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On the Dependence of Avrami Indexes of MDPE on Milling Time

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In the current study, the role of milling time on thermal properties and crystallization behavior of medium density polyethylene (MDPE) was investigated. For this purpose, high energy ball mill and differential scanning calorimetry (DSC) techniques were used. The results of DSC tests indicated that the milling process affected on crystallization behavior and thermal properties of MDPE. Rising crystallization temperature, specific heat capacity and crystallinity index and decreasing Avrami index were caused by ball milling; yet melting temperature was not changed, even at long milling times. In summary, thermal properties of the polymer were not changed significantly by increasing milling time.

Keywords Ball milling; Crystallization behavior; DSC; MDPE; Thermal properties

INTRODUCTION

Ball milling is being used widely to improve the physical properties of materials. This technique can be applied to elemental crystalline powders with different objectives; particle size reduction, amorphization, procurement of nanocrystalline structures, etc. It can be also used for alloying powders in the solid state, the so called mechanical alloying. Although most of the studies employing this technique have been limited to metallic systems^[1–3], but recently, ball milling has been applied to polymeric materials.

The use of ball milling is one of the best methods to dispersion of secondary phase to polymer matrix. Good dispersion and lack of filler agglomeration in matrix and the possibility of blending incompatible polymer mixtures are among the main advantages of this process. First results of applying ball milling to polymers showed that this procedure is adequate for making polymer blends. This technique overcomes some problems associated with conventional methods, such as thermal degradation due to excessive heating in the melting process or the difficulty in removing the polymer from the solvent if the solution method is used^[4–6].

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Based on a literature survey done by the authors, there are many studies concentrated on milling of polymer systems^[7–13]. For example Font et al. showed that the binary mixtures of semicrystalline/noncrystalline polymers could be formed by ball milling. Also some researchers made mixtures of PEEK/PEI, PET/PEI, PBT/PEI, and PBT/PET using the milling method. The results showed that their thermal behavior were comparable with that of blends obtained by melting^[9–13].

Although using mechanical milling in composite producing has some advantages, but the main question is whether any change takes place in polymer structure through milling or mechanical mixing or not. Some modifications of polymer mechanical properties such as strength and hardness have been obtained as a consequence of the milling treatment^[14,15]. Intensive structural changes induced by milling are described in the literature^[16,17]. Font et al. investigated the effect of milling on thermal behavior of poly ethylene terephthalate^[17].

Research results showed that the energy supplied by grinding caused an increase in the amount of amorphous material. The crystallization, on heating the glassy state resulted by milling, took place in two steps. One of them was near the glass transition and the second occurred just at the beginning of melting. When PET was pre-annealed, some differences in the amorphization behavior, caused by mechanical milling, were encountered^[17]. Font et al. investigated the effect of ball milling on semicrystalline bisphenol A polycarbonate (PC)^[18].

They showed that the semicrystalline PC could be amorphized by ball milling. The amorphous state reached by this method was different from what obtained by quenching the melt. For polymer amorphized by grinding, a smaller heat capacity jump in the glass transition temperature was observed. In this case, an additional annealing treatment gave rise to a partial recrystallization which was not observed for quenched PC.

The degree of crystallinity after this recrystallization depended on the temperature of thermal treatment prior to the amorphization by ball milling^[18]. The Avrami theory was applied for crystallization kinetics analysis.

Values of the Avrami index that provide a qualitative indication of the nucleation mechanism and on the form of crystal growth were determined for different polymeric samples^[19,24–30].

Xu et al. investigated the Non-isothermal crystallization kinetics of exfoliated and intercalated polyethylene/montmorillonite nanocomposites. In this research the Avrami plots showed that the crystal growth of PE in the intercalated sample is two-dimensional, while it is three-dimensional in the exfoliated sample. The crystallization activation energy of the intercalated sample is slightly smaller than that of the exfoliated sample^[25].

Apiwanthakorn et al.^[26] investigated the non-isothermal melt-crystallization kinetics and subsequent melting behavior of poly(trimethylene terephthalate) (PTT) by differential scanning calorimetry (DSC). The Avrami, Tobin and Ozawa equations were applied to describe the kinetics of the crystallization process. The Avrami and the Tobin models were all found to describe the non-isothermal melt-crystallization data of PTT fairly well, with the Avrami model being the better of the two.

Both of the Avrami and Tobin crystallization rate parameters (i.e., KA and KT, respectively) were found to increase with increasing cooling rate^[26]. Ziaee et al. investigated the non-isothermal melt- and cold-crystallization and subsequent melting behavior of poly(3-hydroxybutyrate) (PHB). The crystallization kinetics was studied by a direct fitting of the experimental data to various macrokinetic models, namely Avrami, Tobin, and Ozawa models.

All of the macrokinetic models were found to describe the experimental data for both the melt- and the cold-crystallization processes fairly well. They showed that the temperature at 1% relative crystallinity, the temperature at the maximum crystallization rate, and the temperature at 99% relative crystallinity were all shifted towards lower temperatures with increasing cooling rate for melt-crystallization or shifted towards higher temperatures for cold-crystallization with increasing heating rate. For both the melt- and the cold-crystallization processes, the apparent incubation period, the crystallization time at different relative crystallinity values and the apparent total crystallization period showed a linear relationship with cooling or heating rate in their log–log plots^[27].

Thanomkiat et al. investigated the overall isothermal melt-crystallization and subsequent melting behavior of metallocene-catalyzed syndiotactic polypropylene resins of various molecular weights. The kinetics of the overall isothermal melt-crystallization process was analyzed based on various macrokinetic models, i.e., the Avrami, Malkin, and Urbanovici–Segal models. The experimental data were found to be best described by the Urbanovici–Segal model, followed by the Avrami and the Malkin ones, respectively.

For a given resin, all of the overall crystallization rate parameters were found to decrease in their values with

increasing the crystallization temperature, a characteristic of the crystallization in the nucleation-controlled region^[28]. In spite of the importance of MDPE the effect of ball milling on its structural changes and its thermal properties has not been under attention. Therefore, the main goal of current research is to find out the effect of ball milling on thermal properties and crystallization behavior of MDPE. Also it will be tried to clarify the role of milling time on its Avrami indexes.

EXPERIMENTAL PROCEDURE

Material

Medium density polyethylene (MDPE) with density (0.937 g/cm³), vicat softening point (117°C) and melting flow index (MFI) (4.2 g/10 min), supplied by Tabriz Petrochemical Complex, Iran, was used as beginning material.

Specimen Preparation

Milling of polymer was performed at room temperature using a high energy ball mill with constant rotation speed of 250 rpm. A cylindrical stainless steel vessel and steel balls were used. The weight ratio of balls to MDPE powders was kept constant at 30. The 3.5 gram samples were milled for different times (i.e., 0, 0.5, 1.5, 3, 7, and 30 hours). Just for simplicity, the polymers at different milling time were coded as MDPE-0 h, MDPE-0.5 h, MDPE-1.5 h, MDPE-3 h, MDPE-7 h, and MDPE-30 h.

Differential Scanning Calorimetry

The thermal properties of pure MDPE were examined using heat flow differential scanning calorimetry device (Shimadzu DSC-60). Samples were heated from room temperature to 150°C at a heating rate of 10°C/min, followed by cooling at the same rate to room temperature. After that samples were heated in the second heating cycle. The second heating cycle and the first heating cycle were exactly the same. Each sample was subjected to DSC test and average values of DSC results for at least two fresh specimens of each sample were reported for thermal properties.

RESULTS AND DISCUSSION

Crystallization Behavior

Figure 1 shows the variations of heat flow versus time for MDPE-0 h and MDPE-0.5 h at heating, cooling and second heating cycles. Based on Figure 1, the amount of heat flow of milled MDPE powders is more than that unmilled MDPE. It is worth noting that the rising trend due to an increase in milling time was observed for all studied samples.

The heat of fusion (H_f) and solidification (H_s), melting (T_{pf}) and solidification (T_{cp}) temperatures and initial (T_{ci} , T_{mi}) and final (T_{cf} , T_{mf}) temperatures of solidification

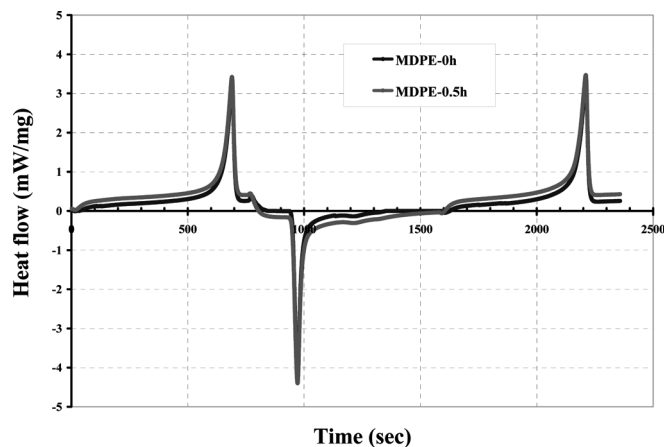


FIG. 1. The variation of heat flow versus time for MDPE-0h and MDPE-0.5h.

and fusion peaks were obtained from DSC curves and summarized in Table 1.

Based on Table 1 and what appears in Figure 2, at first heating cycle, melting temperature including initial, maximum (peak of the curve) and final temperatures of melting have not changed significantly as milling time increase up to 7 hours, while melting temperatures slightly increase for MDPE-7 h and MDPE-30 h respect to other samples. The reason of this effect can be related to severe deformation applied on MDPE powders during long time of milling process, which causes to increase interaction and rigidity of polyethylene chains significantly^[24].

At initial cooling process, maximum and final temperatures promote to higher amounts by progressing of milling. The experimental data indicate that the nucleation sites in MDPE, realized from T_{ci} , increase with increase in milling time. At the second heating cycle, fusion temperatures of all samples is almost the same. But heat of fusion in ball milled MDPE samples is higher than that of MDPE-0h. On the other hand, melting temperature of ball milled MDPE almost do not change by variation of milling time. The reason of this effect can be attributed to the variation of structure of polymer chains during milling process.

Considering solidification cycle, the relative crystallinity fraction can be calculated by the following Eq. (1)^[20]:

$$X(t) = \frac{\int_0^t \left(\frac{dH}{dt}\right) \times dt}{\int_0^\infty \left(\frac{dH}{dt}\right) \times dt} \quad (1)$$

the first integral is the heat generated at time t and the second one is the total heat when the crystallization is completed.

Relative crystallinity versus temperature for MDPE with different milling time is shown in Figure 3. As seen, solidification in milled MDPE occurs in a wide temperature range, and crystallization starts at a temperature higher than MDPE-0h.

Figure 4 shows the variation of relative crystallinity with logarithm of solidification time for milled and unmilled MDPE samples. As it can be realized, both solidification time and solidification rate depend strongly on mechanical milling. Relative crystallinity changes over time can be readily illustrated in the following equation:

$$X(t) = 1 - \exp(-kt^n) \quad (2)$$

where $X(t)$ is a relative crystallinity at arbitrary time t , n is the Avrami index that provides a qualitative indication of the nucleation mechanism and on the form of crystal growth, and k is the constant concluding nucleation and growth parameters^[19]. Equation (2) can be transformed into logarithmic form:

$$\ln[-\ln(1 - X_t)] = \ln(k) + n \ln(t) \quad (3)$$

By applying Avrami theory and plotting $\ln[-\ln(1 - X_t)]$ against $\ln(t)$, a straight line is obtained with the slope and the intercept as n and $\ln(k)$, respectively. The plot of $\ln[-\ln(1 - X_t)]$ versus $\ln(t)$ is shown in Figure 5, The Avrami indexes and $\ln(k)$ achieved from Figure 5 are summarized in Table 2.

As reported by other investigators, Avrami index 3 suggests an instantaneous nucleation with spherulite growth geometry^[21]. It may be concluded that ball milling has no effect on the nucleation mechanism and spherulite

TABLE 1
Thermal properties of ball milled MDPE achieved from DSC test

| Materials | First heating cycle | | | | Second heating cycle | | | | Third heating cycle | | | |
|------------|---------------------|----------|----------|--------|----------------------|----------|----------|--------|---------------------|----------|----------|--------|
| | T_{mi} | T_{mp} | T_{mf} | H_f | T_{ci} | T_{cp} | T_{cf} | H_s | T_{mi} | T_{mp} | T_{mf} | H_f |
| MDPE-0 h | 121.39 | 127.47 | 130.20 | 122.53 | 115.88 | 113.81 | 110.19 | 125.43 | 122.88 | 129.07 | 131.69 | 133.20 |
| MDPE-0.5 h | 121.24 | 126.81 | 129.55 | 141.67 | 116.76 | 114.17 | 110.49 | 144.08 | 122.19 | 128.53 | 131.25 | 156.78 |
| MDPE-1.5 h | 121.07 | 126.42 | 129.07 | 141.06 | 116.48 | 114.22 | 110.70 | 143.78 | 122.01 | 128.09 | 130.75 | 151.30 |
| MDPE-3 h | 122.60 | 127.35 | 130.92 | 139.68 | 117.32 | 114.93 | 110.63 | 136.93 | 121.67 | 128.73 | 131.36 | 146.83 |
| MDPE-7 h | 123.60 | 128.36 | 132.00 | 152.27 | 117.75 | 115.39 | 111.39 | 141.25 | 122.43 | 128.80 | 131.39 | 146.34 |
| MDPE-30 h | 125.27 | 129.42 | 132.08 | 159.26 | 117.79 | 115.84 | 111.22 | 141.89 | 122.20 | 128.67 | 131.10 | 145.36 |

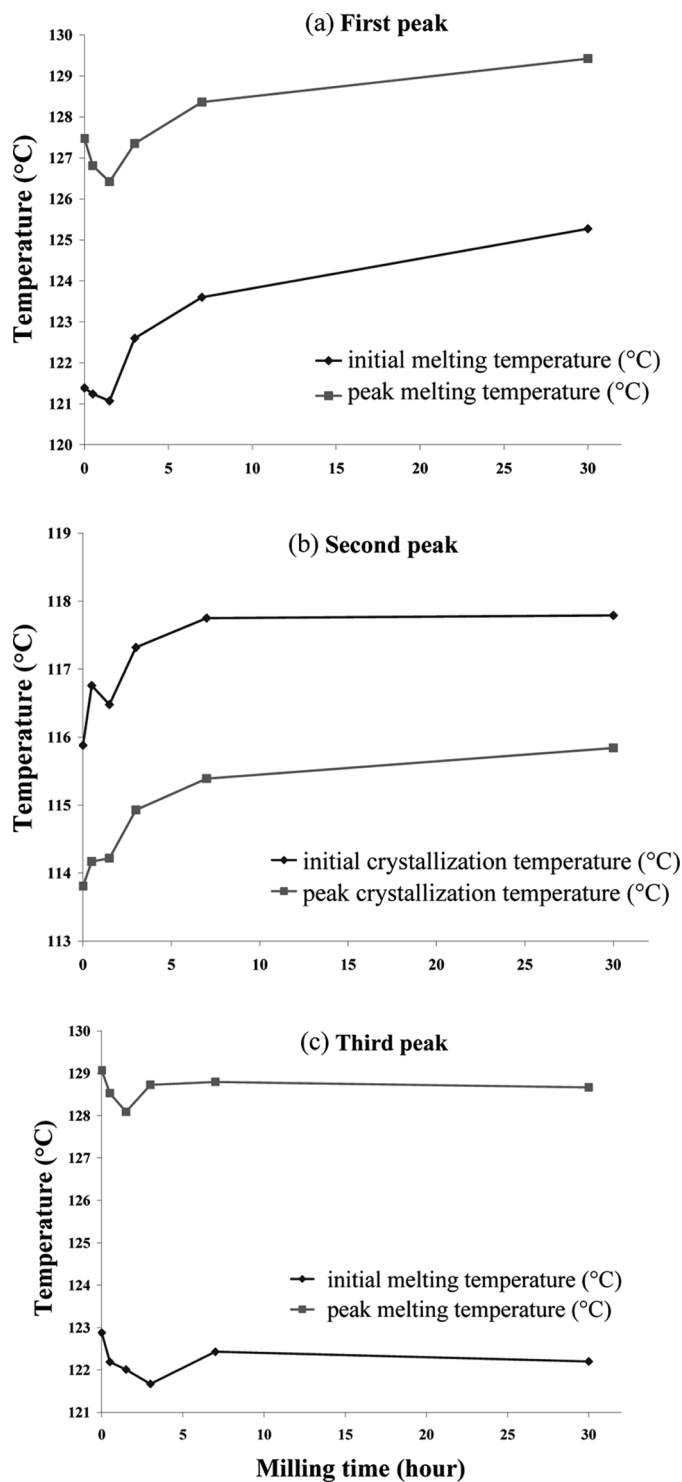


FIG. 2. Melting and crystallization temperatures of milled MDPE plotted against milling time.

growth of MDPE, But unmilled MDPE has a different nucleation and crystallized morphology respect to ball milled MDPE and all milled samples have the same crystallized morphology and nucleation mechanism.

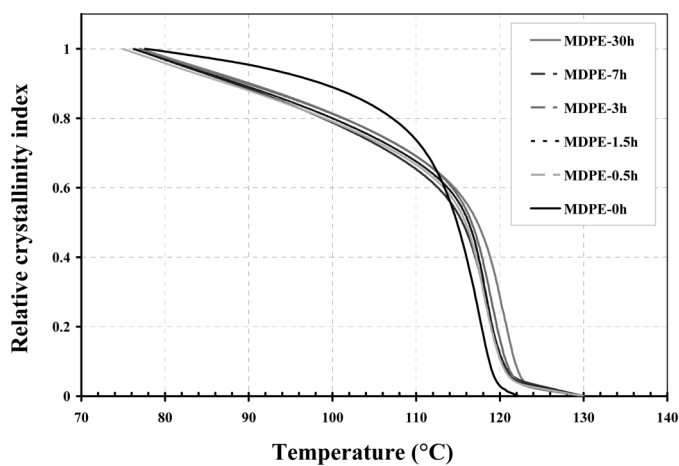


FIG. 3. Relative crystallinity versus temperature of MDPE as function of different milling time.

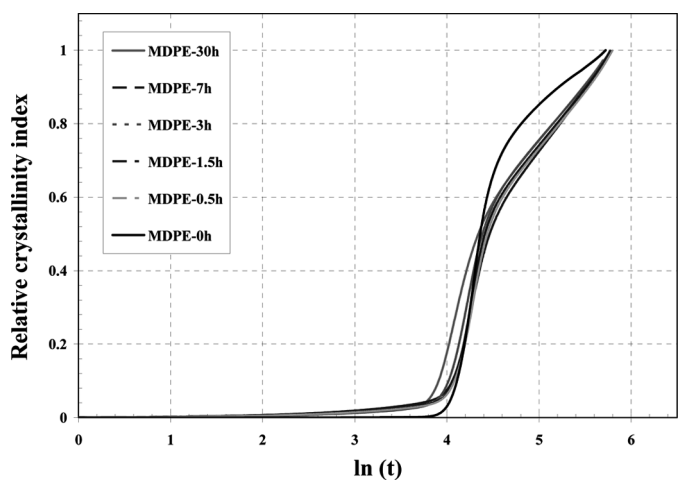


FIG. 4. Relative crystallinity of MDPE versus logarithm of solidification time at different milling times.

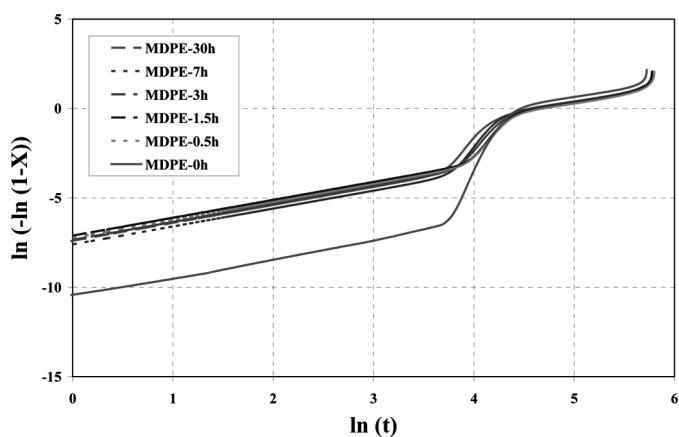


FIG. 5. Plots of the variation of $\ln[-\ln(1 - X_i)]$ versus $\ln(t)$ for MDPE ball milled at different milling time.

TABLE 2
Role of milling on Avrami index of MDPE

| Notation of samples | First crystallization | | Second crystallization | |
|------------------------|-----------------------|-------|------------------------|-------|
| | ln(k) | n | ln(k) | n |
| MDPE-0 h | -13.902 | 1.929 | -5.395 | 1.140 |
| MDPE-0.5 h | -7.495 | 1.058 | -5.779 | 1.158 |
| MDPE-1.5 h | -7.317 | 1.051 | -5.935 | 1.190 |
| MDPE-3 h | -7.593 | 1.057 | -5.691 | 1.152 |
| MDPE-7 h | -7.828 | 1.055 | -5.567 | 1.130 |
| MDPE-30 h | -7.812 | 1.106 | -5.170 | 1.070 |

The Avrami plots exhibited a deviation from linearity at the later stages of crystallization at crystallization temperatures. This deviation has been attributed to the occurrence of second crystallization^[22,23]. According to Figure 5, the volumetric second crystallization of MDPE decreases because of milling condition. Besides, similar nucleation and crystallized morphology at second crystallization are shown based on Table 2.

CONCLUSION

To investigate the role of milling time on crystallization behavior and thermal properties of MDPE, a series of MDPE with different milling time were prepared. Differential scanning calorimetry was carried out. The results of current study might be summarized as follows:

1. Ball milling has a significant effect on crystallinity index of MDPE.
2. High energy milling does not change melting temperature.
3. Nucleation mechanism and crystallization morphology of MDPE powders change with mechanical milling at early stages, while the Avrami index is almost independent of long milling time.

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