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STUDY ON THE CLARIFYING ADDITIVES FOR HIGH DENSITY POLYETHYLENE

Le Thi Bang[1, *], Nguyen Phi Trung[1], Nguyen Van Khoi[2], Tran Vu Thang[2], Trinh Duc Cong[2], Hoang Thi Phuong[2]

[1]*Institute of Research and Development on Novel Materials,*
350 Lac Trung, Hai Ba Trung, Ha Noi

[2]*Institute of Chemistry, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi, Viet Nam*

[*]Email*: banghoak6@gmail.com*

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ABSTRACT

Bis-3,4- dimethyldibenzylidene sorbitol (DMDBS); bis-p-methylbenzylidene sorbitol (MDBS) and the mixture of DMDBS/MDBS (50/50) were studied through optical, thermal, mechanical properties and surface morphology. With the same amount of additive (DMDBS/MDBS mixture and DMDBS) in the material, the results are similar. On the other hand, using an additive mix reduces the cost of production due to MDBS. Furthermore, the additive mixture is used without producing odours. Therefore, the mixture of DMDBS/MDBS (50/50) is chosen.

Keywords: polyethylene, bis-3,4-dimethyldibenzylidene sorbitol, bis-p-methylbenzylidene sorbitol.

1. INTRODUCTION

High-density polyethylene (HDPE) is widely used today in a large number of applications including packaging, coating and films. The optical, machanical, thermal and chemical properties are significantly affected by the crystallization process [1]. Directed modification of the crystalline morphology during solidification from the melt state in HDPE can alter a wide range of physical properties such as optic clarity [2], shrinkage [3], and cycle time in extrusion and molding [4]. As these properties are directly related to the crystalline morphology of the polymer, directed modification to control the crystallization of HDPE can lead to significant improvements in targeted physical properties.

Nucleation and crystal morphology are affected by the addition of a nucleating agent (NA) that promotes heterogeneous nucleation. The addition of effective NAs in most polymers increases the rate of crystallization and the crystallization temperature, Tc. A beneficial result from the addition of effective NAs is reduced cycle times in polymer processing such as extrusion or molding. Fabricated parts solidify faster, increasing the rate of production. Another benefit is greater transparency or clarity in HDPE as NAs reduce crystal sizes to a range smaller than the wavelength of visible light to reduce light scattering [2].

One of the most widely used nucleating agents is the so-called "clarifier", dimethyl dibenzylidene sorbitol (bis-p-methylbenzylidene sorbitol (MDBS) and bis (3,4-dimethylbenzylidene)-sorbitol (DMDBS)). DMDBS is a butterfly-shaped molecule that hydrogen bonds in apolar matrices to form crystalline nanofibers, on whose surface polymer crystallization is nucleated [5]. At high temperature, DMDBS dissolves in polymer melt. Upon cooling, the DMDBS precipitates out in the form of nanofibers, that organize into a 3D-network in polymer [6].

In this paper, we investigated the influence of MDBS, DMDBS, the synergist of MDBS and DMDBS (weight ratio 50/50) to optical, thermal, mechanical properties and morphology of material.

2. EXPERIMENTAL

2.1. Materials

Low density polyethylene (LDPE) (density 0,925 g/cm^3, melt flow index (MFI) 4g/10 min (190 ^{0}C, 2160 g) from LyondellBasell-Netherland.

Linear low density polyethylene (LLDPE) (density 0.924 g/cm^3, MFI 21 g/10 min (190^{0}C, 2160 g) from ExxonMobil – USA.

High density polyetylene (HDPE) (density 0.95 g/cm^3, MFI 4 g/10 min (190^{0}C, 2160 g) from SCG.

Clarifying agents (NAs) were Bis-3,4-dimethyldibenzylidene sorbitol (DMDBS) and Bis-p-methylbenzylidene sorbitol (MDBS) from Tianjin Bestgain Science & Technology – China

Aid dispersion additive particles was zinc stearate from Plastics and Additive Joint Stock Company – Viet Nam.

2.2 Methods

2.2.1. Sample preparation

HDPE films (30 ± 3 µm) were prepared by mixing 0.2 % w/w of clarifying agents (MDBS or DMDBS or MDBS/DMDBS: 50/50) with HDPE in a film blowing machine using single screw extruder SJ-35 (35 mm screw, L/D:28/1). HDPE film has been designated as HDPE-0 and HDPE containing of MDBS or DMDBS or MDBS/DMDBS: 50/50 have been designated as HDPE-MDBS, HDPE-DMDBS, HDPE-MDBS/DMDBS, respectively.

In order to achieve the good dispersion of clarifying agents in films, additives were added to films under masterbatches of PE/MDBS or PE/DMDBS or PE/MDBS-DMDBS (10 wt%) (the date show the weight fraction of MDBS or DMDBS or MDBS/DMDBS in PE, PE is combination of LDPE/LLDPE with 30/70 wt).

2.2.2. Optical properties

Glossiness of specimens were measured according to the standard ASTM D2457-03, using Picogloss 503 instrument in Institute for Tropical Technology - Vietnam Academy of Science and Technology (VAST).

The transparency of sample was measured by using Shimazu 2600 UV-VIS-NIR instrument, according to ASTM D 1003 standard, in Institute of Physics – VAST. The specimens were stable in condition: temperature 23 ± 2^{0}C, moisture 50 ± 6.5%, at least 40 hours before testing.

2.2.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) studies were conducted by using DSC 204F1 Phenix (NETZSCH-Germany) in Institute for Tropical Technology to measure effect of compound proportion to crystallization behavior of MB. The samples were heated from 25 ^{0}C to 220 ^{0}C with a heating rate of 20 ^{0}C/minute, prolonged at 220 ^{0}C in 2 minutes, then cooled to room temperature with cooling rate of 20 ^{0}C/minute.

Percent crystallinity (I_C) were determined from enthalpy of crystallization present in DSC diagram. Percent of crystallittes was calculated by equation:

$$I_C = \frac{\Delta H_{f(DSC)}}{\Delta H_{f(0)}}$$

where: $\Delta H_{f(DSC)}$ is melting enthalpy of samples (obtained from DSC diagram); $\Delta H_{f(0)}$ (= 293 J/g) is melting enthalpy of complete crystallization HDPE.

2.2.4. Scanning Electronic Microscopy (SEM)

The surface morphology of samples were obtained using Scanning Electron Microscope (SEM) JEOL 6390 instrument in Institute of Materials Science – VAST. The samples were cryogenically fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of platinium.

2.2.5 Mechanical measurements

The mechanical measurements, including tensile and elongation at break properties of film samples were performed using a tensile tester (Instron 5980), according to ASTM D882.

3. RESULTS AND DISCUSSION

3.1. Effect of clarifying additives on optical properties

Optical properties of samples were characterized by glossiness and transparency. Effect of MDBS, DMDBS and the mixture of both additives on optical properties are shown in Table 1.

Glossiness and transparency of sample without clarifying additive are lower than those of samples containing additives (HDPE-0: glossiness 64, transparency 56 %). The sample containing DMDBS provided the best result (glossiness 87, transparency 86 %). Generally, optical properties of these samples decrease respectively: HDPE-DMDBS > HDPE-DMDBS-

MDBS > HDPE-MDBS > HDPE-0. The addition of Nas effects the optical properties (greater transparency and clarity) of HDPE by reducing crystal size to a range smaller than the wavelength of visible light to reduce light scattering [1].

Table 1. Effect of various clarifying additives on optical properties of sample.

Sample	Glossiness	Transparent (%)
HDPE-0	64	56
HDPE-MDBS	82	82
HDPE-DMDBS+MDBS	85	83
HDPE-DMDBS	87	86

3.2. Effect of clarifying additives on thermal properties

The crystallization temperature has significantly influence on nucleus and crystal growth of crystalline, so affect to crystallitte shape and size. With higher temperature, the crystallitte has smaller size, so to increase the transparency of light and to increase the clarity of the samples. Differential scanning calorimetry (DSC) gives information of melting and crystallization temperatures. The results were presented in Table 2.

Table 2. Effect of different clarifying additives on thermal properties of samples.

Sample	T_m (^oC)	T_c (^oC)
HDPE-MDBS	129,7	112,2
HDPE-DMDBS	130,1	114,6
HDPE-DMDBS+MDBS	130,5	113,4
HDPE-0	130,3	109,3

Table 3. Effect of different clarifying additives on percent crystallinity of polymer.

	Sample	Percent crystallinity, (%)
1	HDPE-MDBS	84.4
2	HDPE-DMDBS	88.2
3	HDPE-DMDBS+MDBS	86.2
4	HDPE-0	68

The crystallization and melting behaviors of samples are shown in Table 2. The result that the crystallization temperature (Tc) is enhanced from 109.3 ^oC of HDPE-0 film to 112.2 ^oC of HDPE-MDBS film and 113.4 ^oC of HDPE-DMDBS+MDBS film and 114.6 ^oC of HDPE-DMDBS film. Furthermore, the melt temperature Tm of HDPE films has not been influenced by the addition of MDBS or DMDBS apparently.

Crystallization temperature has significant effect on percent crystallinity of polymer, the increasing of temperature leads to increasing of percent crystallinity. Clarifying additives have influence on crystallization temperature, so affect on percent crystallinity. The obtained percent crystallinities were described in Table 3.

In view of results shown in Table 3, percent crystallinity of samples containing clarifying agents are higher than that of the sample without additives. The percent crystallinity of samples containing clarifying agents decrease in the following sequence: HDPE-DMDBS>HDPE-DMDBS+MDBS > HDPE-MDBS > HDPE-0, the percent crystallinity are 88.2; 86.2; 84.4; 68 %; respectively. These results can be explained so that, clarifying agent which having high crystallization temperature promotes the growing of crystallittes. When temperature is increased, molecular carbon chain becomes more flexible due to the decreasing of viscosity of polymer, so they move easily to create crystallittes and enhance crystallization rate.

3.3. Effect of clarifying additives on surface morphology

The surface morphology of samples with and without additives were shown in Figure 1.

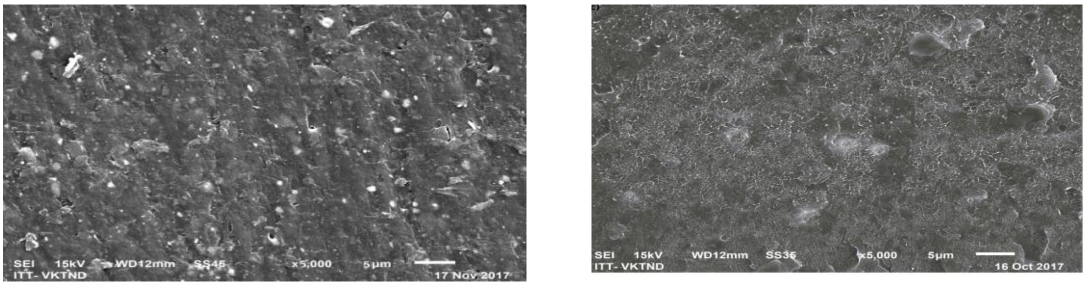

Figure 1. The SEM figure of the samples with and without clarifying additives:
(a)- PE-0; (b)- DMDBS+MDBS.

The figure of surface morphology of sample containing additives indicates that, additive particles distribute greatly in polymer matrix. The nucleating agents promote the crystallization of polymer to form fiber (Fig. 1b). The fiber form isn't seen on the sample without clarifying additives. These results can be explained due to the fact that the clarifying additives control nucleation process and make the nuclei distributed uniformly in polymer matrix. In contrast, the crystallization in HDPE without additives are not uniform in polymer matrix.

3.4. Effect of clarifying additive on mechanical properties

Table 4. Effect of different clarifying additives on mechanical properties of samples.

Samples	**Tensile strength at break (MPa)**	**Elongation at break, (%)**
HDPE-MDBS	31,2	553
HDPE-DMDBS	33,6	548
HDPE-DMDBS+MDBS	32,4	552
HDPE-0	28,5	600

Mechanical properties of samples are characterized by tensile strength at break and elongation at break. Clarifying additives affected to these properties and were described in Table 4.

The results show that, the incorporating of clarifying additive into polymer matrix leads to increasing of tensile strength at break and light decreasing of elongation at break. These results can be explained due to clarifying additives increase the rate of crystallization, leading to increasing percent crystallinity, thus in turn to enhance the tensile strength, increase the density and decrease the elongation at break.

4. CONCLUSION

Through investigating the influences of clarifying additives on physico-chemical properties of HDPE; we can conclude that the use of DMDBS in combination with MDBS could enhance the thermal, optical and mechanical properties; as compared with the MDBS with similar level of additive content. Moreover, the mixture of DMDBS and MDBS didn't generate odour for final products and had the cost lower than DMDBS.

The figure of morphology's samples indicated that, clarifying additives distributed greatly in melting HDPE matrix and crystalized to form fiber during cooling. When loaded 0.2 wt.% of clarifying additive in polymer matrix, the physical and mechanical properties had changed less significantly. Consequently, the synergist of DMDBS and MDBS which had ratio 50/50 was incorporated with HDPE to enhance the clarifying of product.

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