

COEXTRUSION OF TPU AND BaSO₄ FILLED MEDICAL-GRADE TPU

Guangyu Lu, Dilhan M. Kalyon, Iskender Yilgor and Emel Yilgor**

*Highly Filled Materials Institute
and Biochemical, Chemical and Material Engineering
Stevens Institute of Technology, Hoboken, NJ*

** Chemistry Department, Koc University, Istanbul, Turkey*

Abstract

Coextruded products for the medical device industry, involving layers of filled and unfilled polymers, are difficult to fabricate, especially due to the various degradative processes taking place in the absence of stabilizers. Significant differences in the degradation behavior and the subsequent rheological behavior of unfilled and BaSO₄ filled TPUs generally give rise to severe fluctuations at the interfaces and poor coextruded products. It is shown here that the shear viscosity values of the filled and unfilled TPU need to be matched under the extrusion conditions to obtain acceptable coextruded products.

Introduction

In our previous studies it has been demonstrated that the rheological and processing behavior of TPU is strongly dependent on the processing temperature and furthermore it is usually complicated due to thermal and oxidative degradation of the urethane hard segments (1). In BaSO₄ filled TPU suspensions the shear elasticity and viscosity of the system were found to be affected significantly by the moisture and the air entrained into the suspension upon the incorporation of the filler BaSO₄ (2). Figure 1 shows the partial cross-section of stripe tubing that was extruded with unfilled TPU (matrix) and 20% BaSO₄ filled TPU suspension (stripe) extruded at the same temperature, 210°C. The difference in viscosities between the filled and unfilled materials at the same extrusion temperatures results in a phenomenon of "viscous encapsulation" in which the less viscous filled material tends to encapsulate the more viscous polymer producing a rather distorted stripe profile, suggesting that obtaining the desired interface shape is not straightforward.

Coextrusion and dual-extrusion technologies are reviewed by Levy and Carley (3). Han and coworkers conducted a comprehensive study on multilayer film coextrusion and the interfacial instability in flat film coextrusion and the thermo-mechanical history during blown film coextrusion. It was reported that, for a given polymer system, there is a critical value of wall shear stress at which an irregular interface between the layers sets in, giving rise to a pattern similar to that usually found in a wood panel (4).

The coextrusion process for an unfilled and TiO₂-filled polyethylene was studied by White and co-workers. The study aimed at investigating the influence of viscosity ratio, cross-section type, die length and duration of flow on coextrusion. It was observed that low viscosity melts would encapsulate high viscosity melts during flow through cylindrical and rectangular geometries (5). A wavelike distortion of the interface between the two polymers was found to cause intermixing of the layers, and the onset of the instability was associated with a "critical interfacial shear stress".

In this study the impacts of the rheological behavior of unfilled and a 20% by volume (50% by weight) BaSO₄ filled TPU on the types of interfaces obtained during the coextrusion process were investigated and acceptable conditions for the coextrusion were determined.

Experimental Procedure

The TPU used in this study is a polyether based medical grade thermoplastic polyurethane, which contains hard segments based on MDI and 1,4-butanediol. Its solid density is 1.2 g/cm³. It was compounded with 20% by volume (50% by

weight) BaSO₄ with a density of 4.25 g/cm³ (J. T. Baker). The shape of particles is approximately elliptical with a major axis length of between 0.2 and 0.8 microns. The maximum packing fraction ϕ_{max} of BaSO₄ particles was determined to be 0.64 using the method of Ouchiyaama and Tanaka (6, 7).

A Harrel single screw coextrusion system comprising of a 1" extruder for TPU matrix extrusion and a ¾" extruder for BaSO₄ stripe extrusion, were employed in this study. The L/D ratios of both screws were 24. Modified Maddock and Saxton mixer type screws provided dispersive and distributive mixing to eliminate temperature gradients during coextrusion. The extrusion temperature range of the unfilled TPU and the BaSO₄ filled TPU suspension used for this study was 185°C to 210°C.

The dynamic and steady flow rheological behavior of the material was characterized using a rotational rheometer. An Advanced Rheological Extended System (ARES) available from Rheometric Scientific Inc. of Piscataway, New Jersey was used in conjunction with the parallel disk fixtures with a diameter of 8 mm. The temperature range that was investigated was 180-230 °C. An Olympus Vanox LE 8080-006 microscope was employed for the observation of coextrudates at a magnification ratio of 20.

Results and Discussion

Figure 2 shows the evolutions of the magnitude of complex viscosity with time for the unfilled TPU at 200, 210, 220 and 230°C. The magnitude of the complex viscosity values monotonically increase with time over the entire temperature range due to various factors including the increase of the crystallinity and the hard block concentration at the low temperatures and the oxidative crosslinking of the TPU at higher temperatures. With increasing temperature the rate of increase of the storage modulus also increases, consistent with the increased elasticity of the TPU upon oxidative crosslinking. The rates of crosslinking and hence the build-up of elasticity of the TPU increase with increasing temperature (1).

The time and temperature dependence of the 20% by volume BaSO₄ filled suspension is different from the behavior of unfilled TPU as shown in Figure 3. The filled TPU suspension

shows very high viscosity values at 180°C. However, the magnitude of complex viscosity of the filled TPU drops down dramatically at 190 and 200°C. In addition, there is only a modest increase of viscosity with time for the filled suspension when compared to the unfilled TPU.

For co-extrusion process to be successful the melt viscosities of these different materials need to be matched under the extrusion conditions. This could only be achieved by varying the time-temperature history of the two materials. Figure 4 shows the magnitude of the complex viscosity as a function of time for both the filled and unfilled TPU. The comparison and the matching of the viscosity values of the two materials needed to be carried out at the correct residence times of the two materials extruded in two different extruders. The time scans shown in Figure 4 were conducted at the same amplitude of strain and frequency but at different temperatures, i.e., 210°C for the unfilled and 190°C for the filled TPU. For the typical extrusion residence time of 400 to 700 s, Figure 4 suggests that different temperature profiles are necessary for the filled and unfilled TPUs so that the two materials would reach similar values of shear viscosity during 400 to 700 s of residence time in the extruders.

Figure 5 indeed demonstrates that the best results (a rectangular stripe and flat interfaces between the two materials) of co-extruded profile is obtained by employing the suggested temperature ratio of 0.88, i.e., 185°C for the filled TPU suspension and 210°C for the unfilled TPU upholding the viscosity versus the time behavior shown in Figure 4.

Conclusions

The selection of the proper co-extrusion conditions is essential for obtaining stable interfaces between medical grade TPUs and filled TPUs. This only becomes possible if one were to include in the analysis the typical residence time in the extruder and the shear viscosity changing as a function of the time and temperature. In order to match the shear viscosities of the unfilled and filled TPU it was necessary to use two different processing temperature ranges (185-190°C for filled TPU and 210°C for unfilled TPU). Under these conditions stable interfaces between the two materials could be obtained.

References

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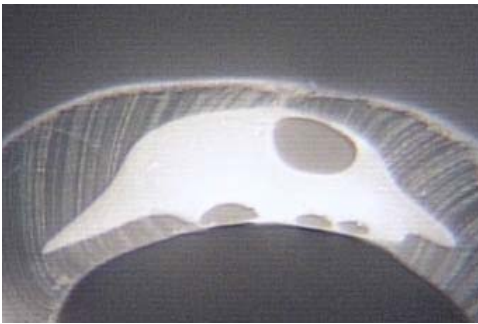


Figure 1. Interface shape of the coextrusion sample at the same temperature of 210°C for both TPU and filled TPU.

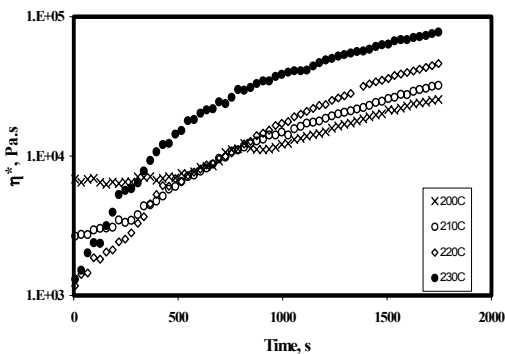


Figure 2. The magnitude of complex viscosity of TPU versus time at various temperatures and the strain of amplitude of 1% and the frequency of 0.5 rps.

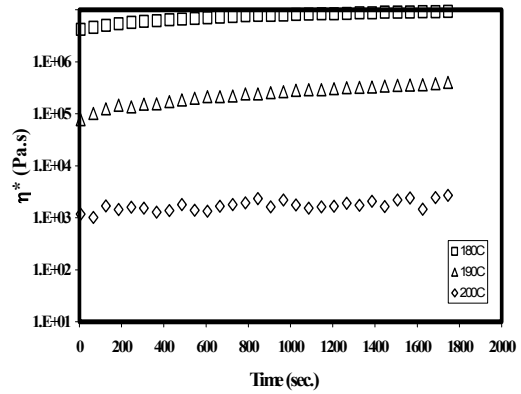


Figure 3. Complex viscosity – time behavior of TPU at various temperatures and the strain of amplitude of 1% and the frequency of 0.5 rps.

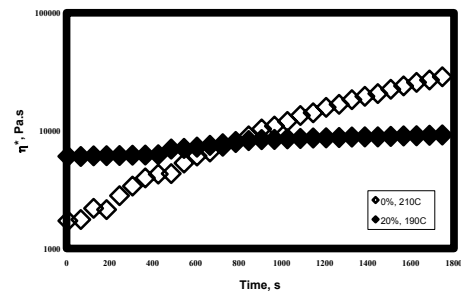


Figure 4. Comparison of complex viscosity of unfilled TPU (at 210°C) and 20% BaSO₄ filled TPU (at 190°C) versus time at 1% strain and 0.5 rps.



Figure 5. Interface shape of the coextrusion sample at the same temperature of 210°C for both TPU and filled TPU.