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Thermochimica Acta 348 (2000) 175–179

thermochimica acta

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Studies on solid–solid phase transitions of polyols by infrared spectroscopy

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Received 24 June 1999; received in revised form 1 November 1999; accepted 8 November 1999

Abstract

This paper chiefly deals with the properties of polyols — a kind of energy storage material, by IR spectra. A series of infrared spectra at various temperatures were obtained for pentaerythritol (PE), pentaglycerine (PG), neopentylglycol (NPG) and their mixture NPG/PG. The experimental results (the shifts of –OH absorption band in IR spectra) support the solid–solid phase transition mechanism, which involves the reversible breaking of nearest-neighbor hydrogen bonds in the molecular crystals at transformation temperature. The correlation between the wave number shifts and the temperatures of phase transition is proposed in this paper. Finally, by means of infrared spectroscopy experiments, it is shown that aging has a great influence on the thermal properties of polyol mixtures. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polyol; Phase transition; Hydrogen bonding; Infrared spectroscopy; Aging; Plastic crystalline phase; Thermodynamics

1. Introduction

Phase change materials (PCM) have been widely studied for thermal energy storage, particularly, the polyols with solid–solid phase transition to which are attached increasing importance owing to their diverse advantages [1]. The polyols offer small change in volume and do not have segregation or phase separation problems. It is even more important that they have high enthalpies and low temperature during the phase transition. These advantages are of great interest in energy storage.

The studies of polyols on thermodynamics and kinetics are explored deeply using a step by step methodology. Drawing the binary phase diagram for polyols is reported gradually [2,3], as well. In the preceding studies the thermal properties of the solid–solid phase change for polyols are mainly obtained by differential scanning calorimetry (DSC) measurement [4–7]. In this paper by IR experiments at various temperatures the thermal properties of polyols are obtained. Moreover, the effect of aging on thermal properties for NPG/PG binary mixtures is shown by way of IR spectra.

2. Experimental

2.1. Sample preparation

Pure compounds (NPG G.R., PG E.P.) were purchased from Chemical Industrial Co. in Tokyo, PE having analytical purity with no additional purification. The polyols (NPG, PG) were ground and then weighed exactly in desired proportion to prepare the different

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PII: S0040-6031(99)00403-7

mixed samples. The two components were heated in sealed glass tube so as to melt them and form a clear liquid. Then they were slowly cooled to form a solid.

2.2. *Infrared spectroscopy*

A Perkin–Elmer M-1730 Fourier transform infrared spectrometer was used to record the infrared spectra of polyols and their mixtures in the spectral region of 4000–2500 cm^{-1} (resolution: 4 cm^{-1} 4 scans for each spectrum). The sample was ground with dry KBr powder and then compressed into dense and fully transparent pellets. To record spectra at different temperatures the sample pellet was placed in a sample holder combined with an external E-01-2A HITACHI temperature-controlling apparatus. The apparatus has the uncertainty of ±1 K. The pellet was heated from an ambient temperature to roughly 400 K with the heating rate 3K/min.

3. Experimental results and data analysis

3.1. *IR analysis for three polyols*

Infrared spectroscopy of the polyols at the room temperature shows a strong absorption centered at about 3300 cm^{-1} which is identified with –OH stretching band. Fig. 1 shows the portion of infrared spectra in the spectral range 4000–2500 cm^{-1}, including –OH stretching band, for three polyols (NPG, PG and PE) at various temperatures. Analysing the infrared spectra at various temperatures for the same pure compound, we can find that the frequency and shape of –OH absorption band notably change with rising temperature while other groups have very small changes in absorption band. The –OH stretching bands become broader and broader upon heating the sample. For all three polyols the frequency of –OH absorption peaks shifts to the higher wave number when the temperature is rising as shown in Fig. 2. And in a certain temperature interval there is a sudden and pronounced change in –OH absorption band. Related data of IR and DSC experiments are listed in Table 1. Comparing the solid–solid phase change temperature by DSC with the temperature interval having the maximum shift by IR. it is easy to discover that the two data are agreeable to each other. That is to say, by IR experiments at various temperatures, the temperature range, in which the polyols exhibit the solid–solid phase change, can be deduced. Moreover, there is a certain relation between the maximum wave number shifts and the transition enthalpies with the former increasing the latter is enhanced (Table 1).

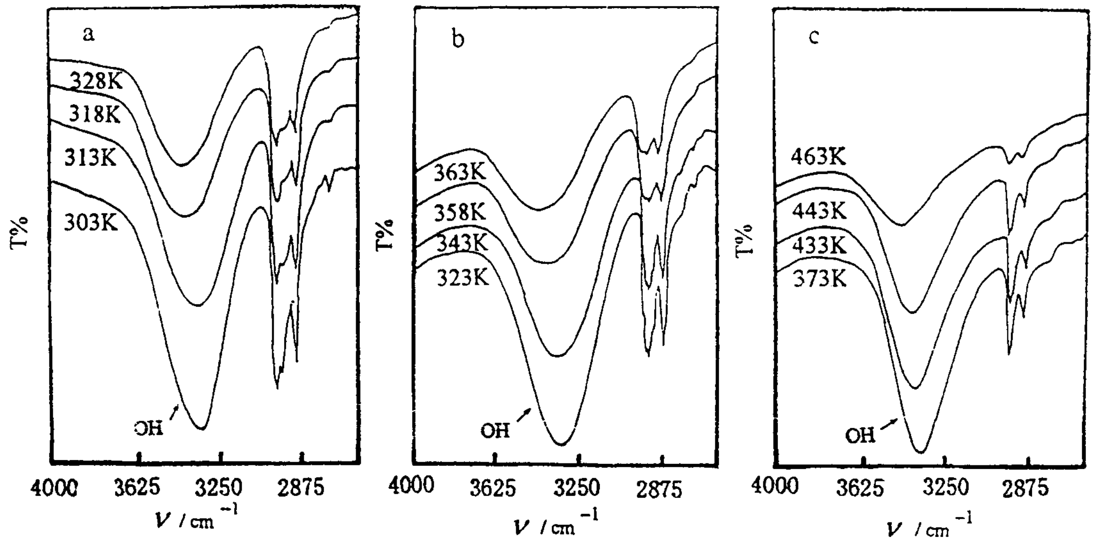
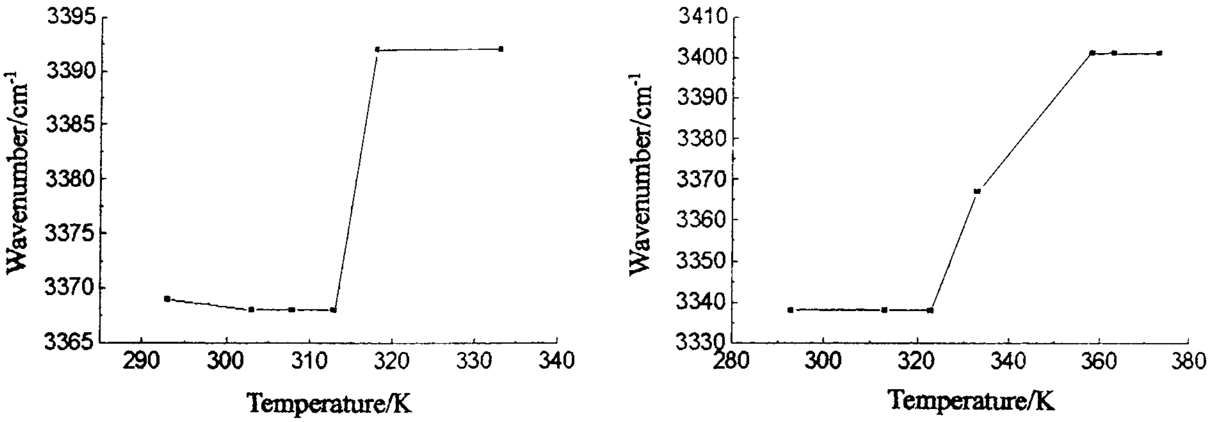
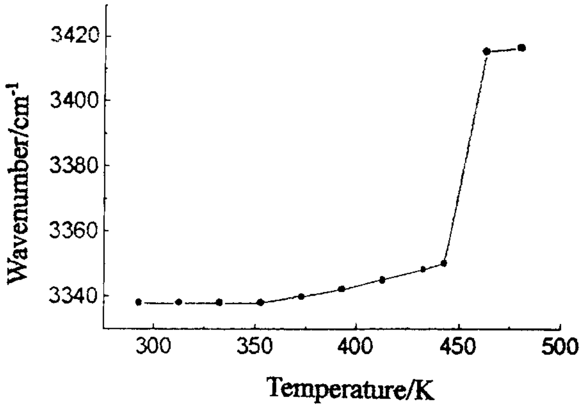


Fig. 1. IR spectra at various temperatures (a) NPG; (b) PG; (c) PE.



a NPG **b** PG



c PE

Fig. 2. Plot of wave number vs. temperature for pure polyol.

At room temperature the alcohols (including polyol) exist in an associated state because the intermolecular hydrogen bonds come into being. When the temperature is going up, the intermolecular hydrogen bonds will weaken. And correspondingly, the hydroxyl bond strengthens gradually. This causes the –OH absorption band to move to a higher wave number [8–10]. The change is especially strong at the temperature of the phase transition because the intermolecular hydrogen bonds are extremely weakened and eventually destroyed. The intensity of hydroxyl bond increases notably. Therefore, there is the maximum shift of –OH absorption band in IR spectra at various temperatures. The solid–solid phase changes of polyols are known to transform from a low symmetric layered crystal structure to a highly symmetric face centered cubic structure [4]. The energy (transition

Table 1
Comparison between IR and DSC experimental result of NPG, PG and PE

Sample	DSC		IR		n
	$(T_{tr})^a$ (K)	$(\Delta H_{tr})^a$ (J g^{-1})	$\Delta T_{\Delta\nu\max}$ (K)	$\Delta\nu_{\max}$	
NPG	317	116.54	313–318	24	2
PG	355	172.58	343–358	33	3
PE	458	209.45	443–463	48	4

[a] The temperature is obtained by DSC.

enthalpy) is absorbed to destroy the intermolecular hydrogen bonds so as to complete the transition between the crystal lattices. Simultaneously, the process involves the vibrational and rotational disorder. In the order of NPG, PG and PE, the number of –OH group increases in turn. And the chance of forming the intermolecular hydrogen bonds changes increasingly [11]. More and more energy is needed to destroy the intermolecular hydrogen bonds in molecular crystals. In other words, the transition enthalpy increases gradually. Because of more and more increment of intensity of hydroxyl bond at the respective transition temperature for NPG, PG and PE the maximum wave number shift increases in order. The maximum wave number shift is approximately in direct proportion to the number of –OH group (Table 1).

3.2. IR analysis for NPG/PG mixture

Table 2 summarizes the test results of IR experiments for NPG/PG mixtures with the different mass concentration. Similarly, the temperature interval with maximum wave number shift is consistent with the solid–solid phase change temperature determined by DSC experiments. Among these, for the three mixtures with the concentrations of 10.33, 27.1, 32.16% the temperature intervals with the maximum shift on wave number are the same. The solid–solid transition temperatures by DSC for the three mixtures are the same as well and equal to 309 K. According the IR and DSC experimental data, below conclusion can be drawn. The mixtures with other concentration exhibit the solid–solid phase change at the temperature going up with the concentration increasing. The location of the transition ($T = 309$ K) does not depend on the composition. In view of the above the NPG/PG binary phase diagram is eutectoidal in the low concentration. The eutectoidal temperature is 309 K. At this temperature the transformation process occurs from α phase (with the same morphism as NPG) and β phase (with the same morphism as PG) to plastic crystal having face-centered cubic structure. This is agreeable to the reported information in other publications [12].

3.3. IR analysis for the effect of aging

For the same sample of NPG/PG binary mixture the IR experiments at various temperatures had been done under two conditions — without aging and after aging at room temperature for several months. Similarly, in each case the –OH absorption band changes gradually with the temperature and has a sudden change in a certain temperature interval. However, the temperature interval and the number of sudden change are

Table 2
Absorption peak of –OH of PG/NPG at various temperatures

W_{PG} (%)										$\Delta T_{\Delta\nu\max}$ (K)	$(T_{tr})^a$
10.33	T (K)	293	303	308	313	323					
	σ (cm^{-1})	3368	3367	3367	3391	3393				308–313	309
27.71	T (K)	293	298	308	313	323	333				
	σ (cm^{-1})	3368	3369	3370	3393	3392	3395			308–313	309
32.16	T (K)	293	298	308	313	323	333				
	σ (cm^{-1})	3363	3370	3368	3391	3393	3392			308–313	309
49.45	T (K)	293	303	308	318	333	343				
	σ (cm^{-1})	3338	3338	3343	3372	3371	3379			308–318	313
53.70	T (K)	293	298	308	323	333	348	358	373		
	σ (cm^{-1})	3337	3343	3353	3359	3383	3385	3392	3391	323–333	326
67.61	T (K)	293	303	313	323	333	343	363	373		
	σ (cm^{-1})	3338	3344	3353	3361	3386	3392	3393	3398	323–333	326
76.00	T (K)	293	303	318	323	328	338	358	373		
	σ (cm^{-1})	3338	3349	3353	3365	3392	3392	3397	3392	323–328	328
80.79	T (K)	293	303	313	323	333	343	353	373		
	σ (cm^{-1})	3338	3343	3349	3358	3366	3398	3398	3400	333–343	338
92.25	T (K)	293	303	313	328	333	343	353	373		
	σ (cm^{-1})	3338	3343	3343	3347	3355	3392	3398	3401	333–343	341

[a] The temperature is obtained by DSC.

Table 3
Absorption peak of –OH at various temperatures under two conditions[a]

W_{pg} (%)											$\Delta T_{\Delta\nu\max}$ (K)	
49.45	WA	T (K)	293	303	313	323	333	343	353	363	303–313	343–353
		ν (cm^{-1})	3338	3338	3349	3343	3349	3349	3392	3392		
	AA	T (K)	293	303	308	318	333	343			308–318	
		ν (cm^{-1})	3338	3338	3343	3372	3371	3379				
76.00	WA	T (K)	293	303	313	323	333	348	358	363	303–313	348–358
		ν (cm^{-1})	3338	3338	3349	3350	3358	3367	3399	3400		
	AA	T (K)	293	303	318	323	328	338	358	373	323–328	
		ν (cm^{-1})	3338	3349	3353	3365	3392	3392	3387	3392		

[a] WA — without aging; AA — after aging.

not same under two conditions for the same sample (Table 3). That is to say, the temperature of solid–solid phase changes is different when the aging time is different. Moreover, the number of solid–solid phase transition processes is not identical. There are two solid–solid phase transition processes to occur without aging. Only one transition does after aging. The transition temperature after aging is between the two transition temperatures without aging. To show the difference of –OH absorption band even more directly the temperature interval under two conditions are listed in Table 3.

The DSC results, corresponding to the above different IR results, have been reported, respectively, in published literatures [13,14]. This disparity under two conditions can be explained by means of the preparation of polyol mixture. It is related to the cooling process of the clear liquid, particularly, the solid–solid transition process. The metastable phase is proposed as in literature [15].

4. Conclusion

The paper deals with the thermodynamic properties of polyols and their mixtures by IR at various temperatures. The transition temperature is determined through the shift of –OH absorption band. The experimental result is tested and verified by DSC data. It is workable to deduce the temperature range of solid–solid phase transition by the infrared spectra at various temperatures.

Aging is a neglected factor, but it greatly influences the properties of the polyols mixtures. The discrepancies of thermal properties in literature are related to the cooling process. Aging has a general significance in guiding experiments with polyols.

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