

Reaction of Polyacrylic Acid and Metal Oxides: Infrared Spectroscopic Kinetic Study and Solvent Effect

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SYNOPSIS

In this work, we performed infrared spectroscopic studies of the reaction of poly(acrylic acid) (PAA) and metal oxides (ZnO, CaO, CuO, Cr₂O₃, and Al₂O₃). Factors such as the amount of metal oxide, reaction time, solvents, the kind of metal oxides, and temperature were also evaluated to derive the optimum condition for this reaction. The reactions of Cr₂O₃ and Al₂O₃ were far from complete. An extra solvent added to the reaction system could increase the solubility of PAA and metal oxide in the solution so as to completely react. The reactivity of the reaction was increased by using the hydrophilic solvent, particularly H₂O and CH₃OH. Moreover, the reaction rate increased when temperature decreased. The reactivity of the reaction was proportional to the pH value of the metal oxide in the aqueous solution. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Some polyelectrolyte cements are formed by certain powdered metal oxides or ion-leachable silicates reacting with concentrated aqueous solutions of poly(alkenoic acids). These materials have been characterized by an extremely rapid rate of hardening compared to hydraulic cements, excellent mechanical properties, low-temperature processing, and good adhesion to many engineering materials. They are found in dentistry and other applications.¹⁻³

In recent years, many investigators have characterized the chemical and physical nature of dental zinc polyacrylate cements by infrared spectroscopy. Crisp et al.⁴ concluded that oxides of divalent metals form cement gels more readily than oxides of trivalent metals. Moharram and Abdel-Hakeen⁵ indicated that the cements interact with enamel, and ionic bonds form between calcium

ions in enamel and carboxyl groups in polycarboxylic acid. The interaction depended on the percentages of ZnO content in the powders and of carboxylic acid in the liquids of these cements. Rabie et al.⁶ studied the temperature differences in the reaction between metal oxide and polyacrylic acid. Hu et al.^{7,8} studied the polyacrylic acid-metal oxide composites by the infrared spectroscopic feature and the mechanical behavior of deformation. However, this new class of composites may have considerable potential in other composite areas. The kinetics of the reaction of metal oxides and polyacrylic acid has not yet been fully investigated. The purpose of the present study is to study the reaction kinetics of metal oxides and polyacrylic acid by infrared spectroscopy. Likewise, the physical and chemical natures can hopefully be more thoroughly understood to offer some valuable data for developing novel materials.

EXPERIMENTAL

Materials

Aqueous polyacrylic acid (Aldrich, 25% by weight of solid PAA, average molecular weight

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of 90,000), metal oxides (Strem), and other reagents were of reagent grade.

Procedure

Materials were prepared by mixing polyacrylic acid solution, solvent, and metal oxide powder on a glass beaker (50 mL) under a required temperature. The magnetic stirrer's agitation rate was 400 rpm. The agitation was stopped to withdraw the sample at a selected time (30 min). The solution was filled by an aspirator, washing by distilled water several times. Next, the solid was dried in an oven for 24 h at 30°C, and then for 3 h at 120°C. The material was mixed with powdered KBr in a proportion of 1/100. The subsequent mixture was compacted until it was a piece with an adequate transparency. The material was submitted for analysis to determine the characterization. The infrared measurements were taken by using KBr disc technique (Perkin-Elmer 1725X).

The number of moles of acrylic acid ($M_w = 72$) monomer units in the poly(acrylic acid) was 1250 ($=90,000/72$). Hence, the equal amounts of ZnO, CaO, CuO, Cr_2O_3 , and Al_2O_3 for 1 mL of PAA aqueous solution are 0.28, 0.20, 0.28, 0.35, and 0.53, respectively.

The equal amounts of metal oxide for 1 mL of PAA aqueous solution and 50 mL of distilled water were introduced in a flask at 25°C. The magnetic stirrer's agitation time was 4 h under 400 rpm. Finally, the sample was analyzed by a pH meter (METTLER 320) to measure the pH value.

RESULTS AND DISCUSSION

Figure 1 shows the Fourier transform infrared (IR) spectrum of unreacted PAA and PAA-ZnO. The spectra of unreacted PAA displayed bands at 2990 cm^{-1} (CH_2), 1717 cm^{-1} (characteristic stretching, COO^-), 1451 and 1405 cm^{-1} (scissors and bending vibrations of CH_2 and $CHCO$), and 1235 and 1170 cm^{-1} (OH bending and CO stretching of neighboring carboxyl group). The spectra of the treated metal oxides PAA-ZnO exhibited bands at 1560 cm^{-1} (asymmetric COO^- stretching), 1415 cm^{-1} (symmetric COO^- stretching), and 1455 cm^{-1} (CH_2 deformation). The characteristic stretching band of the carbonyl group shifted from 1717 to 1560 cm^{-1} . Also, the doublet at 1235

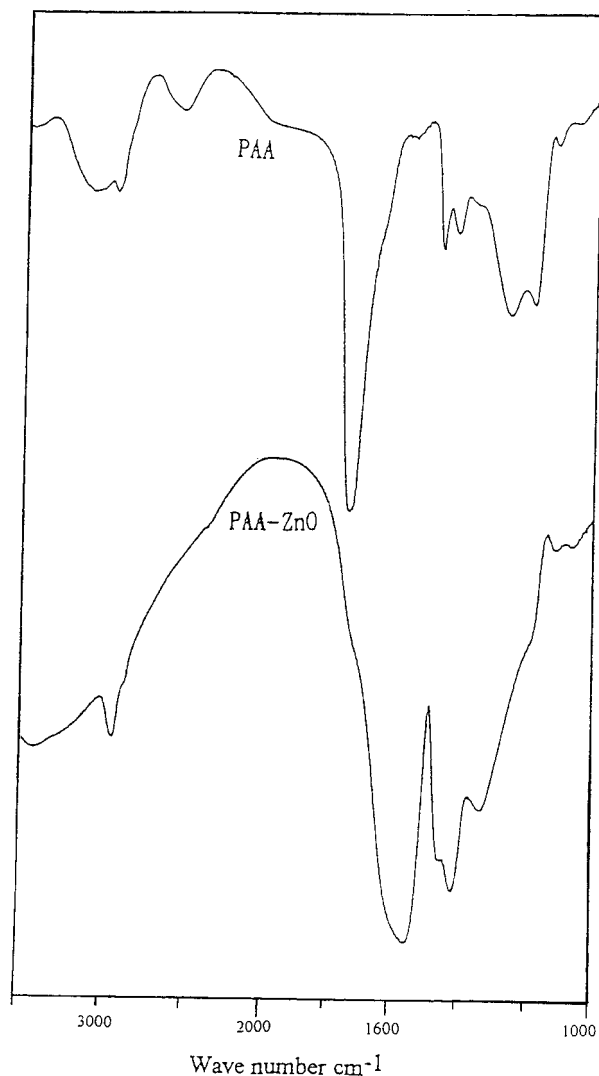


Figure 1 FT IR spectrum of pure polyacrylic acid and PAA-ZnO: 30°C, 400 rpm, 30 min; PAA = 1 mL, ZnO = 0.28 g, CH_3OH = 10 mL.

and 1170 cm^{-1} in the unreacted PAA disappeared. A new peak at 1300 cm^{-1} appeared. This occurrence indicates that polyacrylate ions were present in the PAA-metal oxide material.

Thirteen kinds of solvent were examined to investigate the effects of solvents on the conversion of the carboxylate group, including H_2O , toluene ($C_6H_5CH_3$), chlorobenzene (C_6H_5Cl), diethyl ether ($C_4H_{10}O$), acetone (C_3H_6O), acetonitrile (CH_3CN), hexane (C_6H_{14}), N,N -dimethylformamide (C_2H_7NO), dichloromethane (CH_2Cl_2), benzene (C_6H_6), 2-propanol ($CH_3CHOHCH_3$), methanol (CH_3OH), and ethanol (C_2H_5OH). To observe the effects of solvents on the reaction, an

extra 10 mL of solvent was added to the reaction system. When the lipophilic solvents, including toluene, chlorobenzene, hexane, benzene, and dichloromethane, were introduced to the reaction system, the solution of the reaction system became a two-phase system. The conversion of carboxylate group was the same as that of no added extra solvent: no energy changed at bands of 1500 to 1600 cm^{-1} . They did not contribute to this reaction system.

Effects of solvents for the reaction of PAA and metal oxides are present in Figures 2–4. The attenuated total reflectance infrared spectrum of the freshly prepared PAA–MO showed that a rapid reaction had occurred, with a conversion of some COOH groups (band at 1717 cm^{-1}) to COO^- groups (bands between 1500 and 1600 cm^{-1}). When no extra solvent was added to the reaction system, the amount of water was too little (about 0.75 g) to mix PAA and metal oxide and to allow PAA react with metal oxide completely. The spectrum in Figures 2 and 4 displays a weak shoulder at 1717 cm^{-1} . The order of conversion of the carboxylate group for ZnO is $\text{H}_2\text{O} \approx \text{CH}_3\text{OH}$

$> \text{C}_3\text{H}_7\text{NO} \approx \text{C}_2\text{H}_5\text{OH} > \text{C}_2\text{H}_6\text{O} > \text{CH}_3\text{CHOHCH}_3 > \text{no extra solvent} \approx \text{C}_4\text{H}_{10}\text{O} > \text{CH}_3\text{CN}$ in Figure 2. The order of conversion of the carboxylate group for CaO is $\text{C}_3\text{H}_7\text{NO} \approx \text{H}_2\text{O} \approx \text{CH}_3\text{OH} \approx \text{C}_2\text{H}_5\text{OH} \approx \text{C}_2\text{H}_6\text{O} \approx \text{C}_4\text{H}_{10}\text{O} \approx \text{CH}_3\text{CN} > \text{no extra solvent} > \text{CH}_3\text{CHOHCH}_3$, in Figure 3. Also, the reaction of PAA and CaO was rapid and complete. The bands at 1717 and 1235 cm^{-1} disappeared for any solvent. The order of conversion of the carboxylate group for CuO is $\text{H}_2\text{O} \approx \text{C}_2\text{H}_6\text{O} \approx \text{no extra solvent} \approx \text{C}_4\text{H}_{10}\text{O} \approx \text{CH}_3\text{CN} > \text{CH}_3\text{OH} > \text{CH}_3\text{CHOHCH}_3$, in Figure 4. The reaction of PAA and CuO was slow and incomplete. The sample was too viscous to prepare when the solvent was lipophilic. According to Figures 2–4, an extra amount of solvent enhanced the solubility of the reaction system to react. The reactivity of the reaction was increased by using the hydrophilic solvent, particularly H_2O and CH_3OH . However, if methanol was used as a solvent, the sample was easily prepared. The experimental data of H_2O and CH_3OH are discussed in the following.

Figures 5–7 summarize the effects of amounts of metal oxides for the reaction of PAA and metal

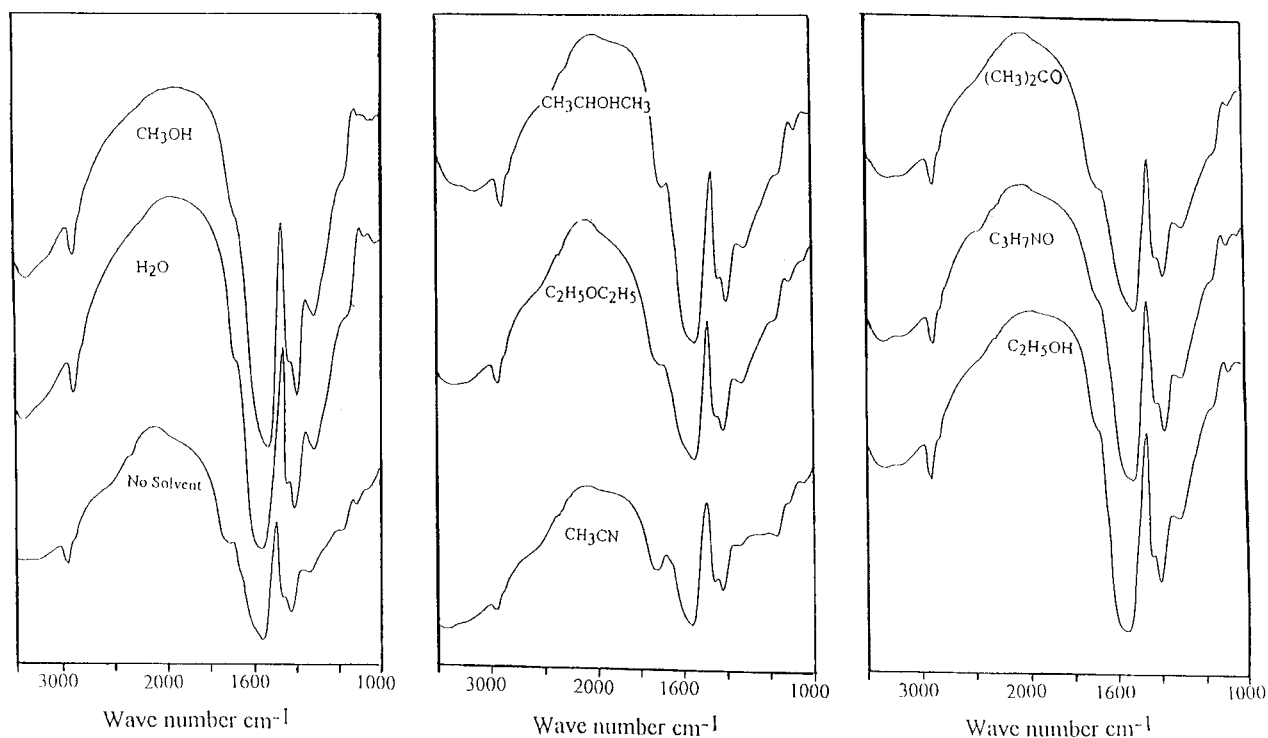


Figure 2 FT IR spectrum of PAA–ZnO for solvent effect: 30°C, 400 rpm, 30 min; PAA = 1 mL, ZnO = 0.28 g, solvent = 10 mL.

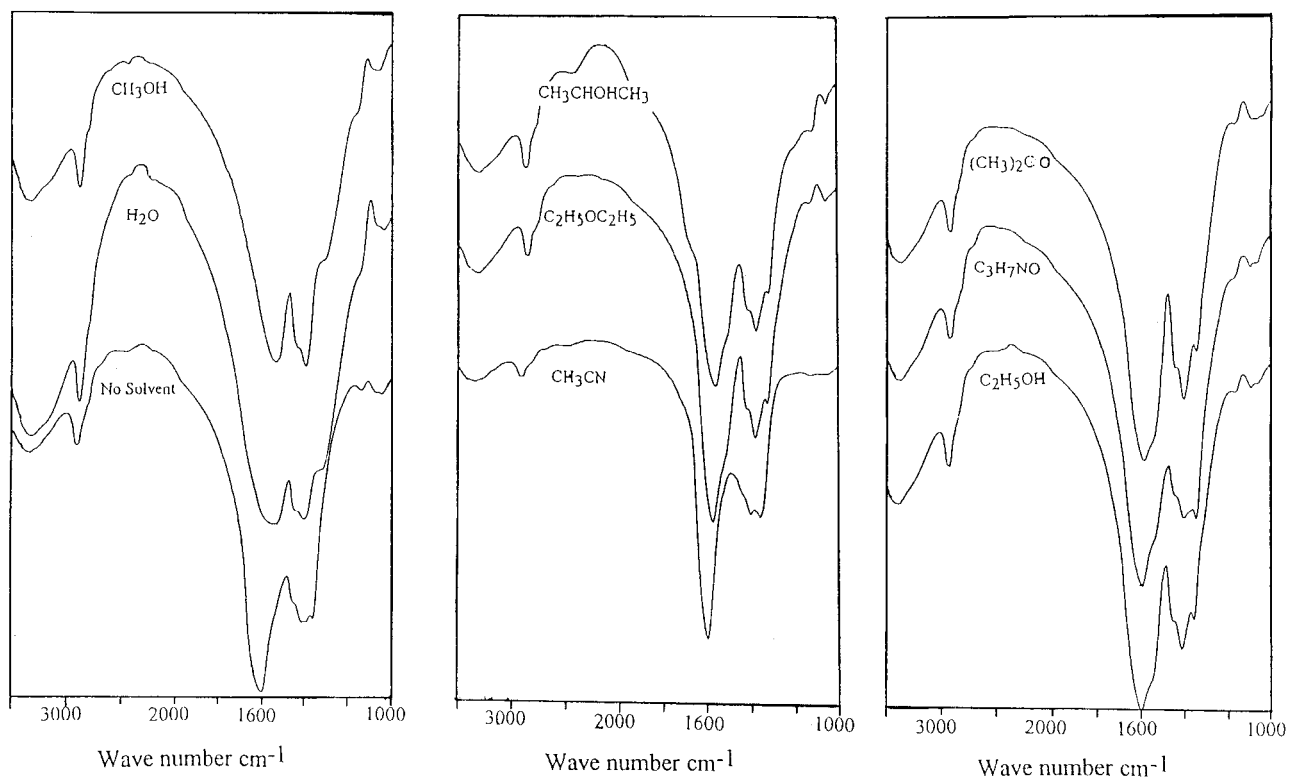


Figure 3 FT IR spectrum of PAA-CaO for solvent effect: 30°C, 400 rpm, 30 min; PAA = 1 mL, CaO = 0.28 g, solvent = 10 mL.

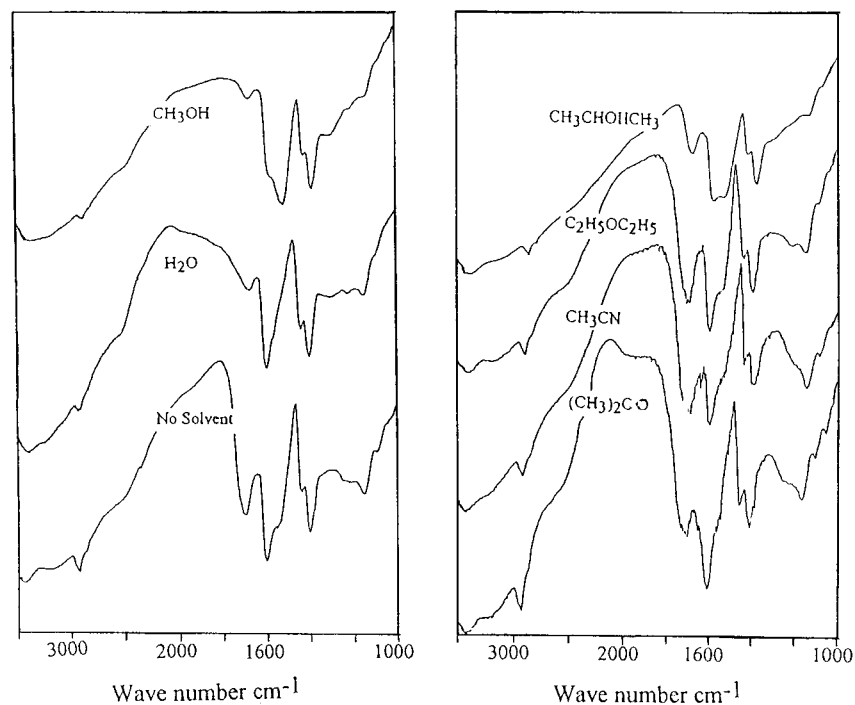


Figure 4 FT IR spectrum of PAA-CuO for solvent effect: 30°C, 400 rpm, 30 min; PAA = 1 mL, CuO = 0.19 g, solvent = 10 mL.

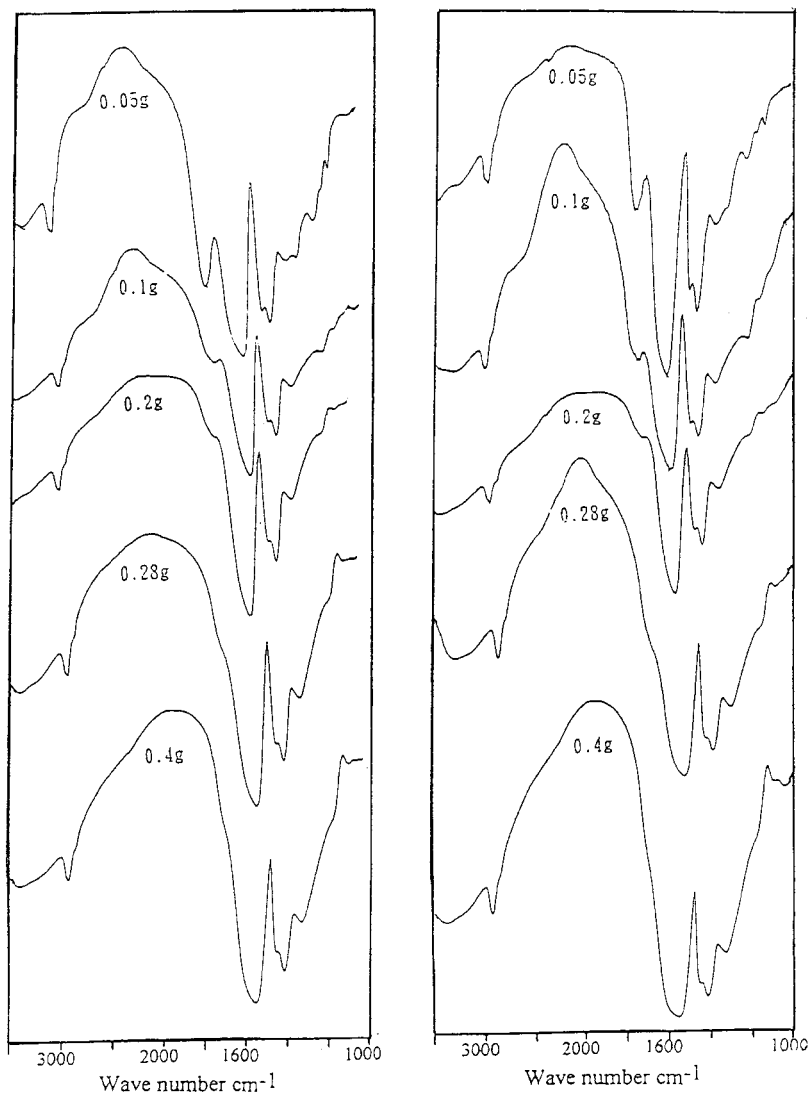


Figure 5 FT IR spectrum of PAA–ZnO for amount of ZnO: 30°C, 400 rpm, 30 min; PAA = 1 mL, solvent (right, methanol; left, H₂O) = 10 mL.

oxides. The energy of band at 1717 cm^{-1} was reduced by increasing the amount of metal oxide. Figure 5 shows that the energies of bands at 1560 cm^{-1} were gradually obvious and became sharp when the amount of metal oxide increased. The energy of band at 2930, 1451, and 1403 cm^{-1} did not change. A new band was found at 1330 cm^{-1} . Figure 6 shows that the energy of bands at 1451 and 1401 cm^{-1} was very strong. The band at 1560 cm^{-1} was broadened when the amount of CaO increased. When the added amount of metal oxide was more than the equal amount of ZnO or CaO (0.28 or 0.2 g; Figs. 5 and 6), the energy of band

at 1717 cm^{-1} disappeared. Whereas, the PAA–CuO reaction was slow and incomplete. The energy of band at 1717 cm^{-1} was high. The excess amount of CuO could not completely react with PAA.

The setting reaction and the phenomenon of ion binding have been widely studied. Ion binding can be general, as for hydrogen and sodium ion,⁹ or occur at specific sites on the polymer chain, notably multivalent ions.¹⁰ Copper(II) is known to bind to poly(acrylic acid) by chelation,^{11–14} and zinc and magnesium form complexes involving two carboxylate ions.^{12,15,16} Hu

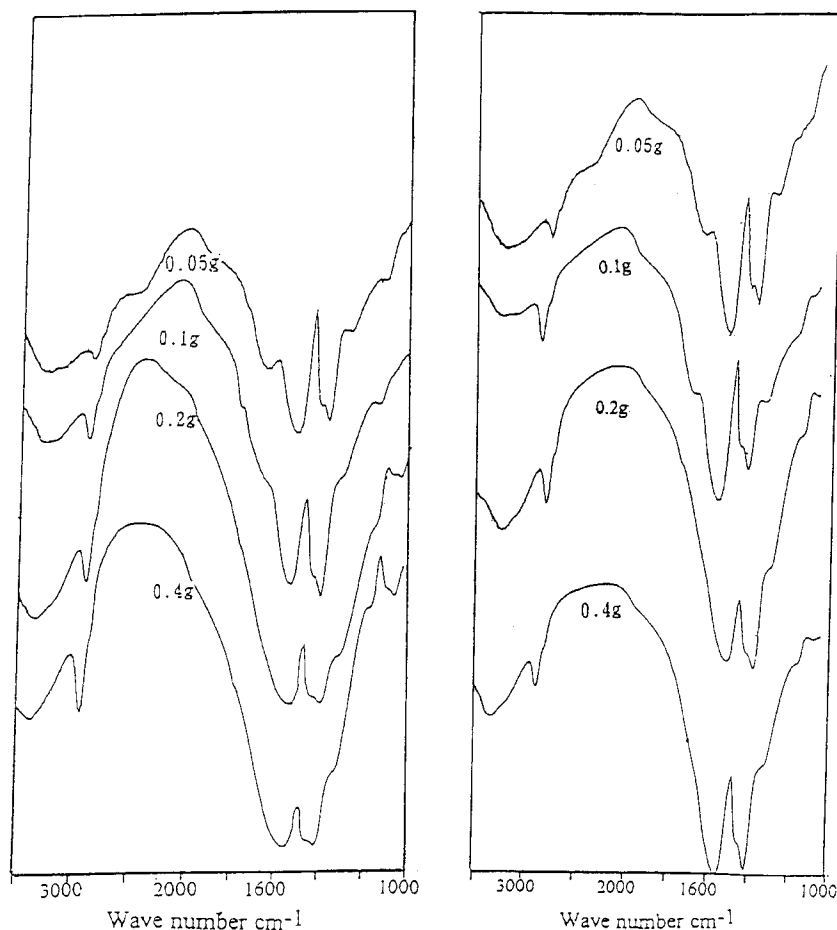


Figure 6 FT IR spectrum of PAA-CaO for amount of CaO: 30°C, 400 rpm, 30 min; PAA = 1 mL, solvent (right, methanol; left, H₂O) = 10 mL.

et al.⁷ used the different values of wavenumbers between asymmetric and symmetric stretching vibration for the carboxylate group to find that the chemical structures of PAA-ZnO, PAA-CaO, and PAA-CuO were the so-called monodentate. This finding suggests that the formation of those composites produces the cross-linking of carboxylate groups through a metal. Although the reaction time was 30 min in Figures 5-7, the reaction was nearly complete when the mole ratio of ZnO (or CaO) to acrylic acid monomer was 1 : 2. The ZnO (or CaO) was considered with divalent ions to polyions, subsequently leading to the formation of salting bridges. Hence, the composites of PAA-ZnO and PAA-CaO were formed by the partial cross-linking style. However, the carboxylate group did not completely react in the composite of PAA-CuO.

Figures 8-11 summarize the effect of the reaction time for the reaction of PAA and metal oxides. During the following 65 min, the COOH band (at 1717 cm⁻¹) was reduced to a weak intensity, while the COO⁻ bands (between 1500 and 1600 cm⁻¹) were enhanced. When the reaction times were more than 25 and 7 min for ZnO and CaO, respectively, the reaction was almost complete. However, the reactions for CuO, Al₂O₃, and Cr₂O₃ could not be complete when the reaction time was more than 65 min. Moreover, the energies of bands (at 1717 and 1500 cm⁻¹) for PAA-CuO remained nearly unchanged when the reaction time was more than 25 min. Furthermore, the reactions for Al₂O₃ and Cr₂O₃ were very slow.

The order of the reactions of PAA and metal oxide was CaO > ZnO > CuO > Al₂O₃ > Cr₂O₃.

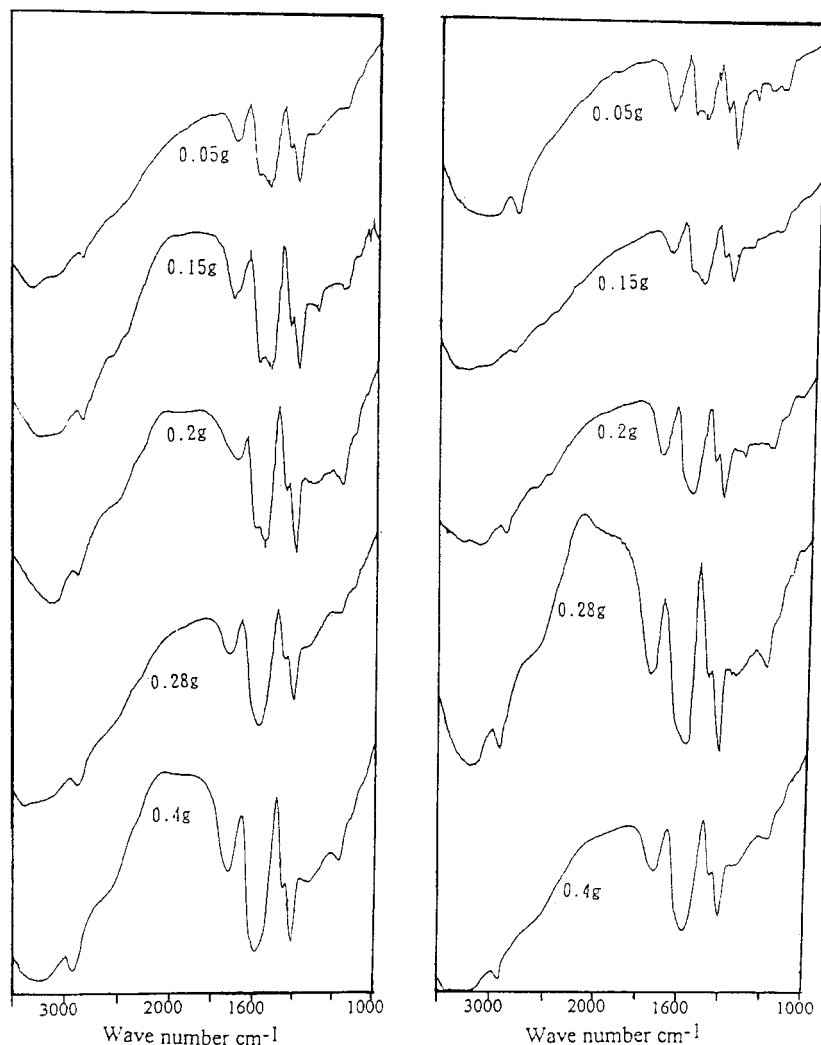


Figure 7 FT IR spectrum of PAA–CuO for amount of CuO: 30°C, 400 rpm, 30 min; PAA = 1 mL, solvent (right, methanol; left, H₂O) = 10 mL.

Rabie et al.⁶ indicated that the metal's reactivity was inversely proportional to the radius of the metal ions. Our results contradicted those of Rabie et al.⁶ As generally known, the reaction is an acid-base reaction. The pH value of the reactant was measured by a pH meter. The pH value of PAA was 3.17. The pH values of CaO, ZnO, CuO, Al₂O₃, and Cr₂O₃ were 12.7, 9.4, 8.1, 8.0, and 7.9, respectively. The reaction's reactivity was proportional to the metal oxide's pH value. According to Figures 9–11, the reactivity for CH₃OH was higher than that of for H₂O.

The reaction of PAA–CaO was rapid (Fig. 9). Preparing the sample was difficult at a short reaction time. When the reaction time was ex-

ceeded 10 min, the reaction had stopped. The reaction's rates of PAA–CuO and PAA–Al₂O₃ were not influenced for varied temperatures. Figure 12 shows the effects of temperature on the reactions of PAA–Cr₂O₃ and PAA–ZnO. The PAA–ZnO spectrum prepared at 60°C displayed a weak shoulder at 1717 cm⁻¹. Also, the intensity of the band decreased with decreasing the temperature to 5°C. The spectrum of PAA–Cr₂O₃ prepared at 60°C showed a weak shoulder at 1565 cm⁻¹. The intensity of the band decreased with increasing the temperature to 5°C. Moreover, the reaction rate increased when the temperature decreased. This result corresponds to that of Rabie et al.⁶

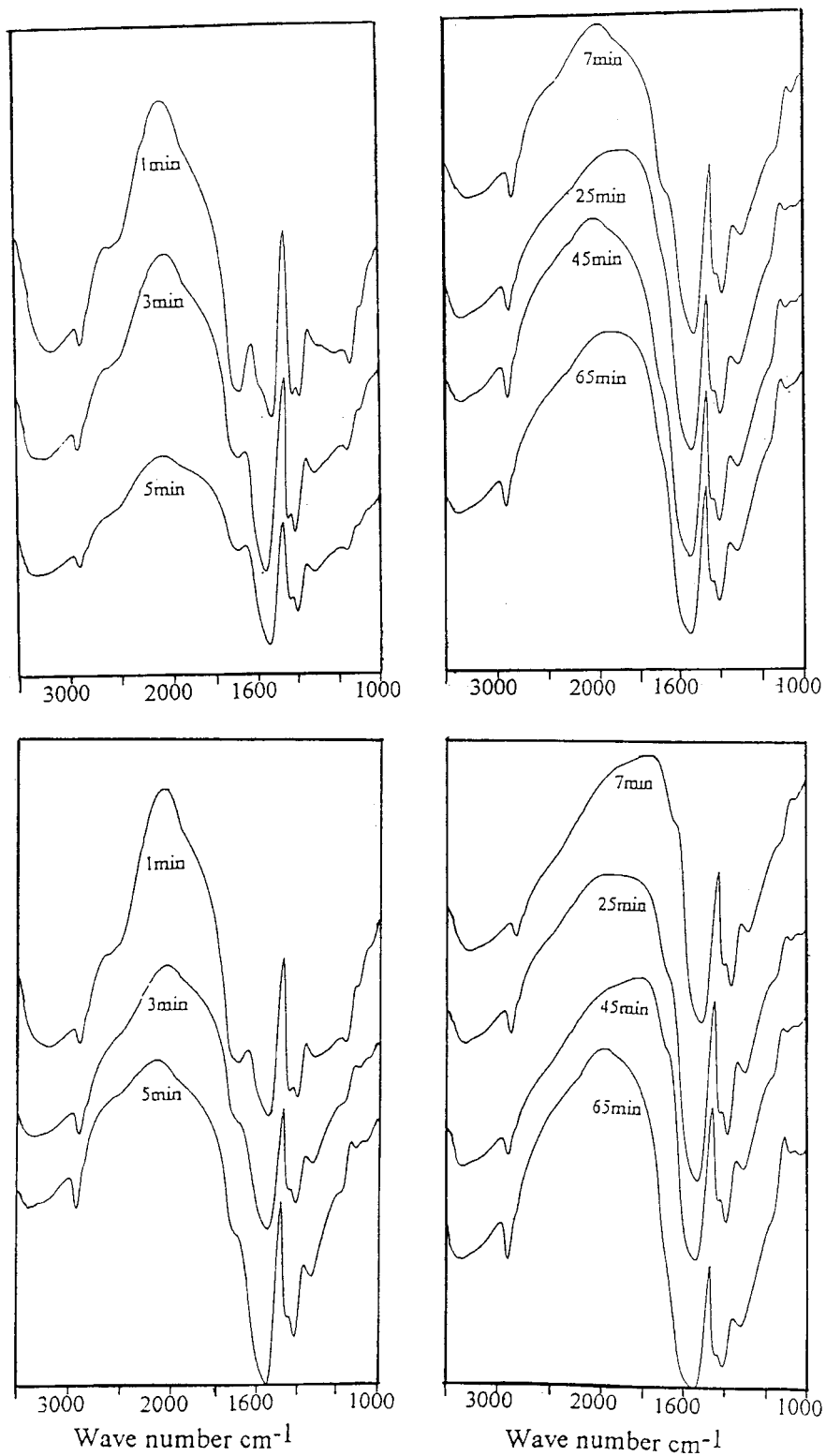


Figure 8 FT IR spectrum of PAA-ZnO for reaction time: 30°C, 400 rpm; PAA = 1 mL, ZnO = 0.28 g, solvent (above, methanol; below, H₂O) = 10 mL.

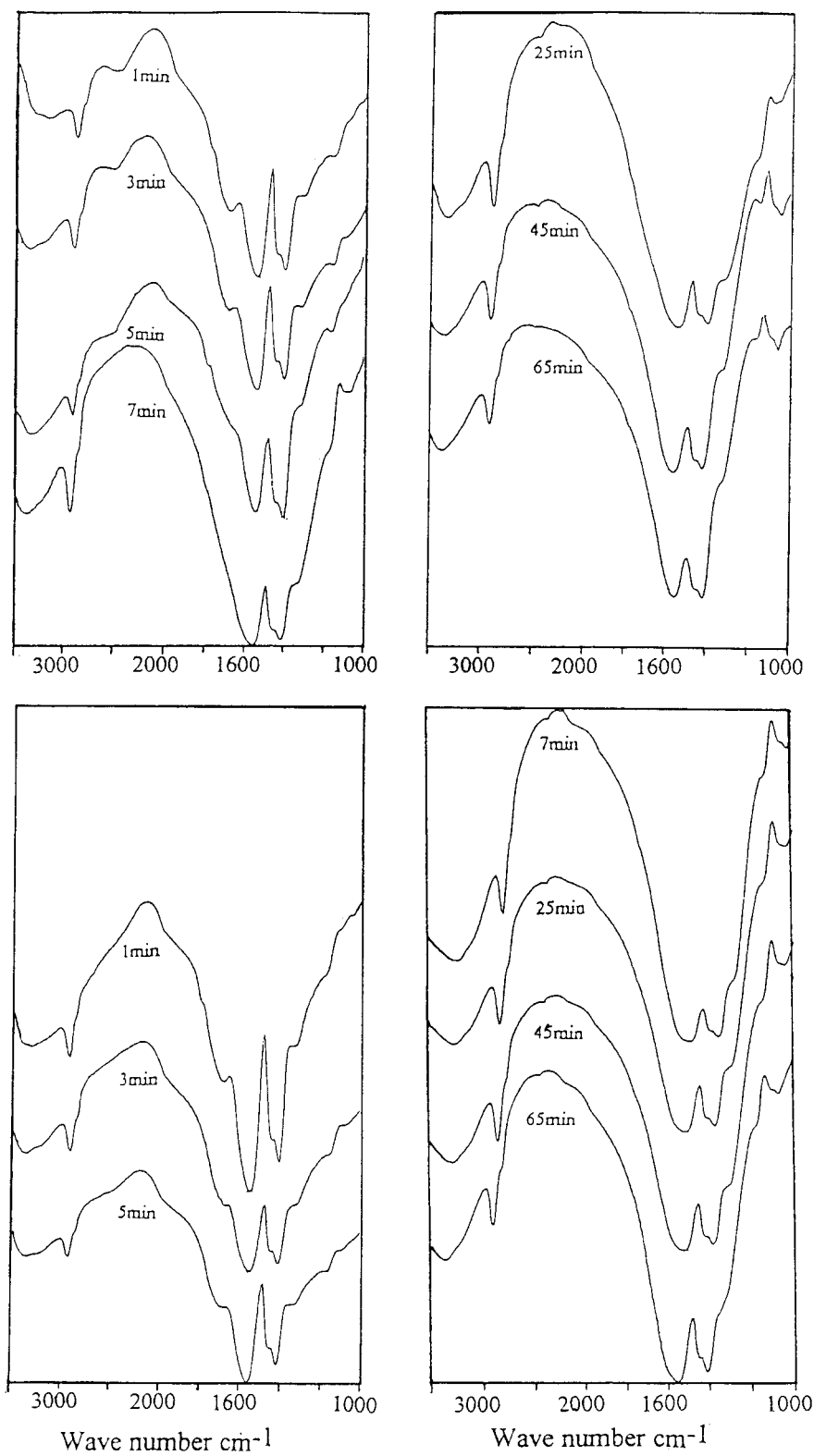


Figure 9 FT IR spectrum of PAA–CaO for reaction time: 30°C, 400 rpm, PAA = 1 mL; CaO = 0.20 g, solvent (above, methanol; below, H₂O) = 10 mL.

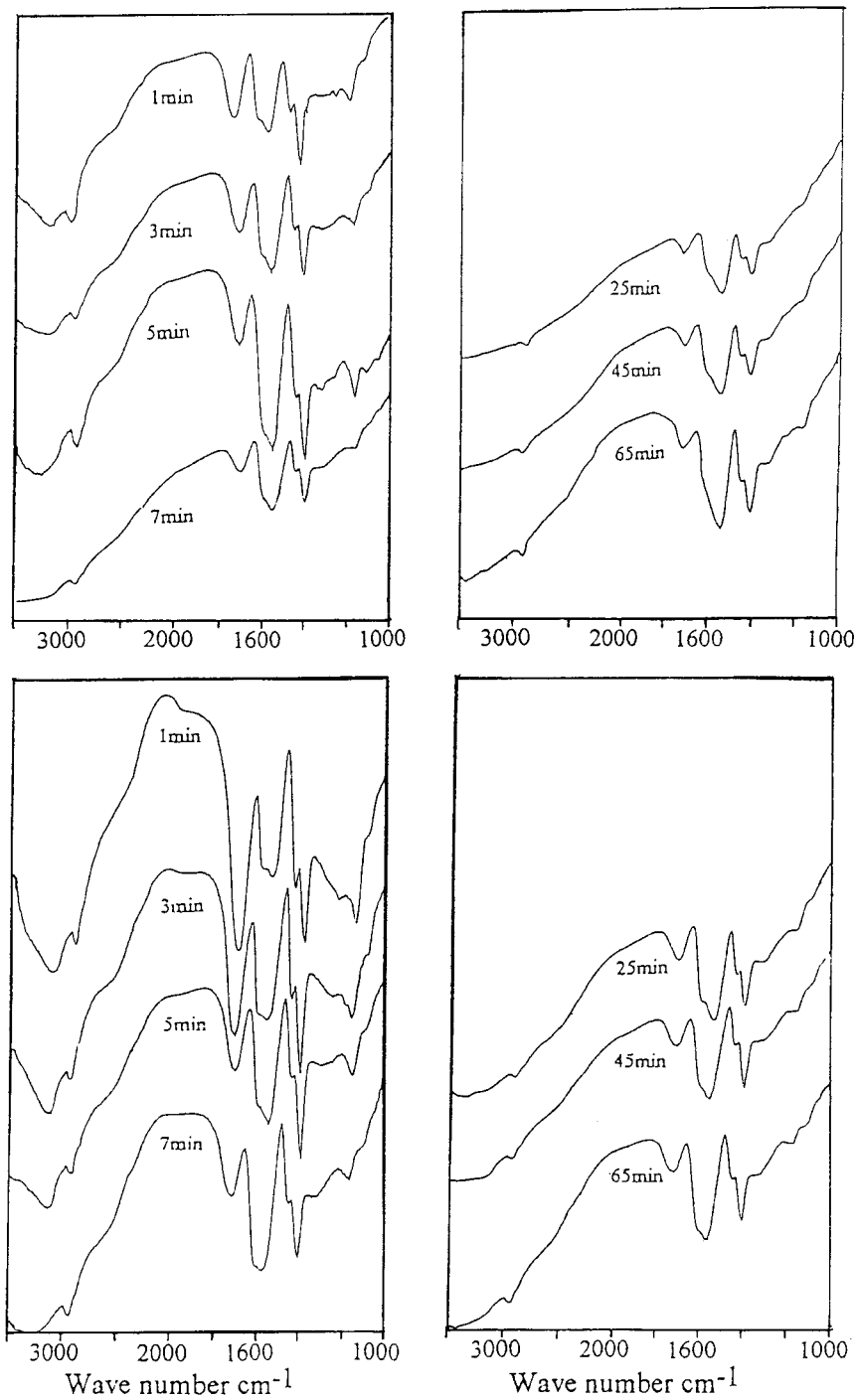


Figure 10 FT IR spectrum of PAA-CuO for reaction time: 30°C, 400 rpm; PAA = 1 mL, CuO = 0.28 g, solvent (above, methanol; below, H₂O) = 10 mL.

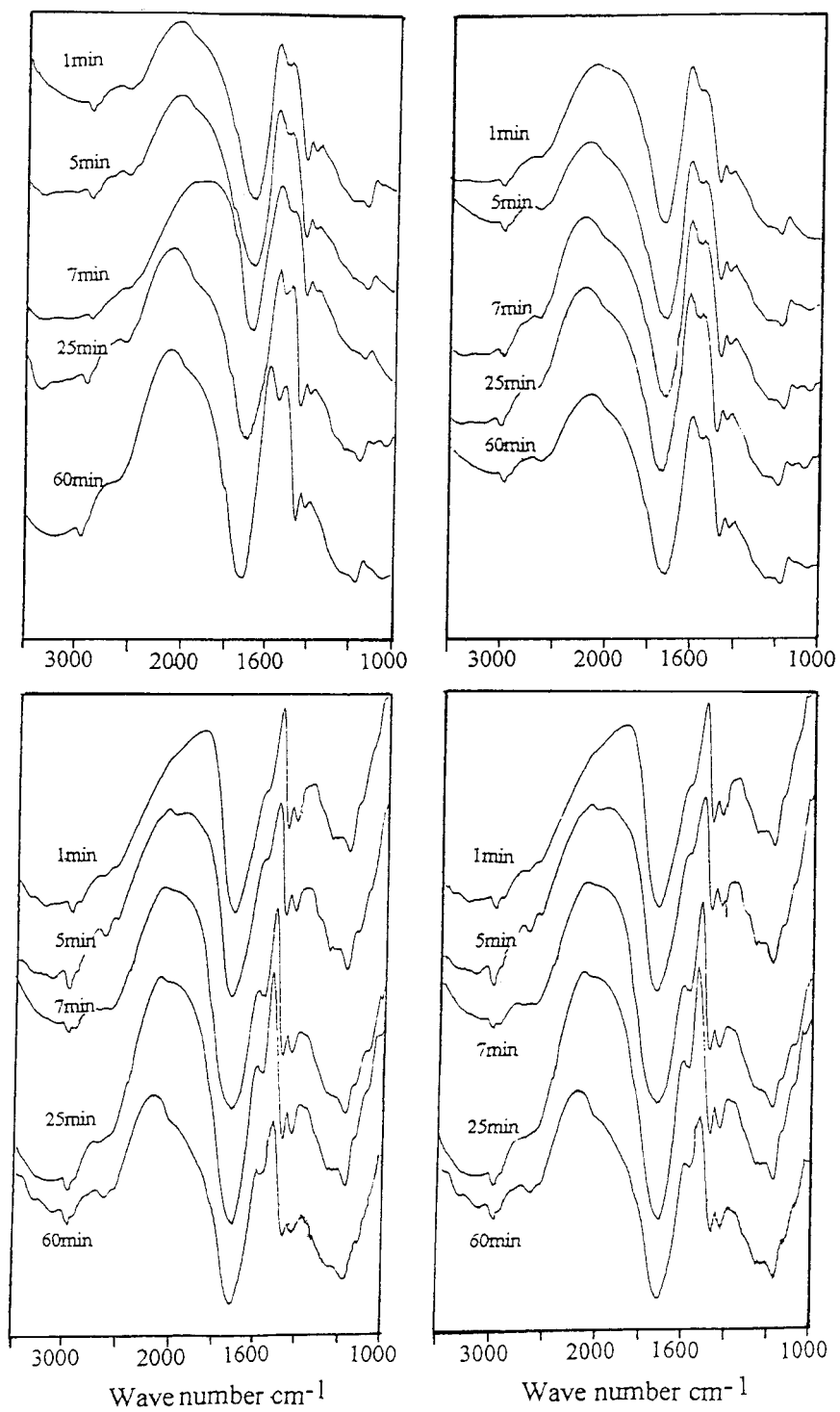


Figure 11 FT IR spectrum of PAA-Al₂O₃ (above) and PAA-Cr₂O₃ (below) for reaction time: 30°C, 400 rpm; PAA = 1 mL, Al₂O₃ = 0.35 g, Cr₂O₃ = 0.53 g, solvent (left, methanol; right, H₂O) = 10 mL.

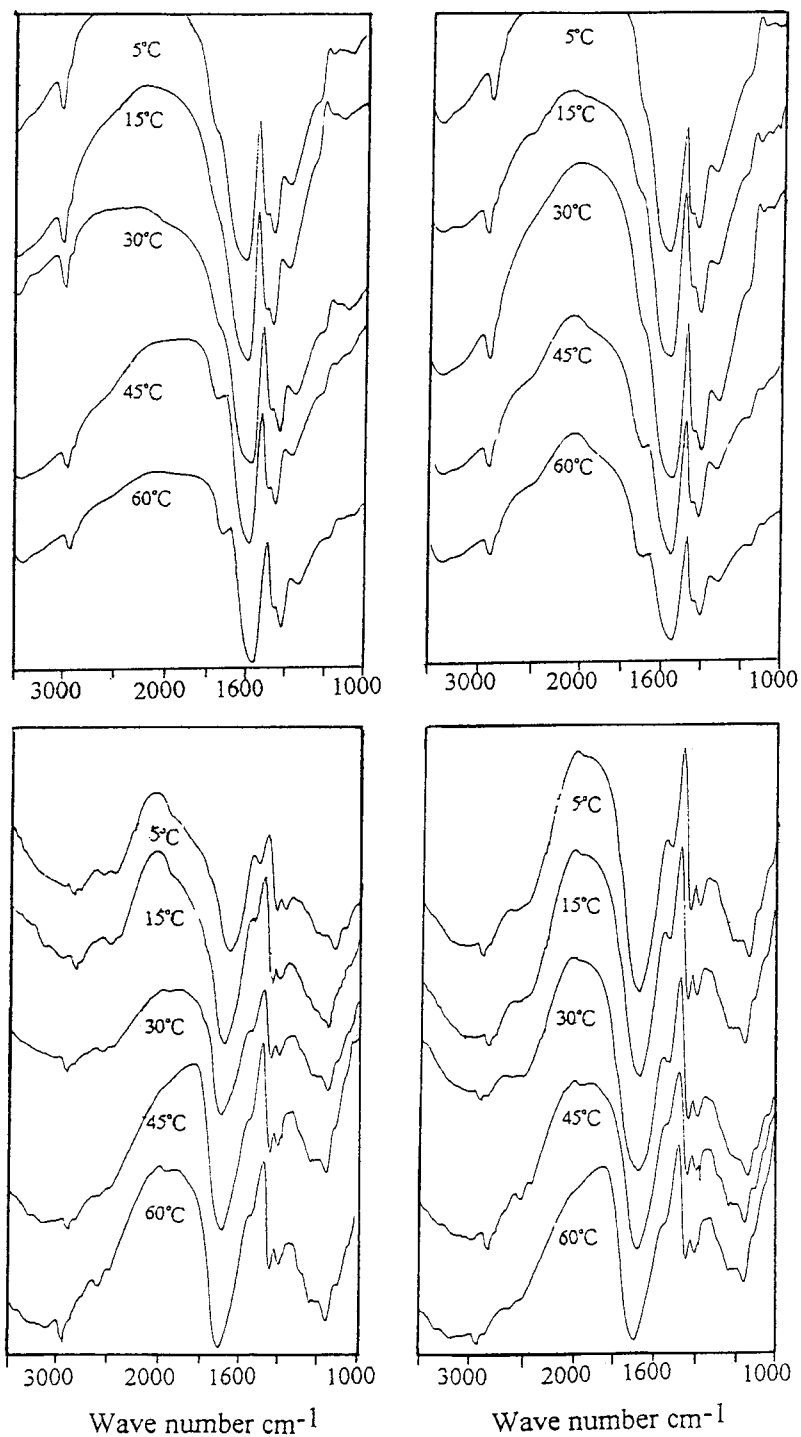


Figure 12 FT IR spectrum of PAA-ZnO (above) and PAA-Cr₂O₃ (below) for temperature: 30 min, 400 rpm; PAA = 1 mL, ZnO = 0.28 g, Cr₂O₃ = 0.53 g; solvent (left, methanol; right, H₂O) = 10 mL.

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