

Study of the Interaction of Poly(acrylic acid) and Poly(acrylic acid-Poly acrylamide) Complex with Bone Powders and Hydroxyapatite by Using TGA and DSC

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ABSTRACT: The thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) were used to study the thermal degradation of poly(acrylic acid) PAA and poly(acrylamide) PAAm as well as the compound obtained from their interactions. The examination of the thermal curves revealed that the characteristics of the curves of the compound resulting from the cooperative interactions are different from those of the constituent polymers. The differences in the characteristics of the thermal curves were attributed to the formation of an interpolymer complex resulting from the interaction of PAA with PAAm at low pH value. These two thermal techniques were also used to investigate the thermal behavior of the compounds obtained from the interaction of PAA and (PAA-

PAAm) mixture with bone powders (BP) and hydroxyapatite (HA). It was found that the TGA, DTG, and DSC curves do not show the peak of formation and degradation of PAA anhydride which provided strong evidence for the consumption of PAA in the reaction between the polymer and BP. The interaction between PAA and the thermally treated BPs and HA was investigated. Moreover the interaction between the mixture of PAA and PAAm at different pH values and the BPs and HA was discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3220–3227, 2007

Key words: thermogravimetric analysis; differential scanning calorimetry; poly(acrylic acid); poly(acrylamide); bone powders and hydroxyapatite

INTRODUCTION

In the recent years, the inter polymer interactions between poly acid, e.g., poly(acrylic acid), and poly (methacrylic acid) and poly base e.g., poly (acrylamide) and poly(vinyl pyrrolidone) have attracted the interest of a number of researchers who used various techniques to study the formation, structure, and properties of these interpolymer complexes.^{1–3} Other workers studied the interactions between such polymers and BP and HA.^{4–8} The characteristics of these complexes resulting from the cooperative interactions are different from those of the constituent polymers. This new class of polymeric materials is used in various applications, for examples, in dialysis, ultrafiltration, reverse osmosis, and production of blood-compatible materials and batteries.⁹ The structure as well as stability of the complexes depend on the type of the interactions, the solution conditions and macromolecules characteristics, pH, ionic strength, temperature, solvent, molecular weight, and conformations. Although the thermal analysis, thermogravimetric analysis (TGA), and differential scanning

calorimetric analysis (DSC) have been used as analytical techniques to study the thermal behavior of PAA and PAAm,^{10–15} the thermal degradation of their interpolymer complexes has not yet been fully investigated.

On the other hand, considerable amount of effort has gone into the study of polymer–hydroxyapatite (or bone) composites from the point of view of material characterization and its biomaterial applications. Extensive studies have been carried out on the polymer–hydroxyapatite composites for their potential use as bone and teeth replacement materials.^{16–22} Very little is understood, however about the interaction between the polymers and the constituents of bone or hydroxyapatites (HA). Indeed the thermal behavior of polymer-HA composites has been studied by many researchers by using the thermal analysis techniques. The interaction between polymers and bone structure or HA has been a subject of interest for many investigators who used the thermal analysis techniques to study the thermal degradation of polymer-HA composites.

The main purpose of this study is to investigate the thermal degradation of PAA, PAAm, bone powders, synthetic HAs, and the compounds resulting from the interaction of PAA, and mixtures of PAA-PAAm with bone powders and HAs by using TGA and DSC techniques.

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EXPERIMENTAL

In the present study, the bone powder (BP) was prepared from freshly removed diaphyses of the calf long bones. Bones were dissected of surrounding connective tissues and alkali treated to leave purely osseous structure free of all traces of tissues, fat, or any organic matter occupying the intraosseous spaces. In alkali treatment, the bones were broken into small pieces and boiled for hours in a 30% sodium carbonate solution followed by thoroughly washing with hot water. The treated bones were then dried at 100°C overnight. The cycle of alkali treatment was currently repeated till a steady state of sample constant weight was reached. Then, bones were ground to fine powders in a hardened steel vial. The BP was sieved to obtain suitable particle size.

The chemically treated BP samples were then heated in a conventional oven at 700°C for 2 h (HBP). The HA used in this study is bovine hydroxyapatite (BHA) whose calcium content is 39% and the phosphorous is 18%. This sample was obtained from Asahi optical, Tokyo, Japan.

Poly(acrylamide) (PAAm) was obtained from BDH Chemicals, Pool, England; its molecular weight is over 5000,000. Poly (acrylic acid) (PAA) was obtained from Nisso Shoji, Japan (PW-110 Lot No. 4029) with a molecular weight 125,000. The two polymers were used without any further purification. A solution of each polymer was prepared by dissolving 1 g in 100 mL of distilled water. Each solution was then stirred overnight to ensure complete dissolution. The chemically treated BP was added to the 1% aqueous solution of PAA with different wt % concentrations. Then the mixtures were stirred with a magnetic stirrer at the room temperature for 2 h without any pH adjustment. The precipitate was filtrated and

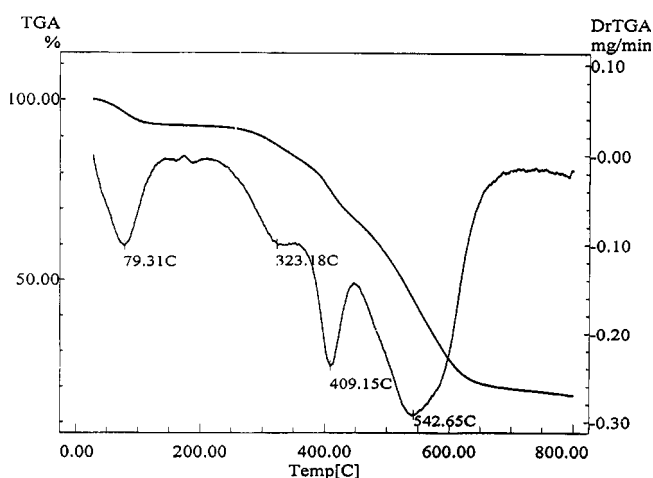


Figure (4.27.a): TGA and DTG curves of PAA sample

Figure 1 TGA and DTG curves of PAA.

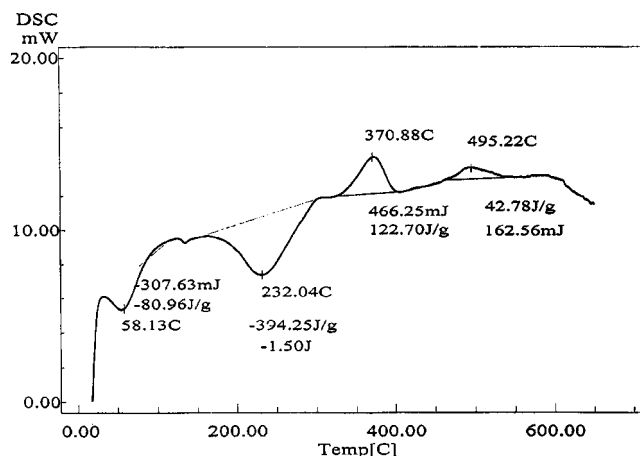


Figure 2 DSC curve of PAA.

washed with distilled water to remove any soluble salts. The samples were dried in an oven at 90°C for 6 h and then ground to suitable particle size. All thermal analysis measurements were carried out by using the TGA and DSC-50, Shimadzu, Japan. The temperature range is from the room temperature to 800°C (for TGA) or 650°C (for DSC) with a heating rate of 10°C/min. The thermal measurements were carried out under nitrogen atmosphere with flow rate of 30 mL/min. The weight of the samples varied from 5–10 mg.

RESULTS AND DISCUSSION

Figure 1 shows the TGA and DTG curves of PAA. It is apparent from this figure that this polymer losses weight in four decomposition steps. The first step occurs between 30 and 154°C with a maximum decomposition rate at 79°C and weight loss of 6.82 wt %. The second step starts at 225°C and ends at 377°C with a maximum decomposition rate at 323°C and weight loss of 11.16 wt %. Then the third step up to 456°C with a maximum decomposition at 409°C and weight loss of 17.53 wt %, and then followed by the last step up to 650°C with a maximum decomposition rate at 542.65°C and weight loss of 44.59 wt %.

Figure 2 shows the DSC curve of PAA. As can be seen from this curve, there are two endothermic peaks at 58 and 232°C, at which the sample consumes energy values of 80.96 and 394.25 J/g, respectively. In addition, the curve shows two exothermic peaks at 370 and 495°C with emitted heat values of 122.7 and 42.78 J/g, respectively.

In the DTG curve of this sample, the first peak at 79°C corresponds to the endothermic peak at 58°C in the DSC curve, and can be attributed to water loss. The second peak at 323°C corresponds to the endothermic peak at 232°C, and can be attributed to for-

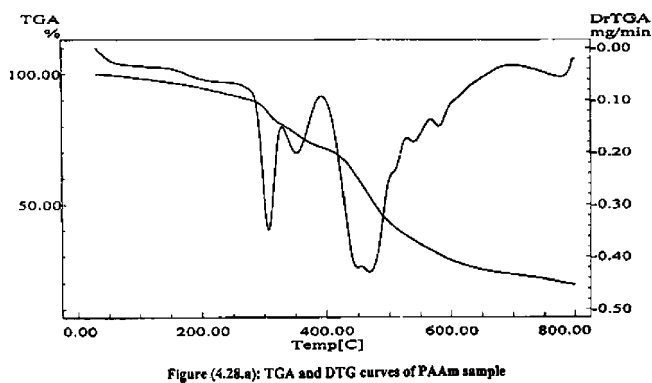


Figure 3 TGA and DTG curves of PAAm.

mation of PAA anhydride. The third peak at 409°C corresponds to the exothermic peak at 370°C and can be ascribed to the degradation of corresponding PAA anhydride. The fourth peak at 542°C corresponds to the exothermic peak at 495°C and can be due to the thermal degradation of PAA.

These results are in good agreement with the data reported in the literature,^{10,14} especially those obtained by Cardenas et al.¹⁰ for the low M_{wt} weight PAA sample. However, the slight shift in the peak positions in the DTG curve may be attributed to a change in the M_{wt} .

Figure 3 shows the TGA and DTG curves of PAAm. It is apparent from Figure 3 that there are four decomposition regions. The first region occurs between 64 and 253°C with a maximum decomposition rate at 142°C and weight loss of 7.79 wt %. The second region starts at 275°C and ends at 339°C with a maximum decomposition rate at 308°C and weight loss of 10.89 wt %. Then the third region up to 390°C with a maximum decomposition rate at 354°C and weight loss of 7.49 wt %, and then followed by the fourth region up to 644°C with a maximum decomposition rate at 456°C and weight loss of 46.43 wt %.

Examination of the DSC curve of PAAm revealed that, there are four endothermic peaks at 76, 214, 326, and 440°C with consumed energy values of 22.75, 32.99, 26.92, and 9.30 J/g, respectively.

These data reflects the high molecular weight of PAAm. Both the TGA and DSC curves of this sample are in consistence. The first peak at 142°C in the DTG curve corresponds to that one at 76°C in the DSC curve, and can be attributed to moisture loss and a minor dehydration. The second peak at 308°C in the DTG curve corresponds to that one at 214°C in the DSC curve and can be attributed to loss of water (by dehydration) and loss of ammonia (by imidization). The remaining thermal events at temperatures higher than 340°C are mainly attributed to the process accompanying the main chain scission.^{11,15}

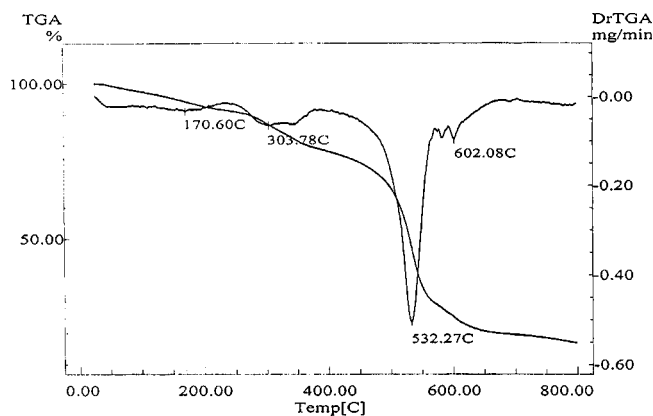


Figure 4 TGA and DTG curves of (1 : 1) PAA-PAAm complex.

An aqueous solution of each of the two polymers PAA and PAAm was prepared by dissolving 1 g/100 mL of distilled water. Then, a mixture from the two solutions was prepared with the ratio PAA : PAAm, 1 : 1. The pH value of the mixture was adjusted at 2.16 at which a precipitate was formed. The dried precipitate was ground to the suitable particle sizes.

The TGA and DTG curves of the resulted precipitate are given in Figure 4. The first decomposition region occurs between 38 and 230°C with a maximum decomposition rate at 170°C and weight loss of 8.44 wt %, followed by the second step up to 417°C with a maximum decomposition rate at 303°C and weight loss of 14.28 wt %. Then, the third region up to 664°C with a maximum decomposition rate at 532.27°C and weight loss of 56.59 wt %.

The DSC curve of this sample is shown in Figure 5. There is one endothermic peak at 232°C with consumed energy of 204.76 J/g. In addition there are two exothermic peaks at 371 and 493°C with values of emitted energies of 70.62 and 58.54 J/g, respectively.

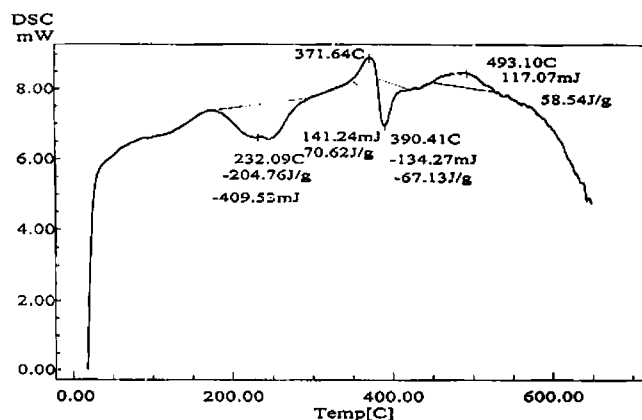


Figure 5 DSC of (1 : 1) PAA-PAAm complex.

Krusic et al.¹³ studied the thermal properties of a complex from poly(itaconic acid) (PIA) and PAAm. The TG curves showed that the thermal degradation of PAAm occurs via two-stage process. The first from 200 to 340°C corresponds to the loss of ammonia and water by imidization, respectively. The second step occurs at temperature higher than 340°C and was attributed to the process accompanying the main chain scission. The complex of PIA with PAAm has higher thermal stability than pure PIA and its degradation can be considered as a multi-stage process. After breakage of the most hydrogen bonds, the degradation of complex component starts. The first stage under 250°C corresponds to anhydride formation; the main chain scission process occurs from 400 to 450°C, while above 450°C, carbonization prevails.

The profiles of each of the TGA, DTG, and DSC curves of PAA-PAAm complex can not be considered as a simple summation of the two components decompositions, i.e., for the PAA-PAAm physical mixture. On the contrary, these profiles denote some form of interaction of the two components.

So one can come to the conclusion that a complex is formed from PAA and PAAm via the hydrogen bonding,³ with new thermal features. In the DTG curve of this complex, the first decomposition peak at 170°C corresponds to the endothermic peak at 232°C and may be attributed to water elimination and minor anhydride formation by the residual PAA and minor loss of ammonia. The second peak at 303°C corresponds to the exothermic peak at 371°C and can be attributed to the degradation of corresponding PAA anhydride. The third peak at 532°C corresponds to the exothermic peak at 493°C and can be attributed to the thermal degradation of the two polymer complex.

The decomposition profile of TGA and associated derivative curves DTG of chemically treated BP are shown in Figure 6. As can be seen in this figure, there are three decomposition regions. The first region

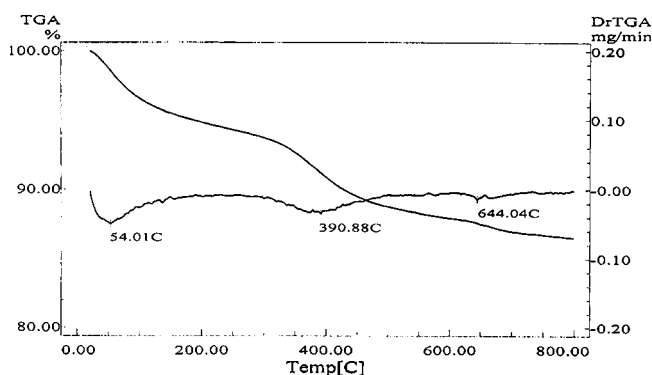


Figure 6 TGA and DTG curves of chemically treated BP.

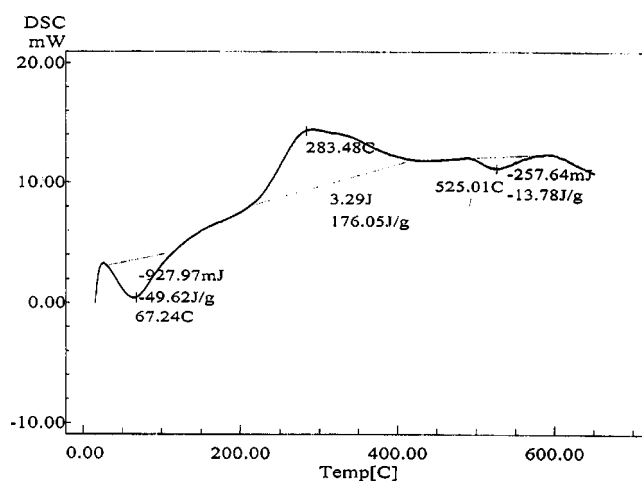


Figure 7 DSC curve of chemically treated BP.

occurs between 24 and 158°C with a maximum decomposition rate at 54°C and weight loss of 4.6 wt %, which is attributed to water decomposition. The second region start at 298°C and stops at 550°C with a maximum decomposition rate at 390°C and weight loss of 4.75 wt % and is assigned to combustion of the organic matter. Then third region up to 750°C with a maximum decomposition rate at 644°C and weight loss of 2.25 wt %.

The DSC curve for this sample is shown in Figure 7 and shows two endothermic peaks at 67.24 and 525°C with consumed energy values of 49.6 and 13.78 J/g, respectively. In addition, the curve shows an exothermic peak at 283°C with emitted energy value of 176 J/g. The absorbed water is being eliminated from the specimen causing the endothermic peak at 67°C, while the exothermic peak that appears at 283°C results from the combustion of the residual organic matter, while the endothermic peak at 525°C can be ascribed to decarbonation of the BP.

The aqueous solution of PAA (1% by weight) was mixed with the chemically treated BP by the concentration ratio 1 : 1.

The resulted precipitate, without any pH adjustment, from 1 : 1 mixture of PAA and BP was thermally investigated. Figure 8 shows the TGA and DTG curves of this sample. Three decomposition regions are appearing. The first region occurs between 28 and 167°C with a maximum decomposition rate at 93°C and weight loss of 8.9%. The second region begins at 324°C and ends at 569°C with a maximum decomposition rate at 470°C and weight loss of 19.59 wt %. Then, the third region up to 728°C with a maximum decomposition rate at 646°C and weight loss of 17.67 wt %.

Figure 9 shows the DSC profile for this sample. As is shown in this figure, the sample exhibits two endothermic peaks at 77.7 and 472°C with consumed energy values of 169.7 and 9.71 J/g, respectively. In

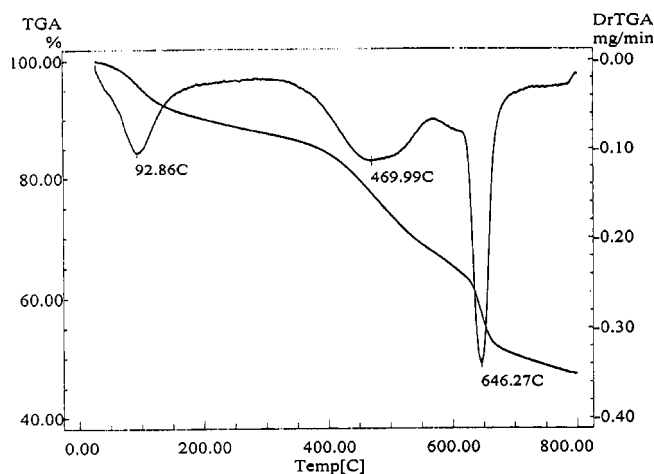


Figure 8 TGA and DTG curves of the precipitate formed from the mixture of (1 : 1) PAA and BP.

addition, two exothermic peaks appear at 477 and 586°C with emitted energy values of 9.07 and 18.61 J/g, respectively.

It is clear that the thermal decomposition profile of the complex of (PAA+BP) is quite different from those of the individual components, PAA or BP. The region at 92.8°C in the DTG curve corresponds to the endothermic peak at 77.7°C in the DSC curve and is attributed to moisture loss. The second peak at 470°C in the DTG curve corresponds to that one at 472°C in the DSC curve and may be attributed to formation of an unknown bond, which is suddenly cleaved causing the exothermic peak at 477°C in the DSC curve. The decomposition region at 646°C in the DTG curve corresponds to the exothermic peak at 586°C in the DSC curve and may be assigned to the cleavage of newly formed bonds between the carbonyl groups of the PAA and the Ca^{+2} or the amide groups of BP. Also, burning of the carbon skeleton of the complex may be indicated by this peak.

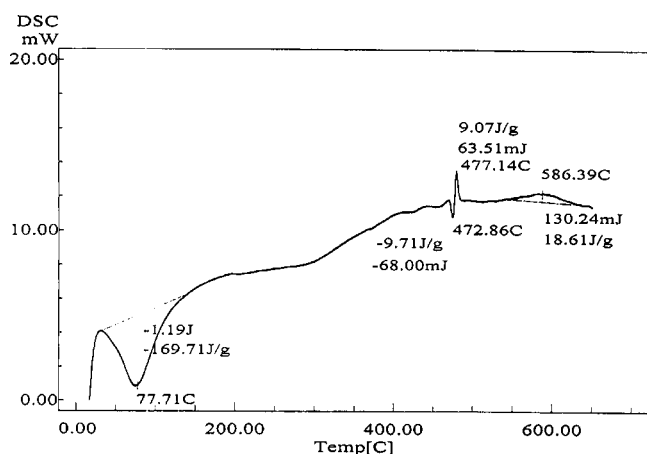


Figure 9 DSC curve of the precipitate formed from the mixture of (1 : 1) PAA and BP.

The present results suggest the occurrence of an appreciable reaction between PAA and BP in this complex. It is notable that both the DTG and DSC curves do not show the peaks of formation and degradation of PAA anhydride at about 270 and 370°C, providing a good evidence for complete consumption of PAA in the reaction between PAA and BP.

The chemically treated BPs were then heated at 700°C for 2 h to eliminate the residual organic part from them. The 1% wt solution of PAA was mixed with the thermally treated BPs with the same ratio mentioned above. Examination of the TGA and DTG Figure 10 of the sample resulted from the mixture of PAA and thermally treated bone powder revealed that there are four decomposition regions. The first region occurs between 40 and 240°C with a maximum decomposition rate at 102°C (elimination of water and weakly adsorbed PAA molecules) and weight loss of 4.54 wt %. The second region occurs between 255 and 430°C with a maximum decomposition rate at 374°C and weight loss of 4.50 wt %, followed by the third step from 499 to 583°C with a maximum decomposition rate at 548°C and weight loss of 6.26 wt %, and then followed by the fourth region up to 681°C with a maximum decomposition rate at 623°C and weight loss of 5.14 wt %. These results demonstrate that the carboxylic acid groups of PAA interact with the calcium ions of bone resulting in the formation of Ca-polycarboxylate. However this reaction seems to be of lower rate than that occurred in case of BP, this is indicated by the presence of the features of PAA in the thermal profile of this sample. The decomposition region at 374°C in the DTG curve can be attributed to the degradation of the corresponding PAA anhydride that may be formed with the residual acid, which is not involved in this reaction. In addition, the appearance of the peak at 548°C is ascribed to the carbonization of the residual PAA. The decomposition peak at 622.7°C

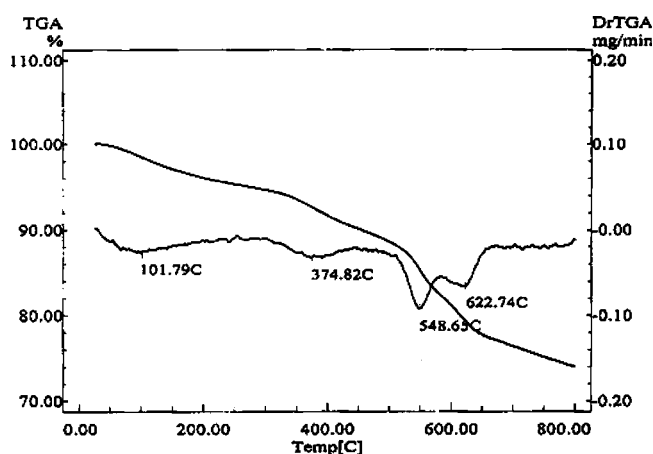


Figure 10 TGA and DTG curves of the compound resulted from the mixture 1 : 1 PAA and HBP.

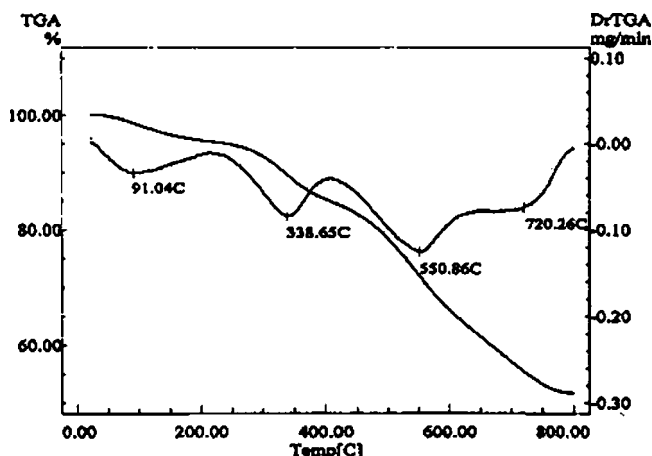


Figure 11 TGA and DTG curves of the resultant of the mixture of (1 : 1) PAA and BHA.

may be due to the pyrolysis cleavage of Ca-polycarboxylate bonds.

Figure 11 shows the TGA and DTG curves of the compound obtained from 1 : 1 wt% mixture of PAA and BHA. This figure shows four decomposition steps. The first step occurs between 23 and 219°C with a maximum decomposition rate at 91°C and weight loss of 4.8 wt %, followed by the second step up to 405°C with a maximum decomposition rate at 338°C and weight loss of 10.23 wt %, and then followed by the third step up to 629°C with maximum decomposition rate at 550.8°C and weight loss of 21.68 wt %. Then the fourth step up to 789°C with a maximum decomposition rate at 720 and weight loss of 11.11 wt %.

The DSC curve for this sample is shown in Figure 12. Three endothermic peaks are appearing at 65, 224, and 462°C with consumed energy values of 72.63 and 5.5 J/g, respectively. In addition, an exothermic peak appears at 379.39 with emitted energy value of 36.4 J/g.

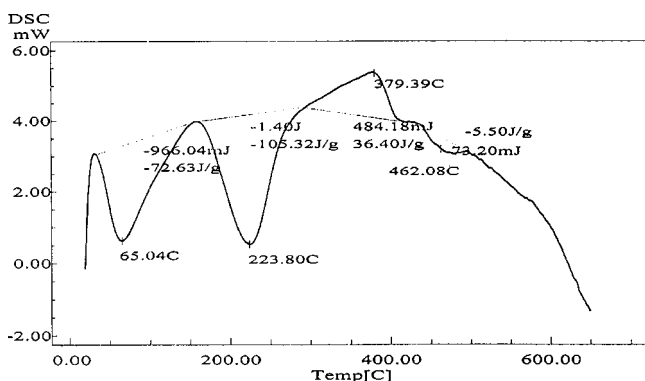


Figure 12 DSC curve of the resultant of the mixture of (1 : 1) PAA and BHA.

The decomposition peak at 91°C in the DTG curve corresponds to that one at 65°C in the DSC curve and is attributed to water loss. The peak at 338°C corresponds to the endothermic peak at 224°C and the exothermic peak at 379°C, and can be attributed to loss of bound water and minor PAA anhydride formation, and the degradation of the corresponding PAA anhydride, respectively, whereas the two decomposition regions at 550 and 720°C correspond to the endothermic peak at 462°C, and may be attributed to the thermal degradation of the non reacted BHA.

Both the DTG and DSC of this sample do not show the peaks that may result from the cleavage of polyacrylate bonds. This means that the reaction of polycarboxylate formation in case of BHA is much lower than that in case of HBP.

The compound resulted from the mixture of 70 wt % of (PAA-PAAm) and 30 wt % BP without any pH adjustment was thermally investigated. The general thermal decomposition features of this sample can be seen in Figure 13. The sample losses weight in four steps. The first step occurs between 25 and 172°C with a maximum decomposition rate at 86°C and weight loss of 6.5 wt %. The second region occurs between 276 and 403°C with a maximum decomposition rate at 382°C and weight loss of 3.3 wt %. Then the third region up to 543°C with a maximum decomposition rate at 460°C and weight loss of 11.55 wt % and then followed by the fourth region up to 787°C with a maximum decomposition rate at 611.5°C and weight loss of 17.95 wt %.

In the DSC curve of this sample there are three weak endotherms at 64, 286, and 459°C with consumed energy values of 48.50, 51.33, and 42.77 J/g, respectively. In addition, an exothermic peak can be seen at 335°C with emitted energy value of 35.12 J/g.

In view of the previously mentioned relevant literature,^{10,11,13,15} the first decomposition peak at 86°C

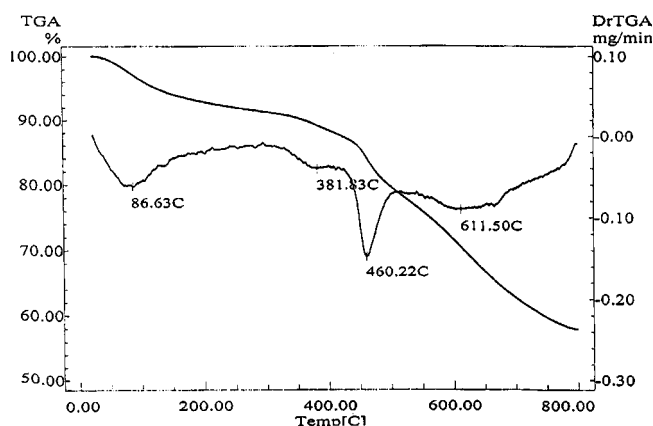


Figure 13 TGA and DTG curves of the resultant of the mixture of 70% (PAA-PAAm) and 30% BP without PH adjustment.

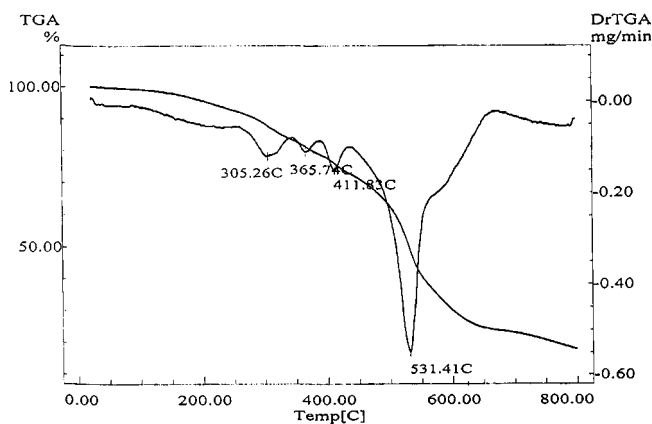


Figure 14 TGA and DTG curves of the complex formed from 70% (PAA-PAAm) and 30% BP at low pH.

in the DTG curve of this sample corresponds to that one at 64°C in the DSC curve, and can be attributed to moisture loss. The second peak at 382°C in the DTG curve corresponds to the endothermic peak at 268°C and the exothermic peak at 335°C, which can be attributed to loss of bound water (by hydration) and loss of ammonia (by imidization), and the cleavage of the formed bonds between PAA and the amide group of BP, respectively. The peak at 460°C in the DTG curve corresponds to the endothermic peak at 459°C and may be due to thermal degradation of the carbon skeleton. The weak broad peak at 611°C may be due to carbonization of BP.

The endothermic peak of imidization in the DTG of PAAm occurs at 214°C with consumed energy value of 32.99 J/g, while in case of PAA-BP-PAAm mixture, it is shifted to higher temperature (248°C) with a higher consumed energy value (51.30 J/g). This means that in case of PAA-BP-PAAm mixture, this peak may be caused by other amide structures rather than those of PAAm; which may be those resulting from the interaction between the PAA and the amide groups of BP.

The formed precipitate as a result of pH adjustment of a mixture of 70% (PAA-PAAm) and 30% BP was thermally investigated. The TGA and DTG curves, Figure 14 show five decomposition regions. The first decomposition region occurs between 83 and 253°C with a maximum decomposition rate at 200°C and weight loss of 7 wt %, followed by the second region up to 346°C with a maximum decomposition rate at 305°C and weight loss of 8.93 wt %, and then followed by the third decomposition region up to 289°C with a maximum decomposition rate at 365°C and weight loss of 3.98 wt %. The fourth region occurs between 392 and 435°C with a maximum decomposition rate at 417°C and weight loss of 5.5 wt %. Then, the final region up to 671°C with a maximum decomposition rate at 531°C and weight loss of 47.96 wt %.

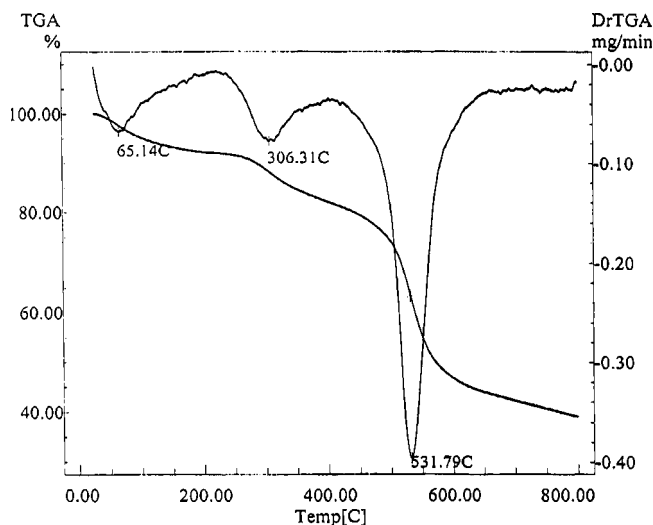


Figure 15 TGA and DTG curves of the complex formed from 30% (PAA-PAAm) and 70% BHA at low pH.

The DSC curve of this sample showed that there are four endotherms at 48, 170, 219, and 383°C with values of consumed energies of 8.67, 39.81, 30.23, and 48.49 J/g, respectively.

The DSC curve of this sample is quite different from that of the pure PAA-PAAm complex, whereas the DTG curve of it shows the thermal features of the PAA PAAm complex at 200, 305, and 531°C beside two new peaks at 365 and 417°C. These two peaks (365 and 417°C) may be due to the degradation of the enhanced amide structures that may be resulted from the reaction between the amide group of BP and the PAA.

The compound resulted from a mixture of 30% (PAA-PAAm) and 70% BHA without any pH adjustment was thermally investigated. The TGA and DTG curves of this sample showed that there are four decomposition regions at 90.52°C and weight loss of

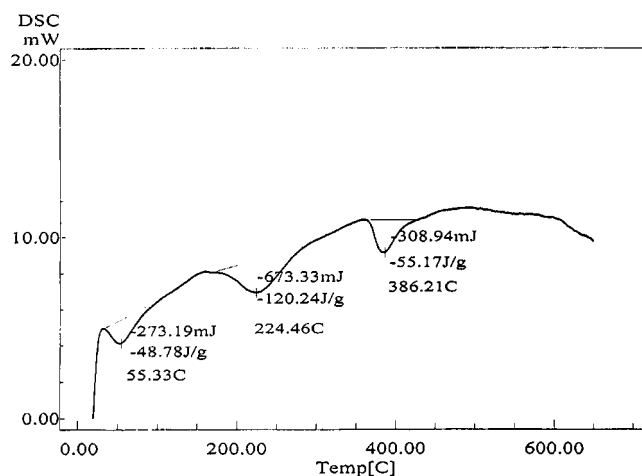


Figure 16 DSC curve of the complex formed from 30% (PAA-PAAm) and 70% BHA.

4 wt %, followed by the second step from 269 to 436°C with a maximum decomposition rate at 342°C and weight loss of 3.7 wt %. Then the third region up to 610°C with a maximum decomposition rate at 496.6°C and weight loss of 11.23 wt %, and then the fourth step up to 771°C with a maximum decomposition rate at 686°C and weight loss of 11.48 wt %.

The DSC curve of this sample displays four weak endotherms at 69, 258, 370, and 527°C with consumed energy values of 12.23, 96.67, 4.54, and 23.21 J/g, respectively.

The first decomposition peak at 90°C in the DTG curve of this sample corresponds to the endothermic peak at 69°C, and may be due to water loss. The second peak at 342°C corresponds to the endothermic peak at 258°C, and can be attributed to the water loss by dehydration and loss of ammonia by imidization. The third peak at 469°C corresponds to the endothermic peak at 370°C and can be attributed to the main chain scission of PAAM. The fourth peak at 686°C corresponds to the endothermic peak at 527°C and may be ascribed to the thermal degradation of BHA.

It may be concluded that the thermal profiles of the PAA-BHA-PAAM mixture reveal that the mixture has higher thermal stability than pure PAA or pure PAAM.

The formed precipitate as a result of pH adjustment of a mixture of 30% (PAA-PAAM) and 70% BHA was thermally investigated. The TGA and DTG curves of this sample are shown in Figure 15.

As is shown in these curves, this sample shows three decomposition regions. The first region occurs between 26 and 170°C with a maximum decomposition rate at 65°C and weight loss of 7.24 wt %. The second region starts at 225°C and ends at 395°C with a maximum decomposition rate at 306°C and weight loss of 9.69 wt %. Then, the third step up to 694°C with a maximum decomposition rate at 531°C and weight loss of 39.52 wt %.

Figure 16 shows the DSC curve of this sample. It can be seen that there are three endotherms at 55, 224, and 386°C with consumed energy values of 48.78, 120.24, and 55.17 J/g, respectively.

The first decomposition peak at 65°C in the DTG curve corresponds to the endothermic peak at 55°C and can be attributed to water loss. The peak at 306°C may be due to the formation of PAA anhydride whereas the decomposition peak at 531°C may be due to thermal degradation of the ternary complex.

CONCLUSIONS

The obtained data revealed that the characteristics of the thermal curves of the compound obtained from the interaction of PAA and PAAM are different from those of the constituent polymers. The profiles

of each of the TGA, DTG, and DSC curves of this compound can not be considered as simple summation of the two components decompositions, i.e., for the PAA-PAAM physical mixture. On the contrary, the profiles denote some form of interaction of the two polymers. Accordingly, the differences in the characteristics of the thermal curves were attributed to the formation of an interpolymer complex resulting from the interaction of PAA with PAAM at low pH via the hydrogen bonding. Careful examination of the TGA, DTG, and DSC curves of the samples under investigation demonstrated that the acid groups of PAA, (PAA-PAAM) mixture, and (PAA-PAAM) complex interact with the chemically treated BP via the Ca ions and the amide groups of the organic part in the bone matrix. These acid groups interact also with the thermally treated BPs and the bovine hydroxyl apatite via the Ca ions only. The rate of interaction of the acid groups with the Ca ions of BHA is always weaker than that in case of the thermally treated BPs.

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