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PROPERTIES OF CALCIUM CARBONATE-FILLED POLYETHYLENE BOTTLES PRODUCED FROM EXTRUSION BLOW MOLDING PROCESS

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ABSTRACT

This research concerns in property testing of $CaCO_3$-filled high density polyethylene (HDPE) for blow molding applications. Both uncoated and stearic acid (SA) coated $CaCO_3$ grades were used at 20%wt filler loading whereas maleic anhydride grafted high density polyethylene (HDPE-g-MA) was used as a compatibilizer (at 0.5-4.0% contents). All compounds were prepared using a twin-screw extruder and an extrusion blow molding machine was used for bottle production. It was found that an addition of $CaCO_3$ increased the compound viscosity, however; the viscosity did not change when SA or HDPE-g-MA was present. From the blow molding process, all the compounds had similar volumetric output rate. The bottle weight of the unfilled HDPE was less than that of the $CaCO_3$-filled HDPE, but the bottle thickness gave opposite results. An incorporation of $CaCO_3$ fillers in HDPE decreased tensile yield strength, elongation at break and impact strength, but these properties could be improved by an addition of SA or HDPE-g-MA. Modulus of the $CaCO_3$-filled HDPE was greater than that of the unfilled one, but decreased when having HDPE-g-MA. It could be possible to use 20%wt $CaCO_3$-filled HDPE compounds for the extrusion blow molding applications since the deleterious effect of $CaCO_3$ incorporation could be reduced by an addition of SA or HDPE-g-MA.

KEYWORDS: Calcium carbonate, Polyethylene, Blow molding process, Mechanical properties

1. INTRODUCTION

High density polyethylene is the most widely used plastic for containers of all types. Uses include extrusion blow molded and injection blow molded bottles for food, beverages and a variety of non-food products, drums and pails [1] due to its very attractive property-cost performance. Polymer properties can be modified by incorporation of additives. Among the additives, mineral fillers are increasingly important, not only by acting as an inactive diluent, or cost reducing additive, but also as active, functional species which impart specific types of property enhancement to polymer compounds [2]. Fillers can change the characteristics of polymers in two ways: the properties of the particles (size, shape and modulus) can have profound effects on mechanical properties of polymer compounds (modulus or strength parameters; melt viscosity) and changes in micro-morphology may give rise to further differences in bulk properties. An increase in the level of a filler that is used, such as calcium carbonate ($CaCO_3$) and carbon black, in polyolefin compounds improves low strain properties such as tensile modulus [3-5], but may decrease properties relating to energy absorption, such as ultimate tensile strength and elongation at break [3-4]. To facilitate filler dispersion, the filler is often surface treated with a coating, which acts as a wetting agent by reducing the specific surface free energy of the additive particles. The treatment of $CaCO_3$ with stearic acid(SA) decreases the surface energy of the filler and particle-particle interactions within agglomerated regions. This facilitates filler dispersion and also leads to enhanced mechanical performance of the compounds [5-8]. Another method for improving properties of the filled polymer compounds is to add some compatibilizer [9-11] such as maleic anhydride grafted polyethylene (PE-g-MA) in the system of PE/polar filler [9]. This is due to both polar and non-polar natures in HDPE-g-MA structure.

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Commonly in processing point of view, the most important step in examining newly formulated compounds in polymer conversion processes such as extrusion blow molding is a study of their rheological behavior. The viscoelastic flow behavior of particle filled polymer melts depends upon the filler characteristics, the interface natures of the polymer/particle and particle/particle, the degree of dispersion and the filler orientation distribution. The presence of other additives, even in small quantities, may be crucial in the composite system because they may interfere the composite system. Generally, the presence of filler particles increases the polymer melt viscosity [3,5,12-15], with highest levels of viscosity being observed at higher filler content [12] or with smaller filler particle size additives [5,13,15].

The objectives of this research were to study rheological behavior of $CaCO_3$–filled HDPE samples with and without SA or HDPE-g-MA and so to link the results with physical and mechanical properties of their bottle products to seek possibility of using modified $CaCO_3$–filled HDPE samples for the extrusion blow molding applications.

2. MATERIALS AND METHODS

2.1 MATERIALS

All mixing ingredients were used as received. High density polyethylene (HDPE), H6420B with MFI of 0.4 g/10 min, was supplied by CCC Chemical Commerce Co., Ltd. Two gardes of calcium carbonate ($CaCO_3$), Omyacarb 2 and 2T, were manufactured by Surint Omya Chemicals (Thailand) Co., Ltd. The latter grade was the former grade treated with 1% stearic acid. Maleic anhydride grafted high density polyethylene (HDPE-g-MA), Polybond® 3009 having MFI of 5 g/10 min, was provided by Uniroyal Chemical Co., Ltd.

2.2 PREPARATION AND TESTING OF HDPE COMPOUNDS

The polymer compounds were prepared using a twin-screw extruder (Brabender PL-200) with a rotational speed of 15 rpm and a die temperature of 190°C and were ground using a plastic grinder. The compound formulation is given in Table 1. Rheological behavior of all the compounds was examined using a capillary rheometer (Rosand V) at 190°C, following ASTM D3835. The volumetric output rate of the compounds on an extrusion blow molding machine (Sinco, VK100) was performed at a rotational speed of 35 rpm and at 190°C die temperature by measuring mass output rate directly from the extruder. These data were then converted to volumetric output rate using melt density parameters that take account of the exact amounts of $CaCO_3$ included.

Table 1 Compound formulation

Code	Composition (% by weight)	$CaCO_3$ Grade
HDPE	100% HDPE	-
CA20	80% HDPE + 20% $CaCO_3$	Uncoated
MA0.5	80% HDPE + 20% $CaCO_3$ (0.5% HDPE-g-MA)	Uncoated
MA1	80% HDPE + 20% $CaCO_3$ (1% HDPE-g-MA)	Uncoated
MA4	80% HDPE + 20% $CaCO_3$ (4% HDPE-g-MA)	Uncoated
SA2T	80% HDPE + 20% $CaCO_3$ (1% Stearic acid)	Coated

2.3 PRODUCTION AND TESTING OF HDPE BOTTLES

The extrusion blow molding machine (Sinco, VK100) was used to produce HDPE bottles using the same condition as the volumetric output rate determination. The bottle products had cylindrical shape with 46 mm in diameter, 107 mm in height and 135 cm^3 in containing volume (as shown in Figure 1).

Before doing any testing, the scraps at the top and bottom of the bottles were cut off. Average bottle weight was taken from weighing at least 10 bottles. Average bottle thickness and its distribution were measured in the middle area of at least 10 bottles (see Figure 2).

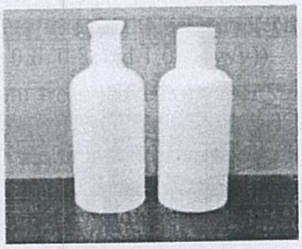


Figure 1 The produced bottles in this research: with a scrap at the top of the bottle (left) and with a cap (right).

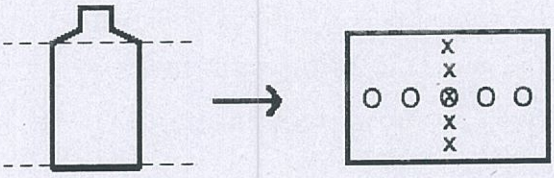


Figure 2 Middle area of the bottle for thickness measurement when X and O are the measuring positions in vertical and hoop directions, respectively.

Tensile properties were determined using a universal testing machine (LLOYD, LR 30K) with a sample gauge length of 20 mm and a testing speed of 80 mm/min, following ASTM D 638. Tensile testing specimens were cut from the middle area of the bottle (as shown in Fig. 2) in both vertical and hoop directions. Impact properties were investigated according to ASTM D 2463 and presented in terms of falling weight impact energy. At least 20 bottles having fully containing water with a cap were used to determine the impact energy.

3. RESULTS AND DISCUSSION

3.1 Effects on rheological behavior of HDPE compounds

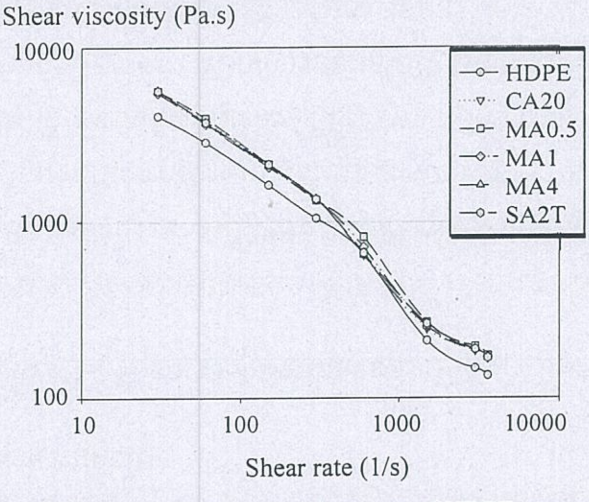


Figure 3 Shear viscosity versus shear rate of HDPE compounds.

The influences of $CaCO_3$ with and without SA and HDPE-g-MA on rheological behavior of HDPE compounds are shown in Figure 3. The results present that all the compounds are pseudoplastic fluids as the viscosity decreases with increasing shear rate. Also shear flow data have shown increases in viscosity due to filler incorporation as the presence of a solid filler like $CaCO_3$ in the compound obstructs the deformation of the polymer molecules [3,5,12-15]. The presence of SA (1%wt) or HDPE-g-MA (0.5-4.0%wt) did not significantly alter the compound viscosity and this may be because their chemical structures are similar to HDPE structure and melt viscosities at high shear rates are not so sensitive with low contents of both additives.

Table 2 **Output rate data of HDPE compounds**

Code	Melt density * (kg/m^3)	Mass output rate (kg/sec)	Volumetric output rate (m^3/min)
HDPE	770	0.53×10^{-3}	4.1×10^{-5}
CA20	904	0.60×10^{-3}	4.0×10^{-5}
MA0.5	916	0.65×10^{-3}	4.3×10^{-5}
MA1	910	0.66×10^{-3}	4.4×10^{-5}
MA4	910	0.68×10^{-3}	4.5×10^{-5}
SA2T	898	0.66×10^{-3}	4.4×10^{-5}

* Note that the calculation was used the same method as mentioned elsewhere [5].

Table 2 shows that mass output is enhanced significantly with filler incorporation due to melt density increases because density of $CaCO_3$ particle (2,700 kg/m^3) is much higher than that of HDPE (962 kg/m^3). However, there are no significant trends relating to the effects of $CaCO_3$, SA or HDPE-g-MA addition on volumetric output rate, which was converted from mass output rate and melt density data. The downward extrusion blow molding operation uses a flood-fed system and so the volumetric output rate of the polymeric material is influenced by the process conditions and the material flow properties, which are affected by the presence of filler [16]. As shown in Figure 3, an incorporation of $CaCO_3$ filler induces greater shear viscosity in the filled compounds, compared with the unfilled polymer and this would decrease the volumetric output rate. However, the addition of $CaCO_3$ would also promote more shear heating and so the temperature increases and so shear viscosity decreases, which will increase the volumetric output rate. Therefore, volumetric output rate of all the compounds are all about the same value.

3.2 EFFECTS ON PHYSICAL PROPERTIES OF THE BOTTLES

The effects of $CaCO_3$, SA or HDPE-g-MA on bottle weight and thickness of HDPE bottles are illustrated in Table 3. The bottle weight is a complicated property since it is influenced by several parameters such as the material volumetric output rate, die swell and melt density. An increase in volumetric output rate and/or melt density can lead to an increase in bottle weight [17]. As shown in Table 3 that the bottle weight of the filled polymer is more than that of unfilled one because of an increase in melt density due to the presence of $CaCO_3$, but ironically this effect is undesirable in the blow molding industry, as a result of increased unit weight of containers. With the presence of HDPE-g-MA compatibilizer in the compounds, the bottle weight order is MA4 > MA1 > MA0.5 and this is the same as the volumetric output rate order (see Tables 2 and 3). In case of SA coating presence, the bottle weight of SA2T is slightly higher than that of CA20 due to slightly greater volumetric output rate (see Tables 2 and 3).

The results in Table 3 show that the bottle thickness in both horizontal and vertical directions are about the same, but thickness distribution in the later direction is bigger. This indicates that the parison expansion during the inflation stage is more uniform around the bottle circumference (horizontal direction) than along the bottle height (vertical direction). This could be due to the cylindrical shape of the product, giving good uniform thickness in horizontal direction. The thicker region near the bottle base implies that there is some parison sag effects (during the parison formation) which causes thinning at the top and thickening at the bottom parts of the parison and so the bottle. The bottle thickness is a less complex characteristic than the bottle weight and is related to the parison swell data. A greater parison swell means a thicker parison wall which leads to a thicker bottle [5,17]. The bottle thickness of the $CaCO_3$-filled HDPE is less than that of the unfilled HDPE because $CaCO_3$ particles obstructs the molecular recovery process, resulting in less parison swell [5,15] and so thinner bottle. With the presence of either SA or HDPE-g-MA, there is no big change in thickness and its distribution.

3.3 EFFECTS ON MECHANICAL PROPERTIES OF THE BOTTLES

Tensile properties of all the blow molded containers in terms of tensile yield strength, elongation at break and modulus are illustrated in Figure 4. In general, slight differences in tensile properties between the samples cutting in hoop and vertical directions are observed. This implies that the bottles have no preferential molecular orientation in any direction. This could be because the bottle shape is cylindrical with only 46 mm in diameter and 107 mm in height and therefore the degree of parison expansion is not so much to make great differences in molecular orientation between hoop and vertical directions.

Figure 4 reveals that incorporation of $CaCO_3$ fillers in HDPE has a deleterious effect on both tensile yield strength and elongation at break, but not modulus (stiffness). Because solid filler like $CaCO_3$ are many times more rigid than the polymer matrix, the modulus of filled HDPE is greater, which gives higher section stiffness to the containers, as previous reported [18]. As reported by some workers [3-4], the presence of a filler decreases the tensile yield strength and elongation at break (ductility) of the material. The reduced effective cross-section of the matrix in a filled material causes an increase in stress concentration, and hence plastic deformation around the filler particles, for a given external load. When the 1% SA surface treatment is introduced, the surface polarity of decreased [4,8,19] and so the filler dispersion is improved and so greater surface area of the coated $CaCO_3$, compared to the uncoated one. This results in slightly higher tensile yield strength and elongation at break. The use of HDPE-g-MA compatibilizer gives slightly greater tensile yield strength and elongation at break because HDPE-g-MA structure is both polar and non-polar, which could help improving compatibility between HDPE and $CaCO_3$ filler particles. However, modulus decreases with incorporation of HDPE-g-MA and this may be due to an increasing polymeric phase in the compounds, making less load resistance at a very short strain range, as reported previously [9-10]. In general there is no trend of the tensile properties among the filled compounds with various HDPE-g-MA contents (0.5-4.0%).

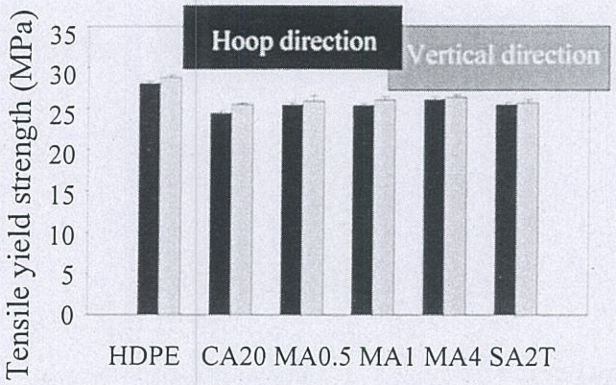
Table 3 Bottle weight, thickness and thickness distribution data

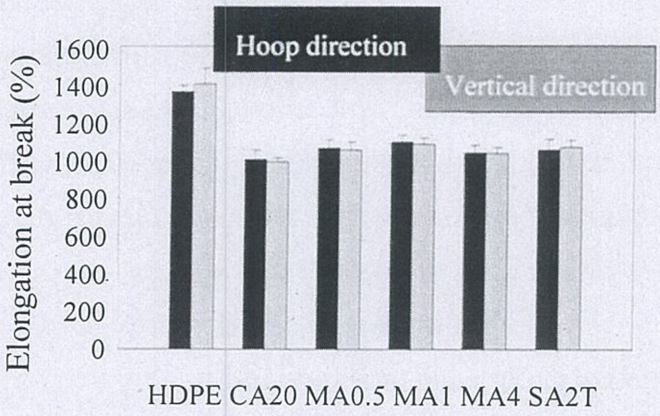
Code	Bottle weight (g)	Horizontal direction Thickness (mm)	Horizontal direction Thickness distribution (%)	Vertical direction Thickness (mm)	Vertical direction Thickness distribution (%)
HDPE	8.0	0.62	1.6	0.61	6.6
CA20	8.4	0.56	3.6	0.58	6.9
MA0.5	8.5	0.57	3.5	0.59	6.8
MA1	8.6	0.57	1.8	0.57	7.0
MA4	8.7	0.61	3.3	0.54	11.1
SA2T	8.5	0.57	1.8	0.58	6.9

The energy absorption characteristics of all the blow molded containers in a high strain rate situation are presented in term of falling weight impact energy in Figure 5. The results show that the impact properties of $CaCO_3$-filled HDPE samples are lower than that of the unfilled HDPE sample. This is because the cohesive strength within the polymer or filler is greater than the adhesive strength between polymer and filler. Hence, voids form within the sample as the matrix pulls away from the particle during the deformation process, resulting in a lower resistance to crack propagation under impact. The better impact property due to SA coating is observed and this is because the SA surface treatment decreases the surface polarity of $CaCO_3$ and so improves filler wettability, resulting in better filler dispersion [4,8,19]. The presence of HDPE-g-MA (0.5-4.0%) also improves impact energy of the $CaCO_3$-filled HDPE containers due to better compatibility between polymer and filler. However, a slight decreasing trend is observed when HDPE-g-MA level is more than 0.5%. This could be due to phase separation at high contents of the compatibilizer as previously reported [9].

4. CONCLUSIONS

An addition of 20% wt $CaCO_3$ increased the shear viscosity of the compounds, however; viscosity did not significantly alter with an incorporation of SA (1%wt) or HDPE-g-MA (0.5-4.0%wt). From the blow molding process, all the compounds had similar volumetric output rate. The bottle weight of the unfilled HDPE was less than that of the $CaCO_3$-filled HDPE, but the bottle thickness gave opposite results. An incorporation of $CaCO_3$ fillers in HDPE decreased tensile yield strength, elongation at break and impact strength, but these properties could be improved by an addition of SA or HDPE-g-MA. Modulus of the $CaCO_3$-filled HDPE was greater than that of the unfilled one, but decreased when having HDPE-g-MA. In general, there is no trend in tensile properties of $CaCO_3$-filled HDPE samples having different HDPE-g-MA contents (0.5-4.0%), however; the one with 0.5% HDPE-g-MA has the highest impact energy.





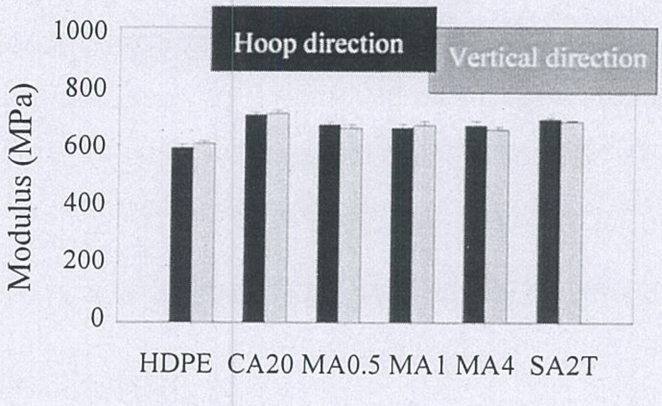


Figure 4 Tensile properties of the bottles.

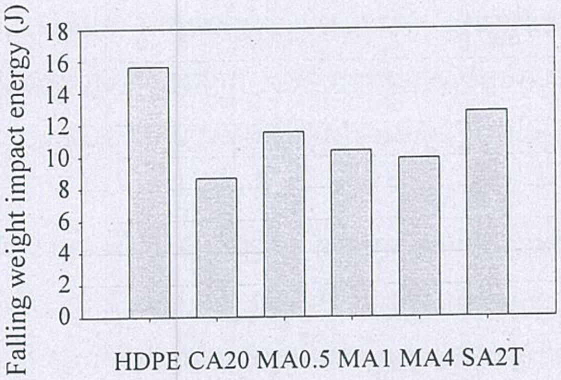


Figure 5 Falling weight impact energy of the bottles.

5. ACKNOWLEDGEMENTS

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