

MECHANICAL PROPERTIES OF OZONIZED HDPE FILLED WITH SERICITE-TRIDYMITE-CRISTOBALITE*

Mian Zhou, Yi Fu, Wen Xu and Xi Xu**

*The State Key Lab of Polymer Materials Engineering of China, Polymer Research Institute of Sichuan University,
Chengdu 610065, China*

Abstract The mechanical properties of ozonized high density polyethylene (HDPE) blended with sericite-tridymite-cristobalite (STC) were studied in this paper. The experimental results show that some oxygen containing polar groups are introduced on the molecular chain of HDPE through ozonization, the compatibility between HDPE and STC is thus improved, the mechanical properties of the blend are markedly enhanced. Compared with untreated HDPE/STC (60/40) blend, the yield strength and notched impact strength of ozonized HDPE/STC (60/40) blend are increased from 27.0 MPa to 29.5 MPa and from 2.8 kJ/m² to 13.3 kJ/m², respectively, the notched impact strength is close to that of HDPE (13.6 kJ/m²), the yield strength is in excess of 3.9 MPa of that of HDPE. The yield strength and notched impact strength will be further increased to 30.7 MPa and 32.4 kJ/m² in case the ozonized HDPE is blended with STC pretreated with silane coupling agent.

Keywords: Ozonization; High density polyethylene; Sericite-tridymite-cristobalite.

INTRODUCTION

Polyolefine makes up over 35% of all plastics produced in the world. Polyethylene and polypropylene are the only high-volume polyolefin. How to increase their stiffness at room temperature without loss of toughness, or increase their toughness at low temperature without loss of stiffness have become the major target in study^[1–4]. The toughness of a polymer can be improved by blending it with some elastomer, however, the modulus, stiffness and heat distortion temperature of the material will be lowered. Some rigid inorganic fillers can be used as reinforcing elements to increase the stiffness of the materials, however, the toughness, especially notched Izod impact strength will be decreased. Sericite-tridymite-cristobalite (STC) is an abundant and naturally occurring flaky sericite. It is a heat stable, weather and corrosion resistant material containing about 70% $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and 30% fibroillary silica. HDPE is a hydrophobic polymer, incompatible with hydrophilic materials, its mechanical properties can not be enhanced through blending. The approach adopted in this paper is to introduce some oxygen containing functional groups into the molecular chain of HDPE through ozonization, then blending it with STC in hopes of improving both stiffness and toughness of the filled HDPE through a simple, clean and efficient method. The mechanical properties of the ozonized HDPE/STC blend as well as the rules of dominating ozonization were studied.

EXPERIMENTAL

Materials

HDPE-5000S: Yangzi Petrochemical Co. Ltd. (China), melt index 1.1 g/10 min, density 0.954 g/cm³. STC: Sichuan Powdering Technology R&D Center (China), density 2.7–3.0 g/cm³, average particle size 2.6 μm.

* This project was supported by the Special Funds for Major State Basic Research Projects of China (No. G1999064809).

** Corresponding author: Xi Xu (徐僖). E-mail: sklpme@scu.edu.cn

Received October 13, 2003, Revised January 2, 2004; Accepted January 9, 2004

Silane coupling agent: KH-550 [$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$], Zhonglan Chengguang Research and Design Institute of Chemical Industry (China).

Ozonization of HDPE

The concentration and flow rate of ozone are kept at about 55 mg/L, 0.1 m³/h, reacting with HDPE at 25°C in a tank-reactor with stirring.

Sample Preparation and Mechanical Properties Testing

The samples (HDPE/STC or ozonized HDPE/STC) for testing their mechanical properties were blended in a twin-roller at 145°C for 10 min, then compression molded at 180°C to sheets of thickness 1 mm and 4 mm, respectively.

The tensile test was conducted according to GB1040-1992 at 23°C with an Instron 4302 tension machine, the impact test according to GB1843-1996 at 15°C with an XJ-40A impact tester.

FTIR Measurement

The FTIR spectra were measured with Nicolet-560 FTIR spectrometer.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 and Fig. 2 show the evolution of the FTIR spectra of HDPE in carbonyl and hydroxyl stretching vibration regions along with the time of ozonization. Peaks appeared at 1767, 1730, 1718 and 1697 cm⁻¹ in carbonyl region are attributed to ester, ketone, carboxylic acids and α , β -unsaturated carboxylic acids^[5-12], the peak appeared at 3532 cm⁻¹ in hydroxyl region is assigned to the non-hydrogen bonded hydroxyl group^[9].

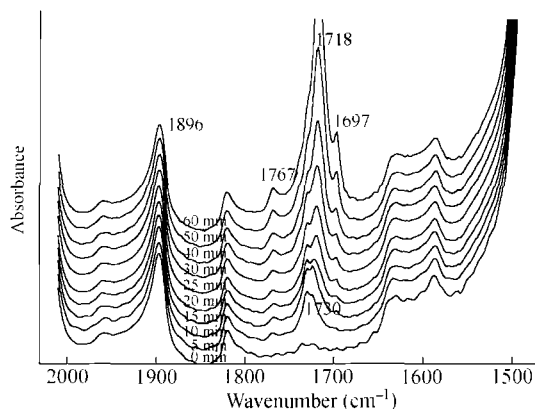


Fig. 1 FTIR spectra of ozonized HDPE in carbonyl stretching vibration region measured at different time of ozonization

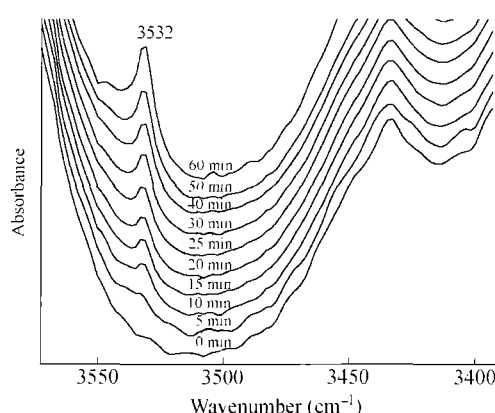


Fig. 2 FTIR spectra of ozonized HDPE in hydroxyl stretching vibration region measured at different time of ozonization

Table 1. Relative content of carbonyl and hydroxyl groups in ozonized HDPE along with time of ozonization

Sample	A_{3532}/A_{1896}	A_{1767}/A_{1896}	A_{1730}/A_{1896}	A_{1718}/A_{1896}	A_{1697}/A_{1896}
HDPE5000S	0.000	0.000	0.00226	0.000	0.00170
5 min HDPE5000S	0.00155	0.0204	0.0211	0.0124	0.00192
10 min HDPE5000S	0.00456	0.0215	0.0199	0.0462	0.00430
15 min HDPE5000S	0.00612	0.0248	0.0232	0.0643	0.00445
20 min HDPE5000S	0.00619	0.0222	0.0208	0.0949	0.00864
25 min HDPE5000S	0.00773	0.0266	0.0221	0.130	0.0110
30 min HDPE5000S	0.00987	0.0355	0.0225	0.190	0.0136
40 min HDPE5000S	0.0108	0.0421	0.0188	0.276	0.0215
50 min HDPE5000S	0.0130	0.0506	0.0164	0.417	0.0365
60 min HDPE5000S	0.0172	0.0625	0.0157	0.546	0.0503

No changes occur for infrared absorption at 1896 cm^{-1} (attributed to crystalline phase of HDPE)^[13]. The relative content of the different kind of oxygen containing groups on HDPE molecular chains could be assessed with the relative ratio of $A_{\text{wavenumber}}$ to A_{1896} , in which $A_{\text{wavenumber}}$ is the integral area of intensity of absorbance calculated by Omnic software. The data listed in Table 1 show that the relative content of OH, COOR and COOH increase with time of ozonization, the content of C=O increases first, then decreases.

Mechanical Properties of Ozonized HDPE/STC Blends

As shown in Fig. 3(a), 3(b) and 3(c), the mechanical properties of ozonized HDPE/STC are different from that of untreated HDPE/STC. The yield strength of ozonized HDPE/STC increases with STC content, the impact strength increases first then decreases with STC content. In untreated HDPE/STC systems, the yield strength gets improved first and then lowered, the impact strength decreases with STC content. However, there is no evident difference in elongation at break between ozonized HDPE/STC and untreated HDPE/STC.

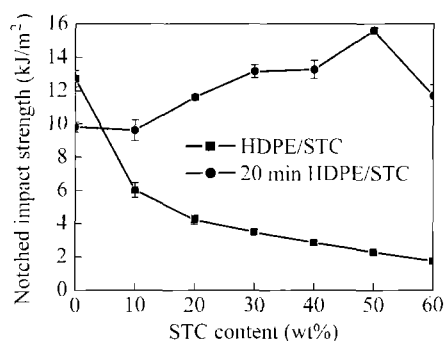


Fig. 3(a) The notched impact strength of HDPE/STC blend versus STC content

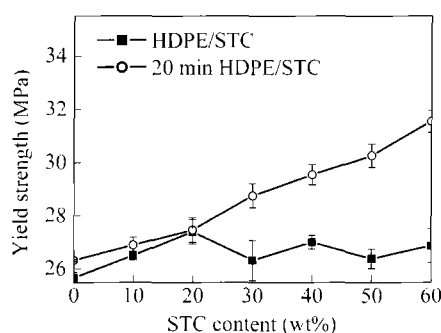


Fig. 3(b) The yield strength of HDPE/STC blend versus STC content

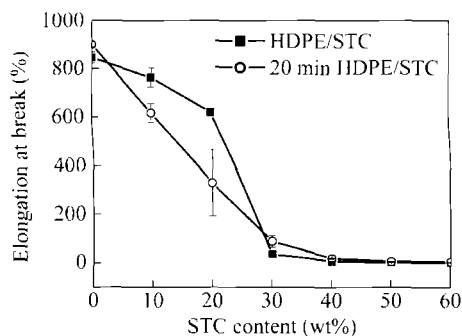


Fig. 3(c) The elongation at break of HDPE/STC blend versus STC content

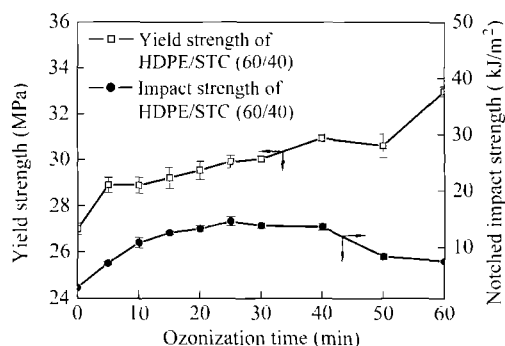


Fig. 4 The yield strength and notched impact strength of HDPE/STC (60/40) blend versus ozonization time

As shown in Fig. 4, the yield strength of HDPE/STC (60/40) blend increases with ozonization time; as far as impact strength, the optimal ozonization time is 20-40min. Data listed in Table 2 are the functionalization index (FI, ratio of peak intensity of infrared band of COOH to that of C=O) of HDPE along with time of ozonization.

Table 2. Functionalization index of HDPE during ozonization

Sample	FI, A_{1718}/A_{1730}
HDPE5000S	0.000
5 min HDPE5000S	0.588
10 min HDPE5000S	2.322
15 min HDPE5000S	2.772
20 min HDPE5000S	4.563
25 min HDPE5000S	5.882
30 min HDPE5000S	8.444
40 min HDPE5000S	14.681
50 min HDPE5000S	25.427
60 min HDPE5000S	34.777

The yield strength of HDPE/STC (60/40) blend increases with FI, the impact strength increases with FI first, then decreases as shown in Fig. 5.

Mechanical Properties of Ozonized HDPE/Coupling Agent treated STC Blend

The results shown in Fig. 6 and Table 3 are the mechanical properties of the ozonized HDPE blended with coupling agent treated STC. Compared with untreated HDPE/STC (60/40) blend, the yield strength and notched impact strength of ozonized HDPE (20 min)/STC (60/40) blend are increased from 27.0 MPa to 29.5 MPa and from 2.8 kJ/m² to 13.3 kJ/m², respectively (Fig. 6). The notched impact strength of this blend is close to that of HDPE

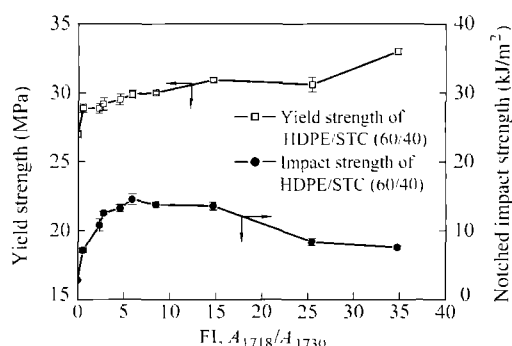


Fig. 5 Mechanical properties of ozonized HDPE/STC blend versus functionalization index

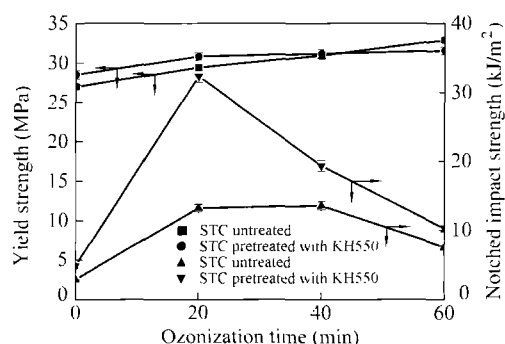


Fig. 6 Mechanical properties of ozonized HDPE/KH-550 treated STC blend versus ozonization time

Table 3. Mechanical properties of ozonized HDPE/KH-550 pretreated STC blend

Sample	STC content (%)	Yield strength (MPa)	Notched impact strength (kJ/m ²)	Elongation at break (%)
HDPE5000S	40	27.0 ± 0.3	2.8 ± 0.1	7.2 ± 0.7
HDPE5000S [*]	40	28.5 ± 0.5	4.9 ± 0.4	14.8 ± 1.4
20 min HDPE5000S	40	29.5 ± 0.4	13.3 ± 0.5	19.0 ± 2.7
20 min HDPE5000S [*]	40	30.7 ± 0.5	32.4 ± 0.9	34.0 ± 2.9
40 min HDPE5000S	40	30.9 ± 0.2	13.6 ± 0.6	10.6 ± 1.0
40 min HDPE5000S [*]	40	31.2 ± 0.5	19.4 ± 0.8	29.6 ± 2.0
60 min HDPE5000S	40	32.9 ± 0.2	7.5 ± 0.3	7.9 ± 0.5
60 min HDPE5000S [*]	40	31.5 ± 0.5	10.2 ± 0.4	15.6 ± 2.0

* STC pretreated with 2 wt% coupling agent KH-550

(13.6 kJ/m²), the yield strength of this blend is much higher than that of HDPE, in excess of 3.9 MPa. In case the STC used has been pretreated with KH-550 then blended with ozonized HDPE, the yield strength and notched impact strength of the blend could be raised to 30.7 MPa and 32.4 kJ/m² (Fig. 6).

CONCLUSION

Some oxygen containing groups (mainly COOH, C=O groups) are introduced on the molecular chain of HDPE through ozonization so as to improve its compatibility with STC (a naturally occurring sericite). The rules of dominating ozonization were mastered. Compared with HDPE/STC (60/40) blend, the yield strength and notched impact strength of ozonized HDPE blended with STC pretreated with a little bit of KH-550 could be raised to 30.7 MPa and 32.4 kJ/m² respectively from 27.0 MPa and 2.8 kJ/m², both stiffness and toughness of HDPE/STC blend are enhanced.

REFERENCES

- 1 Suetsugu, Y., "The Sixth Annual Meeting of Polymer Processing Society", April 17-20, Nice, France, 1990, Preprints 08-03
- 2 Fu, Q. and Wang, G.H., Polym. Eng. Sci., 1992, 32: 94
- 3 Wu, C.Z. and Xie, S.S., Polym. Mater. Sci. Eng. (in Chinese), 1991, 3: 97
- 4 Hindryckx, F., Dubois, P.H., Patin, M., Jerome, R., Teyssie, P.H. and Marti, M.G., J. Appl. Polym. Sci., 1995, 56: 1093
- 5 Ranby B. and Rabek, J.F., "Photodegradation Photo-Oxidation and Photostabilization of Polymers", John Wiley & Sons, London, 1975, p.132
- 6 Dasgupta, S., J. Appl. Polym. Sci., 1990, 41: 233
- 7 Mittal, K.L., "Polymer Surface Modification: Relevance to Adhesion", VSP, Utrecht, 1996, p.233
- 8 Pazur, R., Troguet, M. and Gardette, J.L., J. Polym. Sci., Part A: Polym. Chem., 1997, 35: 1689
- 9 Lacoste, J. and Carlsson, D.J., J. Polym. Sci., Part A: Polym. Chem., 1992, 30: 493
- 10 Simons, W.W., "The Sadtler Handbook of Infrared Spectra", Sadtler Research Laboratories, Inc., Philadelphia, 1978, p.557
- 11 Tidjani, A., J. Appl. Polym. Sci., 1997, 64: 2497
- 12 Macmanus, L.F., Walzak, M.J. and McIntyre, N.S., J. Polym. Sci., Part A: Polym. Chem., 1999, 37: 2489
- 13 Mark, J.E., "Polymer Data Handbook", Oxford University Press, New York, 1999, p.493