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INTERMOLECULAR COMPLEXATION BETWEEN PEG/PBT BLOCK COPOLYMER AND POLYELECTROLYTES POLYACRYLIC ACID AND MALEIC ACID COPOLYMER

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Abstract—The intermolecular complexation (IPC) between PEG/PBT copolymer and polyelectrolytes such as polyacrylic acid (PAA) and ethylene-co-maleic acid (EMa) copolymer was studied by means of DSC, TGA and IR. The study results indicated that the PEG segment which had a molecular weight of 1000 D still had the ability to form IPC with PAA or EMa at lower pH due to the presence of a PBT segment. The presence of the PBT segment stabilized the IPC through hydrophobic or dipole interaction between PBT and PAA or EMa. At slightly basic pH, interaction between PEG and PAA or EMa was also observed, but the interaction was attributed to dipole interaction. These findings indicated that it is possible to modify the bulk properties of PEG-based block copolymers by forming an IPC with polyacid. © 1997 Elsevier Science Ltd

INTRODUCTION

The study of the interactions between macromolecules is important both for understanding the structures and functions of biological systems and for developing new materials. Due to the difficulties in studying the complexation formation of natural macromolecules, synthetic polymers are often used as model systems as well for the study.

In synthetic polymers, it is well known that polyethylene glycol (PEG) is capable of forming complexes with various compounds, with macromolecules such as polyacrylic acid and maleic acid copolymers as well as with low molecules such as urea [1, 2].

The formation of inter-polymer complexes (IPC) between PEG and polyacid is based on hydrogen bonding [1, 2]. A large number of investigations dealing with IPCs formed in aqueous solution and usually containing 1:1 ratios of interacting units have been reported [3–6]. It has been observed that for the formation of an IPC between PEG and PAA, the molecular weight of the PEG has to exceed a value of 6000 [7]. It was also reported that hydrophobic interactions between the two polymers play an important role in the stability of the complexes. Thus, complexes with poly(methacrylic acid) (PMAA) were formed with PEG of molecular weight exceeding 2000, as compared with 6000 for PAA [7]. Introducing hydrophobic groups in the PEG molecule has a similar effect: stable complexes of PAA or PMAA could be obtained with low molecular weight PEG if they were substituted by hydrophobic groups [6, 8–11].

For the formation of IPC with PEG, one interesting question is whether it is possible to decrease the PEG molecular weight further by increasing the chain length of the hydrophobic group? If it is possible, then it will offer a possibility to modify the properties of many PEG block copolymers simply by forming IPC with polyacrylic acid, since it was shown that the bulk physical properties of PEG itself can be significantly improved by forming IPC with polyacrylic acid [12]. To answer the question, a PEG/PBT block copolymer was chosen both for its structural suitability (Fig. 1) and its possible applications.

This poly(ether ester) block copolymer is a representative of thermoplastic elastomers (polyurethanes, polystyrene-block-polybutadienes and other block copolymers). It combines the good physical characteristics of chemically cured elastomers with the easy processing ability of thermoplastics. The first commercialized PEG/PBT block copolymer elastomer was introduced by DuPont under the trade name of Hytrel™. Other similar products are Arnitel™ from Akzo Plastics and Pelprene™ from Toyobo. Recently, it was introduced as a bone replacement material (trade name Polyactive™) because of the bone bonding ability it has [13, 14]. In an effort to make a new bone bonding composite from Polyactive™ and hydroxyapatite (HA), we found that by surface treatment of HA with polyacrylic acid or ethylene maleic acid copolymer (EMa), the interface between the HA and polymer Polyactive™ matrix was significantly improved [15, 16]. Therefore, we speculate that such improvement is due to the inter-polymer complexes formation between the HA surface adsorbed PAA or EMa with PEG segments of Polyactive™. Since the molecular weight of PEG segment within Polyactive™ is only 1000, it was unknown whether such an IPC can be

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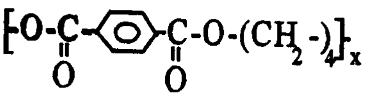
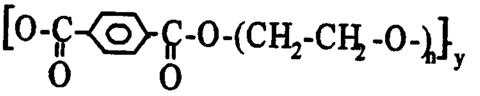


Hard segment (PBT)



Soft segment

Fig. 1. The hard segment and soft segment of PEG/PBT block copolymer used in this study. $n = 22–23$ ($M_w = 1000$). $x > 3$.

formed and what kind of interaction exists between them. Therefore, in this paper we studied the inter-polymer complexation formation ability of PAA or EMa with PEG segments of Polyactive™.

EXPERIMENTAL

Materials

Polyactive™ 70/30 (the figures indicate the weight ratio of PEG/PBT) was obtained from HC Implant bv, The Netherlands. PEG segment has a molecular weight of 1000, and the molecular weight of Polyactive™ is about 100,000. Polyacrylic acid ($M_w = 5000$) 50% water solution and poly(ethylene-co-maleic anhydride) were purchased from Aldrich. Poly(ethylene-co-maleic acid) was obtained by dissolving poly(ethylene-co-maleic anhydride) in water (Fig. 2). Both PAA and EMa were used in 2.5% (w/w) water solution. The pH of PAA and EMa solution were adjusted by using either hydrochloride acid (1 M) or sodium hydroxide (5% w/w).

Preparation of samples

10% Polyactive™ 70/30 chloroform solution was used to make solvent casting film. After fully evaporating chloroform in vacuum at room temperature, the film (0.1 mm in thickness) was put into either PAA solution or EMa solution. The pH of the solution used in the experiment was 3.6, 6.9 and 7.4. After 1 hr swelling in PAA or EMa solution, the films were taken out and briefly rinsed with distilled water and then dried in a vacuum oven. Dried films were used for DSC, TGA and IR spectrophotometer measurement. A Polyactive™ sample which was swelled in distilled water and subsequently dried was used as a control in all the experiments.

Instrumentation

DSC measurements were carried out in a Du Pont 910 series. About 10–15 mg sample was put into a sample pan and put into the sample chamber. After the sample was cooled down from room temperature to −90°C by using liquid nitrogen, DSC curves were recorded from −80 to 350°C at a temperature increase rate of 10°C/min.

TGA was used to study the decomposition behaviour of the polymers. It was performed from room temperature to 350°C at a rate of 10°C/min, 10–15 mg samples were used in each measurement.

A Perkin Elmer 783 IR spectrophotometer was used. Transmission was recorded from 4000 to 200 wavenumber.

RESULTS AND DISCUSSION

DSC analysis

Figure 3(a) gives a typical DSC curve of PEG/PBT block copolymer. Two glass transition temperatures and two melting peaks can be seen from the curve. A glass transition temperature of PEG segments can be observed at −50°C, followed immediately by a crystallization peak and a melting peak of PEG from −20 to 30°C. Another glass transition temperature at 56°C may be ascribed to the amorphous PBT phase in the polymer [17, 18]. A crystallization peak of PBT was observed after T_g^{PBT}, followed by the melting peak of PBT, observed around 155°C. The shape of this broad endotherm is due to the crystallites, which are different in dimensions and regularity depending on hard-segment length [17]. From the DSC curve it is known that at room temperature the polymer consists of two amorphous phases, i.e. one PEG and one PBT phase, and one crystalline phase of PBT. As for the length of PBT segments, x should be larger than 3, because only when the length of PBT exceeds a certain value can PBT form crystals [16].

After the films were immersed in PAA solution and subsequently dried, it could be seen from the DSC curve that the glass transition temperature of the PEG segments was still about −50°C (Fig. 3 and Table 1). The melting of crystalline PEG also took place in the range of −20–30°C. Prominent changes were observed in the melting enthalpy of PEG crystals (Table 1) and in T_g^{PBT}, which was shifted to 61–63°C in all PAA treated samples despite the treatment at different pH. The changes in T_g^{PBT} indicate certain kinds of interaction took place between PAA and PBT segments. The change in the

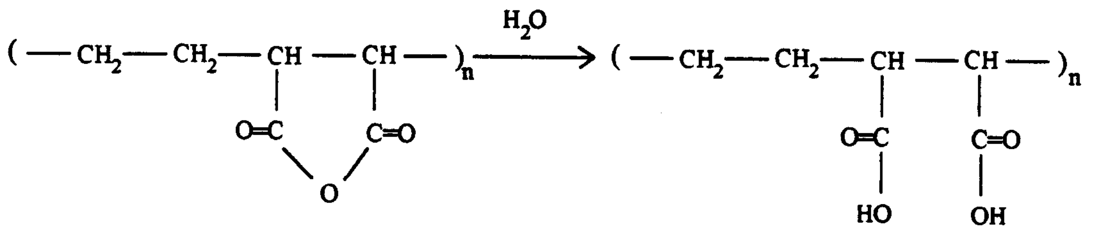


Fig. 2. Preparation of EMa.

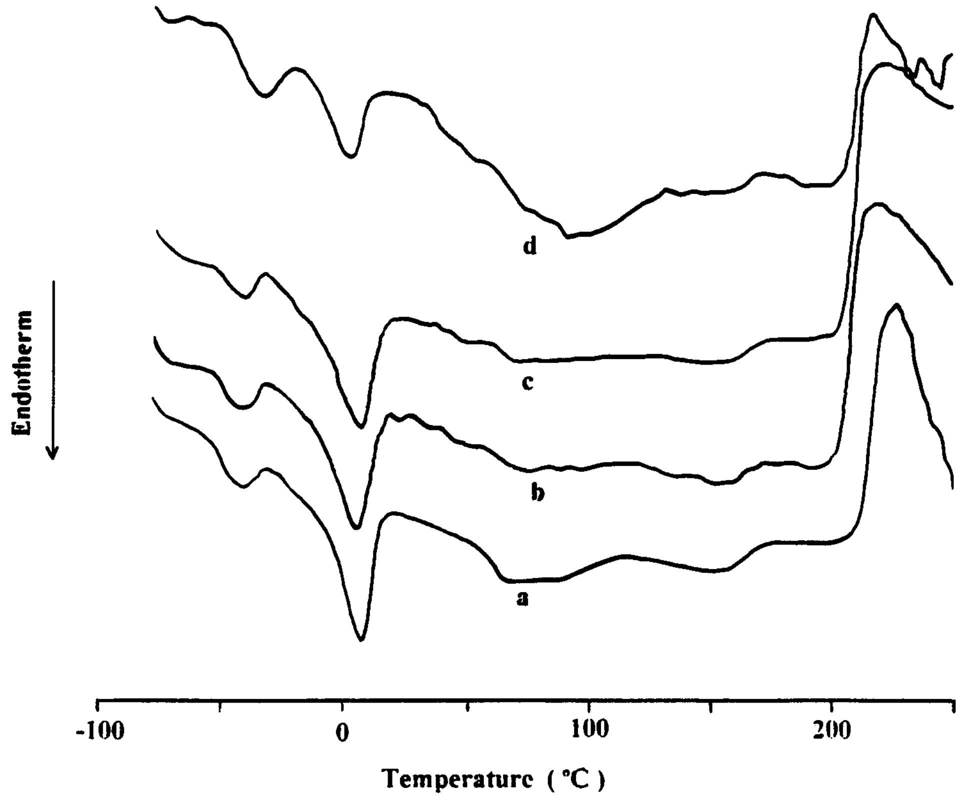


Fig. 3. DSC curves of PAA treated samples at different pH. (a) Control sample; treated at (b) pH 7.4 (c) pH 6.9 and (d) pH 3.6.

shape of the crystallization peak of PBT after the treatment indicates that the mobility of PBT segments was hindered by the presence of PAA due to the interaction, therefore that the melting peak of PBT was diminished in PAA treated samples. Another prominent change was that a broad endothermal peak from 40 to 140°C only appeared in PAA treated samples at pH 3.6.

The decrease in the crystallinity of PEG (Table 1) indicated that the mobility of some PEG segments was inhibited by the presence of PAA. It can also be seen that the decrease of the crytallinity of PEG strongly depends on the pH value at which the samples were treated. At lower pH, i.e. at pH 3.6, ΔH_{m}^{PEG} of PEG was 5.48 J/g, while at pH 6.9, a higher crystallinity of PEG was observed ($\Delta H_{m}^{PEG} = 19.13$ J/g). However, when the pH was further increased to 7.4, the crystallinity was slightly decreased again ($\Delta H_{m}^{PEG} = 17.23$ J/g). These results strongly suggest that the interaction of PAA with PEG depends on the pH. The strongest interaction observed at lower pH (pH 3.6) is probably due to the hydrogen bond formation, since the hydrogen bond IPC can only be formed at a pH lower than 4 [1, 2].

Table 1. T_g and melting enthalpy ΔH^{PEG} of PAA treated samples at different pH

pH	T_g^{PEG} (°C)	ΔH^{PEG} (J/g)	T_g^{PBT} (°C)
3.6	−50	5.48	61
6.9	−50	19.13	63
7.4	−50	17.23	62
Control	−50	21.48	56

The observed broad endotherm peak from 40 to 140°C in samples treated at pH 3.6 is probably due to the disassociation of PAA with PEG, since such hydrogen bond complexes tend to dissociate at elevated temperature [19]. Therefore, it can be concluded that there are interactions between PAA and PEG segments, and that the interaction strongly depends on the pH. The strongest interaction observed at pH 3.6 is most likely due to the hydrogen bond complexes formation between PAA and PEG segments. At elevated pH, hydrogen bond complexes can be easily broken up due to the ionization of PAA. It has been shown that only a small percentage ($< 10\%$) of ionization of the carboxylic groups of PAA was sufficient to break up the complex [20]. However, the interaction between PAA and PEG still exists, but to a lesser extent. Such interaction might be ascribed to dipole or hydrophobic interaction between the PAA and PEG segments [2]. However, the observed T_g^{PEG} for all the PAA treated samples indicates that not all the PEG segments were involved in the interaction with PAA, perhaps this is due to the slow diffusion rate of PAA through the already formed PAA–PEG complexes at the outer surface of the sample.

The observed PBT melting peak in all PAA treated samples indicated that the crystallinity of PBT was not affected by the treatment of PAA. That the

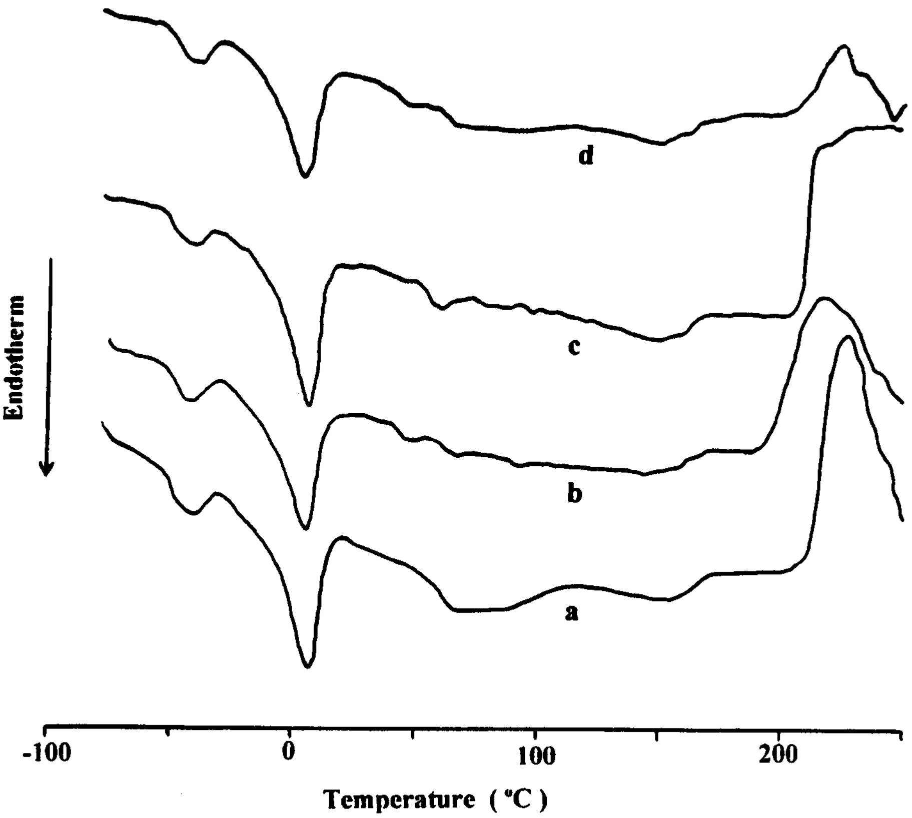


Fig. 4. DSC curves of EMa treated samples at different pH. (a) Control sample; treated at (b) pH 7.4 (c) pH 6.9 and (d) pH 3.6.

observed T_g^{PBT} was shifted to a higher temperature indicated that interactions also exist between PBT segments and PAA. Since the shifting of T_g^{PBT} was independent of pH, the interaction between PAA and PBT is likely to be hydrophobic.

For EMa treated samples, the same T_g^{PEG} and PEG crystallization peak appeared at about −50°C, and −30 to −20°C, respectively. The crystallinity of the PEG in EMa treated samples was also decreased by the treatment both at pH 3.6 and 7.4, but to a lesser extent as compared to PAA treated samples. There were almost no changes in the PEG crystallinity in the sample treated at pH 6.9. The dependence of the crystallinity of PEG on the pH of the treatment also suggested hydrogen bond complex formation between EMa and PEG segments at lower pH.

In EMa treated samples, a slight increase in T_g^{PBT} was observed both at pH 3.6 and 7.4 (Table 2 and Fig. 4), while at pH 6.9, due to the existence of a small endothermal peak, T_g^{PBT} was hardly detectable. The diminishing of the crystallization peak of PBT in EMa treated samples means that the mobility of the PBT segment was affected by the treatment. However, the interaction between EMa and PBT also depends on the pH. Increase of the pH gradually decreases both the crystallization peak and the melting peak of PBT until it is totally diminished at pH 7.4. This result suggests a different interaction mechanism between EMa and PBT segments other than a hydrophobic interaction. A dipole interaction between EMa and PBT segments probably took place in the process.

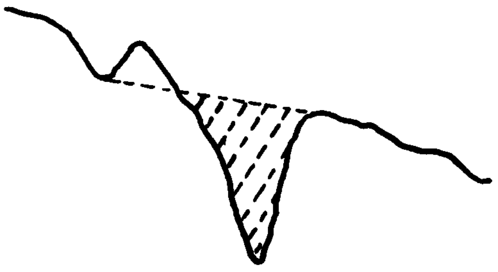


Fig. 5. An illustration of the area (shadowed) used in calculation of the melting enthalpy of PEG crystalline.

Table 2. Transition temperatures of EMa treated samples at different pH

pH	T_g^{PEG} (°C)	ΔH_m^{PEG} (J/g)*	T_g^{PBT} (°C)
3.6	−51	14.72	59
6.9	−50	21.13	?
7.4	−50	17.76	58
Control	−50	21.48	56

*See Fig. 5.

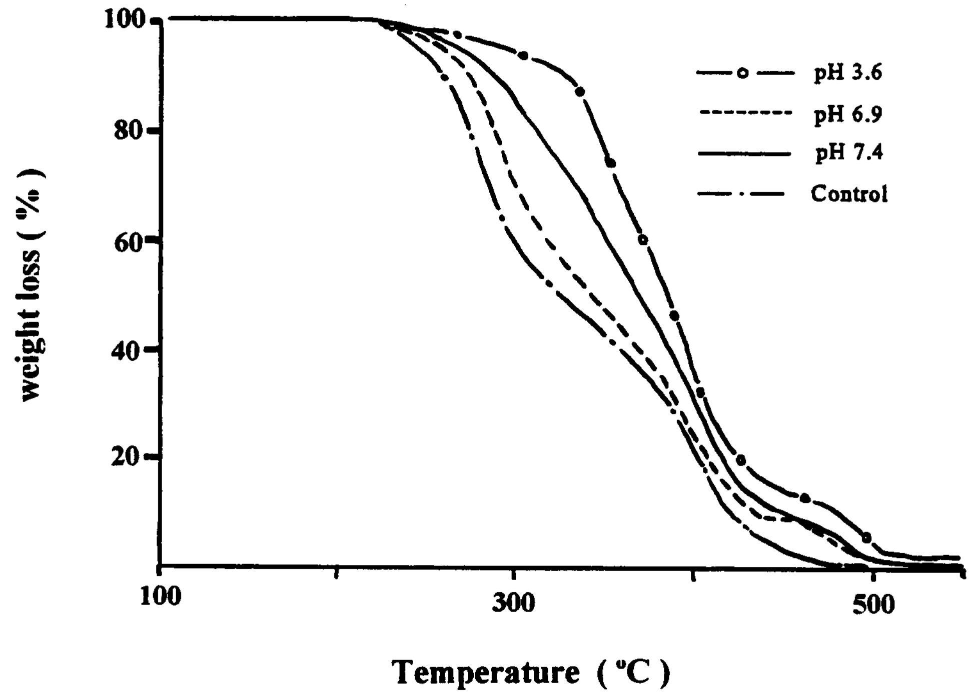


Fig. 6. TGA curves of PAA treated samples at different pH.

TGA analysis

The TGA analysis curves (Figs 6 and 7) clearly show the effect of treatment at different pH. Figure 6 gives the values of the changes in decomposition temperature relative to that of Polyactive™ 70/30. It can be seen that at pH 3.6, PAA treated film has the highest decomposition temperature of 320°C. At slightly basic pH, i.e. pH 7.4, EMa treated samples also have a relatively higher decomposition temperature of 260°C, while at near neutral pH, the changes in decomposition temperature were very small (Fig. 8). These data suggest that at both acidic and slightly

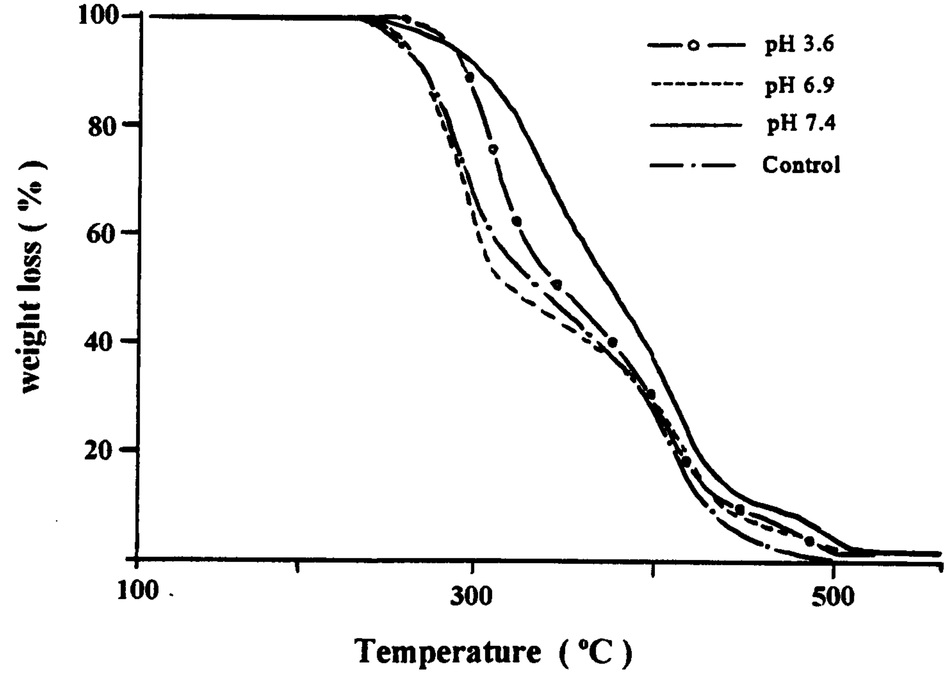


Fig. 7. TGA curves of EMa treated samples at different pH.

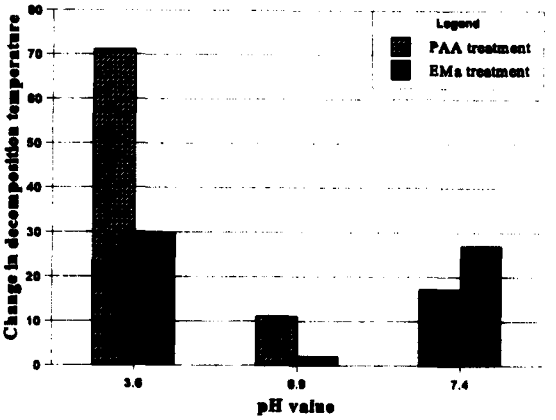


Fig. 8. The changes in the decomposition temperature of Polyactive™ when treated at different pH. The decomposition temperature of untreated Polyactive™ is 249°C.

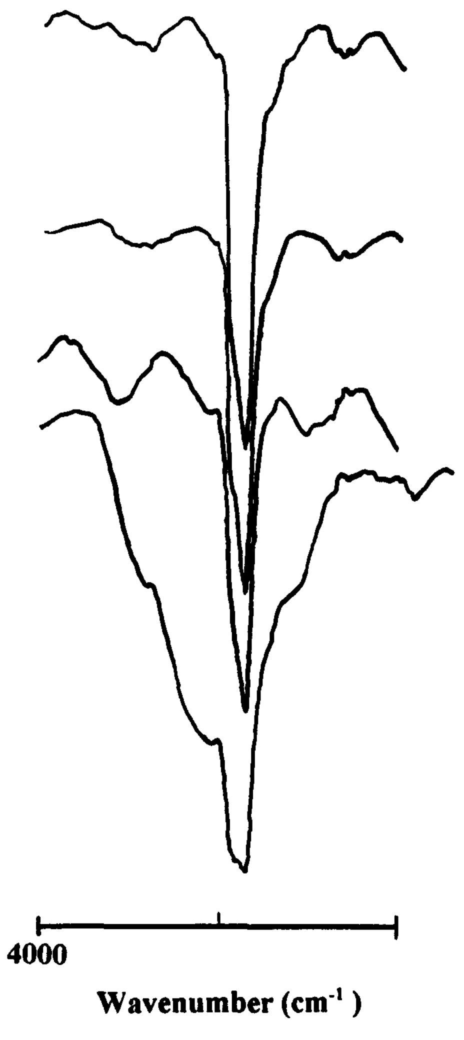


Fig. 9. IR spectra of PAA treated samples at different pH. (a) Treated at pH 3.6; (b) treated at pH 6.9; (c) treated at pH 7.4; (d) control sample. Note a broad peak in curve (a), which indicates the existence of hydrogen bonding in the sample.

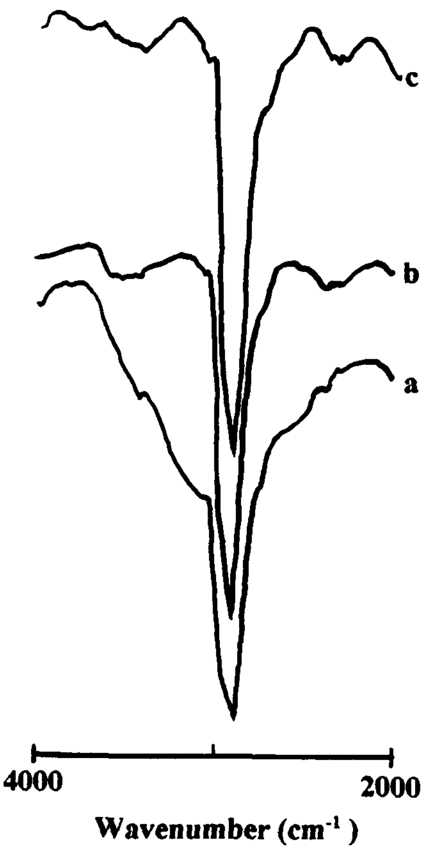


Fig. 10. IR spectra of EMa treated samples at different pH. (a) Treated at pH 3.6; (b) treated at pH 7.4; (c) control sample. Note there is also a broad peak in spectra (a), which indicates hydrogen bonding in the sample treated at pH 3.6.

basic pH, there are stronger interactions between Polyactive™ and PAA or EMa. At nearly neutral pH, there is only little interaction between the polymer and PAA or EMa. These TGA data suggested the same interaction pattern as that suggested by DSC data.

IR spectra study

The IR spectra (Figs 9 and 10) indicated a strong and broad absorption band from 3750 to 2200 cm^{-1} from the samples treated at acidic pH 3.6. Such a broad peak was due to the overlap of bands from hydrogen bonding and CH_2 vibration. The existence of hydrogen bond can be attributed to the hydrogen bond between PAA (or EMa) and PEG segment of Polyactive™ 70/30. No such band could be observed in the other samples treated at near neutral or slightly basic pH.

The above results clearly show that IPC can be formed between Polyactive™ 70/30 and PAA (or EMa) at lower pH. Table 3 summarizes the type of interactions between Polyactive™ and polyacid.

CONCLUSION

Combining the DSC, TGA and IR results, we conclude that at pH 3.6, the PAA can form hydrogen

Table 3. The type and intensity of the interactions between Polyactive™ and polyacid

	pH 3.6		pH 6.9		pH 7.4	
	PAA	EMa	PAA	EMa	PAA	EMa
PEG segments	H-bonding	H-bonding	weak dipole	weak dipole	dipole	dipole
PBT segments	hydrophobic	hydrophobic	hydrophobic	hydrophobic +dipole (?)	hydrophobic	hydrophobic +dipole (?)
Polyactive	+ + + +	+ + +	+/−	+/−	+	+ +

+ + + + = very strong; + + + = stronger; + + = strong; + = medium; +/− = weak.

bond complexes with PEG 1000 segments in a PEG/PBT block copolymer due to the stabilization effect of hydrophobic interaction between PAA and PBT segments. A dipole interaction between PAA and PEG segments was also observed at elevated pH. EMa copolymer can also form IPC through hydrogen bonding with PEG segments in PEG/PBT block copolymer, but the interaction between EMa and PBT might be attributed to dipole interaction rather than hydrophobic interaction. A further study is needed to elucidate the interaction mechanism.

The experimental results also showed the possibility of modifying the properties of such block copolymers by forming an IPC.

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