

Morphological and Thermal properties of HDPE/Caco3 Nanocomposites: Effect of Content of Nano and MFI

Mojtaba Saeedi¹⁺ and Salman Jiryaie sharahi²

¹Young Researchers Club, Farahan branch, Islamic Azad University, Farahan, Iran

²Department of Chemical Engineering, Farahan branch, Islamic Azad University, Farahan, Iran

Abstract. In the present study different series of high-density polyethylene (HDPE) nanocomposites, containing 1, 3 and 5 wt.% of carbonate calcium (CaCO₃) nanoparticles and HDPE with different MFI were prepared by melt-mixing on a internal mixer(plasticorder PL2000 Brabender). From TGA analysis, the decomposition temperature of nanocomposites with surface treatment of nano and HDPE with high MFI increased and has higher resistance to thermal degradation. According to the SEM micrographs, it was found that a much better dispersion of nano CaCo3 in samples with higher MFI also according to the SEM and TEM measurement, was found that nano CaCo3 with surface treatment has better dispersion compared nano without surface treatment. The properties of HDPE and its nanocomposite were investigated through differential scanning calorimetry (DSC) test. The results of DSC tests showed that the addition of nano-sized calcium carbonate to HDPE caused to increase the heat capacity and crystallinity.

Key words: HDPE, Nano CaCo3, Thermal degradation, Nanocomposite

1. Introduction

Polyethylene (PE) is one of the most widely used plastic for many routine applications such as packaging industries, Pipe and fitting manufacturing, etc[1-3]. HDPE has many advantages such as good flexibility, resistance to chemical materials, low cost, high impact and toughness strength[4]. One of the large used range of HDPE in pipe industries that used in agriculture, water supply and gas transition. The HDPE grade material that widespread used in these industries was PE100 and PE80[5]. These grades have low MFI and low permeability and also low thermal stability however for recover of this disadvantage increase nanoparticles to pure HDPE. Chrisaffis and et.al[6] studied properties of HDPE and nanoclay, CNT and nano sio2, they found addition of nano on HDPE increase mechanical properties such as modulus, izod impact and tensile strength. Also Chrisaffis in another paper studied on thermal degradation of HDPE/SIO2 nanocomposites and found addition of sio2 increment thermal stability of HDPE[7].. Akhlaghi and et.al[4] studied properties of HDPE/EVA nanoclay with compatibilizer they found used compatibilizer increased mechanical and thermal properties. so in the present study HDPE/Caco3 Nanocomposites with different of nano caco3 content prepared with melt mixing extrusion for investigate of thermal degradation and effect of nano and compatibilizer on thermal properties

It is well known that HDPE filled with CaCO₃ particles is very brittle. To obtain good interface adhesion between the HDPE matrix and the CaCO₃ filler, two options are possible: One is to chemically modify the HDPE, and the other is to provide a surface graft treatment to the filler. So in this research was tried using nano caco3 with surface treatment.with HDPE at different MFI.

2. Experimental

+ Corresponding author. Tel: +988626622116; fax: +988613571026.
E-mail address: saeedi.polymer@gmail.com.

2.1. Materials

Bimodal HDPE pipe and fitting grade was supplied by Amirkabir petrochemical (Bandar Imam, Iran) with EX3 tradename had melt flow index (MFI) of 0.45/10min at 5kg/190C, density 0.945g/cm³ and T_m 125 C and HDPE supplied by Tabriz petrochemical (Tabriz ,Iran) with HD 5030-UA tradename had melt flow index (MFI) of 2.2kg/190C, density 0.95 g/cm³ and T_m 130 C

A nano-CaCO filler with an average particle diameter of 40 nm was supplied by Omya pars Company, Tehran, Iran. The filler was surface treated with a coupling agent of the stearic acid type by the manufacturer

2.2. Sample preparation

Nanocomposites samples were preparation in internal mixer by melt blending (plasticorder pl2000 brabender), before this the nano caco₃ dried in oven at 130c for 6h and then at first HDPE was mixed in he inernal mixer at 200c for 5 min then the nano caco₃ add to compound, process was continued for 5 min, the samples were cooled and prepared for compression molded. Nanocomposites samples were compression molded with hydraulic press at 210c for 5 min and sheets prepared with 1 mm thickness. The ratio of HDPE was 100 phr and nano CaCo₃ were fixed at 1,3,5 phr.

2.3. Characterization

Thermogravimetric analysis of the nanocomposites samples was accomplished using TGA-7HT from Perkin & Elmer (USA) in the range of 30-600°C with 10°C/min under the nitrogen atmosphere.

Crystallization behaviors of the nanocomposites were investigated with a differential scanning calorimeter, Perkin Elmer DSC-1 . The differential scanning calorimeter was calibrated using indium with sample weight of 10 mg. All processes were carried out in a purge nitrogen. The samples were heated to 200 C and held in the molten state for 5 min to eliminate the influence of thermal history. The sample melts were then subsequently quenched at a rate of 10 c/m in to reach the specific temperature and kept at that temperature for 1 h . When the crystallization process had completed, the samples we re heated to 200 C at a rate of 10 c/m in to measure the melting temperature.

To study the microstructure of HDPE/nano caco₃ nanocomposites, a Philips scanning electron microscopy, XL30, The Netherlands, was employed to study the cryogenical- ly fractured surface.

The morphology structure of the nanocomposites was investigated by an EM 208 Philips, transmission electron microscope, The Netherlands, with an acceleration voltage of 100 kV. The ultrathin slides were obtained by an Ultracut UCT, Leica, Germany, at nitrogen atmosphere.

2.4. Result and discussion

Fig.1 was shown the onset temperature of nanocomposites at various HDPE MFI, so illustrated that the sample with HDPE at high MFI has higher onset temperature compared other samples, this because oof low viscosity of polymer this factor coused nano dispersed on to polymer matrix. The TEM image was shown dispersion of nano particle in HDPE matrix. Also, as seen in fig.1 when nano particle was higher than 5% the decomposition temperature increased but with addition of nano higher than 5% this factor reduced. When nano content increased , accumulation of nano particles im polymer matrix occurs thereby reducing the decomposition temperature caused to the good interaction of nano particles and HDPE.

The compatibilizing mechanism of nano surface treatment in the HDPE/Nano CaCo₃ nanocomposites was proposed as shown in Fig.2, as observed stearic acid surface treatment has created chemical interaction and physical chain entanglement with HDPE.

Fig.3 was shown TEM images of nanocomposites, as illustrated in Fig.3(a) nano dispersion which has been improved with nano surface treatment in comparison nanocomposites without surface treatment Fig.3(b), this because of good interface adhesion between HDPE and nano CaCo₃ surface treatment.

The change of the fracture behavior of the nanocomposite is clearly revealed by the SEM of the fractured surface (Fig. 4–6). It is obvious that there is substantial debonding of two phases before yielding in the nanocomposite of HDPE/CaCO₃, and the surfaces of CaCO₃ particles are perfectly clean (Fig.4).It can be concluded that there is low adhesion at the HDPE/CaCO₃ interface. Figure5 show the SEM micrograph of the fractured surface for the HDPE/CaCO₃ nanocomposite with nano surface treatment. Owing to the

introduction of nano surface treatment with stearic acid, the interfacial adhesion was improved partially. Important morphological changes occurred on addition of nano CaCO₃. The morphology of HDPE/CaCO₃-acid treated nanocomposites shows better interfacial compatibility over the above nanocomposites. As shown in Figure 5, there is an excellent adhesion between matrix and the particles; the two phase structure disappears and many interpenetrating fibriforms are formed on the fractured surfaces which apparently bond the two phases together indicating the presence of interactions between the -OH and -COOH of surface treatment of nanoCaCO₃ particles and HDPE. The scheme for interfacial modification of the HDPE/CaCO₃ nanocomposite is shown in Figure 6. Owing to the incorporation of reactive groups into the nanocomposite, the strong interaction between the nano particle and polymer transformed structurally the nanocomposite into an interpenetrating polymer. So HDPE with higher MFI has better interaction

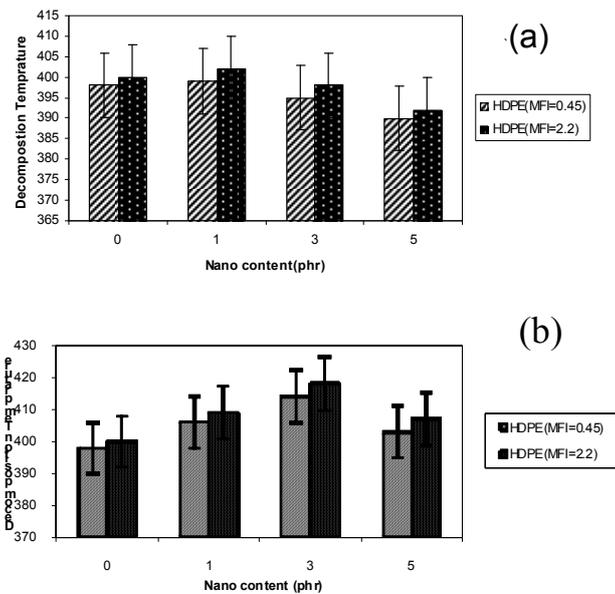


Fig.1: Decomposition temperature (onset temperature) of HDPE/CaCo₃ nanocomposites a)without surface treatment b)with surface treatment in different MFI

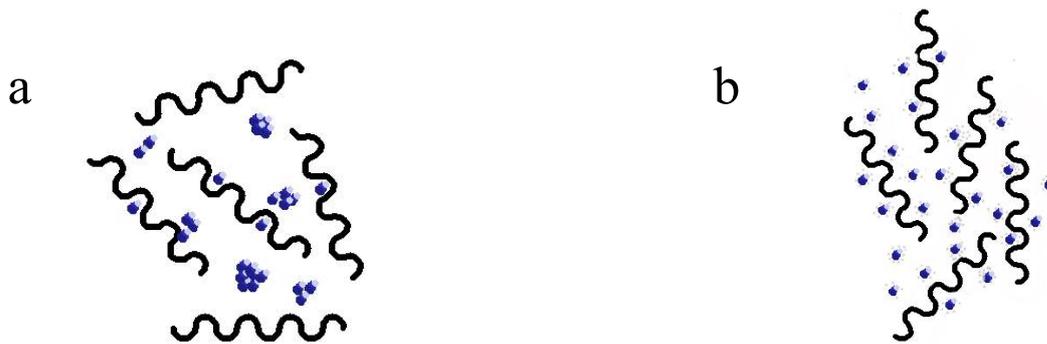


Fig.2: Schematic of interaction between Nano with and without surface treatment and HDPE a)Without treatment b)With treatment

with nano CaCo₃ maybe for low viscosity so in processing nano surface treatment has good dispersion on polymer matrix.

The degree of crystallinity of semicrystalline polymers has a considerable effect on their DSC analysis can be used to obtain the enthalpy of fusion of HDPE in HDPE/nanoCaCO₃ nanocomposites. The crystallinity of sample can be calculated by the following equation:

$$X_c = \left\{ \frac{\Delta H_c}{(1 - \Phi)\Delta H_m^0} \right\} \times 100\% \quad (1)$$

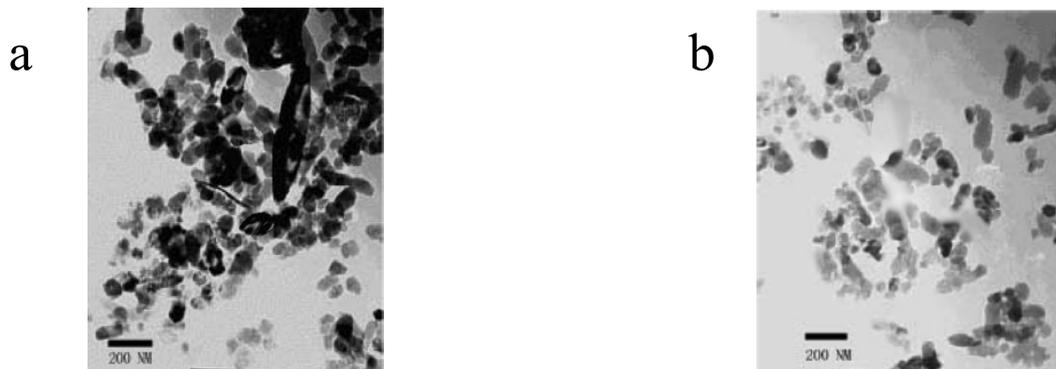


Fig.3: TEM micrograph of HDPE/NanoCaCo3 a) Without surface treatment b) with surface treatment

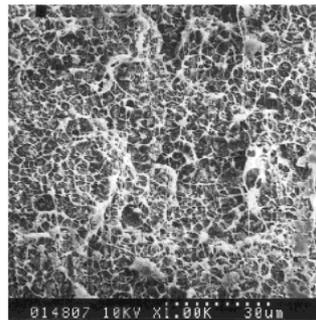


Fig.4: SEM micrograph of impact fractured surface of HDPE/Nano CaCo3 without surface treatment nanocomposites

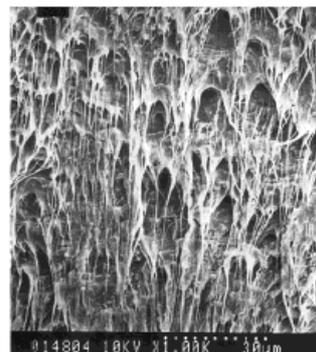


Fig.5: SEM micrograph of impact fractured surface of HDPE(MFI=0.45)/Nano CaCo3 with surface treatment nanocomposites

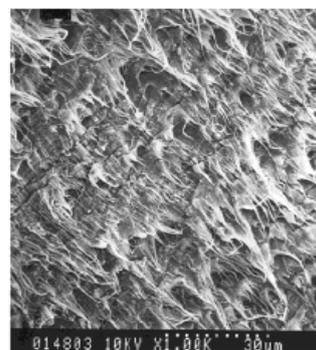


Fig.6: SEM micrograph pf impact fracture surface of HDPE(MFI=2.2)/Nano CaCo3 with surface treatment nanocomposites

where X_c is the crystallinity of sample, ΔH_c is the measured enthalpy of fusion of sample from DSC thermogram, Φ is the mass fraction of nano-CaCO₃ in sample, ΔH_m^0 is a perfect enthalpy of fusion of HDPE (293 J g⁻¹) [8]. the results corresponding to the melting and crystallization temperatures and heat of fusion (ΔH_m) of the blends with different nano CaCo₃ content are summarized in Table I. The CaCo₃ is observed to have significant effect on the melting temperature of PE; rather, it increases the total crystallinity

of the nanocomposites. A comparison between effect of addition of nano CaCo₃ on addition of crystallinity for HDPE with lower MFI and HDPE with higher MFI nanocomposites is shown in Table I.

Table1: Melting Temperature (T_m), Heat of Fusion (ΔH_m), Crystallinity (X_c), and Crystallization Temperature (T_c) of Polyethylene nanocomposites

CaCo ₃ content	HDPE(MFI=0.45)/Nano				HDPE(MFI=2.2)/Nano			
	T _m	T _c	H _c	X _c	T _m	T _c	H _c	X _c
0	130.3	118.75	152	51.87	130.9	119	151.5	51.7
1	130.76	118.98	153.1	52.775	131.1	119.1	153.9	53
3	131.45	120	154.5	54.3	131.78	119.8	154.6	54.35
5	132.65	120.87	153.4	54.97	132.7	119.4	154	55.1

It is seen that this effect of increased crystallinity is much more pronounced for HDPE with higher MFI nanocomposites as compared with HDPE with lower MFI nanocomposites. This is because the HDPE has higher crystallinity. Thus, in this nanocomposites, Nano CaCo₃ dispersed phase has a improvement role in the arrangement of HDPE chain molecules at easier process compared processing of HDPE with lower MFI in a crystal lattice when cooling from melt; as a result, crystallinity is increased. On the other hand, HDPE with higher MFI improves the dispersion of nano-CaCO₃ in HDPE/nano-CaCO₃ nanocomposites. Nano-CaCO₃ particles acting as nucleating agent make HDPE crystallize in a way of heterogeneous nucleation. Thus, the crystallinity of high MFI HDPE samples is higher than that low MFI HDPE samples. . so addition of nano particles in polymer matrix increased this due to above justified.

2.5. Conclusion

The conclusions of this work can be summarized as follows.

(1) Increase of HDPE MFI increase decomposition temperature also with addition of nano CaCo₃ to 3% this temperature increased

(2) According to TEM images, it was shown that using nano with surface treatment dispersion of nano in polymer matrix was better than nano without treatment.

(3) SEM pictures was shown that surface fracture of HDPE/ modified Nano CaCo₃ is brittle compared to HDPE/ Nano CaCo₃ this because of good interaction of modified nano with HDPE.

(4) Addition of nano CaCo₃ increment of crystallinity and heat fusion of nanocomposites also HDPE with higher MFI increase these properties.

3. References

- [1] Jiann-Wen Huang, *J.Applied polymer science*. 2007, **107**, 3163,3172
- [2] Yibing Cai, Lei Song, *J.Energy conversion and Management*,2008,**49**,2055-2062
- [3] Silvia Barus, Macro Zanetti, *J.Polymer*,2009,**50**, 2595-2600
- [4] Shahin Akhlaghi, Alireza Sharif, *J.Material and Design*,2011, **33**,273-283
- [5] Jong-Il Weon, *J.polymer Degradation and Stability*,2010,**95**,14-20
- [6] K.Chrissafis, *J.Thermochimica Acta*, 2009, **485**, 65-71
- [7] K.Chrissafis, *J.Applied polymer science*,2008, **110**, 1739-1751
- [8] Wunderlich B ,*Thermal analysis*. 1990, **Academic Press**, New York