



# THERMAL STABILITY AND COMBUSTION BEHAVIORS OF LLDPE/SILICA NANOCOMPOSITES

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## Abstract

In this paper, nano-silica with and without surface modification was used to prepare LLDPE/silica composites whose thermal stability and combustion behaviors were investigated by thermal gravimetric analysis (TG) and cone calorimeter (CONE), respectively. The results of transmission electron microscopy (TEM) showed that surface modification greatly promoted the dispersibility of nano-silica in LLDPE. As a result of TG, composites with surface modified nano-silica possessed better thermal stability than that with pristine nano-silica. The results of CONE proved better combustion properties of composites with surface modified nano-silica by showing reduced heat release rate (HRR) and mass loss rate (MLR).

## 1 INTRODUCTION

In recent years, polymer/nano-particle composites have attracted much attention because of their remarkable properties, including mechanical strength, impermeability to gases, flame retardancy, etc [1-3]. Much emphasis has been given to the study of polymer/inorganic nanocomposites in search for materials with unique mechanical, electrical and thermal properties [4, 5].

Nano-silica with typical particle size of 10~50nm is widely used as fillers to improve the mechanical and thermal properties of polymers, such as poly(methyl methacrylate) [6], phenolic resin [7], polyolefins [8] and many thermoplastics. Although nano-silica is found to be an effective enhancing filler, it is very difficult to disperse homogeneously due to its large surface area and poor compatibility with polymer [9]. Wang et al. studied the effect of the interfacial structure on the thermal stability of PMMA/silica composites [10]. They found that the thermal stability was affected by the interfacial structure of the composites and the thermal

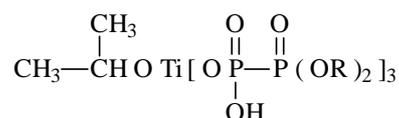
decomposition temperatures of the composites were similar to PMMA and in some cases even decreased with the addition of silica. Surface modification is a usual way to obtain composites with good mechanical properties [11]. However, few reports can be found on the effects of surface modification of nano-silica on thermal stabilities of polymers, not more than combustion properties.

Polyethylene, is one of the most widely used plastics in large volume [12-14]. Nanotechnologies are considered a useful way to overcome the disadvantages of PE, such as low toughness and low service temperature, and to enhance the thermal stability. In this paper, nano-silica after different surface modification was added into linear low density polyethylene to prepare LLDPE/silica nanocomposites. Effects of surface modified silica on the dispersibility of silica in PE, the thermal and combustion properties of nanocomposites were investigated by TEM, TG and CONE.

## 2 EXPERIMENTAL

### 2.1 Materials

Polyethylene (LLDPE, 7042) was a commercial product from Daqing Petrochemical Company. Fumed silica with an average particle size of 20 nm was obtained from Nanjing Haitai Nano-tech Company. Fumed silica without surface treatment was labeled as Si-1. Silica treated with titanium ester was labeled as Si-2. The structure of titanium ester were described in Scheme. 1.



Scheme. 1 Molecular formula of titanium ester

### 2.2 Preparation of composites

PE/silica composites were prepared by melt mixing on rheometer (Hapro Electrical Company,

Harbin, China) with a rotor speed of 60 rpm at 150°C according to the formulations listed in Table 1. After mixing, the samples were hot-pressed under 10 MPa to sheets of suitable thickness for 10 min at 160°C.

Table 1 Formulations for sample preparation

Sample	LLDPE	Silica	
		untreated	Treated with titanium ester
PE/Si-1	95	5	0
PE/Si-2	95	0	5

### 2.3 Characterization

The dispersibility of silica in LLDPE was monitored by transmission electron microscopy (TEM, Hitachi 800). Samples for TEM analyses were cut from ultra-thin specimens. The thermal stability of composites was investigated by using a thermogravimetric analyzer (Pyris 6 Perkin Elmer) at a heating rate of 20°C/min from room temperature to 600°C under nitrogen atmosphere. In order to remove the air well, all samples were kept at 50°C for five minutes during analyses. Stanton Redcroft Cone Calorimeter (made in England) tests were carried out on the samples of 100×100×3 mm<sup>3</sup> according to ISO 5660. Each specimen was wrapped in aluminium and exposed horizontally to an external heat flux of 35 kW/m<sup>2</sup>.

## 3. RESULTS AND DISCUSSION

### 3.1 Morphological analyses

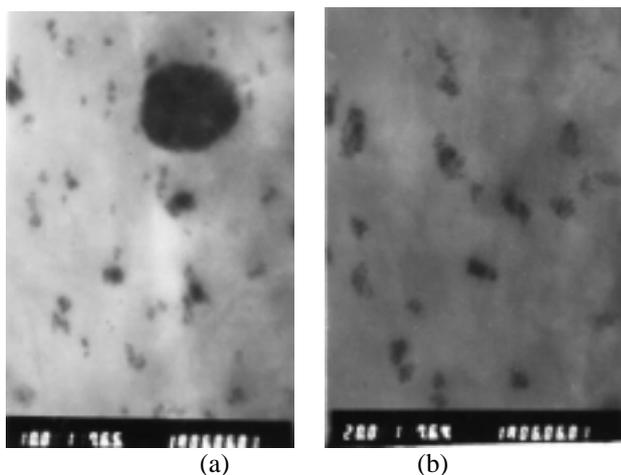


Fig.1 TEM micrographs of PE/Si-1(a) and PE/Si-2(b)

The extent of dispersion of silica in LLDPE was studied by TEM. The high magnification micrographs of all LLDPE/silica samples are

shown in Fig.1. As shown in Fig.1(a), silica without surface modification is not well dispersed in LLDPE owing to the severe aggregation of silica particles and its poor compatibility with LLDPE. Well dispersibility of surface modified silica was found in Fig.1(b) because of its improved compatibility with LLDPE.

### 3.2 TG analysis

TG and DTG curves of PE/silica composites are shown in Fig.2 and Fig.3. The TG data are listed in Table 2.

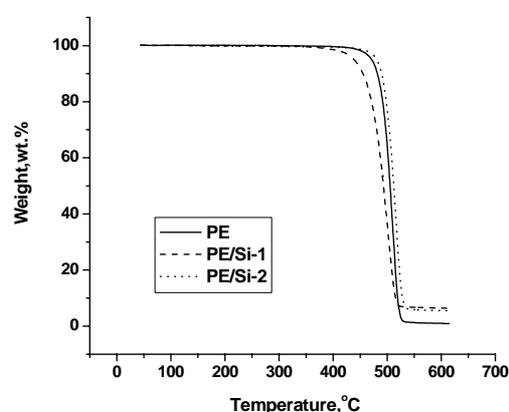


Fig.2 TG curves of PE/silica composites

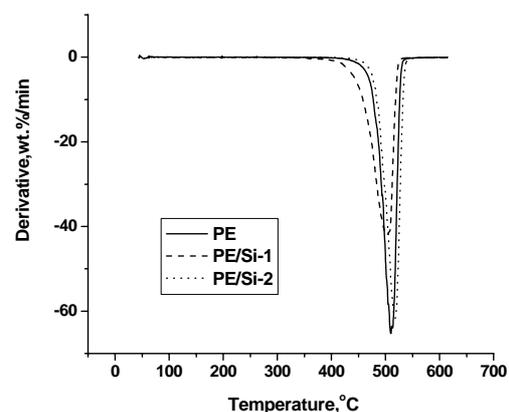


Fig.3 DTG curves of PE/silica composites

The TG curves show a single degradation step for all the composites prepared. The addition of silica with and without modification plays an important role in determining their thermal stability. For LLDPE/silica composites (PE/Si-1 in Fig.2) the 5% weight loss occurs at about 30°C lower than pure LLDPE while for composites with modified silica (PE/Si-2 in Fig.2), the 5% weight loss shifts to higher temperature. Moreover, the TGA traces of

the composite with modified silica indicate a marked increase in thermal stability with respect to pure LLDPE and composites with untreated silica. The shift towards higher temperature may be attributed to the formation of a high-performance SiO<sub>2</sub> network by well dispersed silica in LLDPE, which insulates the underlying material and slows weight loss rate.

Table 2 TG data of PE/nano-silica

Sample	T <sub>5</sub> *	T <sub>max</sub> **	R <sub>max</sub> ***	Residue at
			%/	550°C
				%
PE	472	510	65.3	1.57
PE/ Si-1	439	502	42.5	6.11
PE/ Si-2	482	517	61.8	6.11

\* : Temperature at 5% weight loss ;

\*\* : Temperature at maximum weight loss rate ;

\*\*\* : Maximum weight loss rate.

It can be seen in Fig. 3 that the weight loss rates obtained from the samples with silica are much smaller than that from pure LLDPE. For the composite with pristine silica (PE/Si-1 in Fig.3) DTG curve shows lowest weight loss rate while for the composite with modified silica (PE/Si-2 in Fig.3) the maximum weight loss rate occurs at the highest temperature among all samples. Furthermore, the DTG curves of PE/Si-1 shows wider degradation temperature range than that of PE/Si-2, which to some extent reflects the dispersion of silica in LLDPE.

### 3.3 CONE results

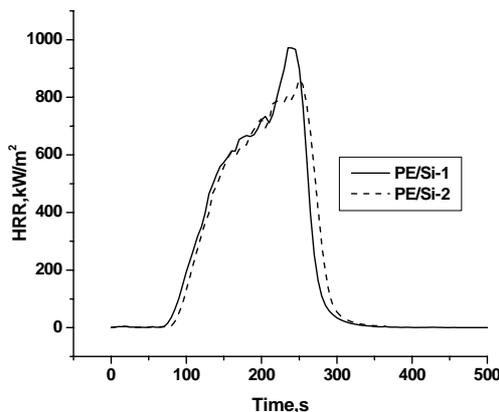


Fig.4 HRR of PE/silica composites

It has been widely reported that the addition of nano-silica can decrease HRR of polymer. But few literatures can be found about the effects of surface modification on HRR. By adding pristine silica and

modified silica into LLDPE, such effects were investigated by CONE. Fig.4 showed the heat release rate (HRR) curves. Obvious decrease of peak-HRR value can be observed. Well dispersed silica after surface modification, as proved by TEM, should be contributed to the decreased peak-HRR. Because the shapes of two curves were similar, it can be concluded that the mechanistic reason for the decreased HRR came mainly from the physical effects of silica on the surface. The formation of a high-performance SiO<sub>2</sub> network by well dispersed silica in LLDPE provided reasonable evidence. The decreased mass loss rate (MLR) in Fig.5 and total heat released (THR) in Fig.6 argued for the results.

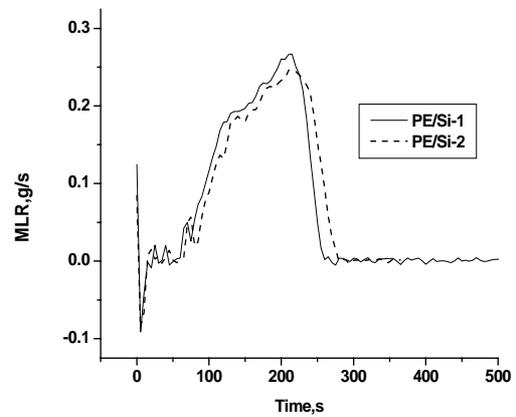


Fig.5 MLR of PE/silica composites

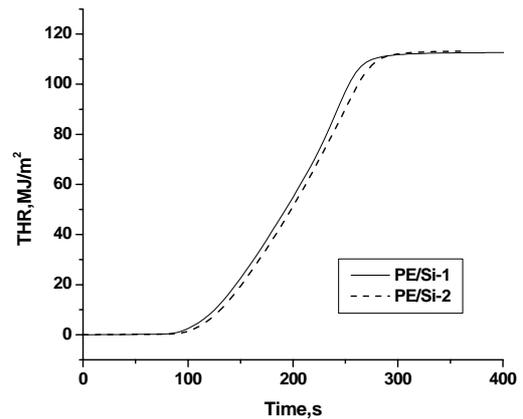


Fig.6 THR of PE/silica composites

## 4. CONCLUSIONS

Well dispersed silica after surface modification was observed by TEM. Improved thermal stability of composites with modified silica was revealed by TG. The formation of a high-performance SiO<sub>2</sub>

network by well dispersed silica in LLDPE should be the reason for the improved thermal stability. As a result, obviously decreased HRR and MLR were found by CONE, which also provided evidence that well dispersed silica was in favor of the formation of more compact char layer on the burning surface. Such layer could efficiently isolate heat and oxygen from polymer.

### Acknowledgement

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### References

- [1] Liang J.. "Dispersion mechanisms and characterization of inorganic nano-particles in polymer melts". *Modern Plastics Processing and Applications*, vol. 17, pp 57-60, 2005.
- [2] Stevenson I., David L., Gauthier C.. "Influence of SiO<sub>2</sub> fillers on the irradiation ageing of silicone rubbers". *Polymer*, vol. 42, pp 9287-9292, 2001.
- [3] Shan W., Liao M.. "Modification of Nanosilica Particles and Research Advances of Polymer/Silica Nanocomposites". *Polymer Bulletin*, vol. 3, pp 1-9, 2006.
- [4] Hu Y., Chen C., Wang C.. "Viscoelastic properties and thermal degradation kinetics of silica/PMMA nanocomposites". *Polymer Degradation and Stability*, vol. 84, pp 545-553, 2004.
- [5] Yang R., Li Y., Yu J.. "Photo-stabilization of linear low density polyethylene by inorganic nano-particles". *Polymer Degradation and Stability*, vol. 88, 168-174, 2005.
- [6] Wang H., Xu P., Zhong W., Shen L., Du Q.. "Transparent poly(methyl methacrylate)/silica/zirconia nanocomposites with excellent thermal stabilities". *Polym. Degr. and Stab.*, vol. 87, pp 319-327, 2005.
- [7] Lin J., Ma C.. "Thermal degradation of phenolic resin/silica hybrid creamers". *Polym. Degr. and Stab.*, vol. 69, pp 229-235, 2000.
- [8] Liauw C., Childs A., Allen N., Edge M., Franklin K., Collopy D.. "Effect of interactions between stabilisers and silica used for anti-blocking applications on UV and thermal stability of polyolefin film 2. Degradation studies". *Polym. Degr. and Stab.*, vol. 65, pp 207-215, 1999.
- [9] Chang T., Wang Y., Hong Y., Chiu Y.. "Organic-inorganic hybrid materials. V. Dynamics and degradation of poly(methyl methacrylate) silica hybrids". *J. Polym. Sci. Polym. Chem.*, vol. 38, pp 1972-1980, 2000.
- [10] Wang Y., Chang T., Hong Y., Chen H.. "Effect of the interfacial structure on the thermal stability of poly(methyl methacrylate)-silica hybrids". *Thermochim Acta*, vol. 397, pp 219-226, 2003.
- [11] Myslinski P., Lazowski Z.. "The effect of silica surface modification on the dielectric properties of silica-filled epoxy compounds". *Materials chemistry and physics*, vol. 33, pp 139-144, 1993.
- [12] Jia S., Zhang Z., Du Z., Teng R., Wang Z.. "A study of the dynamic flammability of radiation cross-linked HDPE/EPDM/silicone elastomer flame-retardant compound". *Radiation Physics and Chemistry*, vol. 66, pp 349-355, 2003.
- [13] Han Z., Dong L., Li Y., Zhao H.. "A comparative study on the synergistic effect of expandable graphite with APP and IFR in Polyethylene". *Journal of fire science*, vol. 25, pp 79-91 2007.
- [14] Hippi U., Mattila J., Korhonen M., Seppälä J.. "Compatibilization of polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with functionalized polyethylenes". *Polymer*, vol. 44, pp 1193-1201, 2003.