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Catalytic effects of sulfates on thermal degradation of waste poly(methyl methacrylate)

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Abstract

The thermal degradation of waste poly(methyl methacrylate) (PMMA) in the presence of ferric sulfate, cupric sulfate, aluminum sulfate, magnesium sulfate, and barium sulfate was studied by using thermogravimetric analysis (TGA) in air atmosphere. The values of apparent activation energies (E_a) calculated by Flynn–Wall–Ozawa method were found to be in the order of $\mathrm{PMMA + Fe_2(SO_4)_3 < PMMA + Al_2(SO_4)_3 < PMMA + MgSO_4 < PMMA + CuSO_4 < PMMA + BaSO_4 < PMMA}$. The mechanism of catalytic degradation of PMMA in presence of the sulfates was discussed and the results showed that the catalytic effects of sulfates have a relationship with the acidity of their respective metal ions.

Keywords: Waste poly(methyl methacrylate); Thermogravimetry; Thermal degradation; Sulfate; Catalytic effect

1. Introduction

Poly(methyl methacrylate), PMMA, a kind of important thermoplastic materials, is widely used in many fields due to its excellent properties, such as transparency, lightness and safety. With the increase of the production and consumption of plastics, wastes are commonly dumped in a landfill or incinerated, which polluted the environment greatly. Plastics degradation or pyrolysis, as an alternative means, may provide for disposal of plastic wastes with recovery of valuable monomer [1]. The price of PMMA is relatively high compared to standard plastics, additionally, the possibility to recover up to above 90% of the monomer. So most industrial process for the pyrolysis of polymers are interested in the production of methylmethacrylate (MMA) from PMMA. In order to depolymerize PMMA, molten metal bath, dry distillation, extruder processes and fluidized bed processes are used [2–4]. However, the degradation would not occur unless PMMA was heated up to the depolymerization temperature. So an attractive method is to use catalyst to decrease the degradation temperature of PMMA.

Over the past few years, the thermal stability of PMMA have been studied [5–12]. A majority of these studies have been conducted in the inert atmosphere. The stability effect of oxygen on thermal degradation of PMMA was first reported by Bresler et al. [13]. Then Kashiwagi et al. [14] proposed the mechanism to explain this effect and Peterson et al. examined the mechanism [15]. On the basis of these studies, our investigations have focused on catalytic degradation to obtain the optimum condition for lower degradation temperature and higher yield of MMA monomer in air atmosphere.

In this paper, the effects of sulfates on the thermal degradation of waste PMMA were studied under air condition. From the experimental results, we suggested the catalytic mechanism and summarized the relationship between the strength of the catalyst and the acidity of sulfates in order to enrich this research field and offer some helpful data for the recycling processes of waste PMMA.

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2. Experimental

Waste PMMA was pretreated by washing clearly with distilled water and air-drying, then filed into powders. Sulfates were dried in an oven at 280 °C in order to remove the crystal water. The sample was prepared by a simple physical combination of the two reagents with a weight ratio of waste PMMA to sulfate powder of 10:1, then ground with a mortar. The thermogravimetric analysis was carried out on a DT-40 thermal analyzer (Japan Shimadzu Co.) which was computer controlled, allowing recording of experimental data for further treatment. Each sample weighing about 10 mg was placed in a platinum crucible and heated at the heating rates of 5, 10, 20 and 40 °C/min. The gas flow rate was kept at 50 ml/min.

3. Results and discussion

3.1. The analyses of TG data

The thermogravimetric analysis (TGA) for each sample is performed at the preset heating rate. With the increase of the heating rate, generally, the temperature of initial weight loss will increase for the same degradation, while the residual fraction of the sample is almost constant regardless of heating rates. Fig. 1 shows the thermogravimetric (TG) curves obtained at a heating rate of 5 °C/min in air for six kinds of samples. Note that the presence of sulfates (especially, $Fe_2(SO_4)_3$ or $Al_2(SO_4)_3$) caused a decrease in the initial temperature of degradation.

The multiple scan method based on Ozawa [16] was applied to calculate the apparent activation energy of the thermal degradation. Eq. (1) is derived from the Flynn–Wall–Ozawa method,

$$\log\beta = \log\left(\frac{AE}{R(g(\alpha))}\right) - 2.315 - 0.4567\left(\frac{E}{RT}\right) \qquad (1)$$

where α is the degree of conversion (=weight loss at a given temperature/total weight loss of the degradation), β is the heating rate (=dT/dt), and $g(\alpha)$ is the function describing the reaction mechanism. A, E, R and T represent pre-exponential factor, activation energy, gas constant and temperature, respectively.

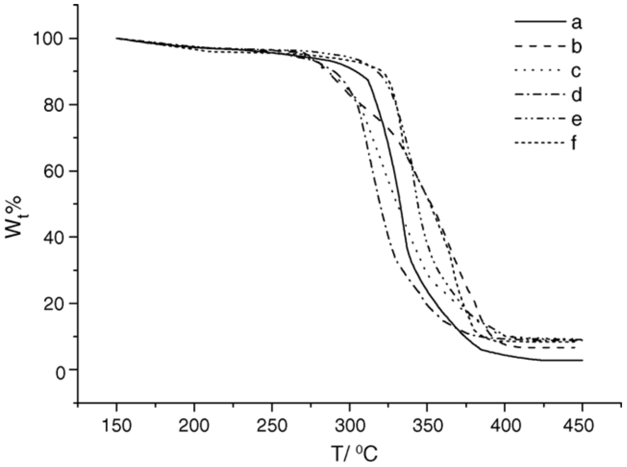


Fig. 1. TGA curves (5 °C/min) for 10:1 by weight blends of waste PMMA with the sulfates in air. (a) PMMA; (b) PMMA + $Fe_2(SO_4)_3$; (c) PMMA + $Al_2(SO_4)_3$; (d) PMMA + $MgSO_4$; (e) PMMA + $BaSO_4$; (f) PMMA + $CuSO_4$.

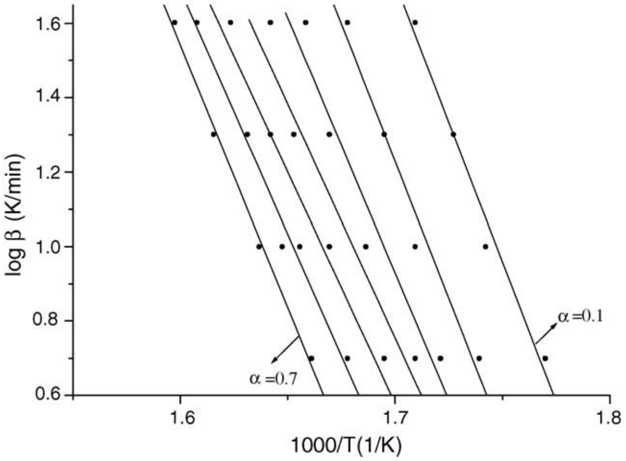


Fig. 2. The dependence of logarithm of heating rate (log β) versus reciprocal absolute temperature (1/T) for the Ozawa method at seven conversions (α) of degradation for waste PMMA in air.

For the same value of α, $g(\alpha)$ is a constant. The straight lines in Fig. 2. show good linearity, which represents the relationship of logarithm of the heating rate (log β) versus 1/T for each value of α.

From the isoconversion curves, apparent activation energies are calculated from the slopes of the lines using the expression,

$$E = \frac{-\text{slope } R}{0.4567} \qquad (2)$$

The apparent activation energies and their average values for the range of conversion 10–70% $\left(E_{\alpha,\text{av}} = \sum_{\alpha=0.1}^{0.7} E_{\alpha,\text{a}}/7\right)$ of the samples, calculate by the Ozawa method, are listed in Table 1.

From Table 1, note that the order of the apparent activation energies for the simple thermal degradation and catalytic degradation of waste PMMA in the presence of sulfate powders is: PMMA + $Fe_2(SO_4)_3$ < PMMA + $Al_2(SO_4)_3$ < PMMA + $MgSO_4$ < PMMA + $CuSO_4$ < PMMA + $BaSO_4$ < PMMA

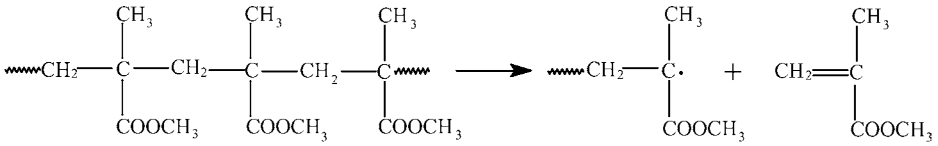
Among five sulfates, note that the presence of $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ powder, different from other sulfates, decrease the E_a of the degradation of waste PMMA by about 100 kJ/mol in comparison with the simple thermal degradation.

3.2. The mechanism of catalytic degradation

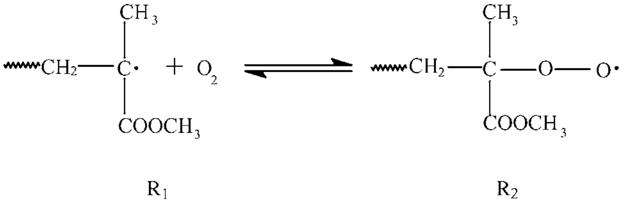
It is known that the simple thermal degradation of PMMA starts with the formation of radicals. When PMMA is heated,

Table 1
Activation energies E_a *(kJ/mol) in air of the sample degradation process calculated by the Ozawa method*

Sample	Conversion							$E_{a,av}$
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	
PMMA	273	269	249	229	227	239	257	249
PMMA + $BaSO_4$	288	221	225	198	189	190	190	214
PMMA + $CuSO_4$	232	212	216	198	202	193	211	209
PMMA+$MgSO_4$	217	220	217	202	166	175	188	198
PMMA + $Al_2(SO_4)_3$	146	158	163	154	155	160	167	158
PMMA + $Fe_2(SO_4)_3$	146	153	151	142	143	138	144	145



Scheme 1.



Scheme 2.

polymer chains undergo scission initially at random, producing radicals, as shown in Scheme 1, then forming the MMA monomer with the β-scission.

However, the conjugative effect of the ester group (–$COOCH_3$) of the side chain reduces the activity of the radical.

In an oxygen-containing atmosphere, the radical R_1 is likely to react with oxygen to form a new polymer radical as shown in Scheme 2 [15]. The peroxy radical R_2 is more thermally stable than R_1 and thus inhibit unzipping of the polymer chain. The formation of the peroxy radical R_2 is exothermic, an increase in temperature should favor the reverse reaction. Therefore, further heating should cause R_2 to ultimately decompose to oxygen and original radical R_1. Here, we suggested a possible mechanism by using the radical R_1 to explain the effect of sulfates on thermal degradation of waste PMMA.

In the presence of sulfates, there is an effect on the thermal degradation of the polymer in those cases where cooperation occurs between the metal ion of the sulfates and the carbonyl oxygen of the polymers, as shown in Scheme 3.

The cooperation will not only weaken the conjugative effect of the ester group, but also inhibit the electron transfer within radicals, which promotes the β-scission of the main chain and accelerate the thermal degradation.

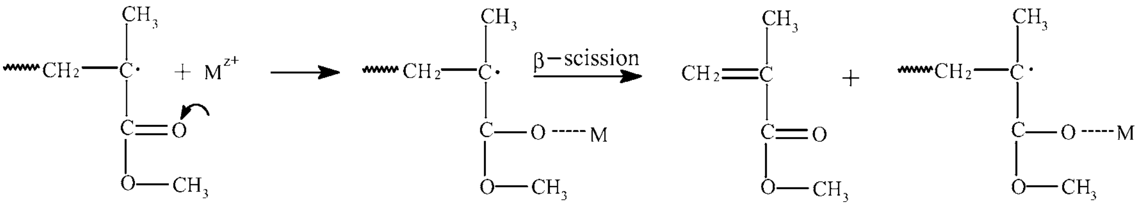
The property of sulfates are similar to that of solid acids [17]. Basically, their catalytic activity has a relationship with their acidity showed after hydrolysis in water. Generally, the stronger the acidity of the sulfate, the stronger its catalytic activity is. The disassociation equilibrium constants (K_a) of various hydrated ions are shown in Table 2 [17]. With the increase of pK_a, the acidity of sulfates decreased gradually after their hydrolysis in water. So the order of the catalytic capability of five sulfates should be: $Fe_2(SO_4)_3 > Al_2(SO_4)_3 > CuSO_4 > MgSO_4 > BaSO_4$.

According to the above paragraph, the order of the apparent activation energies for the catalytic degradation of waste

Table 2
The disassociation equilibrium constant of various hydrated ions

Ion	pK_a[a]
Fe^{3+}	2.2
Al^{3+}	4.9
Cu^{2+}	8.0
Mg^{2+}	11.4
Ba^{2+}	13.2

[a] pK_a represents the negative logarithm of K_a.



Scheme 3.

PMMA should be $PMMA + CuSO_4 < PMMA + MgSO_4$. However, this order is contrary to the experimental result.

According to the soft and hard theory of acid and base [6], a carbonyl is a hard base whereas Fe^{3+}, Al^{3+}, Mg^{2+} are all classified hard acids, and Cu^{2+} is an intermediate one. The principle of this theory is that hard base will combine with hard acids and not combine with soft acids. So it is more difficult for Cu^{2+} to coordinate with carbonyl oxygen than Mg^{2+}, which can explain why $MgSO_4$ shows stronger catalytic capability than $CuSO_4$.

4. Conclusion

Based on our experiments, the different catalytic effects of five sulfates on the thermal degradation of waste PMMA under air were discussed. The order of their catalytic capability is: $Fe_2(SO_4)_3 > Al_2(SO_4)_3 > MgSO_4 > CuSO_4 > BaSO_4$. It was suggested that the coordination between the metal ions of the sulfates and the carbonyl oxygen of the polymers would accelerate the degradation. Generally, the catalytic effects of these sulfates on the polymer degradation have a relationship with their acidity showed after their respective hydrolysis in water. Within a certain range, the stronger the acidity of the sulfate shows, the lower the apparent activation energy of the degradation is. In addition, the catalytic capability of sulfates is also affected by the hard and soft properties of their respective metal ions.

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