

Specific Heats of Neat and Glycerol Plasticized Polyvinyl Alcohol

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ABSTRACT

The specific heats (C_{sp}) of neat polyvinyl alcohol (NPVOH) and 40 phr glycerol plasticized polyvinyl alcohol (PPVOH) were measured using a method known as power compensate differential scanning calorimetry. A high purity sapphire (Al_2O_3) was used as a reference material. NPVOH has a melting temperature of approximately 480 K, while PPVOH has a value of 30 K lower than NPVOH. The amplitude increment of C_{sp} for NPVOH was also higher than PPVOH at melting stage. Overall, C_{sp} of NPVOH is lower than PPVOH because glycerol has reduced the rigidity of PVOH and subsequently induced the motion of molecular structure at an elevated temperature. Based on the specific heat outcomes, neat PVOH and glycerol plasticized PVOH required 1173.544 J/g and 1946.631 J/g, respectively, to heat from 330 to 550 K.

Keywords: Polyvinyl alcohol, glycerol, specific heat, differential scanning calorimetry

INTRODUCTION

Polyvinyl alcohol (PVOH) is one of the most popular biodegradable polymers. When PVOH is exposed to natural environment, it is readily to be consumed by micro-organism. In decades, there has been increasing interest in the use PVOH for the production of disposable plastic articles. However, unlike polyethylene, polypropylene and polystyrene, PVOH is very likely to degrade during processing stage. According to Chiellini *et al.* (2003), the main difficulty in the thermal extrusion of PVOH is the close proximity of its decomposition temperature and melting point. Moreover, PVOH has a high melting point due to the presence of hydrogen bonding interactions among the hydroxyl groups. The hydrogen bond induces crystallization and subsequently requires higher energy to break up the intermolecular forces. According to Tubbs and Ting (1973), the first stage in the degradation of PVOH begins at 200°C which mainly involves dehydration with generation of volatile products; whereas, the melting point of PVOH is 180-240°C (Kuraray, 2003) that includes degradation of temperature. Hence, adding plasticizer is the most effective approach to reduce the melting point of PVOH so that the thermal degradation can be avoided during processing stage. Glycerol is the most common plasticizer (Marten *et al.*, 1991) incorporated with PVOH. This is because glycerol has tri-hydroxyl groups with good compatibility with PVOH in each molecule via hydrogen bond interactions (Kuraray, 2003).

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EXPERIMENTAL DESIGN

Fully hydrolysed PVOH of grade BF-17H (viscosity 25-30 cps, hydrolysis 99.4-99.8 mole %, ash < 0.7 %), manufactured by Chang Chun Petrochemical Co., Ltd. Taiwan, was used. Meanwhile, glycerol (C₃H₈O₃) at 99.5 % purity was purchased from Fisher Scientific, United States. Calcium stearate (CaS) was supplied by Sun Ace Kakoh Sdn. Bhd., Malaysia. Phosphoric acid at 85% purity was obtained from Merck, Germany. CaS and phosphoric acid were used as internal lubricant and heat stabilizer additive, respectively. All the materials were used in the conditions as they were received. PVOH, glycerol, CaS, and phosphoric acid were pre-mixed in Chyau Long Machinery Co. Ltd. Taiwan, CL-10 a high speed mixer for 15 minutes. After that, the mixtures were compounded using a twin screw co-rotating extruder Sino PSM 30 B5B25 (built by Sino-Alloy Machinery Inc., Taiwan) to produce plasticized PVOH (PPVOH). The composition of PPVOH is shown in Table 1. Side feeder was used to transfer the mixtures into barrel with four heating zones. The heating zones were set at 16°C, while the screw speed was set to 250 rpm.

TABLE 1
Composition of plasticized PVOH (PPVOH)

Specimen	Glycerol (phr)	PVOH (phr)	CaS (phr)	Phosphoric acid (g)
PPVOH	40	100	2	4.18

C_p of the specimens were measured by power compensate differential scanning calorimetry (DSC)-Perkin Elmer United States model DSC 7. The original supplied PVOH was labelled as NPVOH, while PPVOH was used as prepared. Synthetic sapphire disc was used as the standard reference material. The measurements were conducted in the temperature ranging from 330-530 K and at the scanning rate of 10°C/min with nitrogen purging at 20 ml/min. Sealed aluminium pans were used to encapsulate specimens or sapphire for measurements. The procedure to determine the experimental specific heat was based on three DSC runs, as depicted in *Fig. 1* below:

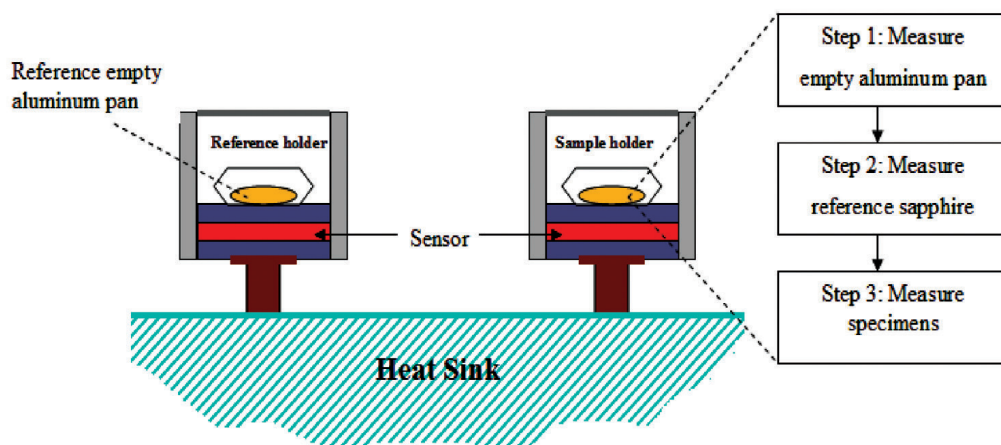


Fig. 1: Procedure of specific heat measurement

Each specimen underwent measurements in duplicate to ensure reproducibility of the results. The specific heat of the specimen is given by:

$$C_{sp} = \frac{M_{rs}}{M_{sp}} \times \frac{\Delta R_{sp}}{\Delta R_{rs}} \times C_{rs} \quad (1)$$

where C_{rs} is the known specific heat of the sapphire standard reference material in BS ISO 11357-4 (British Standard Institutions, 2005), M_{rs} and M_{sp} are the masses of sapphire reference material and specimen, respectively. ΔR_{rs} is the signal difference between the sapphire reference material and empty aluminium pan ΔR_{sp} and is the signal difference between the specimen and empty aluminium pan.

RESULTS AND DISCUSSION

The C_{sp} of the neat PVOH (NPVOH) and PPVOH are tabulated in Table 2. *Fig. 2* shows the relationships of C_{sp} and temperatures of NPVOH and PPVOH. As illustrated, both C_{sp} of PPVOH and NPVOH increased in an almost proportional manner at the initial stage. After that, C_{sp} increased drastically, but it finally dropped back to the original trend after the melting stage was completed. Two endothermic processes were found to have occurred simultaneously during the melting stage. The first endothermic process utilized the external heat to break up the physical bonds of the specimens to reach the melting stage. Meanwhile, the second endothermic process utilized the external heat to increase the temperatures. The polymer substances have different thermal behaviour over their origin monomers. Mono-disperse low molecular weight substances possess narrow melting range which is mainly due to the similarity of entire intermolecular forces. Poly-disperse high molecular weight polymers have different strengths of intermolecular forces within the entire system. The shorter chain molecules in the polymer melt at a lower temperature and it would continue to absorb the external energy to increase the temperature until the entire polymer system achieved the molten state. Hence, the reported C_{sp} of the specimens have included the enthalpy of melting as well.

As expected, the incorporation of glycerol into PVOH showed a decrement in the onset melting temperature. In more specific, NPVOH has a melting temperature of approximately 480 K, while PPVOH has lower melting temperature at 450 K. The amplitude increment of C_{sp} for NPVOH is also higher than PPVOH at the melting stage. This indicated that glycerol had disrupted the genuine strong interactions and crystallinity structure of PVOH. Thus, PPVOH required lower energy than NPVOH to achieve the melting stage. On the other hand, the overall C_{sp} of PPVOH is higher than NPVOH. This is because the high rigidity of NPVOH limits the molecule structures to mere vibration motion while subjected to thermal effects. However, when glycerol was added to PVOH, it reduced the rigidity of PVOH and induced a number of skeletal vibrations, changed conformational and large-amplitude motion that caused anharmonic interactions, subsequently contributed significantly towards higher C_{sp} (Pyda *et al.*, 2004).

TABLE 2
Specific heat of NPVOH and PPVOH

Temperature (K)	Specific heat, C_{sp} (J/g.K)		Temperature (K)	Specific heat, C_{sp} (J/g.K)	
	NPVOH	PPVOH		NPVOH	PPVOH
330	2.293	3.261	440	6.179	10.885
340	2.656	3.759	450	6.293	11.817
350	3.064	4.405	460	6.438	13.094
360	3.508	5.116	470	6.678	13.471
370	3.986	5.871	480	7.071	12.298
380	4.477	6.620	490	8.914	13.115
390	4.950	7.357	500	11.859	13.560
400	5.310	8.075	510	6.429	13.838
410	5.620	8.765	520	6.993	14.115
420	5.882	9.436	530	7.718	14.677
430	6.044	10.100			

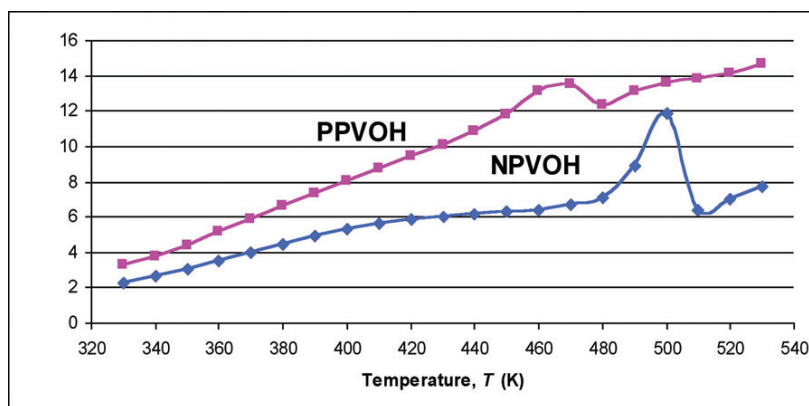


Fig. 2: Specific heat of NPVOH and PPVOH

The overall heat required to increase the temperatures of NPVOH and PPVOH from 330-530 K was calculated as follows:

$$\Delta H = \int_{330}^{530} C_{sp} dT \tag{2}$$

$$\Delta H = \frac{1}{2} \sum_{330}^{530} (C_{sp,i+10} + C_{sp,i}) \times 10 \tag{3}$$

The calculation outcomes showed that NPVOH and PPVOH required 1173.544 J/g and 1946.631 J/g respectively to heat from 330 to 550 K. This information is very important to predict the energy consumption of PVOH in typical polymer processing techniques such as injection moulding and melt extrusion.

CONCLUSIONS

The measurement of the specific heat of neat PVOH and glycerol plasticized PVOH was conducted using DSC. The following findings were therefore obtained:

1. Both neat PVOH and glycerol plasticized PVOH have the highest specific heat values at the melting stage. These values have included the enthalpy of melting as well.
2. Glycerol plasticized PVOH has an overall specific heat higher than neat PVOH. This is because the incorporation of glycerol has reduced rigidity and induced motion of molecules at an elevated temperature.
3. Neat PVOH and glycerol plasticized PVOH require 1173.544 J/g and 1946.631 J/g, respectively, to heat from 330 to 550 K.

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