

EXTRUSION OF BaSO_4 FILLED MEDICAL-GRADE THERMOPLASTIC POLYURETHANE

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Abstract

Extrudability of 20% (vol.) BaSO_4 filled medical-grade (additive free) thermoplastic polyurethanes was investigated. Filled TPU exhibits decreased shear viscosity and elasticity in comparison to unfilled TPU, generating reduced pressure drop at the die and reduced pressurization in the extruder. The moisture remaining in the BaSO_4 may hydrolyze the polymer. However, hydrolysis is not sufficient and air, entrained with the filler into the extruder, reduces the viscosity and elasticity of the compounded TPU.

Introduction

Radiopaque barium sulfate filled thermoplastic polyurethane is widely used in the medical device industry. Here the rheological behavior as well as the extrusion processability of a BaSO_4 filled TPU are studied and compared with the behavior of the unfilled TPU. The medical-grade BaSO_4 -incorporated TPU used in this study is processed without any additives and requires a minimum residence time in the extruder.

Experimental

Materials of the Study

The TPU used in this study is a medical grade thermoplastic polyurethane, based on 4,4'-diphenylmethanediisocyanate (MDI), a polyether glycol and 1,4-butanediol. Its solid density of

1.2 g/cm^3 (ASTM D1505) reflects the relatively high hard segment content. Generally polymeric resins are utilized in complicated formulations which involve various types of stabilizers, antioxidants, lubricants, pigments etc. However, the medical use mandated here precluded the use of any additives and the TPU was thus unusually pure. Additional information on this TPU can be found elsewhere (1).

BaSO_4 with a density of 4.25 g/cm^3 was obtained from J. T. Baker under the product code of 1030. The shape of particles is approximately elliptical with the major axis of the particles ranging from 0.1 to 2.0 microns. The maximum packing fraction of the BaSO_4 particle was determined to be 0.64 using the method of Ouchiyama and Tanaka (2, 3).

Since TPUs absorb moisture rapidly upon exposure to atmospheric conditions, they are properly dried before processing. BaSO_4 powder, however, is usually not dried. It was of interest to determine the moisture concentration of BaSO_4 in the condition that it was compounded in the extrusion process and also upon drying. For the drying conditions the same drying parameters used for the drying of TPU was used, i.e., 5.5 hours under vacuum at 85°C . In the temperature range of 28 to 240°C , the weight percentage loss of moisture of "wet" BaSO_4 upon TGA analysis is 0.09%, while the value for vacuum-dried BaSO_4 is 0.07% indicating that the maximum amount of water that would be available for hydrolysis of the urethane linkages during compounding of TPU with the BaSO_4 is 0.02% of the weight of TPU.

Obviously, only a fraction of this moisture will be accessible during compounding.

Experimental Procedures

The linear viscoelastic dynamic properties upon small amplitude oscillatory shear and the relaxation modulus as a function of time and strain upon a step strain material function of the TPU and filled TPU were characterized using a rotational rheometer. The Advanced Rheological Extended System (ARES) of Rheometric Scientific was used in conjunction with the 8 mm parallel disk fixtures.

TPU chips from the reactor were converted into pellets of TPU in a twin screw extruder. The twin screw extruder was a Leistritz fully-intermeshing co-rotating with 18 mm screw diameter and a length over diameter ratio, L/D, of 35. The rheological characterization of the TPU was carried out on these pellets. TPU chips were also compounded with the BaSO₄ filler using the same twin screw extruder. The die of the extruder was a rod die with a diameter of 2.5 mm and a length over diameter ratio of 10. Keeping the operating conditions in the twin screw extruder the same for both the unfilled TPU and BaSO₄-filled TPU assured that the differences in the rheological behavior and processibility are associated with the incorporation of the filler alone.

The TPU pellets and the compounded TPU, both processed using twin screw extrusion, were also single screw extruded. A Harrel single screw extruder with a 1• barrel diameter and a screw length over diameter, L/D, ratio of 24 was employed. A strand die with a diameter of 0.140• and a length over diameter ratio of 4.0 was used. All three barrel zone temperatures and the temperature of the die were kept at 200°C. This is a flood-fed extruder necessitating that the flow rate be determined independently.

Results and Discussion

Figure 1 shows that the pressure rise in the single screw extruder and the pressure drop at the

extrusion die were significantly affected by the presence of the BaSO₄ filler, but in an unexpected direction. The pressure drop required to extrude the BaSO₄ filled TPU is significantly smaller than the pressure required for the extrusion of the unfilled TPU, indicating that the shear viscosity of the 20% filled TPU is smaller than the shear viscosity of the unfilled TPU under similar conditions. As a result, the operating point is shifted from A to B, suggesting that the production rate does increase with the incorporation of the filler at constant pressurization. The underlying reasons for this “anomalous” finding were not clear and formed the impetus for this detailed study, which is reported here.

Figure 2 shows the variation of the magnitude of complex viscosity values of unfilled TPU, and 20% by volume (50% by weight) of BaSO₄ filled suspension of TPU as functions of frequency at 200°C. As expected on the basis of the single screw extrusion data (smaller pressure drop at the die and smaller pressurization rates for the filled TPU versus the unfilled TPU as shown in Figure 1) the magnitude of the complex viscosity values (hence the shear viscosity) of the TPU, compounded with 20% by volume of BaSO₄, are smaller than the magnitude of complex viscosity values of unfilled TPU at all frequencies. The storage modulus values (indicative of the elasticity of the material as a function of the deformation rate in the linear viscoelastic region) of the 20% by volume of BaSO₄ filled TPU are also smaller than those of the unfilled TPU.

The first factor that we have pursued to explain these processing observations is the possible hydrolysis of the binder TPU upon reactions with the moisture (4, 5). Moisture can be carried into the extruder with the filler, since the TPU itself was very carefully dried prior to extrusion. Upon contact with moisture and especially under typical processing conditions the urethane linkages in thermoplastic polyurethane will be hydrolysed. The hydrolysis reaction involving the urethane linkages yields polymer fragments with amine and carbonic acid end groups. The carbonic acid formed is very unstable and is decarboxylated immediately. As

a result the hydrolytic degradation products of a TPU include amine and hydroxy-terminated species and carbon dioxide (4, 5). We analyzed samples with known moisture content. For example, the shear viscosity values of TPU with 0.65% moisture versus TPU with negligible moisture were compared. The effect of the presence of a relatively large concentration of moisture, i.e., 0.65% is to reduce the molecular weight of the TPU and thus give rise to a reduction of the magnitude of complex viscosity (50%). However, as explained under the materials section above, the amount of moisture, which can be introduced with the filler is only 0.01% of the weight of TPU. Thus, the moisture which can be carried into the extruder with the BaSO₄ and the associated hydrolytic degradation of the TPU cannot explain the almost one order of magnitude decrease in shear viscosity observed upon the compounding of the TPU. What is the major factor missing?

Figure 3 demonstrates that a significant degree of porosity has formed in the suspension upon being extruded. What is the source of the porosity? As determined earlier with the TGA experiment the concentrations of moisture in the TPU or in BaSO₄ are not sufficient to cause the observed porosity. The observed porosity should be caused by the entrainment of air into the system. The subject of air entrainment into suspensions of polymeric materials mixed with rigid particles during extrusion has been investigated by Kalyon and co-workers (6-8). Generally the air comes in through the hopper and is compressed whenever there is pressurization in the extruder. Especially if the solid bed being conveyed is prematurely broken up during the continuous process the air channels are disrupted and the air becomes fully entrained into the suspension.

Why is the air entrained into the suspension associated with BaSO₄ and not with TPU? The major factor should be the greater surface to volume ratio of the filler in comparison to the pellets of TPU. The characteristic lengths of TPU chips are 3-5 mm whereas the characteristic lengths of BaSO₄ particles are only about 0.6 microns. Thus, BaSO₄ particles become the suitable vehicle for

the air to be entrained. Air is introduced within the interstitial volume between the BaSO₄ particles and then is immediately encapsulated within the TPU melt during the compounding process. The incorporated air should decrease the shear viscosity and the elasticity of the suspension and should increase the wall slip coefficient (7). Drastic changes in processability behavior may occur with the presence or the absence of air in concentrated suspensions (8).

The air incorporation effect was probed further by subjecting the extruded specimens to various temperatures. Moldings of the specimens upon drying were kept at various temperatures in the 180 to 220°C range and were then cooled under similar cooling rates to ambient temperature and studied under a microscope. The 20% filled samples in Figure 4 exhibit visible bubbles at temperatures of 200 and 220°C. On the other hand, there are no visible bubbles observed for unfilled TPU at all three temperatures of 180, 200 and 220°C.

The presence of air should be an important factor in the structuring of the extrudates from the compounded TPU. For example, Figure 5 shows cracks in the bulk of the filled TPU. The presence of the void fraction should introduce stress concentration points which facilitate the formation of first crazes and then cracks and thus lead to immediate deterioration of the mechanical properties of the extruded articles.

Conclusions

The compounding of medical grade polymers, which involves minimum or no additives, is a challenge. It is shown here that the compounding of a medical-grade TPU with the requisite BaSO₄ x-ray tracer for in vivo medical device applications leads to unexpected decreases in die pressure drop associated with the shear viscosity and elasticity in comparison to the pure TPU. The general sources of this reduction in viscosity and elasticity are associated with the hydrolytic degradation of the binder upon exposure to the moisture bound to the filler on one hand and the air entrained into the extrusion process through the agglomeration

of the high surface to volume ratio BaSO_4 filler particles. Among these two effects the entrainment of air into the suspension is determined to be the dominant factor for the BaSO_4 incorporated medical grade TPU of this study.

References

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Key words

TPU, thermoplastic polyurethane, extrusion, BaSO_4

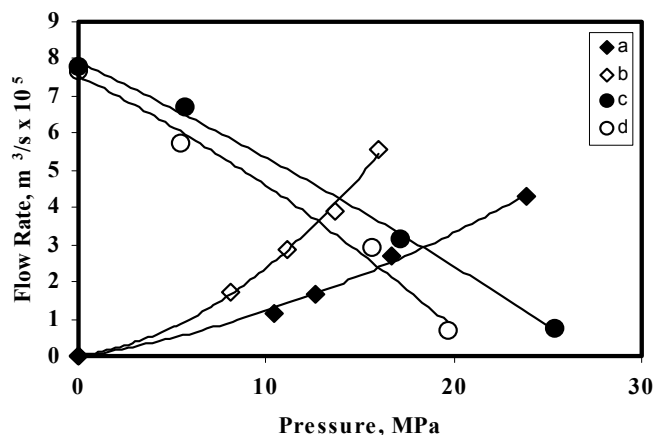


Figure 1. Screw/die characteristic curves for the unfilled TPU and 20% BaSO_4 filled suspension at 200°C: a - die characteristic curve (unfilled); b - die characteristic curve (20% filled); c - screw characteristic curve (unfilled); d - screw characteristic curve (20% filled); A - operating point of unfilled; B - operating point of 20% filled.

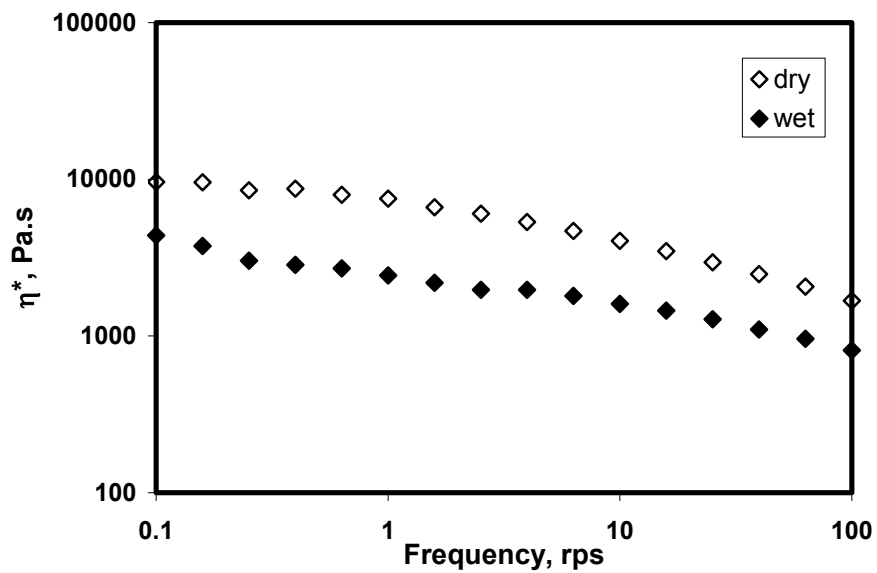


Figure 2. The magnitude of complex viscosities of the unfilled TPU and the 20% filled suspension versus frequency at the strain of 1% and 200°C.

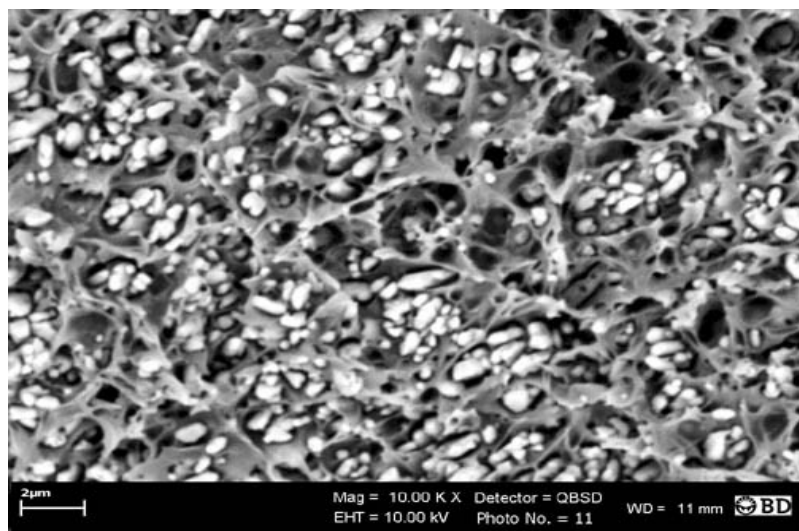


Figure 3. A significant degree of porosity formed in the 20% BaSO₄ filled TPU suspension upon being extruded.

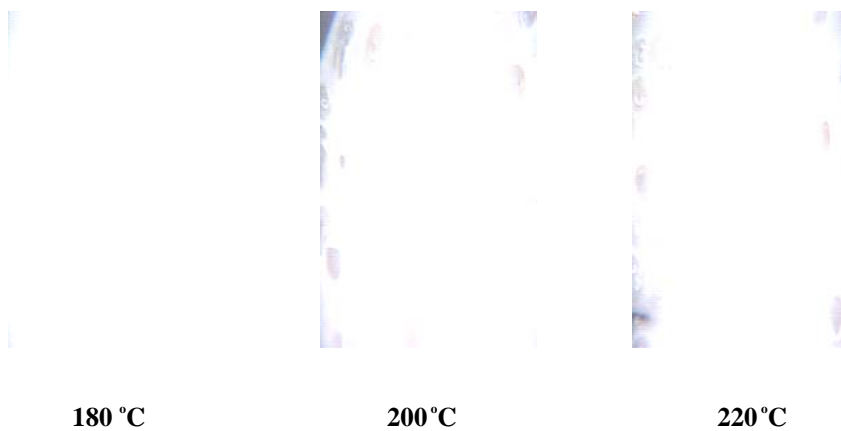


Figure 4. 20% filled TPU samples that are heated at 180, 200 and 220°C respectively (from the left to the right).

