

# Melt Flow Properties of Starch-Filled Linear Low Density Polyethylene: Effect of Photoinitiators

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**ABSTRACT:** Three series of the processed linear low density polyethylene samples containing: 0–15 wt % corn starch, 0.5 wt % of a photoinitiator (PI), and 5 wt % corn starch + 0.5 wt % of a PI were prepared using an internal mixer at 170°C for 5 min in a closed system. The melt flow index (MFI) and apparent viscosity ( $\mu_a$ ) of each sample were measured. The presence of starch in the samples decreased the MFI and increased the apparent viscosity. Increase in the starch concentration has a direct relation to both the MFI and the  $\mu_a$  at various shear rates. A slight

decrease in the MFI and the  $\mu_a$  was observed due to the presence of the PIs in the samples. This was enhanced by the presence of the starch in the samples. Carbonyl group formation showed an increase in the samples containing the PIs. This was also enhanced by the presence of the starch in the samples. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 178–182, 2007

**Key words:** linear low density polyethylene; corn starch; melt flow properties; apparent viscosity; photoinitiators

## INTRODUCTION

Linear low density polyethylene (LLDPE) has always been challenging low density polyethylene (LDPE) for market share because of economic and technological advantages of the manufacturing process as well as of the more superior end-use performance compared with LDPE.<sup>1,2</sup> However, LLDPE has poor performance in the blowing phase of film making, which is related to the low elongational viscosity mostly due to the linear structure of its macromolecules. This can also be overcome by blending the polymer with a small percentage of LDPE.<sup>3</sup>

Starch has been used as a filler to plastics in film production from many years ago.<sup>4</sup> Griffin introduced the idea of blending biodegradable corn starch with polyolefins as a solution to the problem of waste plastic disposal in the environment.<sup>5–8</sup> Raw starch in a polymer satisfies the requirements of adequate thermal stability<sup>9</sup> and low interference with melt flow properties.<sup>10</sup> The inclusion of starch in the polymer reduces the polymer rubbery deformation, swelling, and the entrance corrections of the extrudate emerging from the capillary. These are associated with elastic deformations stored in elastic melts during their capillary flow.<sup>11</sup> Addition of a photoinitiator such as a benzophenone derivative to the starch-filled polymer by melt mixing makes the blend pho-

todegradable.<sup>12</sup> This is essential prior to biodegradation of the polymer.<sup>13</sup>

In the starch-filled polymers, the behavior of polymer blends in the region of high deformation rates (under real technological conditions) is of practical interest. Since the yield stress in such region, especially at low starch concentration, can be neglected, thus a power-law equation which we used in this work reflects correctly all the main features of the flow properties of the starch-filled LLDPE.

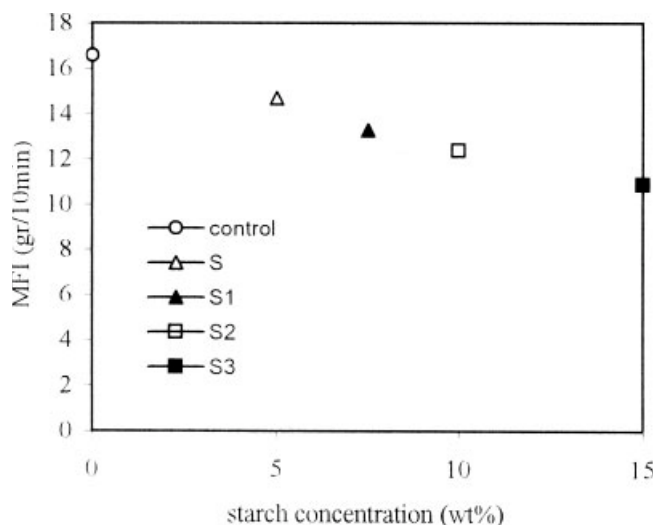
Investigations of melt rheology and processability of the filled LLDPEs are scarce and melt flow behavior of corn starch-filled LLDPE containing a photoinitiator has not yet been reported. In the present work, the effect of various concentrations of corn starch on the melt flow properties of the processed LLDPE in the absence and presence of some photoinitiators (PIs) was studied. Melt flow index (MFI), apparent viscosity versus shear rate, and chemical changes in the macromolecules (i.e. carbonyl formation) of the samples were measured.

## EXPERIMENTAL

### Materials

Linear low density polyethylene (Ladaen, MFI = 17–2.16 kg/190°C,  $d = 0.924$  g/cc,  $T_m = 129^\circ\text{C}$ ) was purchased from Saudi Arabia Petrochemical Co. Corn starch was supplied by Glucosine Co. (Iran) and vacuum dried at 80°C for 12 h before use. Irgacure 651 (dimethoxy-2-phenyl acetophenone) was supplied by

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**Figure 1** Effect of starch concentration on melt flow index of the processed starch-filled LLDPE control (○), S (△), S1 (▲), S2 (□), S3 (■).

Ciba Geigy Co. Benzoin ethyl ether was purchased from Aldrich Chemical Co. Ferric stearate was prepared in our laboratory.<sup>14</sup>

### Sample preparation

The corn starch, PI (or mixture of PI + corn starch) was tumble mixed with LLDPE (42 g) and the compounded polymer was processed in a Haake torque rheometer (HBI System 90) at 170°C for 5 min in a closed chamber. LLDPE was melt-blended with different concentrations of corn starch (0–15 wt %). These samples are designated as control (0%), S (5%), S1 (7.5%), S2 (10%), and S3 (15%). LLDPE was also melt-blended with 0.5 wt % of PI. These processed samples are designated I6, Bin, and Fs, respectively. Mixtures of 5 wt % corn starch and PI (0.5 wt %) were also melt processed with the LLDPE. These samples are indicated by addition of a suffix "S" to the codes of those not containing starch (i.e., I6S, BinS, and FsS).

Films were compression molded at 150°C for 2 min by a bench type Collin press using a special grade of cellophane as mold-release agent. Films (0.15 mm thick) were removed from the press, quenched in cold water, and kept at room temperature.

### Measurements

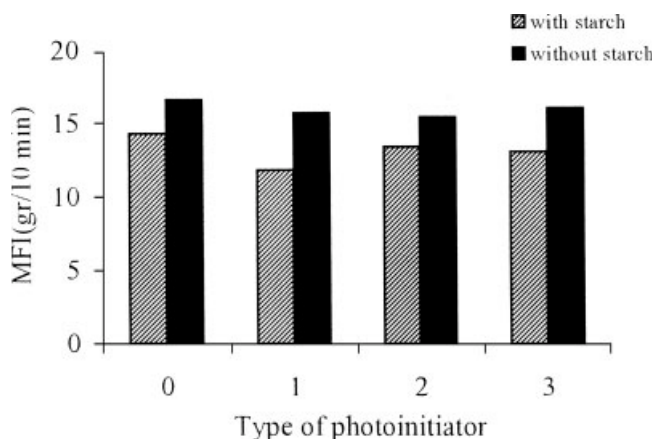
The rheological behavior of the samples was studied by a melt flow index apparatus (MFI, 2.16 kg/190°C) and a Rheoscope 1000, both manufactured by CEAST Co. (Italy). The plunger speed in the Rheoscope was varied in steps from 0.5 to 200 mm/min (9 steps). The power law equation,  $\tau = k(\dot{\gamma})^n$  was used to obtain apparent viscosity–shear rate data ( $\mu$

$= k\dot{\gamma}^n$ ). The two parameters  $k$  and  $n$  are related to the molecular weight and its distribution, respectively.<sup>15</sup> This formula describes the behavior of many polymeric melts sufficiently well in the range of shear stress and rate of shear, which are most vital in technology. A Fourier-transform infrared spectrometer (FTIR, IFS; Bruker Co., Germany) was used to monitor chemical changes occurring in the macromolecular structures. The changes in carbonyl index ( $A_{1721} \text{ cm}^{-1}/A_{1465} \text{ cm}^{-1}$ ) were measured.

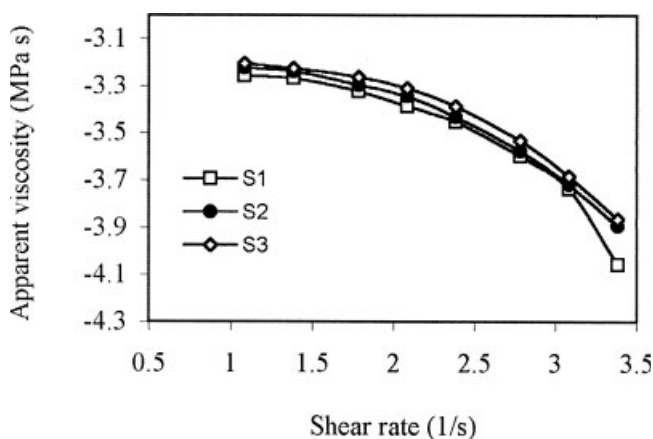
## RESULTS AND DISCUSSION

Figure 1 shows the effect of various corn starch concentrations on the MFI of the processed LLDPE. Increase in the starch concentrations decreases the MFI. There is a linear relation between the amount of starch in the blend and such decrease in the MFI. Figure 2 illustrates the effects of the PI types at 0.5 wt % on the MFI of the LLDPE and the starch-filled LLDPE during the melt mixing. This figure shows that a slight decrease in the MFI compared with the control is found in the presence of each one of the PIs in the samples. Ferric stearate causes the lowest reduction in the MFI of the samples. A comparison between the MFI values of these samples with those of the starch-filled LLDPE at 0.5 wt % of the PIs indicates that the presence of starch in the LLDPE matrix brings about a significant reduction in the MFI of the sample (Fig. 2). The starch + irgacure 651 in the LLDPE is the most effective.

Figure 3 depicts the variation of apparent viscosity versus shear rate of various amounts of the starch in the LLDPE samples. It can be seen that as the shear rate increases from 1 to 3.5  $\text{s}^{-1}$  apparent viscosity of all the samples decreases. An increase in the apparent viscosity at a constant shear rate is observed by increase in the starch concentration. Figure 4 indicates



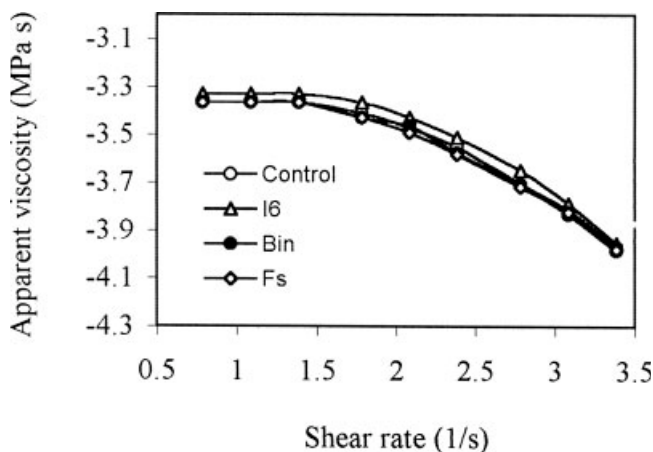
**Figure 2** Effect of photoinitiator's type at 0.5 wt % on MFI of the processed LLDPE and 5 wt % starch-filled LLDPE: (0) control, (1) I6 and SI6, (2) Bin and SBin, and (3) Fs and SFs.



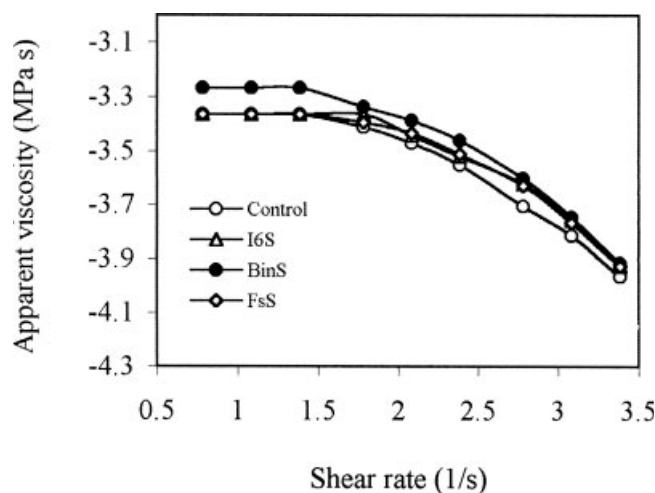
**Figure 3** Variation of apparent viscosity versus shear rate of the processed LLDPE containing different amounts of starch: S1 ( $\square$ ), S2 ( $\bullet$ ), S3 ( $\diamond$ ).

that the presence of irgacure 651 in the LLDPE during the melt mixing causes a high apparent viscosity at various shear rates. The difference between the effect of ferric stearate and benzoethylether on the flow behavior of LLDPE is negligible. Figure 5 shows the effect of the PIs at 0.5 wt % in the processed starch-filled LLDPE on the apparent viscosity of the samples at various shear rates. As the shear rate increases, the apparent viscosity of the samples decreases. Benzoethylether shows the higher apparent viscosity at various shear rates. No difference between the effects of the PIs on the apparent viscosity at shear rates higher than  $2.8 \text{ s}^{-1}$  is observed. Comparison of the curves in Figures 4 and 5 reflects the higher level of the apparent viscosity at various shear rates due to the presence of the starch in the samples.

The changes in the MFI and the apparent viscosity at a constant shear rate due to the effect of the starch (Figs. 1, 3, and 5) are explained by the stiffening effect of the starch particles dispersed in the LLDPE matrix



**Figure 4** Variation of apparent viscosity versus shear rate of the processed LLDPE containing different types of photoinitiators at 0.5 wt %: (O) Control, ( $\Delta$ ) I6, ( $\bullet$ ) Bin, ( $\diamond$ ) Fs.



**Figure 5** Variation of apparent viscosity versus shear rate of the processed LLDPE containing 0.5 wt % of different photoinitiators and 5 wt % starch-filled LLDPE: (O) control, ( $\Delta$ ) I6S, ( $\bullet$ ) BinS, ( $\diamond$ ) FsS.

on the flow. The chemical (branched and linear) and physical (crystalline) structures of the starch as a solid particle in the LLDPE matrix during the melt blending is responsible for such effect.<sup>16</sup> The decrease in the MFI and the increase in the apparent viscosity observed in Figures 2 and 4 could be explained as a consequence of both macroalkyl/macroalkoxy radicals combination, with the radicals produced by the thermal decomposition of the PIs during the initial stages of the melt mixing.<sup>17</sup> This reduces the macroalkoxy radical formation followed by  $\beta$ -scission. As it is known a high concentration of macroalkyl radicals due to the high shearing forces operating on the polymer during the initial stages of the mixing is formed.<sup>18</sup> These radicals combine with oxygen in the mixer resulting in macroalkoxy radicals<sup>18-20</sup>

Table I shows the effect of both the starch concentrations and the PI types on carbonyl formation of the LLDPE and the starch-filled LLDPE during the melt mixing. The starch-filled LLDPE film samples

**TABLE I**  
Effect of Melt Processing on Carbonyl Formation of LLDPE + 0.5 wt % Photoinitiators and 5 wt % Starch-Filled LLDPE + 0.5 wt % Photoinitiators

Sample code	Carbonyl index
Control	1.03
S	1.25
S1	1.3
S2	2.06
S3	2.18
I6	1.3
Bin	1.33
Fs	2.39
I6S	1.98
BinS	1.44
FsS	2.66

show higher amount of carbonyl formation compared with the control. An increase in the carbonyl index of the samples ( $A_{1721} \text{ cm}^{-1}/A_{1465} \text{ cm}^{-1}$ ) is observed by increasing the starch concentrations. A lower increase in the carbonyl index compared with the starch-filled samples is also found in the presence of each one of the PIs in the LLDPE samples. A significant amount of carbonyl is formed owing to the effect of ferric stearate. The presence of starch in these samples promotes the carbonyl formation (see Table I). The carbonyl formation owing to the presence of the starch in the LLDPE matrix is mainly explained by thermal oxidation of the amylose component in the starch. In the present blend, LLDPE forms a continuous matrix (the dispersion medium) and the starch forms a dispersed phase in the LLDPE. The situation is what is known for polymeric systems containing an organic solid dispersed phase. The rheological behavior of this polymer blend depends on the structure, which is primarily governed by the degree of the starch dispersion.<sup>21</sup> During the melt mixing of the blend, the presence of starch particles enhances the viscosity of the melt which increases with the starch concentrations, especially at low shear rates (see Figs. 3 and 5). This depends on the ability of the particles to immobilize molten material and thus restrict the volume of flowable melt.<sup>22</sup> In the region of high deformation rate, the influence of the starch on the apparent viscosity of the melt seems to be weaker than at low shear rates.<sup>23</sup>

The melt temperature of the mixing chamber was set at 170°C. But, because of the particle friction in the blend and a high dissipation of energy, an increase in temperature of the melt is observed. This increase was proportional to the starch content of the blends. The greater the viscosity the higher the increase in the melt temperature. It is worth mentioning that the presence of LLDPE melt also prevented discoloration of the starch at such temperature.

Melt blending of the starch with the LLDPE due to the hydrophilic nature of the starch has compatibility problem and the maximum tolerable amount of starch in the blend, usually, does not exceed 6–9% by weight.<sup>24</sup> To make corn starch compatible with the LLDPE it is necessary to reduce the interfacial tension between the two phases. This can be achieved by (1) the chemical modification of the starch or the LLDPE and<sup>25,26</sup> (2) the use of compatibilizers containing groups capable of hydrogen bonding with starch hydroxyls.<sup>27,28</sup>

In the present work (1) the corn starch used in LLDPE containing the PIs was in the tolerable amount (i.e. 5 wt %), (2) Thermal oxidation of the polymers during the melt processing enhances the compatibility, (3) the interfacial adhesion can also be improved by using the PIs such as irgacure 651 and benzoein ethylether and their thermal decomposition products which are capable of hydrogen bond-

ing with the starch hydroxyls.<sup>27,29</sup> This would be evidenced by mechanical properties and SEM measurements of the starch-filled LLDPE samples containing the PI, which is underway in our laboratory.

Finally, we believe that if the corn starch-filled LLDPE containing 0.5 wt % each of the PIs is processed into fabricated products (i.e. packaging film), it would be bio-assimilated by combined peroxidation (through photodegradation) and biodegradation after being used in outside environment.<sup>13,30</sup>

## CONCLUSIONS

The results of the present work are summarized as follows:

1. There is a linear relation between the starch concentration in the LLDPE matrix and the MFI reduction.
2. The effect of each one of the PI's on the MFI of the samples is not significant, but this effect in the presence of the starch becomes obvious. The I6S sample among the others shows the lowest reduction in the MFI.
3. Apparent viscosity of the starch-filled LLDPE reduces with increase in the shear rate. The higher level of  $\mu_a$  at a constant shear rate is observed by increasing the starch concentration.
4. The irgacure 651 in the LLDPE and the benzoeinethylether in the starch-filled LLDPE cause the higher  $\mu_a$  at various shear rates compared with the other PIs.
5. The presence of the starch in the LLDPE leads to an increase in the carbonyl formation, which is enhanced by the presence of each one of the PIs.
6. The carbonyl formation due to the effect of the PIs is in the order of Fs > Bin > I6.

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