: urea formaldehyde resin incorporating aluminum sulphate salt.

network of urea formaldehyde polymer acquiring amorphous state. On calcining the (RS3) powder at 1000 °C, both the Al^{3+} and PO_4^{3-} reunited to form aluminum orthophosphate $AlPO_4$ (JCPDF card no. 20-45). Firing at 1400 °C aluminum orthophosphate (orthorhombic type, card no. 11-500) is detected as main phase beside α -alumina (Corundum, syn., Rhombohedral (Hex.) type (JCPDF card no. 42-1468)).

This finding confirms the result of IR, which indicated the introduction of aluminum orthophosphate in the form of its ionic components in the resin network.

From peak broadening of resin (RS3) fired at 1400 °C, the crystallite size obtained was found to be (26.96) nm.

The XRD diffraction pattern of S4, resin (RS4) and calcined (RS4) powder, at 1000 and 1400 °C are displayed in Fig. 10. (S4) presents the pattern of the aluminum sulphate precursor used. (RS4) resin pattern showed no particular crystalline phase. This indicates the participation of aluminum sulphate salt in the resin structure.

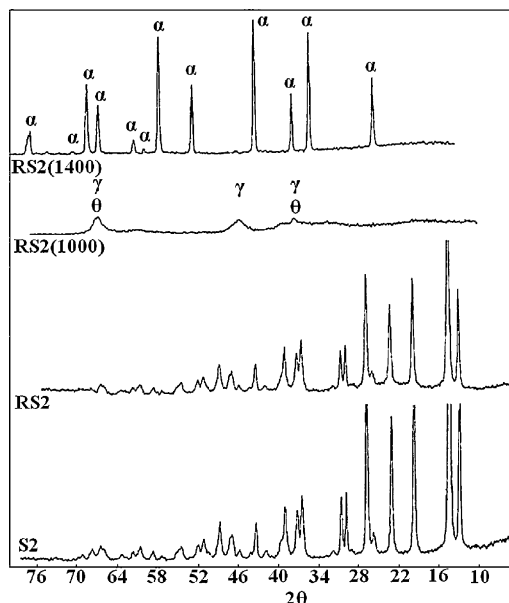


Fig. 7. X-ray diffraction pattern of: S2: aluminum acetate ester. RS2: urea formaldehyde resin incorporating Al. acetate ester. RS2 (1000): RS2 resin fired at 1000 °C. RS2 (1400): RS2 resin fired at 1400 °C.

On calcining the resin (RS4) at 1000 °C, gave rise to the crystallization of ill-crystalline γ and θ alumina phases. On firing at 1400 °C pure α -alumina phase (card no. 11-661) was obtained. Peak broadening of calcined resin (RS4) at different temperatures 1000, 1100, 1200, and 1400 °C are shown in Fig. 11. The calculated crystallite sizes were found to be 26.96 nm and 29.78 nm, at 1200 and 1400 °C, respectively.

3.4. Transmission Electron Microscope Examination (TEM)

TEM of powder obtained by calcining (RS2, RS3 and RS4) resins at 700 °C is demonstrated in Fig. 12(a–c). Fig. 12(a) shows the powder with uniform grains occurring in clusters. On examining the powder obtained after burning out of the resin (RS3) at 700 °C it showed spindle like grains of uniform size characterizing the Al phosphate phase Fig. 12(b).

Wherever the TEM micrograph of powders obtained after calcinations of resin (RS4) at 700 °C, the alumina particles formed in with uniform spherical grains Fig. 12(c).

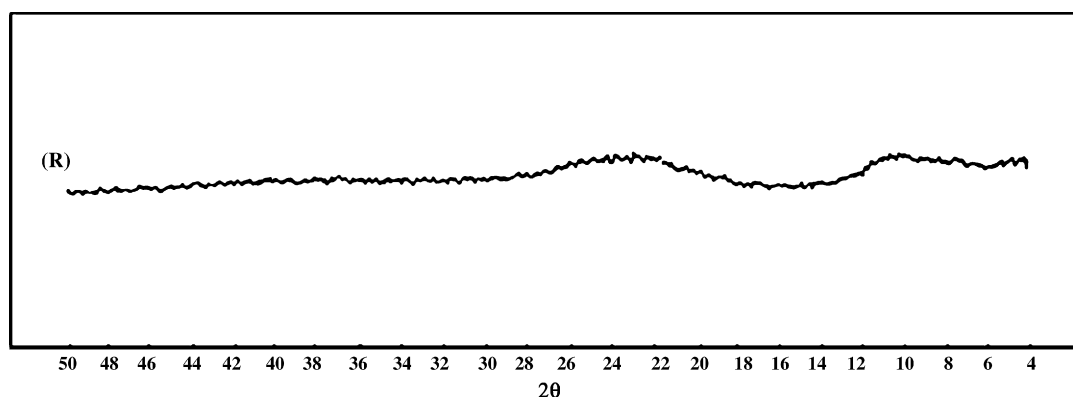


Fig. 6. X-ray diffraction pattern of urea formaldehyde blank resin (R).

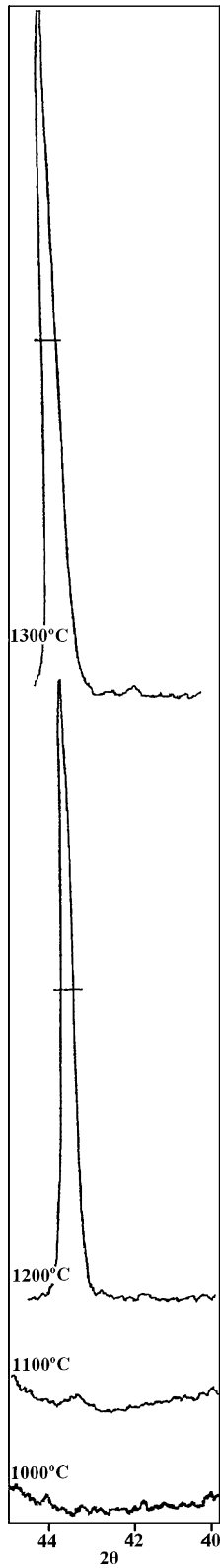


Fig. 8. Peak broadening of α -alumina powder from calcination of (RS2) at: a) 1000, 1100, 1200 and 1300 °C.

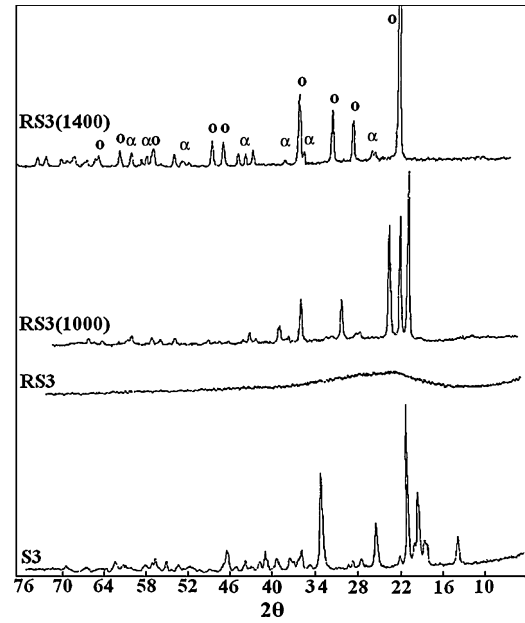


Fig. 9. X-ray diffraction pattern of S3: aluminum orthophosphate salt. RS3: urea formaldehyde resin incorporating Al orthophosphate salt. RS3 (1000): RS3 resin fired at 1000 °C. RS3 (1400): RS3 resin fired at 1400 °C. o=Al. orthophosphate.

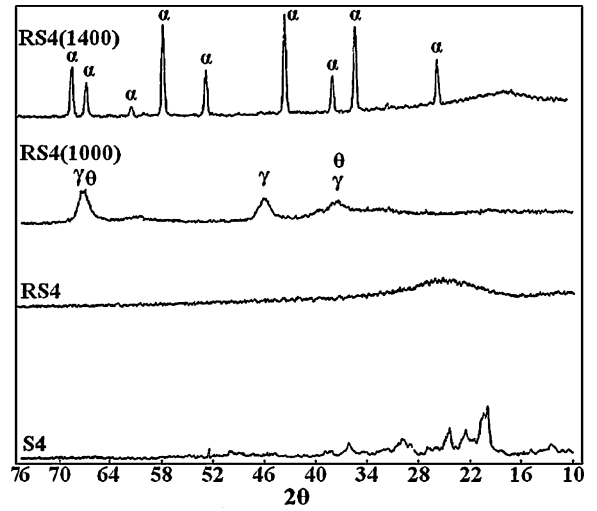


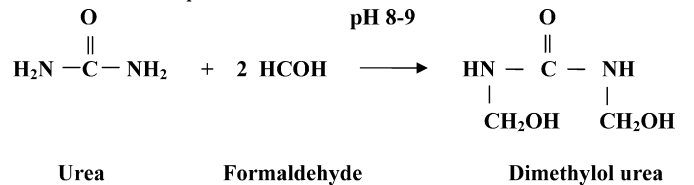
Fig. 10. X-ray diffraction pattern of S4: aluminum sulphate salt. RS4: urea formaldehyde resin incorporating Al sulphate salt. RS4 (1000): RS4 resin fired at 1000 °C. RS4 (1400): RS4 resin fired at 1400 °C.

4. Discussion

4.1. Polymer synthesis

The reaction between urea and formaldehyde to form the resin takes place in two main steps; mainly addition, polymerization reactions as demonstrated by the following.

4.1.1. Addition step



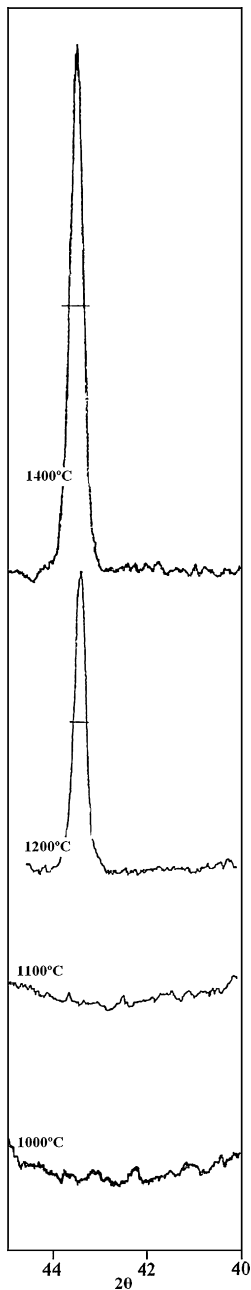
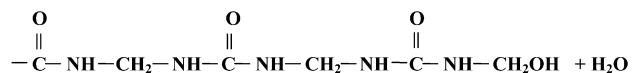
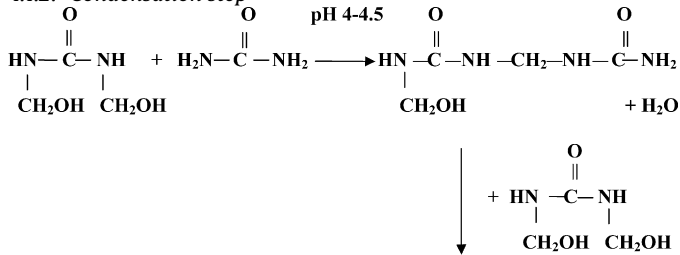


Fig. 11. Peak broadening of α -alumina powder resulted from calcination of (RS4) at: 1000, 1100, 1200 and 1400 °C.

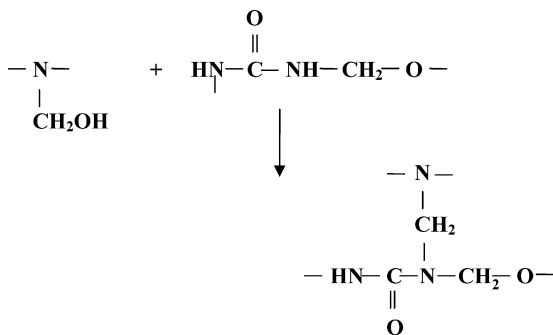
In the addition step, the two formaldehyde moles react with the one mole of urea to form the dimethylol urea.

4.1.2. Condensation step

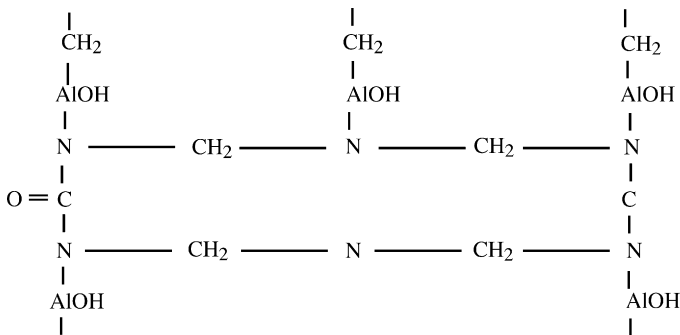


The reaction proceeds in the condensation step with the evolution of water molecules and the crosslinking of dimethylol urea molecules to form intermediate-stage resin.

4.1.3. Crosslinking



The Al precursor added participate in the crosslinking reaction and the Al ions introduced in the resin structure. The crosslinking will increase depending on the number of molecules of aluminum precursor used. Accordingly, the aluminum ions will be evenly distributed as demonstrated by the suggested structure A or B [14].



Structure A

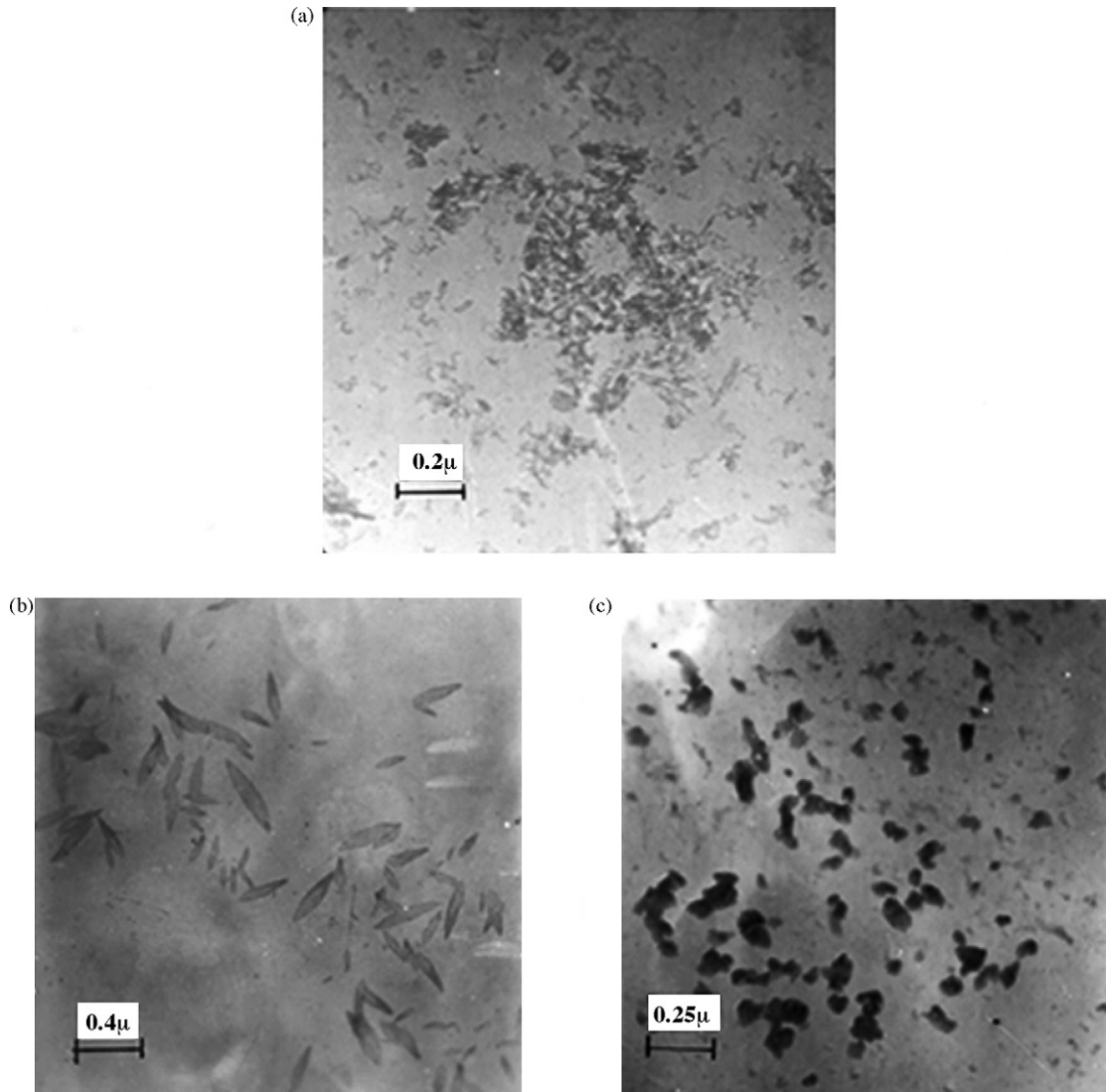
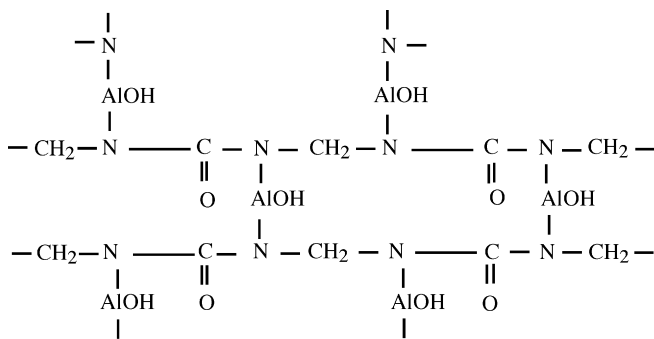


Fig. 12. Transmission electron micrograph of powder of: (a) (RS2) calcined at 700 °C, (b) (RS3) calcined at 700 °C, and (c) (RS4) calcined at 700 °C.



Structure B

5. Conclusion

It was concluded that:

- Using Al acetate ester as a precursor for Al^{3+} during the synthesis of urea formaldehyde resin does not participate in the crosslink-

ing of the resin and is left unreacted. On firing at 1200 and 1300 °C, it results in ultrafine α -alumina with crystallite size of 25.8 and 29.2 nm, respectively.

- Using Al phosphate as a precursor for Al^{3+} , both Al^{3+} and PO_4^{3-} were introduced in the crosslinking reaction of the resin as indicated from IR and XRD results. Firing the resin at 1400 °C result in the reunion of both ions to give Al phosphate (anhydrous) as main product and ultrafine α -alumina with crystallite size of 26.96 nm.
- When Al sulphate salt was used as precursor during resin preparation participated in the crosslinking reaction of the resin. On calcination at 1200 and 1400 °C, ultrafine α -alumina was obtained with crystallite size of 26.96 and 29.78 nm, respectively.

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