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Technical Paper

Effect of Processing Conditions on the Extent of Glass Bubble Survival During Twin Screw Compounding

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Abstract

Reducing the weight of thermoplastics and rubber parts has been a paramount objective in various industries such as transportation, aerospace, hand-held electronics and sports and leisure. 3M™ Glass Bubbles (GBs) are lightweight, micron-sized additives specially engineered to withstand temperature, stress, and strain fields in a wide range of polymer processes, ranging from liquid phase polymer processing to high viscosity melt compounding and high pressure injection molding.

In this paper, we present factors influencing glass bubble survival and discuss processing methodologies to achieve the highest level of bubble survival for a given polymer grade during twin screw extrusion compounding. It is important to emphasize that the majority of the data shown below were generated using glass bubbles of lower collapse strength (3,000 psi to 6,000 psi) with aggressive conditions to show the trend. High strength glass bubbles (10,000 psi and above) are fairly insensitive to these parameters as they can withstand most demanding material and process conditions.

Introduction

Additives, especially inorganic solid fillers, have greatly contributed to the growth of the polymer industry by creating materials with unique properties. Fillers can act as:

1. Mechanical property modifiers, e.g. glass fiber, talc, calcium carbonate
2. Electrical and magnetic property modifiers, e.g. carbon black, carbon nanotube, graphene
3. Surface property modifiers, e.g. silica, molybdenite, graphite, boron nitride
4. Fire retardants, e.g. metal hydroxides
5. Processing aids and stabilizers, e.g. fumed silica and hydrotalcites

In most cases, fillers modify more than one property. Glass bubbles are finely dispersed, free-flowing powders consisting of thin-walled (0.5–1.5 μm) spherical glass particles with an average diameter of 15–65 μm. These inorganic micro additives exhibit low densities (0.12–0.6 g/cc) and are primarily used for weight reduction in plastics. In addition to weight reduction, plastics filled with glass bubbles exhibit reduced thermal conductivity, increased dielectric strength, increased stiffness (modulus) and heat distortion resistance. From a processing point of view, glass bubble-filled plastics have stable dimensions with reduced shrinkage and warpage and shorter cooling time from the melt, resulting in decreased injection mold cycle time or increased extrusion throughput. Glass bubbles are recapturing interest in the plastics industry due to their increased crush strength (up to 28,000 psi) under demanding high pressure polymer processing conditions such as injection molding. The glass transition temperature of glass bubbles is around 650°C, which allows them to be compounded into most demanding polymers, such as PEEK and polysulfones. Glass bubble collapse strength is a function of their diameter and wall thickness according to the following theoretical equation.

$$\text{theoretical collapse strength} = \frac{(0.8E\,(h/r)^2)}{\sqrt{(1-v^2)}}$$

Where **h:** wall thickness of the glass bubble
r: radius of the glass bubble
v: Poisson's ratio for glass

The appropriate glass bubble grade for weight reduction is typically the lowest density with the highest survival rate in a given polymer system. It is important to keep in mind the low density of glass bubbles when formulating with weight percentages commonly used in the plastics industry. For instance, 30 wt% loading of glass fiber (2.5 g/cc) in Nylon 66 (1.15 g/cc) results in 15 vol% inorganic and 85 vol% polymer, whereas the same weight percent loading for glass bubbles (0.6 g/cc) would result in 45 vol% inorganic and 55 vol% polymer. One can easily convert weight percentages to volume percentages and vice versa using the following relationships.

$$\textbf{vol\% GB} = \frac{\dfrac{\text{wt\% GB}}{\text{density of GB}}}{\dfrac{\text{wt\% GB}}{\text{density of GB}} \quad \dfrac{\text{wt\% polymer}}{\text{density of polymer}}}$$

or

$$\textbf{wt\% GB} = \frac{\text{vol\% GB} \times \text{density of GB}}{\begin{array}{c}(\text{vol\% GB} \times \text{density of GB}) \\ + \\ (\text{vol\% polymer} \times \text{density of polymer})\end{array}}$$

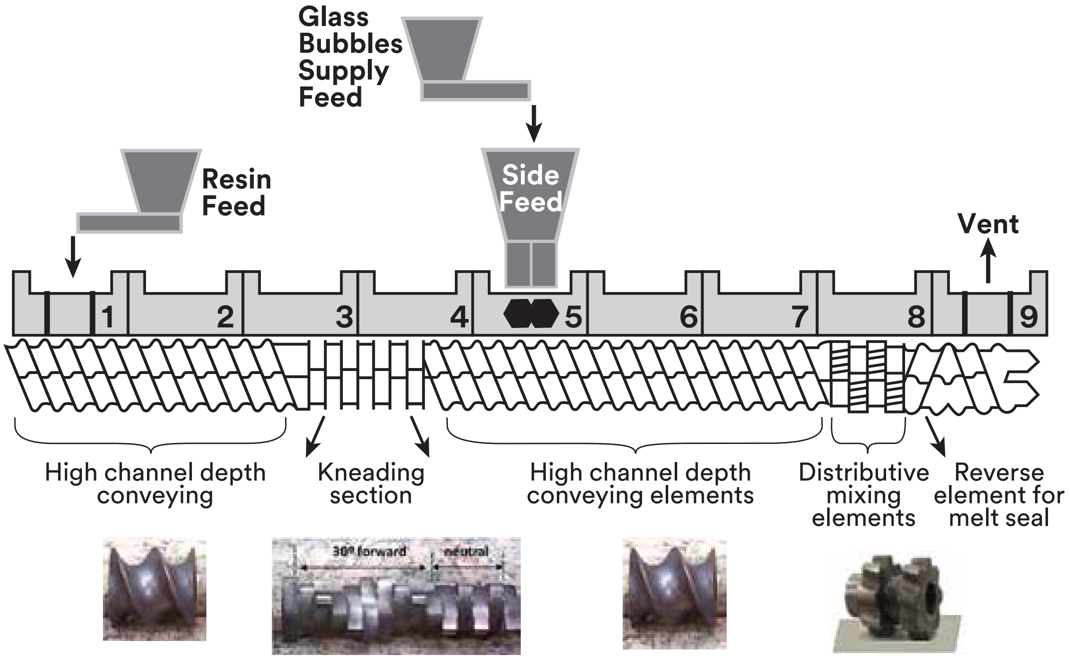

Figure 1. Screw configuration for compounding with 3M™ Glass Bubbles

Twin Screw Compounding Set-up

Co-rotating intermeshing twin screw extruders are typically used for compounding glass bubbles into polymers in a continuous manner. Glass bubbles are preferably introduced downstream in the extruder via side stuffing or top feeding ports into a fully molten polymer stream. Figure 1 shows a twin screw configuration suitable for compounding with glass bubbles. Polymer resin is starve-fed in zone 1 via a resin feeder and passed through a set of kneading blocks to ensure its complete melting before glass bubbles are introduced in zone 5. Glass bubbles should be starve-fed into a side feeder via a supply feeder. It is crucial that high channel depth conveying elements (OD/ID: 1.75 or more) should be used in glass bubble feed zone 5 as well as subsequent zones. Further downstream in zone 8, a short set of distributive elements (preferred but can be omitted if necessary) can be used. One of the advantages of glass bubbles during compounding over fillers such as clay and calcium carbonate is their ability to distribute in the molten polymer without having to resort to aggressive kneading and distributive mixing elements. In fact, simply through mere friction from the barrel wall and conveying elements, they can distribute reasonably well. However, a short distributive section is useful especially at very low loadings of glass bubbles. At high loadings, such as 42 vol%, glass bubbles occupy the entire resin at their closest packing configuration, making distribution irrelevant (Figure 2). Venting, following a reverse element, is optional depending on the application before the compounded material is discharged. If the compounded pellets are to be subsequently injection molded, venting is not crucial since the small amounts of air trapped during compounding can escape through the vents during injection molding.

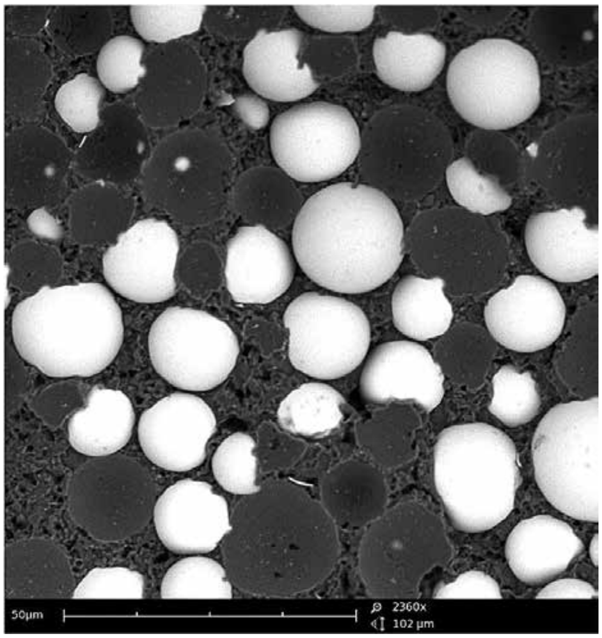

Figure 2. 3M™ Glass Bubbles (0.3 g/cc, 6000 psi) in impact Co-PP at 42 vol%

In order to determine the amount of glass bubbles compounded into the polymer and the volume loss due to bubble breakage, the compounded polymer should be exposed to high temperature in an oven in order to burn and remove the polymer resin. The oven is typically set with a temperature ramp profile to run from 200°C to 550°C in 5 hours and then kept constant for 6 hours. The weight % inorganics, i.e. glass bubbles or glass bubbles with other fillers, is calculated from the known amount of polymer compound before, and amount of ash after the burn process, as shown in the equation below.

$$\text{Weight\% of GBs} = \frac{\text{Mass of residual inorganics after burn}}{\text{Mass of compounded material before burn}} \times 100$$

In order to determine the amount of volume loss due to bubble breakage, the density of residual materials is measured using a helium gas pycnometer. The % glass bubble volume loss due to breakage can be extracted from the following equation using the measured glass bubble density values before and after processing, using a helium gas pycnometer and the density of solid glass (2.54 g/cc).

$$\%\text{ Volume Loss} = \frac{\left(\frac{1}{\text{Initial Density of GB}} - \frac{1}{\text{Density of Solid Glass}}\right) - \frac{1}{\text{Measured Density of GB}} - \frac{1}{\text{Density of Solid Glass}}}{\left(\frac{1}{\text{Initial Density of GB}} - \frac{1}{\text{Density of Solid Glass}}\right)} \times 100$$

Processing Parameters Influencing Glass Bubble Survival During Compounding

After configuring the appropriate compounding system to achieve high glass bubble survival, the next step is to understand the process and polymer resin material parameters. Below we briefly review these parameters. Once again, it is important to emphasize that glass bubbles of collapse strength 10,000 psi and above are fairly insensitive to these parameters as they can withstand most demanding material and process conditions. A majority of the data shown below were generated using glass bubbles with a collapse strength of 3,000–6,000 psi with aggressive conditions to show the trend.

Effect of Pelletizing

Most glass bubble compounded polymers need to be pelletized for further processing, e.g. for injection molding. In a standard water bath pelletizing system, the strands, after cooling, enter into the cutting chamber of the pelletizer, where a rotating blade cuts the strands into small pellets. In a standard pelletizer, extent of glass bubble breakage depends on:

1. Glass bubble collapse strength
2. Type of matrix resin (hard and brittle, soft and rubbery)
3. Temperature of the compounded strand at the point of cutting

As shown in Figure 3, higher strength grades of 3M™ Glass Bubbles, such as iM30K and S60HS, show minimal to zero glass bubble breakage in a standard pelletizer, whereas a fair amount of glass bubble breakage is observed for XLD6000 (9 vol%) and a smaller amount for K42HS (6 vol%). A simple rule of thumb is that glass bubbles with isostatic crush strengths of 10,000 psi and higher can survive standard pelletization substantially.

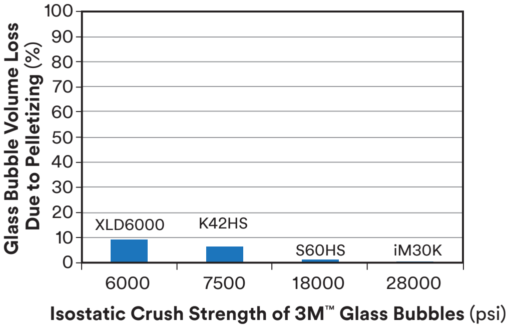

Figure 3. % Glass bubble volume loss due to pelletizing as a function of isostatic crush strength of glass bubble used in homopolymer polypropylene with an MFI of 4 g/10 min at 230°C, 2.16 kg

The level of resin hardness influences the extent of glass bubble breakage during pelletizing. In order to demonstrate this, we used a glass bubble grade with a collapse strength of 6,000 psi. Figure 4 shows that the glass bubbles with 6,000 psi collapse strength do not break when pelletized in elastomeric resins while they do break to some extent in hard thermoplastic polypropylene (PP). This is in spite of the higher glass bubble loadings used in the elastomeric matrices, i.e. 27 wt% for silicone elastomer and polyolefin elastomer versus 17.4 % for homopolymer PP.

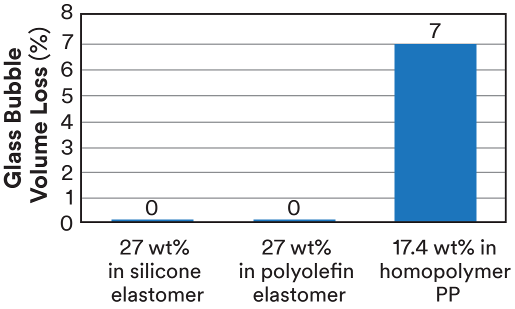

Figure 4. % Glass bubble volume loss due to pelletizing as a function of resin system used. In elastomeric soft resins, glass bubble survival is higher during pelletizing (glass bubble with 6000 psi crush strength, 0.3 g/cc)

The small amount of glass bubble breakage that is observed with low strength glass bubble grades during standard pelletization can be prevented, or minimized, by an underwater pelletizer. In this process, the molten polymer is cut into drops by the fast rotating blades of the pelletizer just when leaving the die holes and emerging into the process water. Since the polymer is cut into drops when it is molten, the bubble breakage is reduced. We have completely prevented lower strength glass bubble (6,000 psi) breakage in a hard polypropylene by switching to an underwater pelletization process. The breakage was about 9 vol% (see Figure 3) when a standard pelletizer was used.

Effect of Polymer Melt Viscosity

It is well known from studies on glass fiber attrition during compounding that increased polymer melt viscosity causes glass fiber breakage. Glass bubbles show the same trend when lower strength glass bubble grades (6,000 psi collapse strength) are used under aggressive compounding conditions. Higher melt viscosities result in higher shear and compressive stresses, which increases the possibility of glass bubble breakage. Figure 5 shows % glass bubble volume loss in polypropylene as a function of melt flow index (MFI). With a high MFI (low viscosity) PP polymer, glass bubble breakage was negligible (3.55 vol%), while it is much higher (25.6%) when a lower MFI (high viscosity) PP was used. Melt viscosity has minimal to no effect on glass bubble breakage when higher strength glass bubble grades are used (10,000 psi and higher). In fact, in large extruders (36 mm and higher) with increased screw channel depths, low density, lower strength glass bubble grades (e.g. 0.38 g/cc, 5,500 psi) were successfully compounded with zero bubble breakage when coupled with underwater pelletizing.

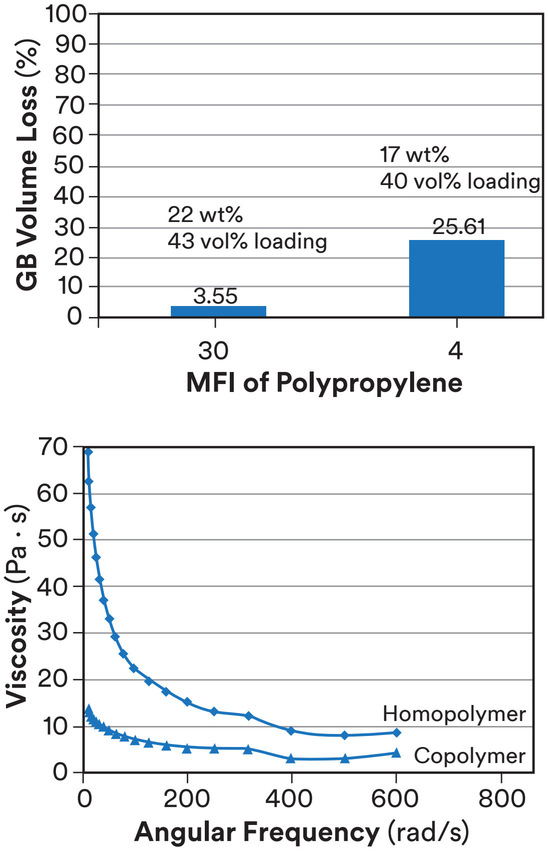

Figure 5. Glass bubble (6000 psi collapse strength) % volume loss in polypropylene as a function of melt flow index (MFI). LyondellBasell Pro-fax™ 6523. MFI (230°C/2.16 kg): 4 g/10 min and LyondellBasell Pro-fax™ SG899 MFI (230°C/2.16 kg): 30 g/10 min. Shear rate dependent viscosity data of neat resins are shown on bottom graph.

Effect of Back Pressure

Back pressure is one of the most critical parameters that influence glass bubble survival. In extrusion, back pressure is the amount of resistance applied to the melt, which can be caused by the presence of downstream equipment such as screens, dies, etc. In injection molding, it is the resistance applied to the rear of the screw as it rotates and collects the melt in front of the screw. In either case, at constant screw speed, increasing back pressure compresses the melt, increasing friction and shear applied to the material. Increased friction and shear can lead to glass bubble breakage.

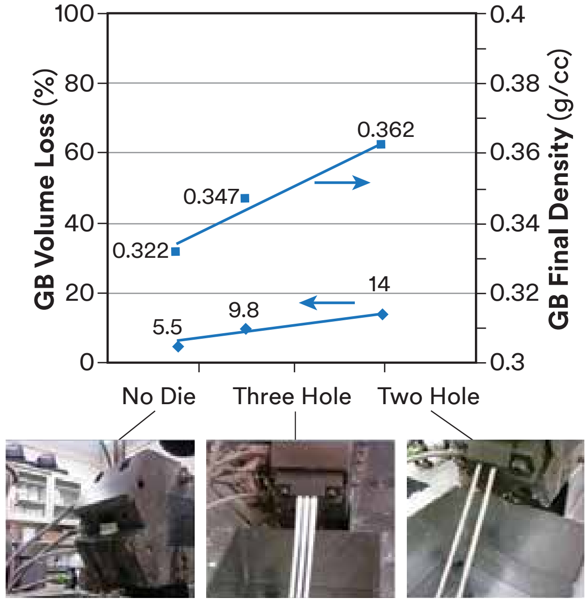

Figure 6. Glass bubble % volume loss and final density of 15 wt% (~ 30 vol%) 3M™ Glass Bubbles XLD6000 (original density 0.318 g/cc, isostatic crush strength 6000 psi) in LyondellBasell Pro-fax™ 6523, MFI-4 polypropylene with no die, die with a three hole strand and die with a two hole strand.

Figure 6 shows volume loss due to glass bubble breakage and final glass bubble density (isostatic crush strength 6,000 psi; original glass bubble density 0.318 g/cc) during compounding with LyondellBasell Pro-fax™ 6523 MFI-4 polypropylene at the same extrusion throughput with:

a) no die

b) die with a three hole strand

c) die with a two hole strand

When using a strand die with 2 holes, 14% breakage is calculated in a high viscosity PP at 15 wt% (30 vol%) glass bubble (6,000 psi; original density 0.318 g/cc) loading. By simply opening another hole in the strand die, glass bubble % void volume loss drops to 9.8%. When we completely eliminate the die and simply collect the extrudate, the glass bubble breakage further reduces to 5.5%, which results in a final density of 0.332 g/cc for the glass bubbles as determined from ash analysis described above. This example shows the effect of back pressure on the survival of glass bubbles and importance of die design. Increasing the number of holes and/or increasing their diameter decreases back pressure and helps minimize bubble breakage.

pressure and helps minimize bubble breakage. However, for a constant volumetric flow rate, it also slows down the flow of polymer coming out of the die, i.e. strand output velocity slows down. When the velocity is too slow, it becomes difficult to synchronize pelletizing with the slow strand speed. Therefore, one must optimize die design with melt handling issues in mind. Similarly, one can imagine the effect of screens with different mesh sizes. Larger openings in the screens result in lower back pressure, minimizing glass bubble breakage.

Effect of Glass Bubble Loading in the Extruder during Compounding

Another important factor is the amount of glass bubble loading in the extruder (shown in Figure 7). High channel depth screw elements are necessary to accommodate large loadings of glass bubbles. For a constant channel depth, high loadings of glass bubbles increase the probability of glass bubble to glass bubble point contact and hence breakage. This is true in the case of low density, low strength glass bubbles but not when high strength glass bubbles are used. In order to minimize breakage for high loadings of low strength glass bubbles, it is recommended that glass bubbles be added in more than one zone downstream.

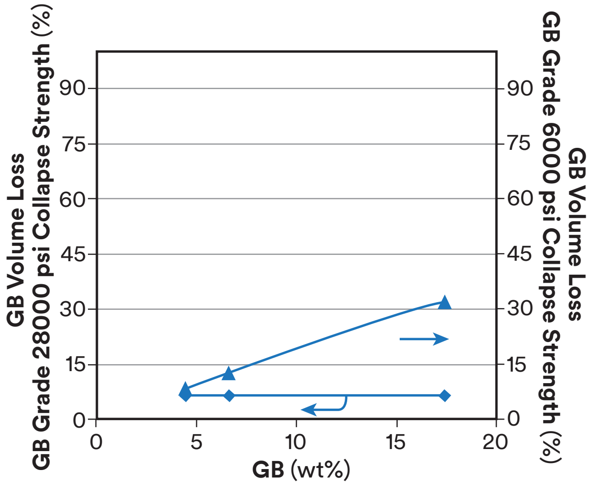

Figure 7. Glass bubble % volume loss as a function of loading in LyondellBasell Pro-fax™ 6523, MFI 4 g/10 min, homopolymer PP

Conclusions

In this paper, we analyzed factors that are influential in glass bubble survival during compounding. The data in this paper were generated using glass bubbles of lower collapse strength (3,000 psi to 6,000 psi) with aggressive conditions to show the trend. Higher strength glass bubbles are much less sensitive to these factors. Regardless, we recommend that the described compounding conditions – developed for lower strength, low density glass bubbles – also be used for higher strength glass bubbles, especially for less experienced compounders. A future publication will further detail the effect of screw configurations and discuss non-traditional glass bubble addition methods. In this upcoming publication, we will demonstrate how high strength glass bubbles can be introduced directly through the feed hopper and compounded into polypropylene-based polymers with high survival rates as influenced by the screw configuration.

Summary of Important Points to Consider During Compounding with Glass Bubbles

- Twin screw co-rotating intermeshing extruders are recommended for compounding glass bubbles.
- It is highly recommended that glass bubbles be added into an already molten polymer at a downstream port via a side or top feeder (side feeder is preferred).
- A side feeder should be fed via a supply feeder. This will ensure starve feeding of bubbles into the polymer melt and allow various volume % loadings to be prepared. If the bubbles are flood fed into the hopper of a side feeder, clogging and bridging may occur.
- The extruder should have a high free processing volume accomplished by deeply cut screw channels with an outer diameter/inner diameter (OD/ID) ratio of 1.75 or more.
- Pre-heating of glass bubbles, although not mandatory, could help prevent rapid temperature decrease of the polymer melt, which could cause rapid increase in viscosity. It is preferable that the glass bubbles are first pre-heated and then added at around 100 to 120°C. Since a side feeder is attached to the extruder, it will get hot due to extruder temperature. If a top feeder is used, it is advised that the glass bubbles be pre-heated.
- After the glass bubbles are added into the molten polymer, they should be conveyed via standard conveying screw elements with a high OD/ID ratio, such as 1.75 or more, for a while before entering distributive block sections (if any need to be used).
- Inlet design of the side feeder into the extruder is very important, especially if high volume percentages of glass bubbles are formulated. The screw elements in the inlet section should be of the conveying type with a very high OD/ID ratio, such as 1.75 or more.
- Minimal back pressure is preferred during compounding with glass bubbles. In this respect, a die design that creates low back pressure is important. Likewise, screens with too large mesh sizes should be avoided.
- An underwater pelletizer is the preferred method of pelletizing and should be used especially when compounding low density, low strength glass bubbles.
- If possible, resin parameters should be considered to prevent breakage – lower viscosity, higher MFI resins are preferred as well as materials that are softer and more elastic.

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Issued: 9/16 11837HB
98-0212-4215-5

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