Tensile, Flow, and Thermal Properties of $CaCO_3$-Filled LDPE/LLDPE Composites

Ji-Zhao Liang

College of Industrial Equipment and Control Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China

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ABSTRACT: Calcium carbonate ($CaCO_3$)-filled low-density polyethylene (LDPE)/linear low-density polyethylene (LLDPE) composites were fabricated by means of a twin-screw extruder, and the tensile mechanical properties of the tubing with thickness of 0.5 mm made from these composites were measured at room temperature to identify the effect of the filler concentration on the properties of these composites. The results showed that the tensile elastic modulus increased roughly linearly with increasing weight fraction (ϕ_f) of the fillers. The tensile fracture strength (σ_b) along longitudinal direction was obviously higher than that along transverse direction under the same test conditions, especially at higher filler concentration. The values of σ_b of the specimens along both the two directions achieved minimum at $\phi_f = 20\%$. Furthermore, the melt flow rate (MFR) and heat enthalpy (ΔH) of the composite materials were measured. It was found that both the MFR and the ΔH decreased with the addition of ϕ_f. The ΔH for the composite with LDPE/LLDPE ratio of 70/30 was higher than that of the composite with LDPE/LLDPE ratio of 50/50 at the same filler concentration, but contrary to the MFR. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1692–1696, 2007

Key words: LDPE/LLDPE blend; $CaCO_3$; tensile; flow property; heat enthalpy

INTRODUCTION

Owing to the good processability, flexibility, and extensibility of low-density polyethylene (LDPE) and advantageous mechanical performances of linear low-density polyethylene (LLDPE), a number of studies on the structure/property of LDPE/LLDPE blends have been conducted. It is necessary for polymer processing and shaping of equipment design that rheological properties of polymer melts are understood. Over the recent decade, the melt flow properties of LDPE/LLDPE blend melts have been conducted.[1–5] Acierno et al.[1] studied the rheological and extensional properties as well as the nonisothermal extensional flow, and found that the melt strength only somewhat decreased and the break elongation ratio was much greater than that of LDPE when the LLDPE content was 25%. Utracki and Schlund[2] researched the flow behavior of LDPE/LLDPE blend melts in capillary and parallel plate rheometer flow, and pointed out that the pressure correction played a significant role in capillary extrusion of the blend melts. Tremblay[3] observed the entrance convergence flow pattern when LDPE/LLDPE blend melts passed through a sudden contraction channel by means of flow visualization technique. The results showed that the length of vortex region was related to the ratio between the extensional stress along the axis direction of flow and the shear stress at the capillary wall. Muller et al.[4] investigated the shear and elongation behavior of LLDPE/LDPE blend melts from capillary rheometry. The results indicated a strong sensitivity of the rheological behavior of the melts to the change in the molecular weight of the LDPE employed. Recently, Liang and Ness[5,6] studied the melt flow properties and elastic behavior of LDPE blended with two LLDPEs with different melt index, and found that the relationship between the blend and component melt shear viscosity accorded with logarithmic rule, while the die-swell ratio (B) achieved maximum value at a blending ratio of 50/50. Lu and Sue[7] researched the morphology and mechanical properties of blown films of a LDPE/LLDPE blend, and found that the film made from the LDPE/LLDPE blend possessed the highest degree of crystal orientation. Ajji et al.[8] measured the elongational behavior of the blends and their constituents at 150°C using an RME rheometer, and the crystallinity and rheological results indicated that 10–20% LDPE is sufficient to provide improved strain hardening in LLDPE. Recently, a set of equations for predicting processing, mechanical, and shrink properties of HDPE/LDPE/LLDPE blends were generated.[9] However, the studies on physical properties of inorganic particulate-filled LDPE/LLDPE composites have been relatively few.

Correspondence to: J.-Z. Liang (scutjzl@sohu.com).

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Because of low price of calcium carbonate ($CaCO_3$), it is usually used to fill into plastics for reducing the cost of plastic products and improve some properties of plastics, such as stiffness, thermal property, and shrinkage. In this work, $CaCO_3$ particles are used to fill LDPE/LLDPE blend, and the influences of $CaCO_3$ particle content on the tensile properties of the tubing, as well as the crystalline and flow properties of the composites, are investigated.

EXPERIMENTAL

Materials

Low-density polyethylene

The resin was the product of Maoming Petrochemical Co. (China), and the trade-mark was 951-000. The resin density at solid state was 920 kg/m^3, and the melt flow rate (MFR) was 1.84 g/10 min (2.16 kg, 190°C).

Linear low-density polyethylene

The resin with trade-mark DFDA-7042 was supplied by Guangzhou Petrochemical Co. (China). The resin density at solid state was 918 kg/m^3 and the MFR was 2.00 g/10 min (2.16 kg, 190°C).

Calcium carbonate

The filler was a light $CaCO_3$ supplied by Jinshan Chemical Industrial Factory (Guangxi, China). The density was 2700 kg/m^3, and the mean diameter of the particles was 1.4 μm.

Sample fabrication

After the surface of $CaCO_3$ particles was treated with a titanate coupling agent with trade mark NXT-100, supplied by Xiangfei Chemical Institute (Nanjing, China), the filler particles with LDPE/LLDPE blend were compounded at the resin melting state in a twin-screw extruder. The temperature was varying from 120 to 200°C, and the screw speed was 50 r/min. The weight fractions (ϕ_f) of the filler were 0, 10, 20, and 30%, respectively. The extrudate was granulated to produce the composites. Then, these composite granules were produced as thin-wall tubes by using a tube-extrusion extruder with screw diameter of 90 mm and head die diameter of 25 mm, and the diameter and thickness of the tubes were 50 mm and 0.5 mm, respectively. Finally, the dumbbell sheets from the tubing were made for tensile test, according to the ASTM D 638 standard. These dumbbell sheets were cut according to the standard method at machine direction (along the flow direction, symbol: d1) and at transverse direction (perpendicular to the extrusion direction, symbol: d2), respectively. The blending ratios of LDPE/LLDPE blend were 50/50 and 70/30, respectively.

Instruments and methods

Tensile test

The tensile properties of the films were measured at room temperature by using a computer-controlled universal material tester (model CTM6104; Shenzhen New Sans Test Machine Co., China). The tests were carried out according to ASTM D 638 standard, and the crosshead speed was 50 mm/min.

Flow property test

The MFR was measured by employing a MFR tester (model XNR-400; Changcun No. 2 Test Machine Factory, China). The tests were conducted at standard test conditions (2.16 kg, 190°C).

Differential scanning calorimetric test

The heat enthalpy of the film materials was measured using a differential scanning analyzer supplied by Shanghai Instrument Factory (model CDR-4P). The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Tensile elastic modulus

Figure 1 shows the dependence of the tensile elastic modulus (E_c) of the sheet specimens on the $CaCO_3$

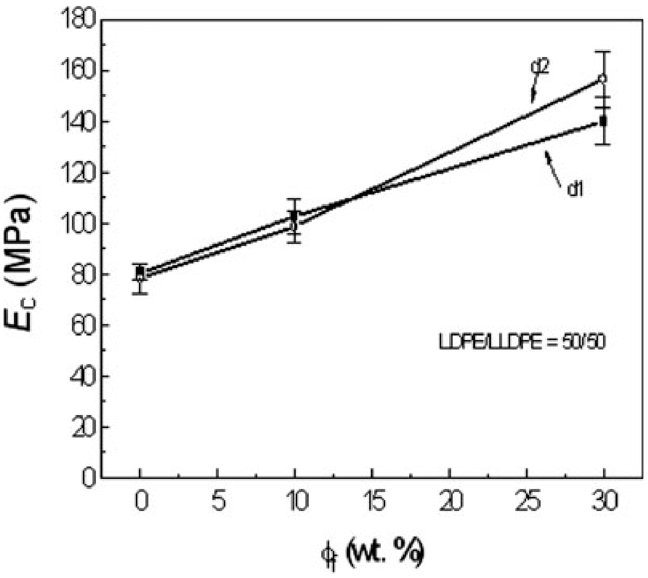

Figure 1 Dependence of Young's modulus on filler weight fraction.

content when the blending ratio of the LDPE/LLDPE blend is 50/50. It can be seen that the E_c of both longitudinal and traverse directions (d1 and d2) is close to each other, and it increases roughly as a form of linear function with increasing ϕ_f. That is

$$E_c = \alpha + \beta\phi_f \tag{1}$$

where α and β are the constants related to the stiffness of materials. In fact, β is the slope of $E_c - \phi_f$ curve, and it characterizes the sensitivity of elastic modulus to the filler concentration. The values of α and β for the sheets can be determined by applying a linear regression analysis method under experimental conditions. The results show that the value of β at transverse direction is 2.655, while the value of β along longitudinal direction is 1.961. This illustrates that the sensitivity of the tensile elastic modulus along transverse direction to the $CaCO_3$ particle content is somewhat stronger than that at longitudinal direction. In addition, when ϕ_f is more than 15%, the value of β at transverse direction is slightly greater than that at longitudinal direction.

When the thin-wall tubes leave the die, they are subjected to both blow-extrusion (the blow-up ratio is 2) and extension, and produce corresponding deformation along both transverse direction and longitudinal direction. In this case, the macromolecules of LDPE/LLDPE blend will be orientated along flow direction. In general, macromolecular orientation may strengthen directly polymeric materials, such as single axial elongation film and twin axial elongation film. Therefore, the tensile modulus of the thin-wall tubes is closely related to the macromolecular orientation and filler concentration in this case. Relatively, the macromolecular orientation along longitudinal direction is greater than that along transverse direction under these operation conditions, and the stiffness of the composite increases relevantly. In other words, the tensile modulus of the specimens along longitudinal direction depends mainly upon the macromolecular orientation in this case. Consequently, the sensitivity of the elastic modulus along transverse direction to the filler particle content is more than that along longitudinal direction.

Tensile fracture strength

When the blend ratio of LDPE/LLDP is 50/50, the dependence of the tensile fracture strength (σ_b) of the sheet specimens on the weight fraction of the $CaCO_3$ particles is shown in Figure 2. For the specimens at longitudinal direction, σ_b decreases somewhat with an addition of the filler content when ϕ_f is less than 20%, while σ_b increases obviously when ϕ_f is more than 20%. Similarly, for the specimens at transverse direction, σ_b decreases obviously with an addition of ϕ_f when ϕ_f is less than 20%, and then increases somewhat. The values of σ_b for both two directions achieve minimum at $\phi_f = 20\%$. It means that there is no reinforced effect in these filled systems at low concentration of the filler. With the particles increasing further, the stress concentration effect in the interface between the matrix and the inclusions will be significant correspondingly, and matrix around the particles might yield first and induce crazes to absorb relevant tensile deformation or fracture energy, leading to improvement of tensile fracture toughness. In this case, the tensile fracture strength increases somewhat.

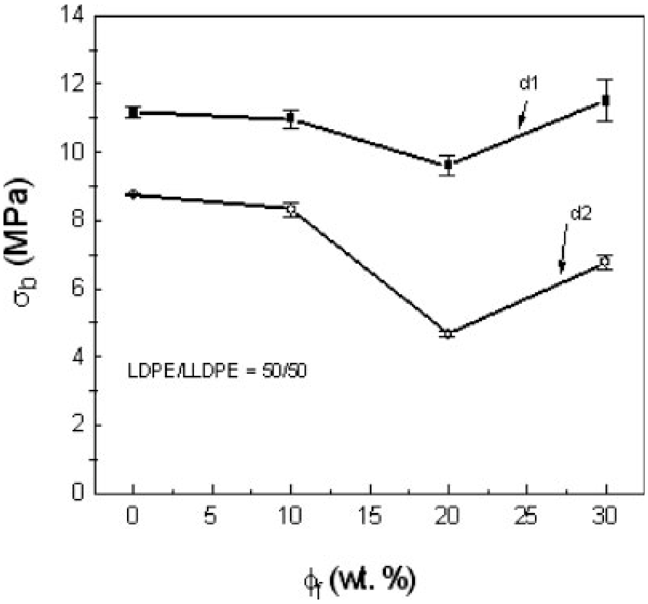

Figure 2 Tensile fracture strength versus filler weight fraction.

Furthermore, the values of σ_b for the specimens at longitudinal direction are obviously greater than those for the samples at transverse direction, especially at higher filler concentration. In general, the orientation of macromolecules may enhance the mechanical strength of polymeric materials along flow or deformation direction, and the difference in orientation degree will form different mechanical strength. As stated earlier, the macromolecular orientation along longitudinal direction is greater than that along transverse direction under these operation conditions, and thus the tensile fracture strength for the specimens along longitudinal direction is higher than that of the specimens along transverse direction.

It is generally believed that the tensile strength of particulate-filled polymer composites depends strongly upon the interfacial adhesion between the filler particles and the matrix. For spherical particles with no adhesion to the polymer matrix, which fail by random fracture, Nicolais and Narkis[10] proposed a tensile strength equation as follows:

$$\sigma_c = \sigma_m(1 - 1.21\phi_f^{2/3}) \quad (2)$$

where σ_c and σ_m are the tensile strength of the composite and the matrix resin, respectively.

In a previous work, Liang and Li[11] proposed a concept of interfacial adhesion angle, and derived a modified tensile strength equation for rigid inorganic particle-filled polymeric composites:

$$\sigma_c = \sigma_m(1 - 1.21\sin^2\theta\phi_f^{2/3}) \quad (3)$$

where θ is the interfacial adhesion angle between the filler particles and the matrix, which is an angle from the pole to the interfacial debonding of the particle. In other words, this is a parameter for characteristic of the interfacial bonding. For a particulate-filled polymer composite system with weak interfacial adhesion, its tensile strength will decrease obviously,[10] or will decrease slightly for a filled system with relatively good interfacial adhesion, with an addition of rigid inorganic particle concentration.[11] For instance, in a case of good interfacial adhesion, $\theta = 0$, and then $\sigma_c = \sigma_m$. Therefore, it might be concluded from the results shown in Figure 2 that the interfacial adhesion between the CaCO$_3$ particles and the matrix is good, especially at the longitudinal direction.

In addition, for both two along longitudinal direction and transverse direction, the variation of the tensile fracture strength with the filler content is similar to each other, whereas the values of the former are greater than those of the latter, which might be attributed to the difference in the molecular orientation between them in this case.

Crystalline property

It has been found that the heat enthalpy (ΔH) of crystalline polymeric resins is proportional to crystallinity.[12] The relationship between them can be expressed as follows:

$$\chi = (\Delta H/\Delta H^*) \times 100\% \quad (4)$$

where ΔH and ΔH^* are the melting heat enthalpy variation of the sample and the polyethylene with 100% crystallinity, respectively.

Figure 3 illustrates the relationship between the heat enthalpy of the samples and the weight fraction of the fillers. It can be seen that ΔH decreases nonlinearly with the increase of ϕ_f. Because ΔH^* in eq. (4) is a constant for a given resin, the crystallinity is a linear function of ΔH. This suggests that the addition of CaCO$_3$ particles does not improve the crystallinity of the composites, while the blending resin decreases with an increase of the fillers, leading to reduction of the heat enthalpy. In the case of the same CaCO$_3$ content, the value of ΔH for the LDPE/LLDPE composite with blending ratio of 70/30 is greater than that of the composite with blending ratio of 50/50. This is because the crystalline property of LLDPE is usually worse than that of LDPE, which results in reduction of the heat enthalpy of LDPE/LLDPE blend with increasing LLDPE content.

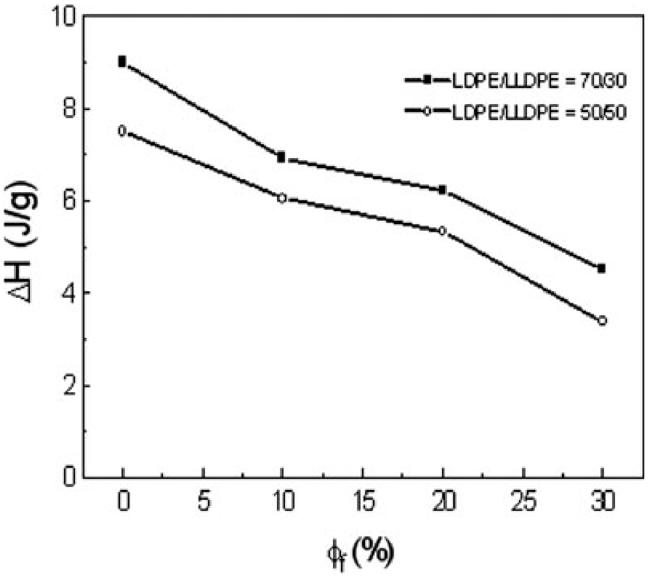

Figure 3 Relationship between melting heat enthalpy variation and filler weight fraction.

Flow properties

MFR is an important parameter for characterization of the processing property of polymeric materials. Figure 4 displays the influence of CaCO$_3$ weight fraction on the MFR of the composites under standard test conditions. It can be seen that, when the blending ratio is 70/30, the MFR of LDPE/LLDPE blend decreases almost linearly with increasing ϕ_f. While for the LDPE/LLDPE blend with blending ratio of 50/50, the values of MFR are slightly higher than those of the former, and the variation of MFR with ϕ_f is more obvious. When ϕ_f is less than 10%, the variation of MFR of LDPE/LLDPE blend with blending ratio of 50/50 is insignificant, while MFR decreases obviously with increasing ϕ_f when ϕ_f is more than 10%. This is because the flow property of LLDPE is somewhat better than that of LDPE, and thus the values of MFR of the LDPE/LLDPE with blending ratio of 50/50 is slightly higher than those of the LDPE/LLDPE with blending ratio of 70/30.

In addition, the MFRs of the unfilled LDPE/LLDPE blend are less than those of both the pure

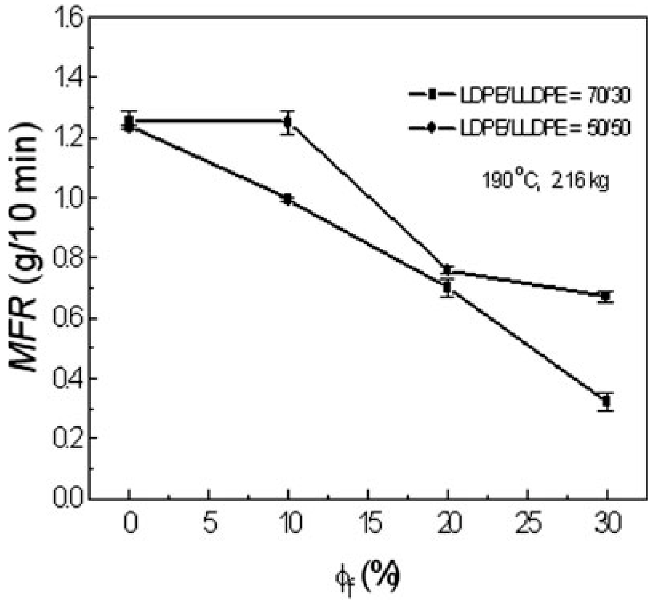

Figure 4 Dependence of MFR on filler weight fraction.

LDPE and LLDPE resins, respectively, which might be attributed to the negative synergetic effect in melt flow behavior for this blending system.

CONCLUSIONS

The effect of $CaCO_3$ particle content on the tensile properties of the filled LDPE/LLDPE tubes is significant. The tensile elastic modulus (E_c) increases roughly linearly with increasing the weight fraction of $CaCO_3$ particles at room temperature. When ϕ_f is more than 15%, the value of E_c along longitudinal direction (along the flow direction) is slightly lower than that along transverse direction (perpendicular to the extrusion direction). The tensile fracture strength of the specimens along longitudinal direction is significantly greater than that at transverse direction. This might be attributed to the difference in the orientation of the macromolecular chains of the resins between both the two directions. Furthermore, the tensile stress at break for both the two directions achieves the minimum at $\phi_f = 20\%$.

The heat enthalpy is an important parameter for characterization of the crystalline property of crystalline polymeric materials. The results show that the heat enthalpy of these ternary composites decreases with the addition of the weight fraction of the filler particles and reduces with increasing LLDPE content.

The MFR reflects the flow property of thermoplastics. Under the standard test conditions, the MFR of the composites decreases with an addition of the weight fraction of the $CaCO_3$ particles, while it increases with the content of LLDPE resin.

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