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Glass-transition Temperature of PECH and GAP

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Glycidyl azide polymer (GAP) is one of the most recognized and prominent azide polymer. Because of its superior properties, GAP is used extensively as a high energetic binder or plasticizer in propellants to increase burning and specific impulse. It is very important to research on the glass-transition temperature (T_g) of GAP and its precursor PECH (poly-epichlorohydrin) due to the T_g of binders is the key factor which can influence low temperature properties of solid propellants.

PECH with different molecular weight and different functionality were synthesized by ring-opening polymerization of epichlorohydrin using different initiators and $SnCl_4/CF_3COOH$ as catalyst, and GAP were prepared by treating the corresponding PECH with sodium azide in DMF solvent at 100 ℃ for 9 – 11 h in this paper. Then the T_g of PECH and GAP were determined by DSC respectively.

The T_g of PECH with different molecular weight of PECH showed in Table 1, the DSC curve of GAP with different molecular weight (1100, 2600 and 4500) was shown in Figure 1.

As shown in Table 1 and Figure 1, the T_g of the PECH and GAP increased as the molecular weight. But the same molecular weight did not represent equal T_g, because the molecular weight distribution also influenced the T_g of PECH. Generally, GAP showes lower T_g compared to corresponding PECH because the azido group in GAP has lower polarity than Cl atom in PECH.

As a result of the difference of steric hindrance brought by initiators, the T_g of PECH based on 3600 molecular weight which were initiated respectively by ethylene glycol, 1,4-bis(hydroxymethyl) cyclohexane and 1,4-butanediol were –27.22 ℃, –27.85 ℃ and –29.30 ℃.

The functionality also influence the T_g. For example, the T_g of difunctional and trifunctional PECH based on 5500 molecular weight were –26.83 ℃ and –28.71 ℃ respectively. It was explained that the trifunctional PECH correspond with that the difunctional PECH added a hydroxyl-terminated flexible branched chain. As a result that trifuctional PECH showed lower T_g than difunctional PECH.

Table 1 The relationship between T_g and molecular weight of PECH initiated by BDO

sample	$\overline{M}_n$	D	T_g/℃	K
PECH-01	1000	1.05	–42.74	
PECH-02	2700	1.15	–32.49	
PECH-03	3600	1.20	–29.30	
PECH-04	3600	1.31	–29.64	18670
PECH-05	4250	1.24	–27.28	
PECH-06	5500	1.27	–26.83	

Note: BDO: 1,4-butanediol; D: molecular weight distribution; K: polymer characteristic constant of PECH calculated by following formulation:

$$T_g = T_g(\infty) - \frac{K}{\overline{M}_n}$$

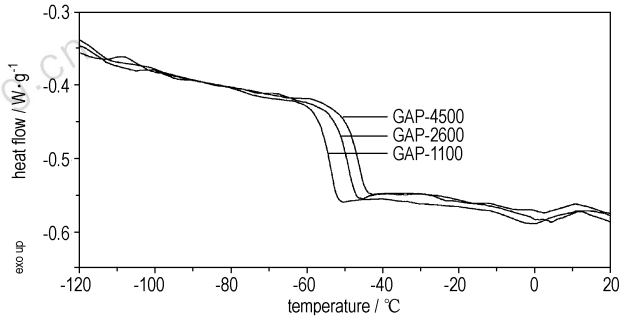

Fig. 1 The DSC curves of GAP with different molecular weight (1100, 2600 and 4500)

The T_g of PECH and GAP increased with increasing of molecular weight and steric hindrance of initiators while decreasing with increasing of molecular weight distribution and functionality. So the T_g of PECH and GAP could be controlled by altering those influencing factors.

Key words: ploymer chemistry; glycidyl azide polymer (GAP); poly-epichlorohydrin (PECH); glass-transition temperature

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