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# Thermal stability of glass-filled polyethylenes

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## Abstract

DSC and TGA studies have been carried out to assess the thermal stability of locally produced polyethylenes with glass fillers. Low and high density polyethylenes (melt flow indices, 20 and 0.35 g per 10 min, respectively) are used with glass powder (GP) or short glass fibers (GF). The filling ratio of glass was varied up to 25% in weight. DSC data showed no remarkable changes in melting point on testing LDPE–glass-filler systems, while a slight reduction in melting point was noticed on measuring different HDPE–GF/GP systems. TGA results indicated a significant improvement in the thermal stability of HDPE–GF/GP systems, while a significant decrease in thermal stability was obtained in the case of LDPE–glass systems.

*Keywords:* DSC; HDPE; LDPE; Polymer; Stability; TGA

## 1. Introduction

During the past fifteen years, thermoanalytical techniques, i.e. DSC, TGA and DTA, have had a particular application in the characterization, thermal behavior and degradation of filled polymers. Many technical articles [1–5] have been published in this field, and they conclude that the addition of inorganic fillers to polyethylenes, e.g. talc/polyethylene (PE), carbon black/PE, coated $TiO_2$/PE, and red phosphorous/PE systems, improves the resistance to thermal degradation.

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The thermal stability and the thermal behavior of PEs with glass fillers have been investigated by some authors [1–9]. The stiffness of the glass fiber, in general, causes steric hindrance of the relaxation process [6]. However, the thermal oxidation was higher for filled than for unfilled PE, due to the differences in thermal conductivity of PE compared with the filler [7]. Rybnikar [8] reported that the formation of a crystalline structure is faster in filled samples, as a result of the nucleation effect due to solid filled surfaces (glass beads). Recently, Hatakeyama et al. [9] concluded that the main DSC melting peak, of pure PE, was moved to slightly lower temperatures and that a broad shoulder peak appeared as the glass fiber content increased. They suggested that filler accelerates the nucleation process and retards the crystal growth of the polymer.

## 2. Experimental

Two grades of commercial polyethylene granules were used: low density polyethylene (Sepilene 23220) of density 0.9235 g $\mathrm{cm}^{-3}$ and melt flow index (MFI) 20 g per 10 min; and high density polyethylene (Sepilex HHM 5022) of density 0.955 g $\mathrm{cm}^{-3}$ and MFI 0.35 g per 10 min. They were produced in the Basrah Petrochemical Complex. The glass powder and fibres were prepared on a laboratory scale as follows:

(a) Alkali glass (composition in Table 1) was supplied by glass and ceramic producers in small pieces, 1–20 mm in length. The pieces were cleaned by washing and drying, and then ground to a fine powder by means of a Herzog swing grinding mill, model HSN 100. The powder was sieved using a Retsch sieve analyzer shaker. The powder collected from −400 mesh was used as the glass powder.

(b) The glass fibers were supplied by Pilkinton Co. (UK) as chopped strand mat (CSM). The fibers were composed of type "E" glass (composition in Table 1). The glass strands were cut from CSM to lengths from 1 to 3 mm.

The GP had an average particle size of 6.5 μm, and an average sphericity of 0.37. The fibres used had a mean strand length of 1.26 mm, (25–50) filament of 10 μm diameter per strand, and an average aspect ratio ($a_r$) of 126.

The particle size analysis and fiber length measurements were performed using microscopic techniques [10].

The glass powder (GP) or short glass fibers (GF) were compounded with PE resins. This was performed using a Brabender cam mixer, type 50N. The melt

Table 1
Glass filler specifications

| Filler type | Density in Mg $\mathrm{m}^{-3}$ | Composition in wt% | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | CaO | MgO | $B_2O$ | $Na_2O$ | $K_2O$ | $Fe_2O_3$ | $F_2$ | $SO_3$ |
| Powder | 2.48 | 72.1 | 1.7 | 6.8 | 4.0 | – | 15.0 | – | 0.1 | – | 0.3 |
| Fibers | 2.53 | 55.2 | 14.8 | 18.7 | 3.3 | 7.3 | 0.3 | 0.2 | 0.3 | 0.3 | – |

obtained was molded into plaques using the press-molding technique, according to ASTM D 1928.

Dynamic thermogravimetric analysis was conducted under nitrogen using a Perkin-Elmer TGA thermogravimetric analyzer, each sample weight being approx. 6 mg, and heating rate being 5°C $\text{min}^{-1}$.

A Du Pont DSC thermal analyzer Model 990 was used to study the melting behavior of filled polymeric samples. The heat of fusion $\Delta H_f$ and the degree of crystallinity $X_H$% were determined according to ASTM D 3417 and the crystalline melting point was measured according to ASTM D 3418. The sample weight was approx. 2.2 mg, and the test was performed at a heating rate of 10°C $\text{min}^{-1}$ under nitrogen. Indium (In) was used as reference. The heat of fusion for 100% crystalline polyethylene $\Delta H_f^*$ was taken from the literature [11], i.e. 298.86 kJ $\text{kg}^{-1}$.

## 3. Results and discussion

### 3.1. *Powder and fiber size analysis*

The relative and cumulative frequency curves of the glass powder and the fiber distribution are presented in Figs. 1 and 2, respectively.

Fig. 1 indicates that the mode, median, and mean values of the powder diameter are 4.35, 5.2, and 6.5 μm respectively. Fig. 2 shows that the mode value of the fiber length is 0.7 mm.

The number-average (mean) fiber length is calculated by

$$L_n = \frac{\sum jL_j}{\sum j}$$

where $j$ is the number of fibers of length $L_j$.

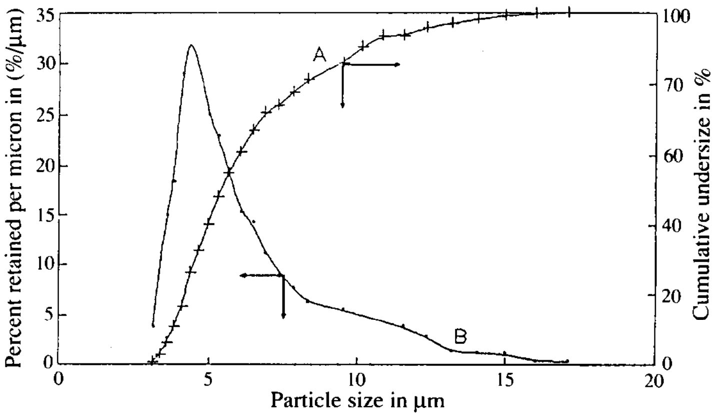


Fig. 1. Curve A, cumulative, and curve B, relative distribution curves of the glass powder.

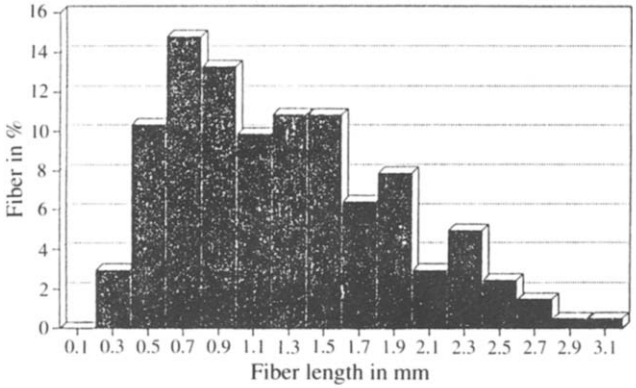


Fig. 2. Fiber length distribution.

In this study, LDPE is referred to as PE1 and HDPE as PE2, and the filled polymeric materials (with glass fillers) are represented as PE$n$/G$Xm$, where $n$ is 1 (LDPE) or 2 (HDPE), G (glass), $X$ is F (fiber) or P (powder) and $m$ the weight percent of filler (wt%).

### 3.2. *Differential scanning calorimetry*

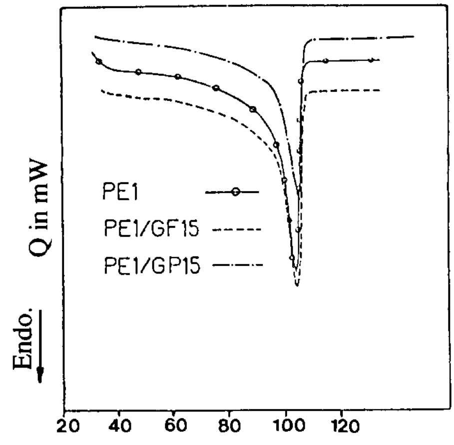
DSC results are listed in Table 2, indicating the melting temperature $T_m$, the actual heat of fusion $\Delta H_f$, and the percent crystallinity $X_H$% as a function of glass type and content. The endothermic melting peaks are presented in Figs. 3–5. DSC runs were carried out for the following samples: LDPE, LDPE + 15%GF, LDPE + 15%GP, HDPE, HDPE + 15%GF, HDPE + 15%GP, HDPE + 25%GP, HDPE + 25%GF.

### 3.2.1. *Low density polyethylene composites*

The filler concentration and shape (fibers or powder) have no significant effect on the crystalline melting point of LDPE, as shown in Fig. 3, while the degree of

Table 2
DSC analysis results for filled polyethylenes

| | Polymer resin | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | LDPE | | | HDPE | | | | |
| Filler type<br>wt% | –<br>0.0 | GP<br>15 | GF<br>15 | –<br>0.0 | GP<br>15 | GF<br>15 | GP<br>25 | GF<br>25 |
| Melting point in °C | 105 | 106 | 105 | 124 | 122.5 | 121 | 121 | 123.2 |
| Actual heat of fusion in kJ kg$^{-1}$ | 188.92 | 156.01 | 148.54 | 270.12 | 230.76 | 245.48 | 223.08 | 223.08 |
| Degree of crystallinity in % | 63.21 | 52.2 | 49.7 | 90.38 | 77.21 | 82.14 | 74.64 | 63.49 |



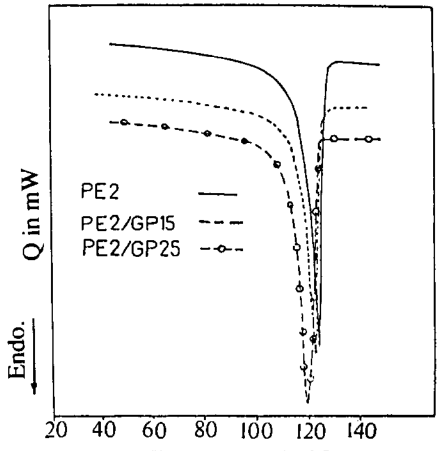


Fig. 3 (left). DSC melting peaks of filled LDPE.

Fig. 4 (right). DSC melting peaks of filled HDPE with GP.

crystallinity is affected significantly. The results obtained suggest that glass powder is a more effective nucleating agent than glass fibers. The present DSC results agree with the observations of Hatakeyama et al. [9].

### 3.2.2. *High density polyethylene composites*

The crystalline melting point and the crystallinity of the matrix are slightly decreased with increasing powder content, as shown in Fig. 4 and Table 2. The inclusion of glass fiber has a variable effect on the DSC results as compared with the glass powder effect, while the $X_H\%$ is decreased sharply by increasing the fiber content, as shown in Fig. 5.

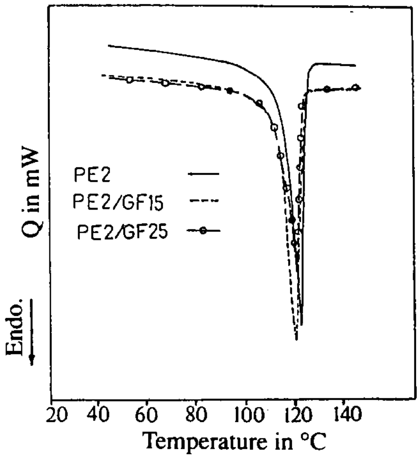


Fig. 5. DSC melting peaks of filled HDPE with GF.

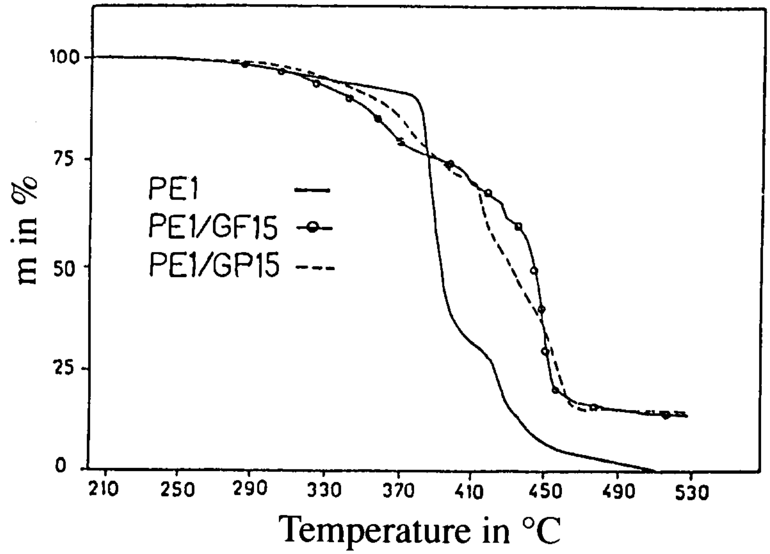


Fig. 6. TGA thermograms of LDPE composites.

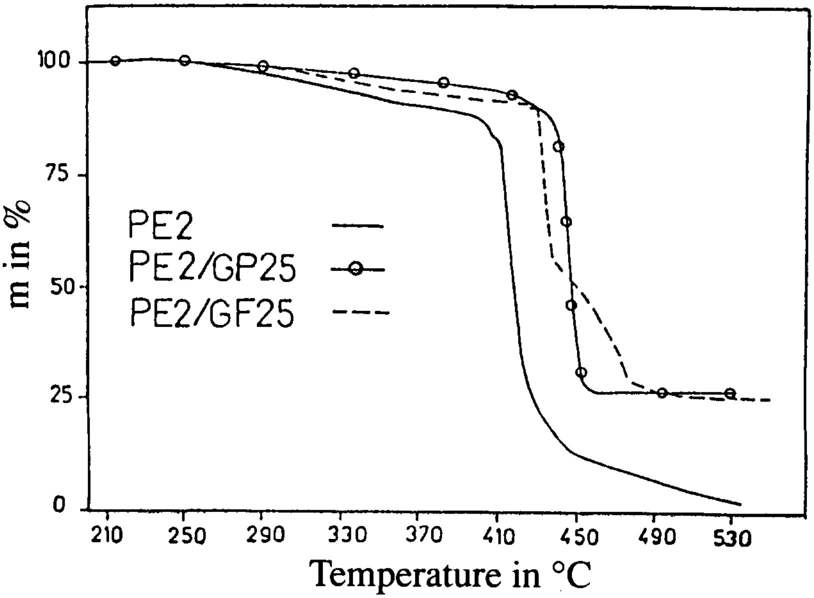


Fig. 7. TGA thermograms of HDPE composites.

### *3.3. Thermogravimatric analysis*

TGA thermograms for the LDPE, HDPE, PE1/GF15, PE1/GP15, PE2/GP25, and PE2/GF25 systems are illustrated in Figs. 6 and 7.

### *3.3.1. Low density polyethylene composites*

Addition of 15%GP to LDPE slightly improves the thermal stability of LDPE in the range of 250–330°C, e.g. at 290°C the percent weight of pure polymer remaining is about 96.9%, compared with 98.8% for PE1/GP15 and 97.6% for PE1/GF15, as shown in Fig. 6. Moreover, in the 330–370°C temperature range, the thermal degradations of PE1/GF15 and PE1/GP15 are more propagated and significantly affect the remaining weight (*m*%). This behavior of composite materials may be related to the separation of the filler from the polymer matrix due to differences in thermal conductivities between the matrix and the glass, e.g. the thermal conductivity values for LDPE and glass are 0.33 and 0.9 $\mathrm{W\ m^{-1}\ K^{-1}}$ respectively [12]. The sharp decrease in weight remaining above 370°C for the PE1/GF15 and PE1/GP15 composites, as observed in practice, is due to the volatile products produced as a result of the degradation.

The thermal stability of filled LDPE is improved significantly within the temperature range of 370–470°C. TGA thermograms after degradation indictated that only 15% of the original composite was remaining. This quantity refers to the weight of glass that was already present in the composite during preparation and that would be unaffected by degradation.

### *3.3.2. High density polyethylene*

The thermal degradation behavior of HDPE appears to improve in the presence of 25% GP or GF in the temperature range 210–530°C. As shown in Fig. 7, the weight loss of HDPE at 430°C is 23.4% in comparison with 89.5% and 89.1% for PE2/GP25 and PE2/GF25 composites respectively. This behavior of the fillers in improving the thermal stability of HDPE is believed to be related to the highly crystalline structure of the base polymer [13], good compatibility, and possibly to the close thermal conductivities, e.g. 0.63 and 0.9 $\mathrm{W\ m^{-1}\ K^{-1}}$ for HDPE and glass respectively [12], between the filler and matrix, whereas the glass fillers act as retardants and protectors to the early degradation of the base polymer.

## 4. Conclusions

DSC results showed that the presence of glass fillers in LDPE has no effect on $T_m$, but slightly reduces the crystalline structure. In addition, the glass fillers decreased the melting temperature, and reduced the crystalline structure of HDPE.

The TGA results obtained reconfirmed that the thermal stability of HDPE and LDPE are significantly improved for the former and diminished for the latter in the presence of glass fillers.

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