DOI: 10.1002/masy.201051045

Control of Nano-Scale Structuring and Reinforcement in Rotational Molding of Polyethylene

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Summary: Polyethylene (PE) resins used for Rotational Molding have usually particle sizes less than 0.8 mm and used as powders or micro-pellets. During heating in a rotating mould, these particles get fused and merge into one piece. A disadvantage of the rotomolding process is long cycle times that affect the production rate and increase thermal degradation of the polymer. One of the problems in rotomolding is bubbles of gasses trapped during sintering of the PE powders which reduce mechanical strength of the article produced. We propose to use reacting mixtures of PEG with citric acid as Processing Additive (PA) to rotomolding grades of PE. Silica fume and vinyl-silanes can be other ingredients of the additive package. The PA accelerates sintering of the PE particulates and greatly reduces number of bubbles in the melt but at high concentrations it impedes flow of the particles. Powders are characterized by low flowability while micro-pellets have too high flowability for rotomolding. To improve the rotomolding process we propose to fabricate micro-pellets by extrusion of PE resins comprising the PA at reduced temperatures and pelletizing in open air. The same PA reduces extrusion pressure and suppresses flow instabilities during pelletizing as well as adjusts flowability of micro-pellets to optimum, accelerates sintering of the PE particulates and removes bubbles from the PE melt. Mechanisms of the observed improvements are discussed.

Keywords: additives; polyethylene (PE); rotational molding; sintering; voids

Introduction

Rotational molding, also referred to as rotomolding or rotational casting, is a plastics processing technology for producing hollow seamless articles and it comprises four steps: charging of polymer as solids (free-flowing powder or pellets) or liquids (melt) into the mold; heating of the mold in an oven to processing temperatures with simultaneous rotation in two axes, see Beall (1998), Crawford and Kearns (2003), Dodge (2004). While heated, the polymer adheres to the mold and gets fused completely. Next steps are cooling of the mold by air or a water spray, and unloading of a produced item from the mold. In contrast to other polymer forming processes like extrusion or injection molding, fusing of the particles occurs at conditions of nearly ''zero-shear'' stress, because only forces of surface tension govern the flow of the melt. Advantages of the rotational molding in comparison with other techniques are the following: larger size of molded parts; lower cost of tooling and easer prototyping; thicker outer corners of the parts that impart higher strength and structural stability to the molded items; an opportunity to produce large and small parts of complicated shapes as one piece.

One of the problems in rotomolding is bubbles of gasses trapped during sintering of the PE powders. Pick and Harkin-Jones (2004) report a correlation between the number of voids (bubbles) in a rotomolded

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article and its impact performance, with a higher number of voids resulting in lower impact performance. According to Spence and Crawford (1996) the particle size distribution affects the porosity of the product while overheating of the polymer melt for bubble removal results in lowering of mechanical properties of the product. Greco and Maffezzoli (2004) predicted existence of an optimum sintering temperature at which the density of the sintered product gets to its maximum for a good quality rotationally-molded product having limited number of voids. Kontopoulou et al. (1999) as well as Kontopoulou and Vlachopoulos (1999) investigated the formation and dissolution of bubbles during sintering of PE powders to evaluate how it is affected by powder properties, chemical structure, thermal properties and rheology. Bellehumeur and Tiang (2000) conclude that the polymer rheological properties seem to dominate the initial size of the bubbles formed.

In production of the PE powders for rotomolding with particle sizes less than 0.5 mm (35 mesh) a raw resin powder from the polymerization reactor is blended with pigments and additives in an extruder, mixed and extruded through a set of dies and pelletized in conditions of water cooling. The produced pellets are ground and classified to proper particle size. The pelletizing and grinding operations are costly because of high energy consumption. An attempt was made to produce PE powders for rotomoding without pelletizing and grinding, see Kallio et al. (2001) in U.S. Patent Appl. 20010025092, but from a practical view point it is more convenient to manufacture micro-pellets for rotomolding. With the use of micro-pellets the number of post-processing steps is reduced thereby reducing the cost of the material, see Nugent (2006). Opposite to micro-pellets for rotomolding with regular oval shapes and averaged sizes from about 0.5 to 0.6 mm, PE powders for rotomolding have smaller averaged size of the particles (from 0.3 to 0.35 mm) and wide particle size distribution as well as irregular shapes. Potentially, powders can be compacted so that fine particles would fill the voids between the larger ones. Wang and Kontopoulou (2007) observed fewer bubbles in the melt and better mechanical properties of the rotomolded articles when powders were used in comparison to the use of micro-pellets. Nevertheless, last ten years the use of micro-pellets is considered as a step forward for the rotomolding technology with following benefits: uniform melting; improved handling; elimination of dusting; faster sintering times (10–12% reduction); more uniform wall thickness; and improved surface finish.

Free-flow behavior of the PE particulates is important to get even thickness of the walls of the rotomolded articles. The fluidity of PE powder is influenced by various properties, such as particle sizes, shapes and surface roughness of the particles. As a general tendency fine powders show less fluidity, see Yokoyama (1997). Fine powders of PE often demonstrate low fluidity because of elongated shapes of the particles, sharp edges as well as such features like ‘‘fibers’’ and ‘‘tails’’ at the surface of the particles. With low fluidity of the particulate matter, an inner surface of the rotomolded parts gets wavy appearance with high variations of the wall thickness. With PE powders a bridging often occurs and air gets trapped in the corners of the mold so that the produced parts are not suitable for use, see Beall (1998). Large pellets (> 2 mm) have too high fluidity, they are bouncing inside the mold and do not stick easily to flat surfaces but accumulate in the corners of the mold. Also sintering of such pellets creates a lot of bubbles that do not dissolve in polymeric melt. Optimization of flow and fewer voids can be achieved by downgaugeing of the pellets to sizes from 0.3 to 0.8 mm (micro-pellets).

Polyolefin composition containing wax and metal salts of long-chain fat acids were proposed long ago to improve processability of PE resins, e.g. Happoldt et al. (1945). Chaudhary et al. (2001) used low Molecular Weight (MW) additives like wax, mineral oil and glycerol monostearate as sintering enhancers in rotational molding. With this, melt viscosity and elasticity were reduced while much faster densification and bubble removal were observed. Suitable sintering enhancers include aromatic or aliphatic hydrocarbon oils, esters, amides, alcohols, acids, and their organic or inorganic salts as well as silicone oils, polyether polyols such as PEG, glycerol monostearate (GMS), pentaerytritol monooleate, erucamide, stearamides, adipic acid, sebacic acid, styrene-alpha-methyl-styrene, calcium stearate, zinc stearate, phthalates and blends thereof. The sintering enhancers allow a reduction in sintering time, cycle time and/or maximum mold temperature but problems in the use of the additives are following: The sintering enhancers that are dissolvable in polyolefins work as plasticizers and reduce toughness of the rotomolded articles. The low-viscous sintering enhancers that are immiscible with polyolefins, e.g. silicone oils and PEG, coalesce inside the melt into large beads. The macroscopic discontinuities in the polymer matrix concentrate mechanical stresses and certainly reduce impact strength of the rotomolded parts.

A considerable number of patents are dedicated to removing of bubbles in rotomolding. Maziers (2005) mentioned in U.S. Patent Appl. 20050255264 that micro-pellets exhibit a better bubble removal as a function of temperature than do powders. Swain (2004) proposed in U.S. Patent 6 682 685 to use resin pellets and from 20 to 40% by weight of ground resin powder to yield rotomolded objects having fewer bubbles. Densification aids were proposed recently by Maziers (2008) in his U.S. Patent Appl. 20080018019 and U.S. Patent Appl. 20080103264.

We propose here hydrophilic processing additives for manufacturing of micro-pellets and removing of bubbles from PE-melt during rotomolding. Underwater pelletizing is used in industry nowadays to produce micro-pellets. Instead of underwater pelletizing we propose extrusion at reduced temperatures and pelletizing of strands in air or gas atmosphere. Amazingly, the same formulations of the densification aid work as Polymer Processing Additives (PPA) for extrusion. Micro-pellets produced with novel PPA manifest better flow than industrial grades of PE-powders for rotomolding.

Experimental Part

In series of experiments on sintering of PE particulates we used powder of LLDPE (LL6301RQ, melting point 125 °C, MI = 5.0 g/10 min) from ExxonMobil Chemical and a grade of LMDPE (M9001RW, MI = 3.2 g/10 min) for rotomolding from the SCG Chemicals. A fraction of fine particles with sizes below 350 μm was separated from the LL6301 grade for some experiments by sieving the coarse powder of LLDPE. To mix PE powders with additives we used as a blender a meat grinder equipped with a heater and a thermostat to keep the metal body of the grinder at temperatures in range from 80 to 90 °C. To facilitate mixing of the additives with the PE powders we added some amount of methanol to the blender. In the process of mixing the methanol was evaporated. To sinter particulates we used a simple mold that was assembled from a 3 mm steel plate and a thick (about 15 mm) steel ring at the plate with an inner diameter of 50 mm. Samples in the amount of 5 g were loaded to the mold and gently compacted by a disk from PMMA to ensure equal thickness of the polymer material in the mold. A digital camera equipped with a magnifying objective lens was arranged at the top side of the mold to record process of sintering of PE particulates under magnification. Some of the recorded photos are presented in Figure 1 and Figure 2 and arranged in vertical rows for comparison. Width of the photos corresponds to about 6.8 mm of the mold inside in its central area.

An induction oven with maximum electrical power of 1.8 kW was used to heat the steel mold to controlled temperature in

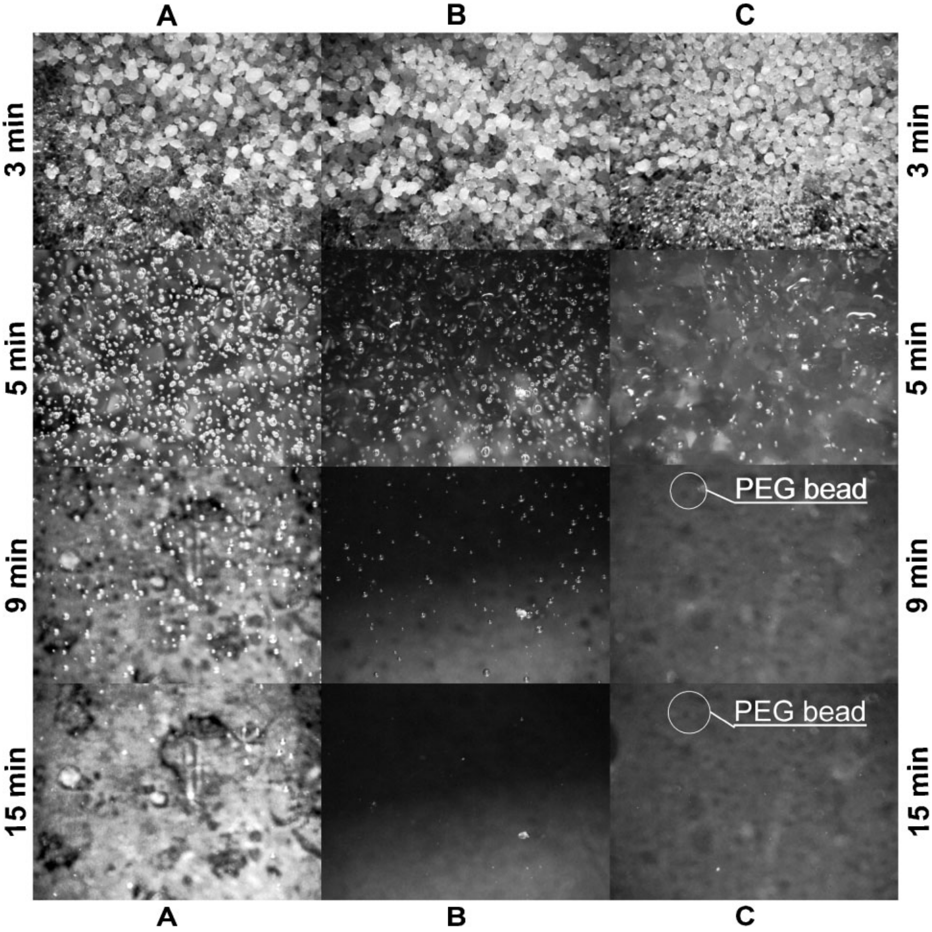

Figure 1.

A: Sequence of photos showing sintering of fine LLDPE-powder. B: Sequence of photos showing sintering of fine LLDPE-powder with additives of Glycerol Mono-Stearate (0.2%). C: Sequence of photos showing sintering of fine LLDPE-powder with additives of PEG 400 (0.2%).

open air. Heating was going in two stages: first, preheating of the mold to 70 °C for 5 min and, second, a main sintering period with the temperature of the bottom plate of the mold rising up to 230 °C. The steel ring was coated by a thin layer of silicone rubber to ensure easy separation of polymer from the mold. The same ring was used after cooling to room temperature in next experiments. The bottom plate in our experiments was not coated and therefore we replaced the used plate by an identical one for every experiment. The used plates were cleaned from molten polyethylene and heated overnight in an electrical oven to temperatures up to 400 °C to burn out organic residues.

In experiments on extrusion of PE resins to demonstrate an opportunity to produce micro-pellets with novel Polymer Processing Additives (PPA) we used a screw-extruder from Extrudex. A barrel of the extruder is made with 4 shallow grooves in its feeding zone. The grooves are 8 mm width and the depth of them is made with gradual slope to zero thicknesses in the direction of a conveying of polymer material. It is well known that extruders with axial grooves in the feeding zone of the barrel produce stable conveying of pellets

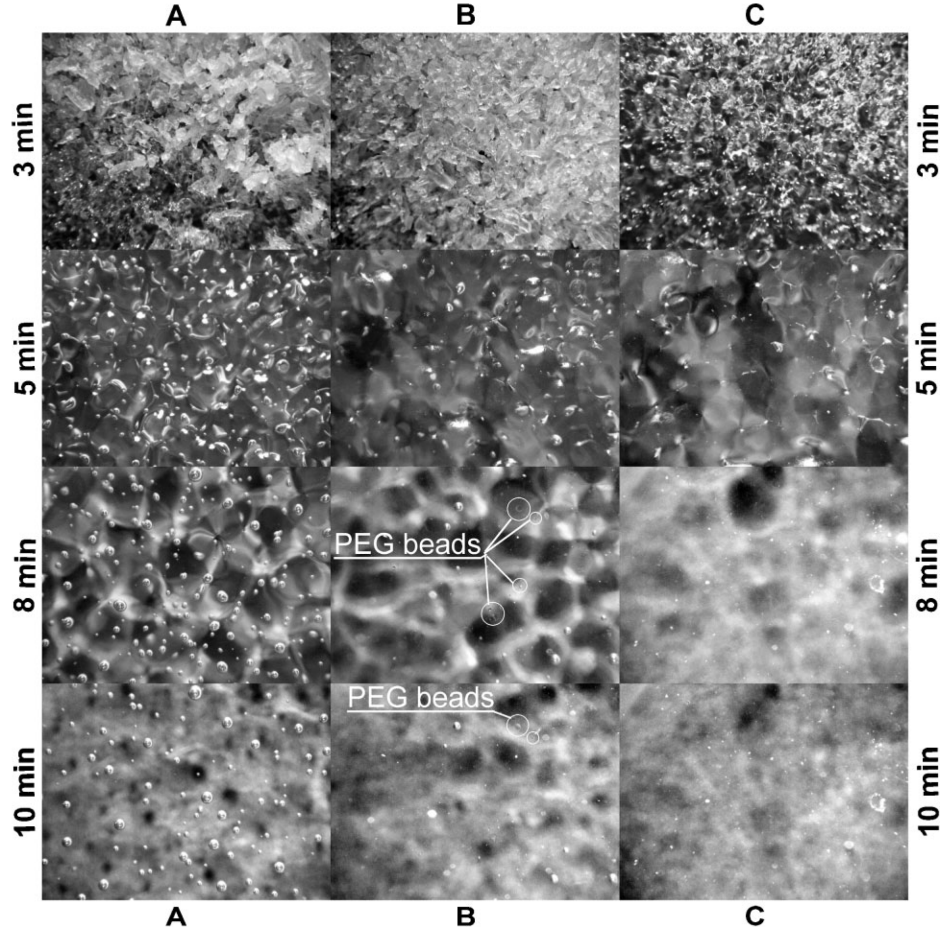

Figure 2.

A: Sintering of fine MDPE-powder without any additives in time from top to bottom. Bubbles are trapped inside the melt. B: MDPE-powder with additives of PEG 6000 (0.4%). Number of bubbles is reduced but PEG is coalesced to a few beads inside the melt. The beads are shown by circles. C: MDPE-powder with additives of PEG 6000 (0.4%) and Citric Acid (26 ppm). Sintering of PE powder goes virtually without any bubbles or beads of PEG.

and powders, see Gruenschloss (2003) and Rauwendaal (1986). A feeding zone of the extruder is cooled by water to room temperature. All parts of the extruder that are in contact with molten polymer are produced from a steel alloy (34CrAlNi7) and nitrided, that is saturated by Nitrogen to harden a thin (about 0.1 mm) surface layer of the parts. The die for extrusion is made with diameter 2 mm and length 60 mm also from this nitrided steel. The 2 mm hole of the die is conjugated with a 50 °Cone having 8 mm diameter at the entrance of the die. To produce some amount of micro-pellets we used the same screw extruder but the die was replaced.

Narrow MW distribution of PE resin is important for rotomolding and therefore we used for our extrusion experiments the grades of LLDPE from ExxonMobil Chemicals with such MW distribution: LL1201 XV (density 0.925 g per cc, melting point 123 °C and MI = 0.7 g/10 min) and LL 1001 XV (0.918 g per cc, melting point 120 °C and MI = 1 g/10 min). We also used for comparison LDPE with wide MW distribution from the ExxonMobil Chemicals:

LL166 BA (0.923 g per cc, melting point 110 °\C and MI = 0.2 g/10 min).

First, we made experiments on sintering of LLDPE (LL6301RQ) powders from ExxonMobil Chemicals. In sintering of coarse LLDPE powder a lot of bubbles of various sizes are trapped inside the melt. While small bubbles dissolve and disappear, a number of larger bubbles stay inside the melt after 20 min of heating and longer. In contrast to the coarse powder, in melting of fine powders of LLDPE with particles of sizes below 350 μm even a greater number of bubbles is present soon after merging of the PE particles but the bubbles mostly dissolve and disappear in about 15 min of heating to high temperatures, see Figure 1A. In further experiments we used only fine powders.

Glycerol monostearate (GMS) is known as a densification and processing aid to accelerate fusion of LLDPE powder. In our experiments, additives of GMS indeed show some improvement in sintering of the blend of LLDPE powders with 0.2 weight % of GMS. In 9 min of heating of the LLDPE particulate we observe approximately two times fewer bubbles trapped inside the melt, see Figure 1B. Surprisingly, additives of polyethylene glycol (PEG 400) at the same concentration 0.2% show a sharp reduction in the number of bubbles as well as a shortening in a sintering time about 30%, compare photos in Figure 1A and Figure 1C. The observed reduction of amount of bubbles in the melt can be explained by very high permeability of PEG to water vapors and Oxygen. So, these gasses may escape from the melt along the boundaries coated by PEG. Sintering of PE powder is accelerated further at higher concentrations of PEG. The optical refraction index of PEG is higher in comparison with LLDPE and therefore we can distinguish in photos of high resolution macroscopic beads of PEG inside the melt, see Figure 1C. It seems so that the PEG evenly distributed among the LLDPE powder coalesces under heating to a few large beads inside the melt. In Figure 1C a white circle shows location of one large inclusion of PEG inside the melt. Macroscopic inclusions of foreign material inside the polymer matrix are not desirable. It was also detected that PEG seriously impedes flowability of the PE powder if it is used in concentrations above 0.2%.

In experiments on sintering of LMDPE grade (M9001RW) for rotomolding from SCG Chemicals we observe a large number of bubbles trapped inside the melt, see Figure 2A. These bubbles are larger in size in comparison with the case of fine powders of LLDPE powder from ExxonMobil and they do not disappear after long heating of the melt. We can clearly see in Figure 2B that additives of PEG 6000 to the LMDPE powder in the concentration 0.4 wt. % shorten duration of sintering and nearly eliminate bubbles inside the melt similar to additives of PEG to fine LLDPE powders. Similar to the experiments with LLDPE we can distinguish at photos in Figure 3C macroscopic beads of PEG trapped inside the melt. White circles in Figure 2B show some locations of them. Viscosity of PEG 6000 is higher and these inclusions are of smaller size in comparison with the use of PEG 400. Particles of LMDPE are characterized by elongated shape and jagged surface and therefore they resist to flow. Additives of PEG impede flow of LMDPE powders further. For example, an angle of free repose of the LMDPE powder is increased from 45° to 72° with additives of 0.4% of PEG 6000.

In extrusion experiments at first we compared extrusion of LLDPE with and without PPA at various temperatures: 130, 135, 145, 165, 185, 205, 225, 235 °C. Characteristic curves that are the curves of Pressure at the extrusion die versus Extrusion Rate (linear velocity of the extrudate derived from volumetric extrusion rate) for extrusion trials of LL1201 XV without PPA are presented in Figure 3A for two temperatures: 145 (a solid line) and 225 °C (a dashed line). The best-fit curves connect experimental data: symbols of open circles (145 °C) and open squares (225 °C). At the characteristic curve for extrusion at 145 °C an onset of sharkskin (at

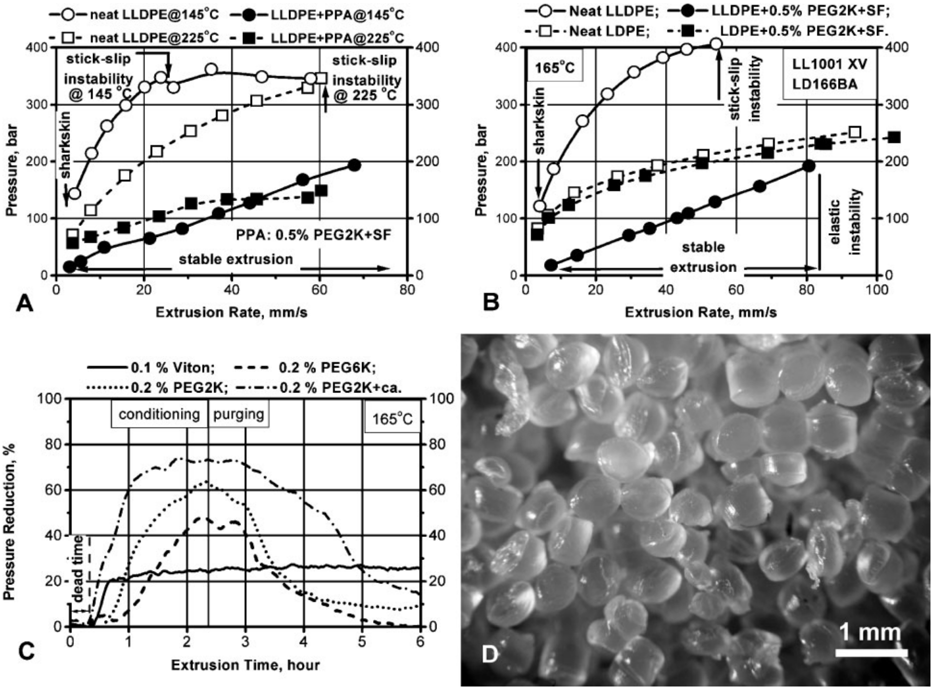

Figure 3.

A: Characteristic Flow Curves (Pressure vs. Extrusion Rate that is averaged extrudate velocity) for extrusion of LLDPE (LL1201 XV) with (0.5%) and without Polymer Processing Additives (PPA, PEG 2000 + 1% of Silica Fume) at two temperatures: 145 and 225 °C. Onsets of Sharkskin and Stick-slip instabilities are marked by arrows. B: Characteristic Flow Curves for extrusion of LLDPE (LL1001 XV) and LDPE (LD166 BA) with (0.5%) and without PPA (PEG 2000 + 1% of Silica Fume) at 165 °C. Onsets of Sharkskin and Stick-slip instabilities are marked by arrows. C: Curves of Pressure Reduction vs. Extrusion Time for extrusion of LLDPE (LL1201 XV) at 165 °C and Extrusion Rate about 40 mm/s with various PPAs: Viton, PEG 6000, PEG 2000, PEG 2000 + 1% of citric acid. A vertical line separates a stage of conditioning of the die and a stage of purging by neat LLDPE. D: Micro-pellets produced by extrusion at 132 °C of LLDPE with melting point 125 °C in conditions of air-cooling.

2 mm/s) and stick-slip (at 27 mm/s) instabilities are marked by arrows. For extrusion at higher temperatures onsets of surface instabilities are delayed. However, for LLDPE with narrow MW distributions the sharkskin instability appears at low rate of extrusion (below 6 mm/s for LL1201 XV) even at temperatures as high as 225 °C. The sharkskin instability greatly disturbs surface of the extrudate and therefore manufacturing of pellets for rotomolding with smooth surface from LLDPE with narrow MW distribution is hardly possible. The instabilities can be eliminated by the use of recently proposed PPAs made from a blend of PEG with silica fume, see Kulikov et al. (2009). For extrusion experiments with such PPA we mixed under heating PEG 2000 with silica fume (1%) and added 5 g of this PPA per 1 kg of the LLDPE pellets. Extrusion trials were made at various temperatures, see above. In the range of extrusion rates from 2 to 45 mm/s and for temperatures below 185 °C the measured pressures manifested little variations versus temperature. Surprisingly, we observed an increase of the extrusion pressures at temperatures from 185 to 235 °C. Characteristic curves of extrusion of LLDPE with PPAs for two temperatures: 145 (a solid line) and 225 °C (a dashed line) are presented in Figure 3A. The best-fit curves connect experimental data: symbols of solid circles (145 °C) and solid squares (225 °C). We can see from comparison of the curves that pressures

at the extrusion die can be considerably less for reduced temperatures of extrusion than for elevated temperatures if LLDPE is blended with PPA. This result is very opposite to extrusion of neat LLDPE where apparent viscosity of melt drops at elevated temperatures.

To compare an impact of PPA on extrusion of PE with wide and narrow MW distribution we used a blend of PEG 2000 with 1% of silica fume as PPA for extrusion of LDPE (LD 166BA) and LLDPE (LL 1001 XV) in concentration 0.5% at the temperature 165 °C and for extrusion rates from about 4 to 100 mm/s. For comparison we extruded these PE resins also without PPA. Characteristic flow curves that are the curves of Pressure at the extrusion die versus Extrusion Rate are presented in Figure 3B. The best-fit curves connect experimental points for extrusion of PE resins without PPA: a solid line with symbols of open circles for LLDPE and a dashed line with open squares for LDPE. For extrusion of PE resins with PPA the best fit curves connect experimental points: a solid line with symbols of solid circles for LLDPE and a dashed line with solid squares for LDPE. At the characteristic curve for extrusion of LLDPE without PPA an onset of sharkskin (at 4 mm/s) and stick-slip (at 52 mm/s) instabilities are marked by arrows. Opposite to extrusion of neat LLDPE, extrusion of LLDPE with PPA goes stable at extrusion rates up to 80 mm/s where so called elastic instability or "gross melt fracture" occurs. While extrusion of LLDPE is greatly improved by the PPA and pressures at the extrusion die are reduced 4-5 times in comparison with extrusion of LLDPE without PPA there is only marginal pressure reduction for extrusion of LDPE with PPA.

In one set of experiments we used a reacting mixture of PEG 2000 with 2% of citric acid as PPA in the concentration 0.2% for extrusion of LLDPE (LL1201 XV) and compared it with other processing additives. For comparison we used also PEG 6000, PEG 2000, and Viton that is a standard Processing Additive in industry to improve extrusion of LLDPE with narrow MW distribution. First, we extruded 1 kg of PE pellets with every one of the additives and then purged the extruder to see how quick it can be cleaned from the additives. The curves of Pressure Reduction vs. Extrusion Time are presented in Figure 3C for extrusion at 165 °C and at Extrusion Rate (averaged extrudate velocity) about 40 mm/s. We start the time counting at the moment when LLDPE with PPA is loaded to the hopper of the extruder. A vertical line separates a stage of conditioning of the die and a stage of purging by neat LLDPE when neat LLDPE is loaded to the extruder. We observed suppression of sharkskin when Pressure Reduction gets above 20%. Dead time in Figure 3C corresponds to the time to convey the polymer material through the extruder. The conditioning time by definition is the time duration that is necessary to suppress sharkskin since the PE resin with PPA starts to flow through the die. In Figure 3C we can see that a composition of the additive comprising PEG 2000 and citric acid (PEG2K + ca) shows best pressure reduction at the extrusion die as well as a shortest conditioning time in comparison with other additives. It seems so that catalytic properties of the extrusion die are important and we observed much longer conditioning times for extrusion with the die made from stainless steel. It appears also that silica fume in amount about 1% in the composition of PPA helps to shorten conditioning times and to get good lubrication at the die. We observed a reduction in these performances if no silica fume or concentrations of silica fume different from 1% were used to prepare the PPA. Without silica fume in the composition of PPA curling of the extrudate of small diameters, e.g. 0.5 mm, may happen so that it leaves the die shaped like a helix. Details of our extrusion experiments and manufacturing of micro-pellets we are going to publish elsewhere.

Pelletizing of LLDPE material in air without PEG additives is hardly possible at low temperature of extrudate, e.g. 132 °C, not only because of high pressures at the die but also because of pronounced die drool and accumulation of molten PE resin at the die exit. PE melt does not stick to the metal surface wetted by PEG while the low viscous PEG lubricates surface of a rotating knife. If pellets are cut by the rotating knife at higher temperatures, e.g. 165 °C, they stick together. Therefore pelletizing with air cooling would be not possible at such temperatures. Extrusion of LLDPE with additives of low viscous PEG, e.g. PEG 2000, at temperatures below 130 °C cannot be recommended too as the extrudate surface gets rough, friction losses at the die oscillate in time while the averaged pressure is increasing. With the use of PEG 8000 extrusion goes stable down to temperatures as low as 128 °C but at higher pressures at the die as compared to the use of PEG 2000.

To demonstrate an opportunity to produce micro-pellets by extrusion at reduced temperatures and pelletizing in open air we used as a die set a pack of 7 injection needles with inner diameter about 0.5 mm and 20 mm length soldered by silver alloy inside a steel housing. We used no additional cooling in the process but convection of air. LLDPE (LL1201 XV) was blended inside a screw extruder with additives (0.5 wt. %) of a reacting blend of PEG 8000 and 1.6 wt. % of citric acid. We started extrusion at 165 °C and after a conditioning time about one hour that is necessary to get stable lubrication at the die we reduced gradually a temperature of the die. We used a rotating knife from a meat grinder to cut strangle to pieces at averaged melt velocity about 22 mm/s. The produced micro-pellets do not stick to each other at temperatures from 130 to 135 °C. With this simple appliance it is possible to cut micro-pellets as cylinders or disk-like pellets of oval shape with thickness about half of the diameter by varying the rotation speeds of the knife. Appearance of the micro-pellets is presented in Figure 3D. The produced micro-pellets demonstrate good flow properties (an angle of free repose is about 40°) and obviously can be used for rotomolding or flood feeding of an extruder. In one more trial we fabricated some amount of micro-pellets by cutting thin strands of LLDPE by a rotating knife of a wood planer. The strands were extruded at reduced temperatures (about 132 °C) and stretched by rollers in conditions of air cooling to diameters about 0.3 mm before they were cut.

Discussion

PEGs are slightly dissolvable in PE resins at high temperatures. They reduce surface tension and viscosity of molten PE and the additives of PEG are already known in industry as an agent to improve cohesive strength of a weld joint in hot sealing of PE films. So, it is no wonder that additives of PEG accelerate sintering of the PE powders but mechanism of the PE melt densification with additives of PEG is not yet understood. We can tentatively explain the observed improvements by high permeability of PEG to Oxygen and water vapors. To our knowledge a systematic research on gas permeability of PEG and PEG-based esters is missing but from the data in literature, e.g. Metz (2003), Massey (2003), Lin and Freeman (2004), we can derive that diffusion of water vapors and Oxygen through PEG is much better in comparison to PE resins. Zhang and Cloud (2006) proposed a qualitative mechanism of gas permeability of silicon rubber: thermal motion of long and flexible siloxane molecules provides ‘‘openings’’ in silicones for the gas molecules which permit diffusion of gasses. Chemical structure of PEG molecules resembles molecules of siloxanes and gasses can diffuse through the PEG and PEG-based esters in a similar way. In fact, hydrophilic properties of PEG make diffusion of water vapors through the bulk of PEG and PEG-based esters much easier in comparison with silicone rubbers.

PEG reacts with citric acid (ca) at temperatures above 160 °C with release of water. Additionally, citric acid is decomposing at temperatures above 175 °C to water and Carbon dioxide. PEG is characterised by very high permeability to these gasses. We believe that ‘‘purging’’ of the merging PE grains with water vapours combined with easy diffusion of water through the foamed mixture of PEG + ca can be a mechanism that reduces amount of trapped gasses inside the melt. We may think that foaming of the PA impedes its flow under capillary forces and therefore we do not observe any large beads of PEG + ca inside the melt. Additionally, the foamed hydrophilic substance at the surface of PE grains may keep channels between the PE grains open so that gasses can escape from the voids.

Polyethylene is exposed during grinding to extreme shear stresses and to temperatures close to its melting point in presence of Oxygen. If PE powders with high surface area are stored in an air atmosphere for prolonged periods, oxidative degradation of PE molecules would continue. Additionally, surface of grains of the PE powder is enriched by chemical components of low molecular weights (MW) that migrate from the bulk of PE grains. Presence of low MW PE and waxes significantly reduces entanglement of long PE molecules at the boundaries of the sintered PE grains and causes local weakness of cohesive strength of the polymer. We believe that if PPA comprises silica fume and vinyl-silanes the cohesive strength can be enlarged by cross-linking of PE molecules across the grain boundaries and by anchoring nano-particles of silica fume in both contacting grains of PE during the fusion process. In our experiments we added vinyl-silane to the blend of the PE powder with silica fume in hope to get reinforcement of the boundaries between the merging grains of PE. Vinyl-silanes VTMOS and VTEOS dissolve in PE resins and they would migrate in time to the surface of PE grains and react with silica and water vapors. During rotomolding process the vinyl-silanes molecules that are grafted to the surface of silica particles may create chemical bounding between the modified silica particles and molecules of PE as well as cross-linking of the PE molecules in a boundary layer of the merged grains of PE. Yet, direct measurements of impact strength to confirm integration of silica particles to polymer matrix are missing and have to be done in future.

Flow performances of the PE particulates are important to get uniform thickness of the walls and to avoid ‘‘bridging’’ inside the mold between opposite walls and in the corners of the rotomoded article. The use of PEG and reacting mixtures of PEG with carboxylic acids as PPA impede flow of PE powders. Additionally, blending of the PE powders with additives is costly. We propose that blending of PPA with PE resins has to be done inside an extruder for production of micro-pellets. Micro-pellets of oval shape with sizes from 0.3 to 0.8 mm provide superior handling and processing performances in rotomolding, see Beall (1998), Whatcott (2008) as well as Crawford and Kearns (2003). Our experiments demonstrate that micro-pellets can be produced by extrusion of PE resins at reduced temperatures. High fluidity of micro-pellets is considered sometimes as a disadvantage of the material while flowability of PE powders is below optimum. The proposed PPAs adjust flowability of micro-pellets in proper direction, i.e. reduce it. Yet, micro-pellets with PPA show better flowability than PE powder without PPAs.

It is amazing that the same composition and concentration of additives used as a densification aid in sintering of PE particulates helps to improve extrusion of the PE melt: to suppress sharkskin and to reduce extrusion pressure. As a tentative mechanism of the observed lubrication we can propose following: Commercially available LLDPE grades comprise low MW organo-phosphites as antioxidant additives. The antioxidants deplete Oxygen from the PE melt and get converted to organo-phosphates that are low MW esters of alcohols and phosphoric acid. PEG reacts with these esters at the surface of the die so that high MW esters appear in the reaction of trans-esterification. Reaction rates depend on presence of catalysts. We used in our experiments the die that is made from a steel alloy comprising Aluminum and Vanadium. These metals are good catalysts for a poly-condensation and trans-esterification reactions. The high MW esters of PEG and phosphoric acid have high affinity to metal surface and therefore they accumulate at the die surface and form a layer of a plastic lubricant. With the use of the catalytic die we observe relatively short conditioning times while with the dies having low catalytic properties, e.g. a Chromium coated die, the conditioning times is much longer.

The use of citric acid in the composition of PPA for extrusion of PE resins with narrow MW distribution allows to shorten conditioning times and to get better lubrication at reduced temperatures of extrusion. Actually, inside an extruder the temperatures can be higher (185 – 195 °C in our experiments) while the die is at the reduced temperatures. Extrusion can go at temperatures of the die so close to the melting point of the PE resin that the extrudate with cold surface can be pelletized by a rotating knife at the die exit in conditions of air cooling. We observe that at reduced temperatures of extrusion the additives are ejected from the extrudate to its surface. We have some indirect indications from our experimental observations that if silica fume is suspended in PEG it moves to the extrudate surface together with PEG. If pelletizing goes in air or gas atmosphere, these additives would stay at the surface of the micro-pellets and therefore they can be reused as densification and sintering enhancers for rotomolding.

Conclusion

We present here first experimental results on the use of reacting mixtures of PEG with citric acid (ca) as sintering and densification enhancers for rotational molding of PE particulates. Sintering of PE grains with these additives goes virtually without bubbles of trapped gasses and duration of heating of the mold in rotomolding can be 20-30% shorter. Therefore, higher productivity and better mechanical properties of the rotomolded articles can be achieved. From our observations we can conclude that reacting mixtures PEG + ca do not coalesce into a few large beads like neat PEG does but stay trapped inside the melt as small-size inclusions.

We demonstrated here that reacting mixtures of PEG with citric acid improve sintering of PE powders but impede flow of them. So, it is not advisable to use them with PE powders. Surprisingly, the same mixtures that are helpful to reduce sintering time of PE particulates do work as Polymer Processing Additive (PPA) for extrusion of PE resins with narrow Molecular Weight (MW) distributions. These PPAs suppress extrusion instabilities, reduce extrusion pressure 2-5 times and allow extrusion at temperatures close to solidification points of the PE resins. Extrusion at so low temperatures allows manufacturing of micro-pellets with sizes less than 0.8 mm by cutting the extrudate with a rotary knife at the die exit in conditions of air-cooling. Flow of micro-pellets produced with novel PPAs is better than flow of the powder from the same PE resin without the additives. Rotomolding experiments with such micro-pellets we reserve for next publications.

The use of micro-pellets fabricated by underwater pelletizing for rotational molding is already cost efficient in comparison to the use of PE powders. It seems so that cost of micro-pellets can be reduced by pelletizing in air with proposed PPAs while the rotomolded articles can be produced in shorter times and of better quality. More experimental and analytical investigations are required to prove better Impact Strength and Environmental Stress Crack Resistance of the rotomolded articles made from micro-pellets and novel PPA as well as to get deeper insight in the mechanisms of the observed improvement of sintering and extrusion of PE resins. However, we believe that manufacturing of micro-pellets with proposed PPAs from PE resins in conditions of air cooling and the use of these micro-pellets for rotomolding can be a quantum leap in technology of rotomolding. Patent pending.

Acknowledgements: We would like to thank Dr. Winyu Tanthapanichakoon and Dr. Chris Rauwendaal for stimulating discussions. We thank gratefully ExxonMobil Chemicals and SCG Chemicals for presenting us Polyethylene resins for our experiments. Financial support by the German Science Foundation (Deutsche Forschungsgemeinschaft) is gratefully acknowledged.