

Temperature Dependence of Hydrogen Bond in Fe-OCAP/Polyurethane Blends

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ABSTRACT: Fourier transform infrared (FTIR) thermal analysis was utilized to study the temperature dependence of hydrogen bond in Fe-octacarboxyl acid phthalocyanine (Fe-OCAP)/polyurethane (PU) blends. Two regions in the FTIR spectra were concerned to investigate the difference of the degree of hydrogen bond in the samples: the —NH stretching region ($3210\text{--}3460\text{ cm}^{-1}$) and carbonyl stretching region ($1680\text{--}1760\text{ cm}^{-1}$). It was found that the average strength of hydrogen bond in the modified samples was stronger than that in pure PU. With increasing Fe-OCAP content, the hydrogen bonded —NH and carbonyl groups were increased, while with increasing temperature they decreased. The equilibrium between free and hydrogen bonded carbonyl groups was discussed. The dissociation enthalpy for hydrogen bonded carbonyl of the samples was increased with increasing Fe-OCAP content. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2265–2271, 2013

KEYWORDS: blends; films; polyurethanes

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INTRODUCTION

Polyurethane (PU) has a wide range of applications as coatings, adhesives, fibers, foams, thermoplastic elastomers, etc.^{1–6} The modification of PU for improved physical and chemical properties is of great interest among researchers.^{7–15} Cai et al.¹¹ prepared PU/grapheme oxide (GO) blends. The incorporation of GO significantly improved PU's mechanical and thermal properties. Gao et al.¹² prepared PU/ CaCO_3 blends and found that the thermal stability of PU was improved with the addition of CaCO_3 .

In our previous work,¹⁶ Fe-octacarboxyl acid phthalocyanine (Fe-OCAP)/PU blends were prepared by solution blending. Improved mechanical, dynamic mechanical, and thermal deformation properties of the samples were obtained with increasing Fe-OCAP content. The improvement of the properties was attributed to the strong interaction formed between Fe-OCAP and PU matrix. It is well-known that PU is extensively hydrogen bonded. Hydrogen bond in polyurethane can be characterized as a hard–hard segment hydrogen bond (NH— —O=C bond) and a hard–soft segment hydrogen bond (NH— —O— bond). The proton donor is —NH group of urethane, while the acceptor group is carbonyl and ester carbonyl or ether oxygen

atom of urethane. Hydrogen bond in PU can significantly influence PU's properties.

In order to give a detailed description to the interaction between Fe-OCAP and PU, the temperature dependence of hydrogen bond for Fe-OCAP/PU blends should be investigated. Since Fourier transform infrared (FTIR) is very sensitive to hydrogen bond,^{17,18} this technique has been applied to the characterization of hydrogen bond in PU in a wide range of studies.^{17,19–29} Chen et al.²⁷ prepared a pyridine containing PU. With the analysis of the temperature dependent FTIR spectra, they found that strong hydrogen bond was formed in the urethane group and in the pyridine ring. The hydrogen bond in the pyridine ring served as the molecular switch, while the hydrogen bond in the urethane groups served as physical cross-links. Mishra et al.²⁸ studied the effect of chain extender and NCO/OH ratio on the properties of hyperbranched polyurethane (HBPU)-urea and HBPU-imide coatings. The structure properties of the samples were investigated by FTIR. Results suggested that hydrogen bond in the samples increased with increasing NCO/OH ratio. Zhang et al.²⁹ prepared polyester-based aliphatic PU elastomers containing hyperbranched polyester segments (HB). The degree of hydrogen bond of the samples was studied by FTIR. The result showed that PU elastomers

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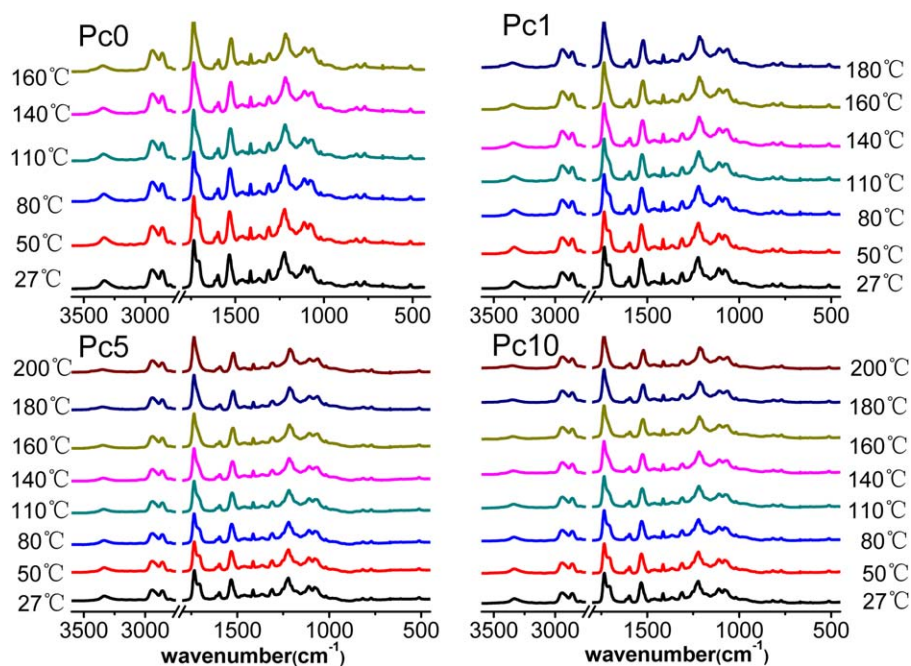


Figure 1. FTIR spectra of the samples as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing small amount of HB exhibited increased degree of hydrogen bond.

In this article, the temperature dependence of hydrogen bond for Fe-OCAP/PU blends was investigated by FTIR. The —NH and carbonyl stretching region in the FTIR spectra were concerned. With the method of curve fitting procedure, the difference of the degree of hydrogen bonded —NH and carbonyl groups with increasing Fe-OCAP content was investigated. The equilibrium between free and hydrogen bonded carbonyl groups, the dissociation enthalpy and entropy of hydrogen bonded carbonyl groups were also discussed.

EXPERIMENTAL

Materials

Pyromellitic dianhydride, urea, FeCl_3 , and ammonium molybdate tetrahydrate were purchased from Sinopharm Chemical Reagent Co. Dimethylacetamide (DMAc) was purchased from Shanghai Jingwei Chemical Co.. All the chemicals were of analytical grade and used without further purifying. PU sample (TPU 1180A) was obtained from BASF. The hard segment is composed of 4,4'-diphenylmethane diisocyanate (MDI) chain extended with butanediol and the soft segment is composed of poly(tetramethylene ether) glycols (PTMEG).

Sample Preparation

Fe-OCAP, synthesized in the same way as that used in our previous work,³⁰ was dissolved in DMAc first, and then added into PU/DMAc solution at 75°C stirring for 6 h. The mixture was then casted on glass plates, and placed in vacuum at 50°C for 3 days to remove the residual solvent. In this manner, four samples with Fe-OCAP content of 0, 1, 5, and 10 wt % were prepared, which were named Pc0, Pc1, Pc5, and Pc10, respectively.

Fe-OCAP: IR (KBr) ν/cm^{-1} 3440 (OH), 1703 (O=C), 1627, 1508, 1400, 1313, 1258, 1064, 728 (Supporting Information Figure S1).

Characterization

Infrared test was performed on a Nicolet 8700 infrared spectrophotometer and the spectra were recorded by averaging 64 scans at a resolution of 1 cm^{-1} . The films for infrared analysis were sufficient thin to be within the absorbance range where the Beer–Lambert law was obeyed. For the temperature scans, the samples were placed in a heating cell which connected to a temperature controller. The temperature range was from 27 to 200°C with the control accuracy of $\pm 0.1^\circ\text{C}$. The temperature of the sample was held constant for about 10 min before FTIR scan. Curve fitting procedure was carried out by using the software “OMNIC,” which is developed by Nicolet company to analyze IR spectra.

RESULTS AND DISCUSSION

Infrared Spectra

Figure 1 shows the FTIR spectra of PU/Fe-OCAP blends as a function of temperature. Pc0 and Pc1 shrunk at the temperature of 180 and 200°C, respectively, and the related FTIR spectra could not be obtained. Pc5 and Pc10 showed good thermal stability at the temperature of 200°C. It indicates that the thermal stability of the samples is improved with the introduction of Fe-OCAP. The similar conclusion was obtained in our previous study.¹⁶ Two regions in the FTIR spectra can be related to hydrogen bond in PU: the —NH stretching region ($3210\text{--}3460 \text{ cm}^{-1}$) and carbonyl stretching region ($1680\text{--}1760 \text{ cm}^{-1}$). The —NH stretching region is composed of separate absorptions attributed to free (peaks centered near 3443 cm^{-1}) and hydrogen bonded —NH groups (peaks centered near 3335 cm^{-1}),^{17,19}

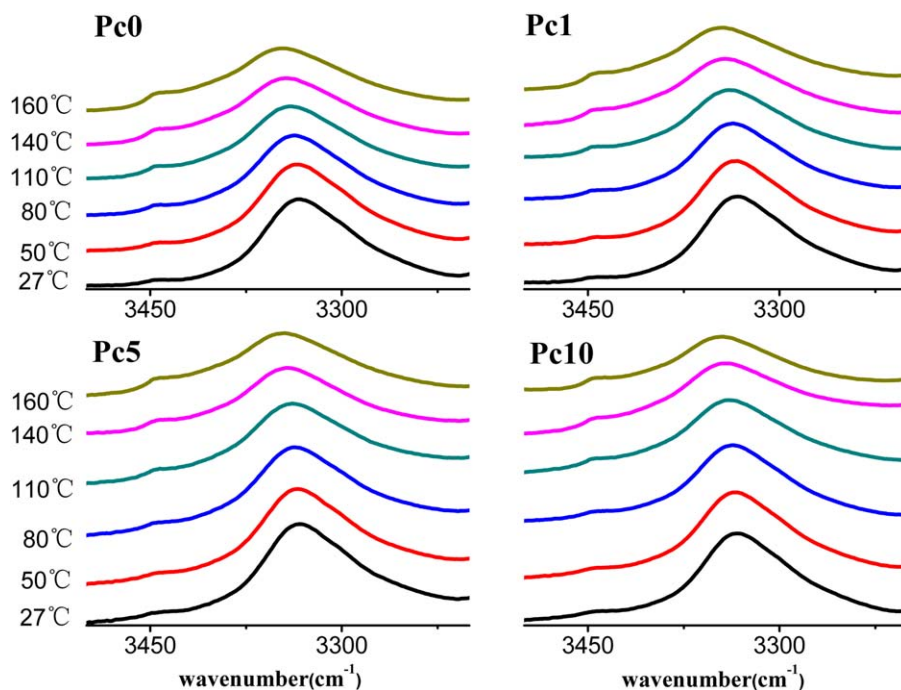


Figure 2. FTIR spectra of -NH stretching region of the samples as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

while the carbonyl stretching region is composed of free (peak centered near 1735 cm^{-1}) and hydrogen bonded carbonyl groups (peak centered near 1706 cm^{-1}).^{20,21} From Figure 1, the intensity of peaks at 3335 and 1706 cm^{-1} decreases with increasing temperature, while the intensity of peaks at 3443 and 1735 cm^{-1} increases. The extent and strength of hydrogen bond in the samples were studied through the infrared absorptions of the two spectral regions as a function of temperature.

-NH Stretching Region

Figure 2 shows the FTIR spectra of -NH stretching region of the samples at different temperature. With increasing

temperature, the intensity of free -NH groups increases and the intensity of hydrogen bonded -NH groups decreases. At the same time, the absorbance peaks of hydrogen bonded -NH groups in Pc0, Pc1, Pc5, Pc10 shift from 3333 to 3349 cm^{-1} , 3333 to 3347 cm^{-1} , 3333 to 3345 cm^{-1} , and 3333 to 3344 cm^{-1} , respectively. The shift of absorbance peak to lower values at high temperature indicates that the average strength of hydrogen bond in modified samples is stronger than that in pure PU. It implies that strong hydrogen bond is formed between Fe-OCAP and PU matrix.

According to Coleman,^{24,31} the -NH stretching band can be curve fitted by two Gaussian bands, corresponding to free and hydrogen bonded -NH band near 3443 and 3335 cm^{-1} , respectively. Representative spectrum of Pc0 recorded at 50°C in the -NH stretching region is shown in Figure 3. Y_b is defined as the fraction of hydrogen bonded -NH and can be expressed by the following equation²³:

$$Y_b = \frac{1}{1 + rC_f/C_b} \quad (1)$$

where r is the absorption coefficient and equals 3.5, C_f and C_b is the area of free and hydrogen bonded -NH band, respectively.

Figure 4 shows the plot of the fraction of hydrogen bonded -NH (Y_b) of the samples as a function of temperature. In Figure 4, the fraction of hydrogen bonded -NH decreases with increasing temperature, and increases with increasing Fe-OCAP content. The result supports that hydrogen bond is formed between Fe-OCAP and PU matrix.

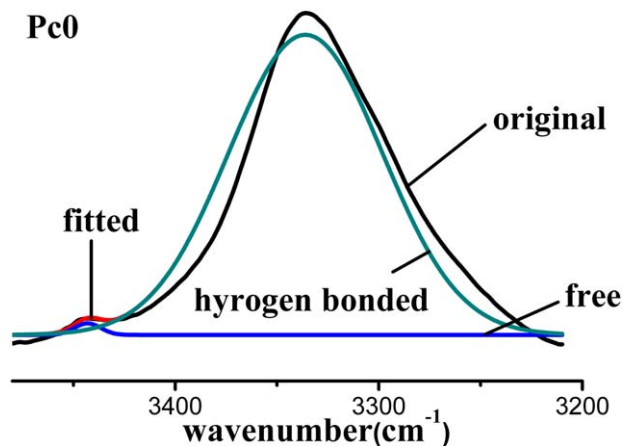


Figure 3. Curve fitting results in the -NH stretching region of Pc0 at 50°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

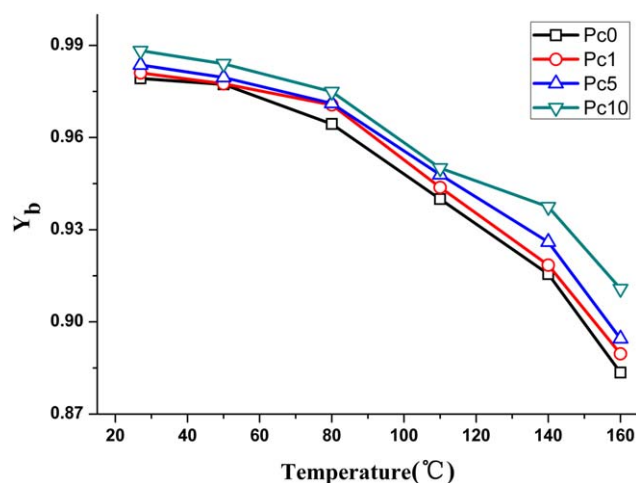


Figure 4. The fraction of hydrogen bonded $-NH$ of the samples as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Carbonyl Stretching Region

Figure 5 shows the FTIR spectra of the carbonyl stretching region of the samples at different temperature. With increasing temperature, the intensity of hydrogen bonded carbonyl (centered near 1706 cm^{-1}) decreases, while the intensity of free carbonyl (centered near 1735 cm^{-1}) increases. Previous papers^{7,29} have pointed out that hydrogen bonded carbonyl could be divided into disordered and ordered hydrogen bonded carbonyl band. Thus, With the curve fitting procedure, the carbonyl

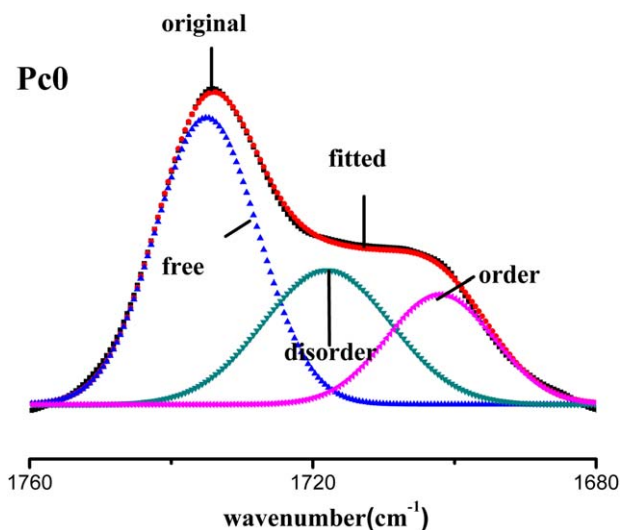


Figure 6. Curve fitting results in the carbonyl stretching region of Pc0 at 50°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stretching region of the spectra of the samples can be curve fitted by three Gaussian bands, corresponding to free, disordered, and ordered hydrogen bonded carbonyl band near 1735 , 1718 , and 1702 cm^{-1} , respectively.

Representative spectrum in the carbonyl stretching region of Pc0 recorded at 50°C is shown in Figure 6. The absorption coefficients for free, disordered, and ordered hydrogen bonded

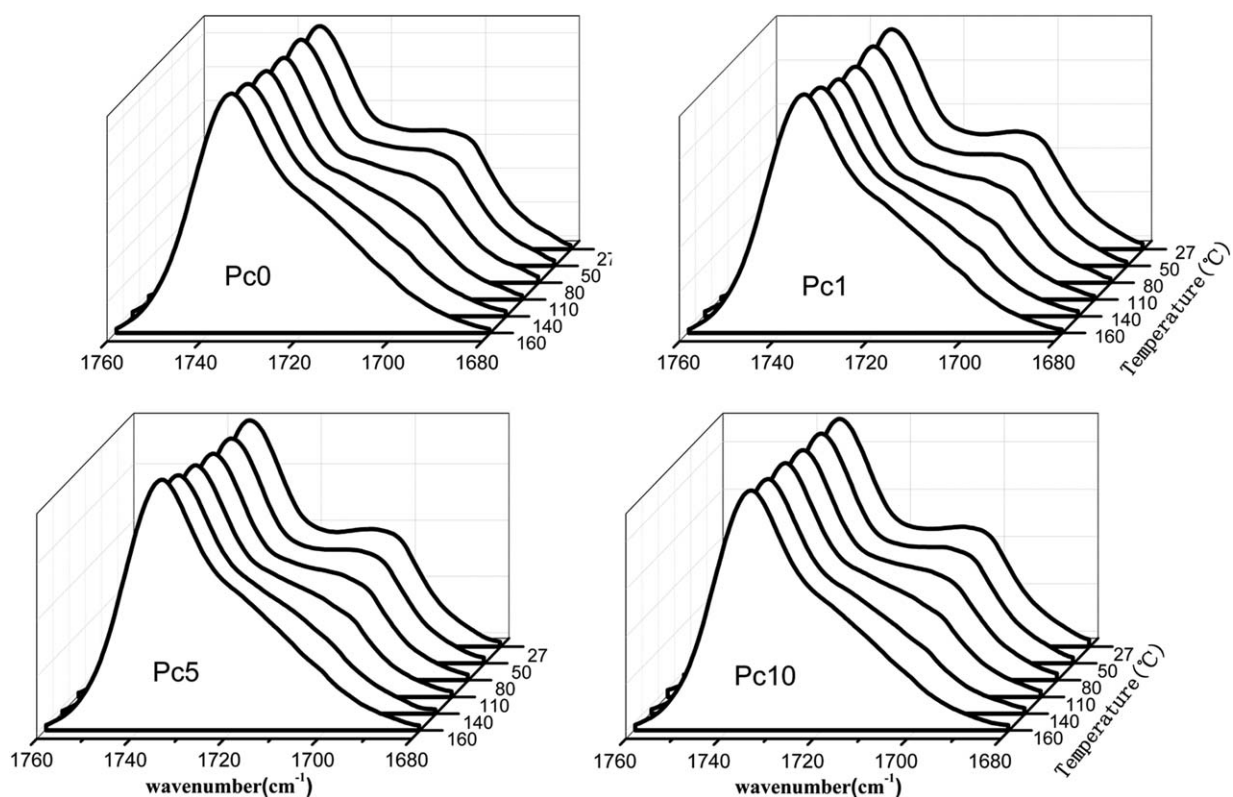


Figure 5. Infrared spectra of the carbonyl stretching region of the samples as a function of temperature.

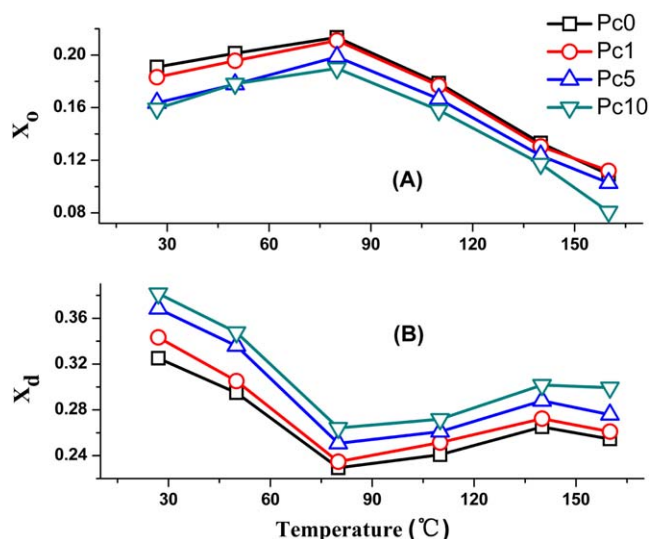


Figure 7. The fraction of (A) ordered and (B) disordered hydrogen bonded carbonyl of the samples as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carbonyl band were 1.0.²⁰ The fraction of disordered (X_d) and ordered hydrogen bonded carbonyl band (X_o) can be expressed by the following equations^{20–22}:

$$X_d = \frac{A_d}{A_f + A_d + A_o} \quad (2)$$

$$X_o = \frac{A_o}{A_f + A_d + A_o} \quad (3)$$

where A_f , A_d , and A_o is the area of free, disordered, and ordered hydrogen bonded carbonyl band, respectively.

Figure 7 shows the fraction of disordered and ordered hydrogen bonded carbonyl of the samples as a function of temperature. In Figure 7(A), X_o decreases with increasing Fe-OCAP content. The incorporation of Fe-OCAP influences the ordered region of hard segments of PU. With increasing temperature, X_o does not change very much before 80°C (the slight increase may be caused by the error of curve-fitting procedure) and then it can be seen a significant decrease above 80°C. The change in the slope is obvious. It demonstrates that the onset temperature for the dissociation of the ordered hydrogen bonded carbonyl is 80°C. Figure 7(B) shows increasing X_d with the addition of Fe-OCAP. The incorporation of Fe-OCAP facilitates the formation of disordered region of hard segments of PU. When the temperature increases, X_d decreases significantly at first, which is corresponding to the dissociation of disordered hydrogen bonded carbonyl groups. Then, a slight increase is seen at the temperature above 80°C. It can be explained by the procedure of the transformation from the ordered hydrogen bonded carbonyl groups to the disordered structure, where the dissociation of the ordered hydrogen bonded carbonyl occupies a dominant position. Above 140°C, the dissociation of disordered hydrogen bonded carbonyl plays a dominant role again and as a result, X_d

decreases. Figure 8 shows the fraction of hydrogen bonded carbonyl (both disordered and ordered hydrogen bonded carbonyl) of the samples as a function of temperature. It shows that hydrogen bonded carbonyl (X_b) increases with increasing Fe-OCAP and decreases with increasing temperature. The result indicates that strong hydrogen bond is formed between Fe-OCAP and hard segments of PU.

The mechanism of this interaction may be described as follows. First, additional disordered hydrogen bonded carbonyl groups is formed between free $-C=O$ in PU and $-COOH$ in Fe-OCAP ($-OH- -O=C$). As a result, the degree of hydrogen bonded carbonyl groups increases. Second, a part of $-NH- -O=C$ bond in PU is substituted by $-OH- -O=C$, and thus causes the dissociation of the original hydrogen carbonyl bond and the formation of new disordered hydrogen carbonyl bond. The interaction between $-C=O$ and $-OH$ is stronger than that between $-N-H$ and $-C=O$. It is because that the electronegativity of oxygen atom in $-OH$ is stronger than that of nitrogen atom in $-NH$. In that case, the extranuclear electron of hydrogen atom is much easier to access to the oxygen atom. As a result, the higher degree of “bare proton” can form hydrogen bond much easier with other atoms with lone pair electrons. Therefore, the hydrogen bond strength of $-OH- -O=C$ bond is higher than that of $-N-H- -O=C$ bond.

Analysis of the Dissociation of Hydrogen Bonded Carbonyl

The dissociation enthalpy of hydrogen bonded carbonyl groups can be used to characterize the strength of hydrogen bond in PU. The equilibrium of the dissociation of hydrogen bonded carbonyl can be characterized as the following balance equation.

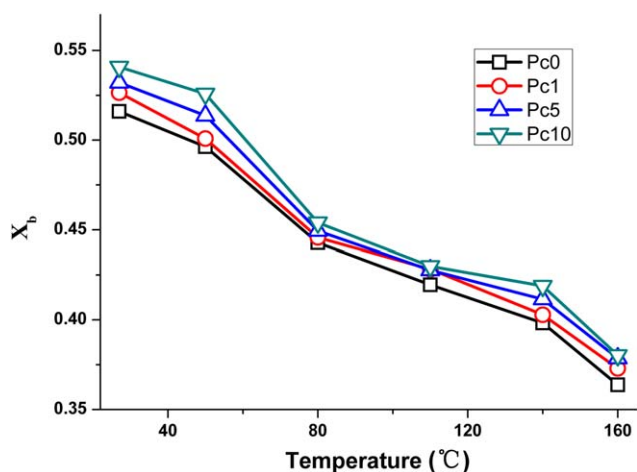
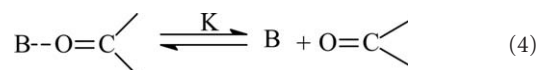


Figure 8. The fraction of hydrogen bonded carbonyl (both disordered and ordered carbonyl band) of the samples as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

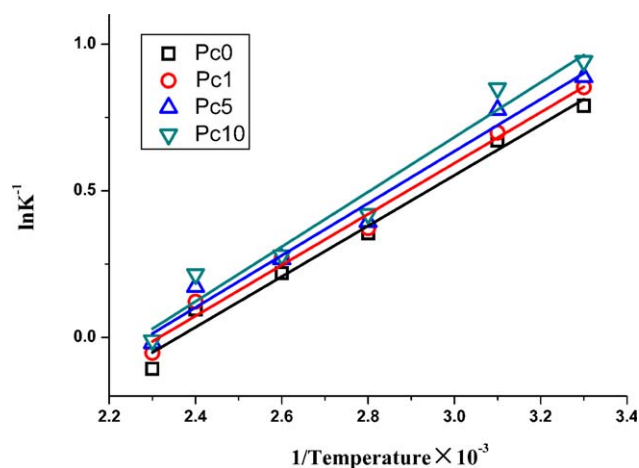


Figure 9. The data and linear fit of $\ln K^{-1}$ versus $1/T$ of the samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The equilibrium constant for the dissociation of hydrogen bonded carbonyl can be determined by the following equation^{27,32,33}:

$$K = \frac{[B][C=O]}{[B \cdots C=O]} = \frac{(1-X_b)^2}{X_b} \quad (5)$$

The change in enthalpy (ΔH_m) and entropy (ΔS_m) for the dissociation of hydrogen bond is then calculated from the temperature dependence of the equilibrium constant:

$$\ln K^{-1} = \frac{\Delta H_m}{RT} - \frac{\Delta S_m}{R} \quad (6)$$

Figure 9 shows the data and linear fit of $\ln K^{-1}$ versus $1/T$ of the samples. The values of ΔH_m and ΔS_m can be calculated from the slope and intercept and are summarized in Table I. The values of ΔH_m are increased with increasing Fe-OCAP content. It supports that strong hydrogen bond is formed between Fe-OCAP and hard segments of PU. The hydrogen bonded carbonyl increases with increasing Fe-OCAP content.

CONCLUSION

The average strength of hydrogen bond in modified samples was found to be stronger than that in pure PU. Hydrogen bonded $-\text{NH}$ groups and carbonyl groups increased with increasing Fe-OCAP content and decreased with increasing temperature. Strong hydrogen bond was formed between $-\text{COOH}$

Table I. Values of ΔH_m and ΔS_m of the Sample

Samples	ΔH_m (kJ/mol)	ΔS_m (J/mol·K)
Pc0	7.1	16.9
Pc1	7.2	16.7
Pc5	7.4	16.9
Pc10	7.8	17.5

in Fe-OCAP and carbonyl groups in PU. The increase of the values of ΔH_m for hydrogen bonded carbonyl from 7.1 to 7.8 kJ/mol with increasing Fe-OCAP content in PU supported the conclusion. The incorporation of Fe-OCAP influenced the ordered and disordered region of hard segments of PU. It facilitated the formation of disordered region of hard segments of PU.

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