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POLYURETHANE/POLYETHYL ACRYLATE INTERPENETRATING POLYMER NETWORKS

Thermal decomposition kinetics

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Abstract

The thermal decomposition kinetics of polyurethane/polyethyl acrylate interpenetrating polymer networks (PU/PEA IPN) were studied by means of thermogravimetry and derivative thermogravimetry (TG-DTG), and compared with those of polyurethane (PU) and polyethyl acrylate (PEA). The decomposition temperature (T_i) of PU/PEA IPN was found to be higher than T_i of PEA, but lower than T_i of PU. Thermal decomposition kinetic parameters, n and E, estimated using Coats-Redfern method, are found for PU/PEA IPN, PU and PEA to be 1.6, 1.9 and 1.1, and 196.6, 258.6 and 139.2 kJ mol^{-1}, respectively. The results show that PU/PEA IPN is neither a simple mixture of PU and PEA nor a copolymer of them. The mechanism of thermal decomposition of PU/PEA IPN is different from those of PU and PEA. The special network in PU/PEA IPN effectually protects weak bonds in the molecular chain of PU and PEA.

Keywords: polyurethane/polyethyl acrylate interpenetrating polymer networks (PU/PEA IPN), TG-DTG, thermal decomposition kinetics

Introduction

'Interpenetrating polymer networks (IPN)' was first reported by Millar in 1960 [1]. Sperling made systematic studies on this material in 1969–1971 [2, 3]. Since then, new IPN materials have been found and applied in various fields [4, 5]. Polyurethane/polyethyl acrylate interpenetrating polymer network (PU/PEA IPN) is a new material with a potential application in paint. The film of it is as bright as that of polyethyl acrylate (PEA) and as pliable and tough as that of polyurethane (PU). In order to study thermal stability and thermal decomposition mechanism of PU/PEA IPN, the thermal decomposition kinetics were studied by means of TG-DTG and compared with those of PU and PEA alone.

Experimental

The sample of PU/PEA IPN

The linear polyurethane (The soft and hard segment were polyethylene glycol adipate and polyethylene dis(4-phenylene iso-cyanate) ethylene glycol) and the linear polyethyl acrylate were dissolved in a suitable solvent. The crosslinking agent

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(1,2,3-hydroxy-methyl-propane) was added to the above solution to form PU/PEA IPN. The fraction of PU and PEA in IPN is 1/1 (*w*/*w*).

TG-DTG experimental equipment and conditions

TG-DTG experiments were carried out on a Perkin-Elmer TGA-7 Thermogravimetric Analyzer, in a nitrogen atmosphere (80 ml min^{-1}) and a heating rate of 10°C min^{-1}. The sample sizes were 8–10 mg.

Results and discussion

TG data and thermal decomposition behaviour in the first stage

The TG-DTG curves of PU/PEA IPN, PU and PEA are shown in Fig. 1.

It can be observed from Fig. 1 that the TG-DTG curve of PU/PEA IPN is different than those of PU and PEA, and also is not a simple 'sum' of them. On the TG curve of PU/PEA IPN, there is a longer 'terrace' from 350 to 450°C.

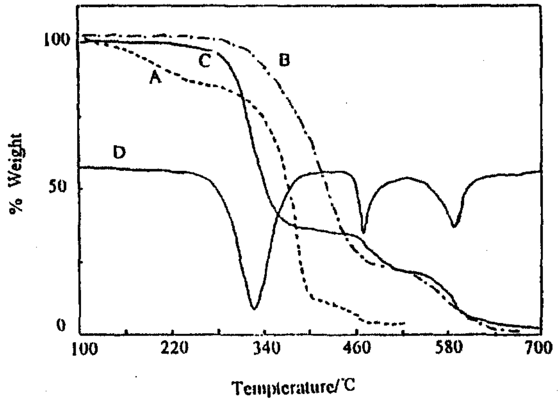

Fig. 1 The TG-DTG curves of PU/PEA IPN, PU and PEA A:PEA B:PU C:PU/PEA IPN

Their thermal decomposition data in the first stage are listed in Table 1.

In Table 1, T_i is the initial temperature or procedural decomposition temperature, which is the temperature at which the cumulative mass-change reaches a magnitude that the thermobalance can detect. T_f is the final temperature, which is the temperature at which the cumulative mass-change first reaches its maximum value,

Table 1 Thermal decomposition data of PU/PEA IPN, PU and PEA

Sample	T_i /°C	T_f /°C	T_p /°C	Mass loss/%
PU/PEA IPN	281.6	392.2	331.7	61.6
PU	296.8	462.1	412.9	70.2
PEA	172.3	278.5	206.4	11.8

corresponding to complete reaction. T_p is the DTG peak temperature at which the mass-change rate reaches its maximum value. The data in Table 1 show that the all TG parameters of PU/PEA IPN are higher than those of PEA and lower than those of PU.

Thermal decomposition kinetics

For a reaction in which the order (n) is unknown, Coats and Redfern [6] derived the following expression:

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT} \qquad (n\neq 1)$$

Where α is the fraction of the sample decomposed at time t, and β is the heating rate. A plot of either $\log[1-(1-\alpha)^{1-n}/T^2(1-n)]$ *vs.* $1/T$ $(n\neq 1)$, should result in a straight line of slope $-E/2.3R$ for the correct value of $\bar{n}$. The quantity $\log\{(AR/\beta E)[1-RT/E)]\}$ appears to be reasonable constant for most values of E and in the temperature range over which most reactions occur.

Processing of the TG data of PEA, PU and PU/PEA IPN gave the plots for the relationships between $\log[1-(1-\alpha)^{1-n}/T^2(1-n)]$ and $1/T$ as Fig. 2.

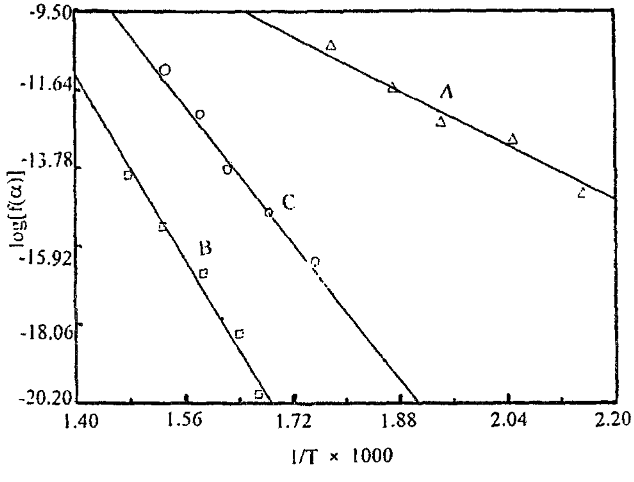

Fig. 2 The relationships between $\log[f(\alpha)]$ and $1/T$ of PU/PEA IPN, PU and PEA.
A: PEA $n=1.1$; B: PU $n=1.9$; C: PU/PEA IPN $n=1.6$

Processing the TG data by Coats-Redfern method, their thermal decomposition kinetic parameters are listed in Table 2.

In Table 2, n is the reaction order, E is the apparent activation energy and A is the pre-exponential constant. As a linear polymer, the thermal stability of polyethyl acrylate (PEA) is lower [7]. Because the molecule chains of polyurethane (PU) for this experiment is crosslinked, the thermal stability of it is higher. Had the sample of PU/PEA IPN for this experiment been a simple mixture of PU and PEA, 'Mass

Table 2 Thermal decomposition kinetic parameters of PU/PEA IPN, PU and PEA

Sample	n	E/kJ mol^{-1}	ln$A$/s^{-1}
PU/PEA IPN	1.6	196.59	36.32
PU	1.9	258.63	37.59
PEA	1.1	139.21	35.04

loss' at 172.3 and 296.8°C would have appeared on the TG curve of PU/PEA IPN, respectively. But the fact is not. On the other hand, PU and PEA also can't form a copolymer. The experimental results have proved that the sample of PU/PEA IPN prepared by us really has formed a new material with interpenetrating polymer networks. The special networks effectually stabilize those weak bonds in the molecular chains of PEA and PU. With the increase of temperature the networks are destroyed. Since the sample is heated to high enough temperature, the molecular chains of PU and PEA speedily decompose at the same time.

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