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TG-DTG study on the thermooxidative stability of AS containing different stabilizers[1]

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Abstract

The thermooxidative stability of acrylonitrile–styrene copolymer (AS) containing different kinds of stabilizers was determined by thermogravimetric analysis (TGA) in air. According to the Coats–Redfern equation, the kinetic parameters were evaluated from the TG curves. The results showed that 1010 combining DPDP had obvious synergistic effect on AS thermooxidative stability and the new type nonpoisonous rare-earth composite (REC) thermostabilizer could effectively inhibit the degradation of AS in air. The degradation temperatures of AS added Stabilizers were increased and the activation energy (E) of degradation reaction which ranged from 228 to 253 kJ mo1^{-1} was approximately 50±10 kJ mo1^{-1} larger than that of AS resin (189 kJ mo1^{-1}).

Keywords: AS; TGA; Rare earth; Stabilizer; Thermooxidative degradation

1. Introduction

It is well known that polymer materials degrade during the processing or application influenced by the oxygen, thermal and so on, which makes the materials age and decrease the properties in advance [1]. Thus, it is necessary to inhibit plastics degradation by adding stabilizers during the processing. Generally speaking, a whole stabilizing system of plastics includes three parts: main antioxidant, co-antioxidant and acidoid-absorbent. The thermooxidative degradation of polymer is a radical reaction, and like other radical reaction, it proceeds by a free radical chain mechanism. The main antioxidant, such as hindered phenols and aromatic amines, also known as chain breaking antioxidant, can suppress the normal propagation processes either by reaction with peroxy radical or by reaction with alkyl radical. The co-antioxidant, such as phosphites, also known as peroxide decomposer, can react with hydroperoxides to give nonradical products. Using this two kinds of antioxidants simultaneously may produce synergistic stabilizing effect on polymers, which makes polymers reach "real" stabilization. Acidoid-absorbent, also named thermal stabilizer, such as stearates, can absorb the acidoid resulting from the process of polymer degradation, which deactivates the catalytic effect of acidoid on the degradation [2,3]. In practical application, we shall choose the proper stabilizers according to the material properties and processing technology.

The stabilization of AS is important for its performance. The thermal stabilization of As has been discussed by a number of authors [4–6]. This paper

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has investigated the effect of different stabilizing system on the thermooxidative stability of AS by thermogravimetric analysis. Treated with Coats–Redfern equation the Kinetic parameters of the thermooxidative degradation of AS added different stabilizers were evaluated from the TG curves. The effect of REC on AS stability has also been investigated specially. REC (rare-earth composite thermo-stabilizer) is a new style stabilizer developed in recent years using the abundant resource of light rare earth in China, which has been produced in commercial scale and awarded 'The Invention & Innovation Sci-Tech Star for the Remarkable Achievements in Science & Technology Invention & Innovation by UN TIPS National Bureau in China. Being nonpoisonous and flavorless and with other special properties, such as lubrication, fluxibility, good dispersity, outstanding plasticization and so on [7], REC has been mainly applied to PVC at present. However, there are few theory researches about the stabilizing mechanism of REC, especially, there is no literature report about the application of REC to AS. It is significant to study and spread the application of REC to AS.

2. Experimental

2.1. Materials

1. AS: manufactured by Asashi, Japan, AS783.
2. Main antioxidant (M): 1010 (Tetrakis[methylene-3-(3′,5′-di-*tert*-buty1-4′-hydroxyphenyl)propionate]methane).
3. Co-antioxidants (C): DPDP(Diphenylisodecyl phosphite), TPP (Triphenyl phosphite), 618 (Dipstearylpentaerythrital cylicdiphosphite), and 168 (tris(2,4-di-tertbutylphenyl phosphite).
4. Thermal stabilizers (T): ZnSt (Zinc stearate), CaSt (Calcium stearate), PbSt (Lead stearate), TLS(Tribasic Lead Sulphate), RE (rare earth compound), and REC.

All aids were purchased from domestic markets, except the RE (prepared in laboratory).

2.2. Sample preparation

AS resin was (or not) mixed fully with different stabilizer system, respectively, (the base ratio was M/C/T=7/3/5 w/w), then was plasticized in a XSS-300 blender at 240°C and 32 rpm for 6 min, and then a few blends were broken to prepare TGA specimens.

2.3. Methods

TG studies were conducted by using Perkin-Elmer TGS-2 type thermogravimetric analyzer in a flow air of 45 ml min^{-1} at a heating rate of 10°C min^{-1}, a sample mass of 5–6 mg and temperature ranged from 25°C to 550°C. All specimens were dried in an air oven at 80°C for 2 h before test.

2.4. Kinetic parameters evaluation

According to the Coats–Redfern equation [8]:

$$\ln[F(\alpha)] = \ln[(AR/\beta E)(1 - 2RT/E)] - E/RT,$$

As $n \neq 1$

$$\ln[F(\alpha)] = \ln[(1 - (1 - \alpha)^{1-n}/T^2(1 - n)],$$

As $n=1$

$$\ln[F(\alpha)] = \ln[-\ln(1 - \alpha)/T^2],$$

where E, A, β, R, α and T represent reaction energy, frequency factor, heating rate, gas constant, reaction degree and absolute temperature, respectively). Given different n, a plot of ln[F(a)] against $1/T$ should yield a straight line by the least square method. When the line is best fit, the value of n is the correct order of the reaction, and then E and A can be evaluated from the slope and intercept of the line.

3. Results and discussion

3.1. Effects of different co-antioxidants phosphite on thermooxidative stability of AS

The thermooxidative degradation of AS added different phosphites was investigated. Fig. 1 Shows the TG-DTG curves of Sample 1. The TG-DTG curves of other samples are similar to it. The curves indicated that the termooxidative degradation of AS was a single-step chain reaction, which accorded with the literature result [9]. The typical degradation temperatures obtained from TG curves were listed in Table 1. The results showed that the beginning weight loss

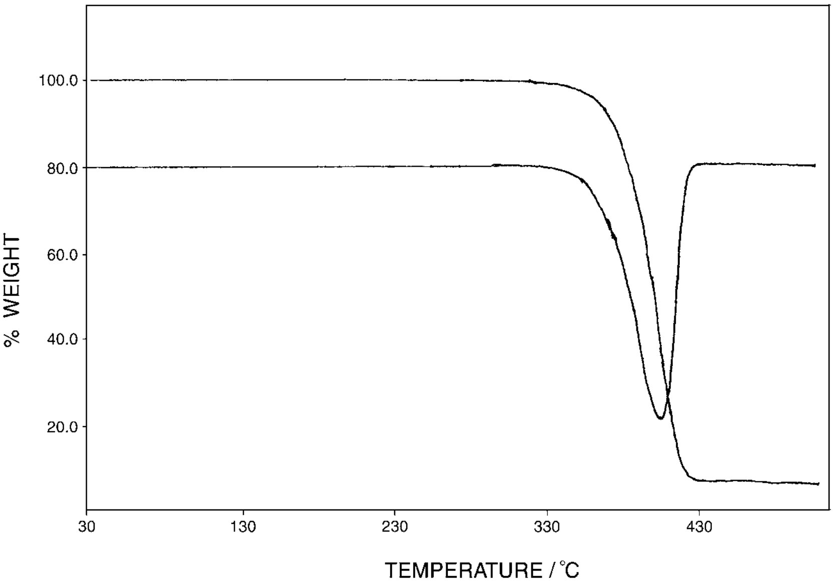

Fig. 1. TG-DTG plot of AS added 1010/DPDP/REC at a heating rate of 10°C min^{-1} and an air flow rate of 45 ml min^{-1}.

temperature of AS added no stabilizers was much lower, whose micro-weight loss temperature (0.4% weight loss temperature, T_b, 193.2°C) and 5% weight loss temperature (T_l) were about 20–60°C and 15°C, respectively, lower than those of AS added different stabilizers. The T_b of sample 2 was the highest with 270°C, T_l and the onset temperature (T_o) of sample 1 were the highest than those of any other samples with the value of 364.4°C and 385.4°C, respectively. The maximum weight loss temperature (T_m) of sample 3 was the highest. T_b ,T_l, T_o, T_m of each sample added stabilizers were higher than those of AS resin added no stabilizers. These indicated that it is necessary to add stabilizers in commercial AS and the thermooxidative stability of AS were improved after being added stabilizers, and the synergistic effect of 1010/DPDP system was the best. Since the T_l of sample 1 was the highest, AS containing such stabilizing system must have the best processing stability. The system of 1010/618 had better effect also. As DPDP is liquid, While 618 is dustlike particles in the ordinary state, we shall choose the proper phosphite according to the actual processing technology.

3.2. *Effect of different thermal stabilizers on AS thermooxidative stability*

The TG-DTG Curves' profiles of AS added different thermal stabilizers were similar to Fig. 1. Table 2. lists the degradation temperatures of each sample. The

Table 1
The degradation temperatures of AS added different co-antioxidants in air

Sample No.	C	T_b (°C)	T_l (°C)	T_o (°C)	T_m (°C)
0	–	193.2	343.4	378.8	395.1
1	DPDP	245.9	364.4	385.4	405.3
2	168	270.0	359.5	378.9	402.3
3	TPP	229.0	358.2	378.2	410.0
4	618	239.9	359.5	380.3	401.6

T_b, T_l, T_o, T_m are the temperatures of 0.4% weight and 5% weight loss, onset and maximum weight loss, respectively. Each sample has been 1010 and REC.

Table 2
The degradation temperatures of AS added different thermal stabilizers in air

Sample No.	T.S.	T_b (°C)	T_l (°C)	T_o (°C)	T_m (°C)
0	–	193.2	343.4	378.8	395.1
1	REC	245.9	364.4	385.4	405.3
2	RE	210.8	367.3	391.6	411.4
3	ZnSt	239.6	363.1	383.7	407.2
4	CaSt	230.5	357.4	383.5	404.8
5	PbSt	251.8	361.4	386.8	406.2
6	TLS	247.8	360.1	382.8	402.2

T_b, T_l, T_o, T_m are the temperatures of 0.4% and 5% weight loss, onset and maximum weight loss, respectively. Each sample has been added 1010 and DPDP.

results showed T_l, T_o, T_m of sample 2 were the highest with the value of 367.3°C, 391.6°C and 411.4°C, respectively, while, T_l of sample 4 was the lowest with 357.4°C and T_b of sample 5 was the highest with 251.8°C. The degradation temperatures of other samples were similar except sample 0 which added no stabilizers. The studies of the effect of thermal stabilizers also indicated it is necessary to add stabilizers in commercial AS. As we know, being poisonous to human, PbSt and TLS shall be restricted to use, although they had good effects. ZnSt would promote the degradation reaction when added too much or the processing temperature was too high [10]. REC is a new type multi-functional aid as what is described previously in this paper. RE was prepared in lab, which was used as thermal stabilizer for a control experiment to REC in order to investigate the stabilizing property of rare earth compound in more detail. To sum up, we think REC is the best fit thermal stabilizer for AS.

3.3. Kinetics of AS degradation in air

The kinetic parameters of AS thermooxidation degradation were obtained according to the Coats–Redfern equation, which were listed in Table 3. The reaction order of each sample was similar with an average value of 0.67. The activation energies of AS added stabilizers which ranged from 228 to 253 kJ mol^{-1} was approximately 50±10 kJ mol^{-1} larger than that of AS resin added no stabilizers. In accordance with the stabilizing mechanism of stabilizers and the equation [11]: $E{=}E_p{+}1/2E_i{-}1/2E_t$ (Where E_i ,E_p and E_t are the activation energies for the initiation, propagation and termination steps, respectively), the E_t of AS degradation must decrease after being added stabilizers, which resulted in the increase of E. Using the Arrhenius equation: $K{=}A \exp(-E/RT)$, the reaction speed constant (k) of each sample degradation at 300°C in air were evaluated and listed in Table 3. The k value of sample 1 added 1010/

Table 3
The kinetic parameters of AS added different stabilizers degradation in air

Sample No.	Stabilizers	E (kJ mol^{-1})	A	n	$K/10^{-4}$	R
0	–	189.0	1.26×10^{14}	0.68	7.36	0.999
1	1010/DPDP/REC	248.6	6.90×10^{18}	0.67	1.48	0.999
2	1010/DPDP/RE	238.6	8.00×10^{17}	0.67	1.40	0.999
3	1010/DPDP/ZnSt	241.9	2.04×10^{18}	0.67	1.79	0.999
4	1010/DPDP/CaSt	228.1	1.94×10^{17}	0.68	3.08	0.999
5	1010/DPDP/PbSt	244.4	3.61×10^{18}	0.67	1.87	0.999
6	1010/DPDP/TLS	236.0	8.46×10^{17}	0.68	2.56	0.999
7	1010/168/REC	241.9	2.88×10^{18}	0.67	2.52	1
8	1010/TPP/REC	236.5	1.12×10^{18}	0.68	3.05	0.999
9	1010/618/REC	253.3	2.21×10^{19}	0.67	1.77	0.999

k: The reaction speed constant of AS degradation at 300°C in air.

DPDP/REC stabilizers was the least one in all sample (except sample 2). It is attributed to the excellent inhibiting effect of 1010/DPDP/REC stabilizing system.

4. Conclusion

From the TG-DTG studies of stability on AS containing different stabilizers, it is found that, adding stabilizers promoted the thermooxidative stability of AS significantly and the micro-weight-loss temperature, which had effect on the performance of the finished products, was increased 20–60°C. 1010 combining DPDP had obvious synergistic effect on AS long-term thermooxidative stability. The new type nonpoisonous rare-earth composite (REC) thermal stabilizer could restrain effectively the degradation of AS. Treated with Coats–Redfern equation, it is found that the activation energy of AS thermooxidative degradation was improved about $50\,\mathrm{kJ\,mol^{-1}}$ after being added stabilizers. In all stabilizer systems in question, the 1010/DPDP/REC system was the best one for AS.

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