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ROLE OF METAL OXIDES IN THE THERMAL DEGRADATION OF BISPHENOL A POLYCARBONATE

M. C. Gupta and S. G. Viswanath[1]

Chemistry Department, Nagpur University
[1]Laxminarayan Institute of Technology, Nagpur University, Nagpur 440010, India

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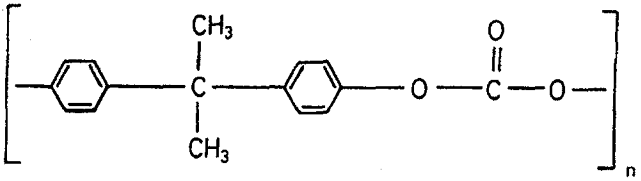
Abstract

Thermal degradation of poly(2,2',-propane-bis-4-phenyl carbonate) or bisphenol A polycarbonate (PC) alone and in presence of metal oxide as additives have been discussed. Thermal degradation of PC in presence of metal oxide additives may be surface induced catalytic thermo-oxidative degradation. Some metal oxides retard thermo-oxidative degradation of PC.

Keywords: kinetics, polycarbonate

Introduction

Polycarbonate or bisphenol A polycarbonate (PC) is commercially available, poly(2,2,-propane-bis-4-phenyl carbonate), i.e.



which has many attractive and useful properties. However, change in these properties results in the modification of chemical structure of the polymer induced by degradation. Davis *et al.* [1] observed that PC possesses high degree of thermal stability and processing at high temperature leads to thermo-oxidative degradation due to chain scission and crosslinking. Gupta *et al.* [2] studied thermo-oxidative degradation in air and reported that this is a two-step process with activation energy 125 and 230 kJ mol^{-1} respectively. Various other studies like the effect of UV radiation, high energy radiation [3], weathering [4] and aging [5–7] have been reported and suggested that side chain and ring photo oxidation occur by the photo Fries mechanism path way resulting in chain scission and crosslinking. The object of the present studies is to understand the kinetics of the thermal degradation of PC in presence of metal oxide additives through kinetic analysis.

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Experimental

Materials

Bisphenol A polycarbonate commercially available Lexan, manufactured by G.E. Company, USA is used in the studies. Various metal oxides were used as additives to bisphenol A polycarbonate for studying thermal degradation. Their physical characteristics and source are listed elsewhere [8].

Sample preparation

The commercial PC sample was purified by repeated dissolution in THF and precipitation by acetone [9]. This purified sample is dried and dissolved in chloroform. To this solution metal oxide (to give polymer to oxide ratio 5:1) was added. After stirring for 1/2 h, the solvent was removed by evaporation. The residue was metal oxide coated with a film of PC.

TG

TG curves were recorded on a Perkin-Elmer TG Thermal Analysis system TGS2 in a flow of nitrogen gas at a heating rate of 10 K min^{-1} using 5–10 mg sample at Regional Sophisticated Instrumentation Center, Nagpur University.

Results and discussion

TG curves in nitrogen atmosphere for the degradation of PC and PC in presence of some metal oxide additives are shown in Fig. 1. It is evident from Fig. 1 that in most cases degradation is a single stage process and residue left varies between 15–35%. The residue in case of PC is 29.95%, which may be due to carbon char. However, in presence of metal oxides it is less than the carbon char residue left for PC. The melting temperature of PC is 265°C and this melting temperature is influenced by the additives. That means, during TG the reaction occurs between polymer and additive at lower temperature. These observations indicate that at higher temperature PC residue does react with metal oxides leading to thermo-oxidative degradation and formation of a volatile products from polymer melt. The onset temperature of degradation in case of PC is 450°C, whereas for samples with metal oxide additives is less than 450°C which indicates the catalysis of degradation by metal oxides.

Kinetic parameters for thermal degradation

TG data for thermal degradation of PC with and without metal oxide additives is analyzed by newly developed methods of Viswanath and Gupta [10],

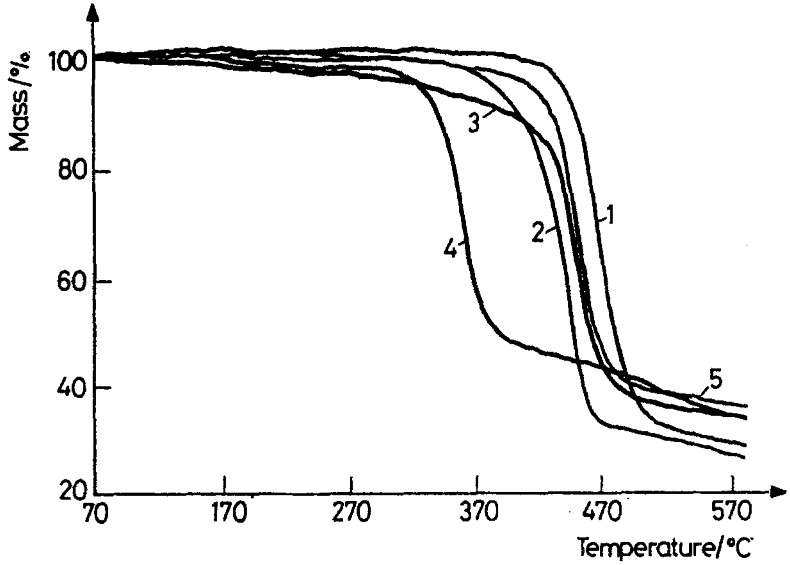


Fig. 1 TG curves of (1) PC and metal additive (2) CuO, (3) Al_2O_3, (4) MoO_3 and (5) CeO_2

which use the inflection point data to estimate all nonisothermal parameters. One of the methods is briefly given here.

The fraction decomposed, C is defined as,

$$C = \frac{W_o - W_T}{W_o - W_f} \tag{1}$$

where W_o, W_f and W_T are the initial mass, final mass and mass of the substance at temperature, T respectively. The Arrhenius rate equation is written as

$$\frac{\mathrm{d}C}{\mathrm{d}T} = (1 - C)^n \frac{A}{\beta} \exp\left(-\frac{\Delta E_a}{RT}\right) \tag{2}$$

where n, A, β, and ΔE_a are order, pre-exponential factor, rate of heating and activation energy of a reaction respectively. At the inflection point the second derivative, $(\mathrm{d}^2C/\mathrm{d}T^2) = 0$ and $(\mathrm{d}C/\mathrm{d}T)$ is maximum. Hence Eq. (2) can be written as

$$\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)_s = \frac{1 - C_s}{n} - \frac{\Delta E_a}{RT_s^2} \tag{3}$$

The subscript defines the quantities at inflection point respectively, and Eq. (3) is rearranged as

$$\frac{\Delta E_a}{R}=\frac{nT_s^2}{1-C_s}\left(\frac{\mathrm{d}C}{\mathrm{d}T}\right)_s \qquad (4)$$

($\Delta E_a/R$) value from Eq. (4) is substituted in the Eq. (2) and then logarithmic form of equation is written as

$$\ln\frac{\mathrm{d}C}{\mathrm{d}T}=n\left[\ln(1-C)-\frac{\theta_s}{T}\right]+\ln\frac{A}{\beta} \qquad (5)$$

where $\theta_s=[T^2/(1-C_s)](\mathrm{d}C/\mathrm{d}T)_s$. The plot of $\ln(\mathrm{d}C/\mathrm{d}T)$ *vs.* $\{\ln(1-C)-\theta_s/T\}$ gives a linear plot with slope equals to n, order of reaction and intercept equals to (A/β). By substituting the value of n in Eq. (4), ΔE_a is obtained. If the n value obtained in this way is substituted in the logarithmic form of Arrhenius equation $\ln k$ *vs.* $1/T$ plots can be obtained.

Kinetic analysis

The kinetic parameters so estimated using TG data are presented in Table 1 and plot of $\ln A$ *vs.* ΔE_a is shown in Fig. 2. Figure 2 shows a linear relationship between $\ln A$ and ΔE_a though there are some deviations. This is represented in equation form as,

$$\ln A = 0.171\ \Delta E_a - 3.84 \qquad (6)$$

Table 1 Kinetic parameters for the thermal degradation of PC in presence of metal oxides

S. No.	Additive	n	ΔE_a/kJ mol^{-1}	A/s^{-1}
1	V_2O_5	1.2	180.5	$8.4\cdot10^{11}$
2	ZrO_2	0.8	231.3	$5.3\cdot10^{14}$
3	CuO	1.1	238.5	$9.6\cdot10^{15}$
4	MoO_3	1.2	253.9	$3.0\cdot10^{19}$
5	ZnO	0.8	254.1	$2.4\cdot10^{17}$
6	Al_2O_3	1.4	271.1	$2.3\cdot10^{18}$
7	Cu_2O	1.0	295.4	$6.2\cdot10^{19}$
8	TiO_2	2.1	336.6	$9.2\cdot10^{23}$
9	Cr_2O_3	1.2	366.3	$1.9\cdot10^{25}$
10	NIL	2.1	375.0	$1.9\cdot10^{23}$
11	CeO_2	2.2	434.9	$7.3\cdot10^{29}$
12	MnO_2	1.5	501.6	$8.8\cdot10^{36}$
13	SnO_2	1.1	731.4	$7.2\cdot10^{52}$

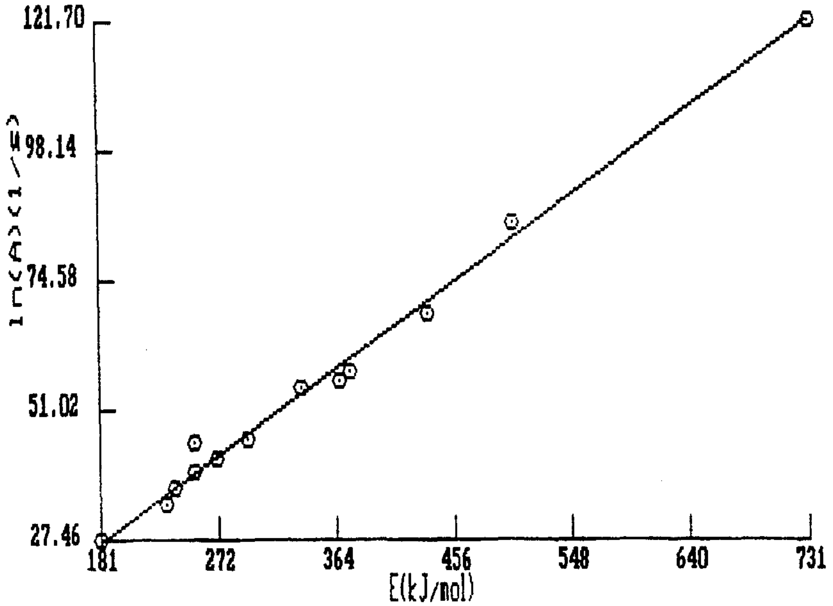


Fig. 2 ln$A$ vs. ΔE_a plot for thermal degradation of PC with and without metal oxide additives

The linear relation is treated as an apparent kinetic compensation effect [8, 11, 12]. Comparing this with logarithmic form of Arrhenius equation, the rate constant is 0.022 and the temperature is 702 K. At this temperature rate constant of all metal oxide catalyzed reactions should be same. We can also propose that the existence of such relationship may be due to either reactions follow similar mechanism or an artifact of error in kinetic data.

However, it has been suggested [13, 14] that true compensation effect will be observed only when ln$k$ vs. $1/T$ plots exhibit a point of concurrence. However, the TG data on PC do not exhibit such point of concurrence as shown in the Fig. 3. Ranganathan *et al.* [15] have interpreted this nonconcurrence due to the dependence of reaction on the intrinsic properties or surface properties of the metal oxides but not on the bulk properties. Therefore it is suggested that the linear relationship between ln$A$ and ΔE_a and nonconcurrence point in the plot of ln$k$ vs. $1/T$ shows that the thermal degradation of PC in presence of metal oxides is surface induced catalytic thermo-oxidative degradation.

Discussion

It is observed from the Table 1 that the degradation of PC in presence of nitrogen atmosphere at elevated temperature is a complex process as noted from the non-integer order of reaction. Since the order of reaction for PC is nearer

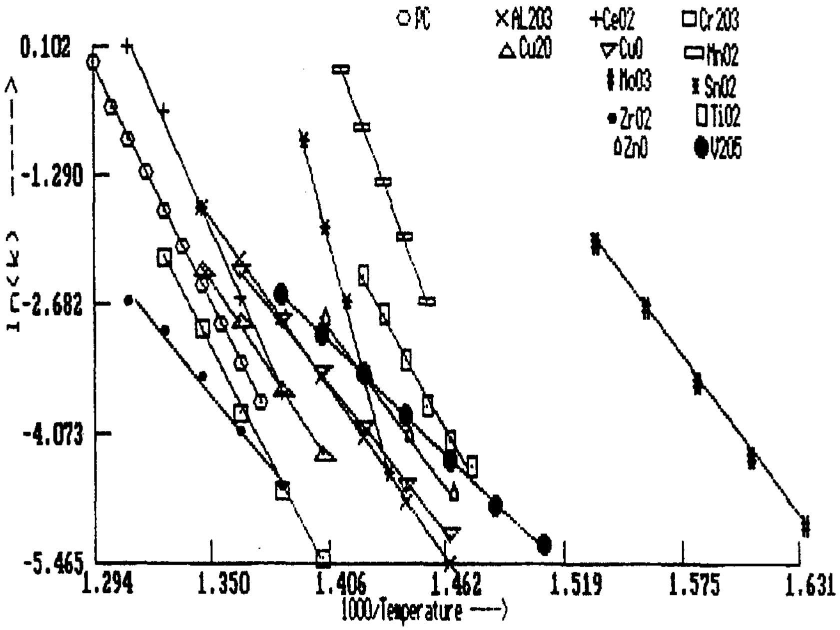
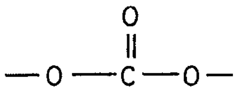


Fig. 3 ln*k* *vs.* 1/*T* plots for thermal degradation of PC with and without metal oxide additives

to two, it may be assumed that the thermo-oxidative degradation of PC follow a second order kinetics. Similarly, it may be assumed that the degradation in presence of metal oxides mainly follows first order kinetics. But for those metal oxides whose order deviates large from whole number may be treated as very complex reaction. In PC there are two links which are susceptible to degradation. At low temperature the carbonate link



$$—O—\overset{\overset{\displaystyle O}{\|}}{C}—O—$$

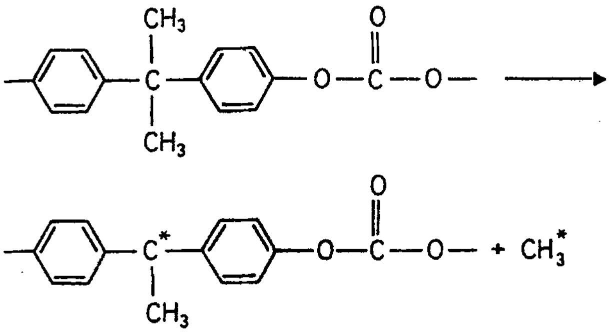
may decompose by the elimination of CO_2 or CO whereas at higher temperature loss of methylene radical from isopropylidene can occur [16]. The degradation of carbonate group leads to a series of reactions by elimination of CO_2 and CO without undergoing free radical reaction which has been found to be a first order reaction by Davis *et al.* [1] in their studies by monitoring the average molecular mass as function of degradation time, at different temperatures. However, if carbonate bond in PC produces a peroxyradical as O–O bond of alkyl peroxide (autooxidation), abstraction of hydrogen by peroxide radical is the rate determining step in such autooxidative degradation process [17, 18]. This can be written as

$$R\text{—}O\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—} \longrightarrow R\text{-}O_2^* + CO$$ (Fast reaction)

$$R\text{-}O_2^* \longrightarrow \text{products}$$ (Slow, rate determining step)

With increasing rate constant, the rate of oxidation is increased and yield of peroxide will increase. Thus it would be second order kinetics.

The degradation at isopropylidene site would be through the formation of tertiary free radical by the removal of CH_3^*. This free radical is eventually more stable. In such case branching and crosslinking will predominant when volatile products are removed [18]. From TG curves, the weight loss from 170°C to onset temperature is very small which may be interpreted as crosslinking. When crosslinking or branching occurs, only small amount of mass loss takes place due to elimination of hydrogen or weak group. This mass loss can not be due to water loss or volatile matter present in substance since it is above 150°C.



(Fast reaction at high temperature)

(Isopropylidene free radical)

Isopropylidene free radical ⟶ crosslinked and/or Branched chain products (Slow, rate determining step)

It will be second order reaction.

However, in presence of metal oxide additives, it is probable that this above step also involves peroxide free radical formation [19] and these peroxide free radicals interact with metal oxides before decomposition. In such cases the rate determining step is the decomposition of metal oxide peroxide radical adduct which may be written as

$$RO_2^* + M_xO_y \longrightarrow RO_2\text{–}M_xO_y^*$$ (Fast reaction)

$$RO_2\text{–}M_xO_y^* \longrightarrow \text{products} + M_xO_y$$ (Slow, rate determining step)

Hansen *et al.* [20] have studied the effect of copper oxides on the degradation of polypropylene and observed that Cu compounds are effective catalysts for the decomposition of tertiary alkyl peroxides. In case the adduct formation is a slow step as it may be in case of Ce, Mn, Sn, and Ti oxides the effect would be retardation of degradation. The activation energy may be large and the decomposition of adduct would be fast step. It has been observed that Sn, compounds leads to retardation of degradation of PC [21].

Conclusion

The studies suggest that the thermal degradation of PC follows a second order rate kinetics which could be due to crosslinking and branching resulting from the degradation which is by the formation of tertiary or peroxide free radical. However in presence of metal oxides, these metal oxides interact with free radical and peroxide-metal oxide adduct formation may result which subsequently decompose to non-peroxide products. Thus chain scission will predominant in presence of metal oxides and the reaction will be largely first order. The presence of some oxide may also retard the degradation of PC. Thus there will be an apparent reaction rate compensation.

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