

Effect of Preparation Methods on Thermal Properties of Poly(acrylic acid)/Silica Composites

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ABSTRACT: Poly(acrylic acid)-silica composites have been prepared by two different methods and thermally characterized. The glass transition temperature (T_g) of the PAA-SiO₂ system prepared by mixture method was found to be 120°C irrespective of the type and amounts of silica involved in this work. However, the T_g varied between 132°C and 113°C in the systems prepared by polymerization reaction depending upon the type of silica and percentage conversion. The composites prepared by mixture and polymerization method have been investigated by using thermogravimetry (TGA) to follow the kinetics of anhydride formation and thermal degradation reactions. The activation energy of thermal anhydride formation and thermal degradation reaction was not found to change very much with ratio of PAA-SiO₂ when the composites were prepared by simple mixing. For the composites prepared by polymerization method the activation energy of anhydride formation and thermal degradation reaction were observed to change with percentage conversion. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 891–895, 1998

Key words: composites; thermal properties; preparation method; poly(acrylic acid); silica

INTRODUCTION

In the polymer industries, inorganic particles (mica, talc, calcium carbonate, etc.) are combined with polymer materials to improve some of their mechanical properties and thermal stability. This is a rapid method of increasing mechanical resistance of the samples against compression, abrasion, and so forth.^{1–7} The properties of the composite materials are affected by the chemical properties of the components and the nature of the interaction between the phases. Studies of reinforcement indicate that stress is effectively

transferred between the polymer matrix and embedded particulate phases over an interfacial region of finite dimension.⁸ The macroscopic properties of the composites are therefore a function of the microscopic properties of this interface. The distribution and contact of the dispersed phase within the matrix polymer are also of great importance in influencing the strength of the interface. In addition to the chemical and physical properties of the components of the composite, the method of preparation is another factor affecting the properties of the composite.

Previous investigations on poly(acrylic acid) (PAA)–alumina systems have demonstrated that there is a strong interaction between the polymer and the filler and this interaction originates from the attraction of the acidic groups of the polymer by the surface of the alumina.⁹ An interaction of

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this type is likely to enhance the binding of PAA onto the surface of silica as well.

The purpose of the present study is to prepare a composite material consisting of PAA-silica by two different methods and compare the thermal properties and stabilities of these systems.

EXPERIMENTAL

Two different methods were employed for the preparation of the composites: polymerization and mixing. In the polymerization method, after AA (BDH Chemicals Ltd.) was distilled twice in a vacuum, it was placed in glass ampoules, mixed with the commercial (97.3% SiO₂ by atomic absorption, coarse powder) and precipitated silica (BDH Chemical Ltd., 99% SiO₂, fine powder) in various AA/SiO₂ weight ratios, and sealed in a vacuum line. Irradiations were carried out in a Gammacell 220 type ⁶⁰Co γ irradiator at room temperature at a dose rate of 0.85 kGy/h. The polymerized product was washed with ether and dried to constant weight in a vacuum oven.

In the mixing method, the PAA (BDH Chemicals Ltd., 25 wt % aqueous solution) was first dried then dissolved in methanol and mixed with commercial silica and precipitated silica in different PAA/SiO₂ weight ratios. Then the suspension was dried for several days under a vacuum at 50°C.

Due to the differences in densities of commercial (3 g/cm³) and precipitated (2 g/cm³) silica, it was not possible to prepare composites with the same compositions for these two silica samples.

Composite Characterization

Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_g) of the composites prepared by the mixing and polymerization methods were determined by using a DuPont DSC 910 thermal analyzer system. All samples were tested in crimped aluminum pans at a heating rate of 10°C/min under dry N₂ gas (25 mL/min) over a temperature range from room temperature to 180°C. The thermogram of a recycle run was used to determine the T_g of the samples kept over CaCl₂ in a desiccator. The T_g s were determined as the average of at least three separate measurements as the midpoints of reverse S shapes. The experimental errors in the

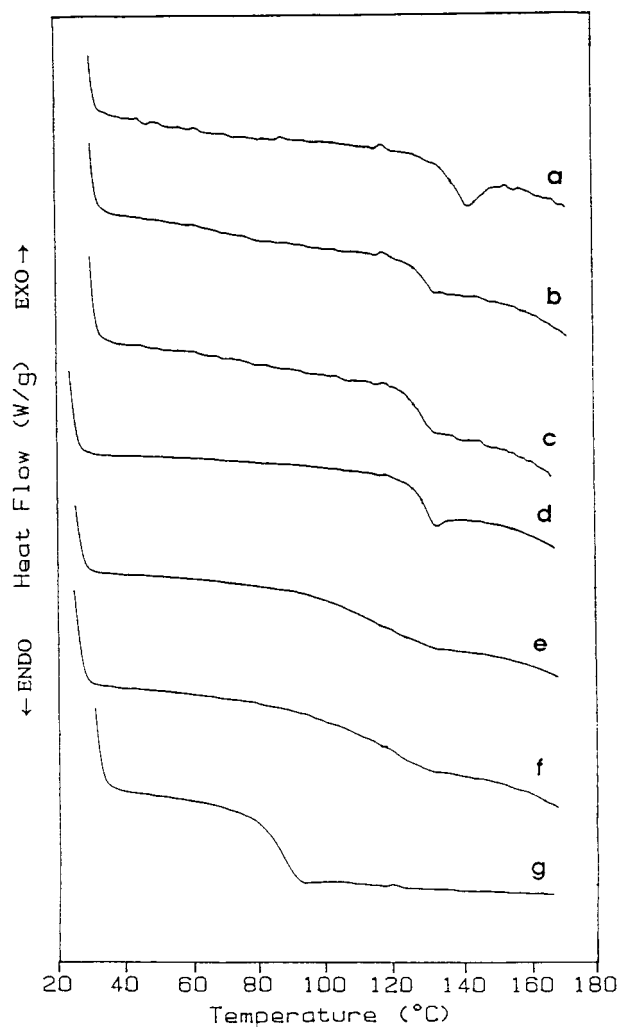


Figure 1 DSC thermograms of unfilled PAA and composites: (a) PAA/Com.SiO₂ ($\phi_{\text{PAA}} = 0.13$), (b) PAA/Com.SiO₂ ($\phi_{\text{PAA}} = 0.25$), (c) PAA/Com.SiO₂ ($\phi_{\text{PAA}} = 0.38$), (d) PAA/Pre.SiO₂ ($\phi_{\text{PAA}} = 0.69$), (e) PAA/Pre.SiO₂ ($\phi_{\text{PAA}} = 0.82$), (f) PAA/Pre.SiO₂ ($\phi_{\text{PAA}} = 0.85$), and (g) unfilled PAA.

individual measurements were estimated to be less than 0.5°C.

Thermogravimetric Analysis (TGA)

The dynamic weight loss tests were conducted by using a DuPont 951 thermogravimetric analyzer. All tests were conducted in a nitrogen purge (25 mL/min) using sample weights of 10–15 mg at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

DSC

DSC was used to locate the T_g of the composites prepared by the mixture and polymerization

Table I Glass Transition Temperature (T_g) of PAA/SiO₂ Composites Prepared by Polymerization Method

| System | Dose (kGy) | Conversion (%) | ϕ_{PAA} | T_g (°C) |
|-------------------------|------------|----------------|---------------------|------------|
| PAA | — | — | — | 85 |
| AA/Com.SiO ₂ | 0.14 | 21 | 0.13 | 132 |
| AA/Com.SiO ₂ | 0.28 | 49 | 0.25 | 130 |
| AA/Com.SiO ₂ | 0.71 | 91 | 0.28 | 129 |
| AA/Pre.SiO ₂ | 0.07 | 35 | 0.69 | 129 |
| AA/Pre.SiO ₂ | 0.14 | 71 | 0.82 | 115 |
| AA/Pre.SiO ₂ | 0.28 | 88 | 0.85 | 113 |

methods. The results are shown in Figure 1. The T_g of PAA with a molecular weight of 230,000 was found as 85°C (Table I). This value is lower than the common T_g ($\sim 106^\circ\text{C}$)¹⁰ of pure PAA. This difference is most probably due to the plasticizing effect of the “bound water” in PAA that was obtained by drying from a 25 wt % aqueous solution. Although the PAA was dried in a vacuum at 50°C for several days, it is clear that this treatment was not sufficient to completely remove the bound water.¹¹ The effect of bound water on the T_g of the PAA may be analyzed by the following equation:

$$1/T_g = W_{\text{H}_2\text{O}}/T_{g\text{H}_2\text{O}} + W_{\text{PAA}}/T_{g\text{PAA}}$$

where $T_{g\text{H}_2\text{O}} = -145^\circ\text{C}$ ¹² represents the T_g of water; $W_{\text{H}_2\text{O}}$ the weight fraction of water that is found from the peak area of the derivative TGA thermograms; and $W_{\text{PAA}} = 1 - W_{\text{H}_2\text{O}}$, which is the weight fraction of PAA. After the correction was made on the effect of bound water, $T_{g\text{PAA}}$ was found to be 108°C, which agrees with the literature value. The presence of bound water in PAA (3.25 wt % in the present case) was found to decrease its T_g by 23°C.

The T_g of the PAA/SiO₂ systems prepared by mixture method was found to be 120°C, irrespective of the type and amounts of silica involved in this work. Because the segmental mobility of the chains near the silica particles are reduced, the T_g of the composites increased.

The insensitivity of the T_g of these composite systems to the amount and type of silica indicates that coverage and consequently the interaction among PAA and silica surfaces are not strong. This is most probably due to the difficulty of obtaining a perfectly mixed system when trying to mix polymer and filler.

However, the T_g varied between 132 and 113°C in the systems prepared by the polymerization reaction, depending upon the type of silica and percentage conversion (Table I). A better dispersion of the silica particles was achieved in this latter system due to the wetting of silica surfaces by AA monomer; consequently, PAA formed a skin on the silica surface. Therefore, the silica–PAA interaction was higher than the systems prepared by the mixture method. Increases in T_g were documented in a number of other composite systems and were explained on the basis of reduced mobility of molecular segments in the vicinity of the filler.¹³ When the polymer/silica ratio is low, the interaction between the polymer and silica phases becomes more effective and this causes a significant rise in T_g . The polymer/silica ratio is highest with precipitated silica containing composites. When the weight ratio of polymer to silica is low as in the presence of commercial silica, the amount of polymer that interacts with the surface of the silica is low. This causes the T_g of the systems containing commercial silica to be higher than the precipitated silica.

TGA

The composites prepared by the mixture and polymerization methods were investigated by using TGA to follow the kinetics of the anhydride formation and thermal degradation reactions. The dynamic TGA traces of the composites prepared by the mixture and polymerization methods are shown in Figure 2.

Three distinct reaction peaks at around 240°C (I), 290°C (II), and 420°C (III) are identified in the dynamic TGA thermograms of the composites prepared by the mixture method [Fig. 2(a)]. These peaks were attributed to bound water removal (I), anhydride formation (II), and polymer degradation (III).⁹ Two distinct reaction peaks at 283°C (I) and 432°C (II) were identified in the dynamic TGA thermograms of the composites prepared by the polymerization method [Fig. 2(b)]. These peaks were attributed to anhydride formation and polymer degradation.

When precipitated silica was used in the preparation of composites, a similar TG behavior was observed for both methods of preparation; three peaks for the mixing method and two peaks for the polymerization method [Fig. 2(c,d)].

The TGA thermograms of the composites prepared by the mixture and polymerization methods were evaluated by the Freeman–Carroll¹⁴

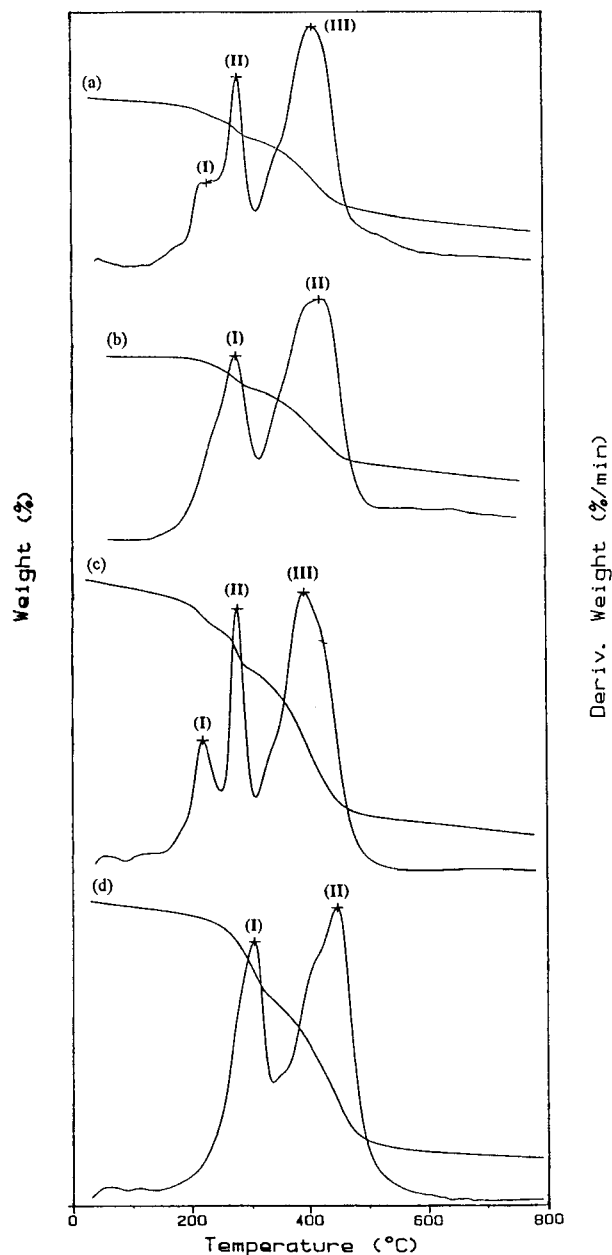


Figure 2 TGA thermograms of (a) PAA/Com.SiO₂ ($\phi_{\text{PAA}} = 0.25$, mixture method), (b) PAA/Com.SiO₂ ($\phi_{\text{PAA}} = 0.25$, polymerization method), (c) PAA/Pre.SiO₂ ($\phi_{\text{PAA}} = 0.82$, mixture method), and (d) PAA/Pre.SiO₂ ($\phi_{\text{PAA}} = 0.82$, polymerization method).

procedure to determine the activation energies of anhydride formation and thermal degradation reactions. The activation energy of thermal anhydride formation reactions of PAA used in the preparation of mixtures was found to be approximately 59 kJ/mol in the temperature range of 280–306°C. The activation energy of the thermal

anhydride formation reaction of commercial silica containing systems prepared by the mixture method was found to be 66 kJ/mol and that of the precipitated silica containing system was 61 kJ/mol in the same temperature range. The activation energy of thermal anhydride formation did not change very much with the ratio of PAA/SiO₂ when the composites were prepared by simple mixing.

For the composites prepared by the polymerization method the activation energy of anhydride formation and thermal degradation reactions were observed to change with the percentage conversion (Table II). The activation energy of the anhydride formation reaction of the commercial silica containing system was determined to be in the range of 73–109 kJ/mol and that of the precipitated silica containing system was in range of 61–69 kJ/mol.

According to these results, the activation energy of thermal anhydride formation reactions of the system is dependent on the preparation method. There is little bound water (~ 3%) in PAA that was dried from a dilute (25 wt %) aqueous solution, which is used for the preparation of composites by the mixture method. The presence of bound water in the system inhibits the formation of anhydride.⁹ In the composites prepared by the polymerization method the thermal anhydride formation reaction was influenced by the good interaction between the silica and polymer and the absence of water bound to the system; consequently, the activation energy of this reaction was found to be high. It has been reported that the anhydride is formed in PAA at higher temperatures by decarboxylation occurring simultaneously with water elimination.⁹

The activation energy of the thermal anhydride formation reaction of the commercial and precipitated silica containing composites prepared by the polymerization method decreased with increasing conversion of AA. The polymer–silica interaction decreases with increasing percentage conversion and the polymer/silica ratio becomes higher.

The activation energy of the thermal degradation reaction of PAA was 40 kJ/mol in the temperature range of 370–410°C. The activation energy of the same process for the commercial silica containing systems prepared by the mixture method was determined to be 44 kJ/mol in a range of 327–371°C and that of the precipitated silica containing system was 43 kJ/mol in a temperature range of 327–377°C. The activation en-

Table II Activation Energy of Thermal Anhydride Formation Reaction (I) and Thermal Degradation Reaction (II) of Systems Prepared by Polymerization Method

| System | Dose (kGy) | Conversion (%) | ϕ_{PAA} | (I) E (kJ/mol) | (II) E (kJ/mol) |
|--------------------------|------------|----------------|---------------------|------------------|-------------------|
| PAA | — | — | — | 59 | 40 |
| AA/Com.SiO ₂ | 0.14 | 21 | 0.13 | 109 | 51 |
| AA/Com.SiO ₂ | 0.28 | 49 | 0.25 | 85 | 45 |
| AA/Com.SiO ₂ | 0.71 | 91 | 0.28 | 73 | 43 |
| AA/Prec.SiO ₂ | 0.07 | 35 | 0.69 | 69 | 44 |
| AA/Prec.SiO ₂ | 0.14 | 71 | 0.82 | 64 | 40 |
| AA/Prec.SiO ₂ | 0.28 | 88 | 0.85 | 61 | 42 |

ergy of the thermal degradation reaction did not change very much with the ratio of PAA/SiO₂ when the composites were prepared by simple mixing. In other word, the thermal stability of PAA was not affected by the two types of silica, provided that the composites were prepared by the simple mixing method.

The activation energy of thermal degradation reaction of the commercial silica containing system prepared by the polymerization method was determined to be between 43 and 51 kJ/mol in a temperature range of 320–430°C, and the precipitated silica containing system was found to be between 40 and 44 kJ/mol in a temperature range of 305–430°C.

Due to the high PAA content of this latter system, its thermal stability was found to be similar to the degradation behavior of pure PAA.

CONCLUSION

In this study we tried to see the effect of preparation techniques on the thermal stability of PAA/SiO₂ composites. As is very well known, the properties of composites are controlled by a number of factors, most notably the chemical and physical properties of the ingredients. In the preparation of PAA/SiO₂ composites it is clearly shown in this work that if the monomer AA is used instead of starting with PAA and the composite is prepared by polymerization of AA in the presence of silica, these composites acquire better thermal stabilities. This can be achieved by soaking the particles in AA and then irradiating the system by γ rays.

The same conclusion can be applied when a coating of silica particles by PAA is considered. To achieve a better surface coverage, the recommen-

dation is to mix the monomer and filler and then irradiate them to get polymer films on the surface rather than mixing the polymer with the particles. This method is especially advantageous when polymers to be used in coatings or composites are highly hydrophilic.

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