



# Effect of shear condition on the thermal stabilization of ethylene–propylene–carbon monoxide terpolymer



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## ABSTRACT

The thermal decomposition behavior of the terpolymer of ethylene, propylene, and carbon monoxide (EPCO), stabilized by calcium hydroxyapatite (CHA) as an acid scavenger and 2,2'-oxamidobis-[ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (OHP) as a radical scavenger, was investigated in terms of shear, temperature and stabilizer composition. The optimum composition of two stabilizers was affected by shear condition as well as thermal history. The thermal stability at the static state evaluated by DSC indicated that the simultaneous use of CHA and OHP produced a synergistic effect and the optimum composition of CHA/OHP ranged from 4/1 to 8/1 by wt at the total content of 0.5 wt%. However, dynamic rheological analysis revealed that shearing changed the optimum composition of the stabilizers to 7/1 by wt but had little effect on the total stabilizer content. In addition, the synergistic effect was not observed at the particular composition of 1/4 by wt. The increase of melt viscosity of EPCO with time ascertained that the thermal decomposition of EPCO accompanied crosslinking through the intermolecular aldol condensation reaction.

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## 1. Introduction

Owing to excellent physical properties the aliphatic polyketone is one of the most promising candidates of high performance polymers. It was first announced in 1950s by Shell Co [1–3]. The first generation was the copolymer of ethylene and carbon monoxide (ECO) in a perfectly alternating sequence, whose  $T_m$  was as high as 260 °C [2,4]. ECO is developed as engineering fibers by wet spinning process. To be used as melt-processable plastics the terpolymer of ethylene, propylene, and carbon monoxide (EPCO) was developed (Scheme 1) [5]. Owing to excellent mechanical properties and high resistance to chemicals it is expected to be used in the automotive and other industries by replacing nylon 6 and nylon 66. In spite of many advantages in mechanical properties the aliphatic polyketones have a serious problem in melt and even in solution processes because of degradation [6–10]. ECO is reported to be thermally degraded in two ways. One is the aldol condensation caused by residual acid catalyst [11–13]. Polymer chains are crosslinked or form the ring structure [14]. The other is degradation by radicals, which brings about chain scission [7,8,15]. Shkolnik and

Weil [16] reported that calcium hydroxyapatite (CHA) acted as an effective acid scavenger.

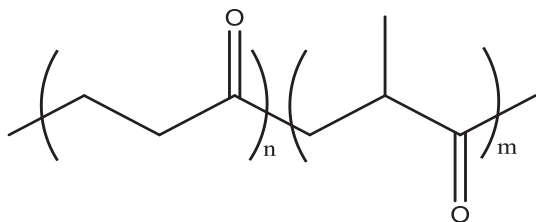
Most studies on the thermal stabilizers have been focused on ECO but little literature on the thermal stability of EPCO is available [17]. Further, it has a practical significance to understand the effect of shear condition on the thermal stabilization of EPCO because shearing is unavoidable in the melt fabrication processes. We selected two kinds of stabilizers, CHA as an acid scavenger and 2,2'-oxamidobis-[ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (OHP) as a radical scavenger. The effect of the thermal stabilizers on EPCO was investigated in terms of the composition and total content of the two stabilizers at the dynamic as well as static states.

## 2. Experimental

### 2.1. Materials

EPCO (melt index = 67 g/10 min at 240 °C and 2.16 kg load) was kindly supplied by Hyosung Co. (Korea). CHA and OHP were purchased from Budenheim Co. (Germany) and Crompton Co. (USA), respectively, whose details are given in Table 1. The raw materials were vacuum dried for 12 h prior to use. Four kinds of stabilized EPCO samples listed in Table 2 were prepared as follows. CHA and OHP were dispersed and dissolved in acetone, and the EPCO powder was immersed in the solution to uniformly coat the stabilizers

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**Scheme 1.** The chemical structure of EPCO.

on the powder. Then acetone was evaporated and dried. The dried samples were melt-mixed in an internal mixer (Haake PolyDrive; Thermo Electron Co., USA) at 240 °C, and at 80 rpm for 4 min.

## 2.2. Measurement of physical properties

Thermal properties were measured by differential scanning calorimetry (DSC Q20; TA Instruments, USA) in the nitrogen atmosphere. The samples were heated to 280 °C at the scan rate of 10 °C/min to obtain melts. The non-isothermal crystallization behavior of EPCO was examined at the heating and cooling rate of 5 °C/min. All samples (5 mg each) were kept at 240 °C for 3 min to obtain an equilibrium state.

Rheological properties were measured by Advanced Rheometric Expansion System (ARES; TA Instruments, USA). In ARES measurement, a parallel plate geometry was adopted whose diameter and gap were 25 and 0.8 mm, respectively. The strain level was 5%. The specimens were melted at 230, 240, and 250 °C between the parallel plates, and the excess flushed-out samples during gap setting were trimmed off. The specimens were kept for 150 s at the given temperatures to remove the residual stress, and then the time sweep measurement was conducted at 3 rad/s.

The FT-IR spectrum was obtained by Nicolet Magna-IR 760 (USA) coupled with an attenuated total reflectance accessory between 600 and 4000  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  resolution.

## 3. Results and discussion

Fig. 1 shows the DSC heating thermograms of EPCO containing two stabilizers, CHA and OHP, with different compositions at the

**Table 2**  
Formulation of stabilized EPCO samples.

Sample code	EPCO (g)	CHA (g)	OHP (g)	Nucrel 535 (g)
C-0.1	60	0.06		0.12
C-0.3	60	0.18		0.12
C-0.5	60	0.30		0.12
C-0.7	60	0.42		0.12
C-0.9	60	0.54		0.12
O-0.1	60		0.06	0.12
O-0.3	60		0.18	0.12
O-0.5	60		0.30	0.12
O-0.7	60		0.42	0.12
O-0.9	60		0.54	0.12
C/O-0/5	60		0.3	0.12
C/O-1/4	60	0.06	0.24	0.12
C/O-2/3	60	0.12	0.18	0.12
C/O-3/2	60	0.18	0.12	0.12
C/O-4/1	60	0.24	0.06	0.12
C/O-5/0	60	0.3		0.12
C/O-7/1-0.1	60	0.048	0.012	0.12
C/O-7/1-0.3	60	0.144	0.036	0.12
C/O-7/1-0.5	60	0.24	0.06	0.12
C/O-7/1-0.7	60	0.336	0.084	0.12
C/O-7/1-0.9	60	0.432	0.108	0.12

total loading level of 0.5 wt% (To have clear presentation curves of CHA/OHP-5/1 to 8/1 by wt were omitted in figure because they are similar and overlapped with that of CHA/OHP-4/1 by wt). The thermal degradation of EPCO takes place by chain crosslinking and/or chain scission, which would generate peaks on the DSC curve. However, distinguishable peaks are not observed on the curve. This suggests that two types of chemical reactions caused by acid catalyst and radical occur simultaneously. When the degradation of EPCO takes place with acid catalyst multi-bonding is formed by aldol condensation leading to an exothermic reaction. On the other hand, degradation by random chain scission of EPCO leads to an endothermic reaction. Consequently, the peak is not observed because of the offset effect in thermodynamics.

The thermal degradation surely lowers the degree of crystallization of EPCO whether chain scission or crosslinking takes. Hence, the change of crystallization temperature ( $T_c$ ) and heat of crystallization ( $\Delta H_c$ ) can be measures of the extent of thermal degradation of EPCO. The first and second cooling DSC thermograms of EPCO containing CHA and OHP with different compositions at the total

**Table 1**  
Chemical structure and molecular weight of stabilizers.

Stabilizer name	Chemical composition	Molecular weight (g/mol)
CHA		502
OHP		697

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