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Thermal, mechanical, and rheological comparison of stereoblock flexible polypropylenes

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Abstract

For medical fluid delivery applications, clear materials with both low modulus and high temperature resistance are highly sought after. Many of the currently available materials are either optically opaque, or far too expensive to be suited for the majority of applications. The recently available stereoblock homo-polypropylene polymers, where atactic and isotactic sequences are placed on the main-chain, present an attractive opportunity. We have examined some of these commercial as well as experimental polymers by thermal analysis, rheology and mechanical analysis for their potential suitability in medical applications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polypropylenes; Polymers; Thermal analysis; Rheology; Mechanical analysis

1. Introduction

The medical device and packaging industries require that a material provide unimpeded light transmission to allow visual inspection for particulate matter contamination or the completion of dissolution of mixed or compounded medications in order to safeguard patients. Also, the need for sterile delivery of therapies makes compatibility with steam autoclaving (the preferred method of sterilization) a must. But this seriously challenges a material's properties due to the high temperature of 121°C (250°F) and pressure.

In the last few years, we have witnessed a fundamental material revolution not seen in the last half century of polymer history. The single site catalysts, many of which are metallocene compounds, are creating novel compositions with properties unheard of only a few years ago. In the medical plastics and packaging markets, the achievement of cost performance similar to that of flexible PVC has always been a technological challenge. With the metallocene catalysts, unprecedented co-monomer incorporation can be achieved with high homogeneity. However, with the steady reduction in crystallinity and modulus, the melting point also decreases monotonically. Thus, materials with both the flexibility and high temperature capabilities are still rare.

More recently, several developments on propylene based elastomers have been discussed. Combining the high melting point of isotactic polypropylene with a suitable elastomeric block structure appears to be promising in achieving these properties [1–3]. Researchers at E.I. DuPont discovered a catalyst with moderate productivity, which could produce elastomeric products with interesting properties.

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Furthermore, these DuPont researchers conducted extensive studies on the melt blending of the elastomeric PP and commercial high isotactic content PP. Since in the molten state both types of polymer should be miscible with each other, a single phase is expected. Upon cooling, some of the crystallizable segments from the elastomeric PP could co-crystallize with the isotactic PP, thus forming the physical crosslink sites required for TPE behavior. In this way, different mechanical properties can be achieved simply by varying the ratio of the elastomeric and isotactic PP fractions. Although research of this catalyst family continued, no commercial product from this novel invention has been available.

In the early 1990s, based on their experience in producing amorphous polypropylene for adhesive and asphalt modification applications, the Rexene began semi-commercial and commercial production of the flexible polyolefin (FPO®) and, Rexflex® [4]. This line of polymers was characterized as having previously unheard-of low modulus, as low as 7–10,000 psi (49–70 MPa), relatively high strength, and peak melting points of about 155°C. This line of specialty polymers met many of the requirements in medical plastics where high melting point and low modulus were needed. However, the polymer was still not ideal, due to the relatively high amorphous and low molecular weight fractions in the polymer. This resulted in sticky and hard-to-handle pellets. Although difficulties in polymer manufacturing and fabrication were overcome, products made from these polymers were still sticky and prone to exudation, especially over time and with elevated temperature storage.

More recently, the exciting work of R. Waymouth of Stanford University showed great promise to be the most versatile catalyst system studied to-date. The catalytic behavior is controlled by the stereo conformation of the catalyst center. The asymmetric indenyl ligands are coordinated to a zirconium or hafnium metal center. Since the two ligands are unbridged, they are free to rotate in the same plane of their respective aromatic rings. Their relative orientation controls the stereo regulation of the inserting propylene monomer. In one orientation, predominantly isotactic polypropylene is produced, and in the other, atactic (Fig. 1). Hence in an elegant way, the requirements for the alternating blocky constructions of crystalline and elastomeric segments are met.

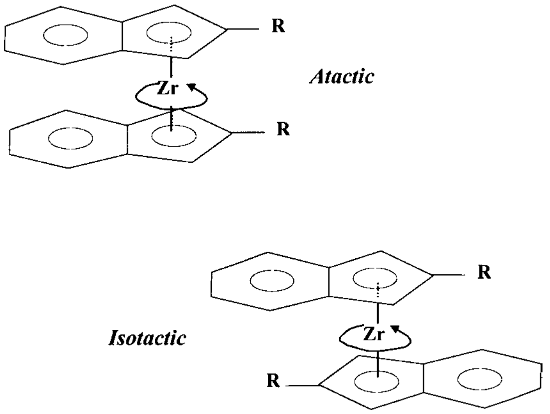

Fig. 1. Rotating metallocene catalyst for stereoblock PP.

The BP Amoco has produced experimental quantities of these materials and our characterizations are based on these samples [5].

2. Experimental

The thermal characterization of these polymer samples was done using a TA Instrument 2920 MDSC at 10°C/min heating and cooling rate in the normal DSC mode under nitrogen gas environment (flow rate of nitrogen gas $= 50\,\mathrm{ml/min}$). Typical sample mass of about 10 mg in a thin film form was used throughout the series.

Dynamic viscoelastic characterization was carried out using a Rheometrics Fluids rheometer in the frequency sweep mode between 0.1 and 200 rad/s. Samples of about 2 mm in thickness were used while the strain amplitude was adjusted at different temperatures to achieve the best signal to noise ratio.

Steady shear rheological characterization was done at 200°C using an Instron Capillary rheometer with a capillary of approximately 24 *L*/*D* ratio.

3. Results and discussion

Dynamic viscoelastic data of a Rexflex® flexible polyolefin sample at 1 rad/s covering a wide temperature range clearly indicates the elastic plateau

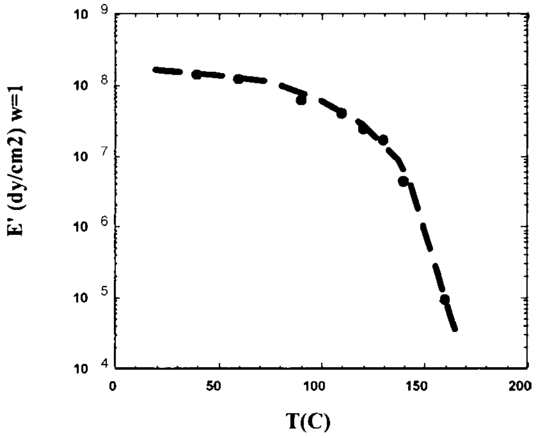

Fig. 2. Flexible PP modulus.

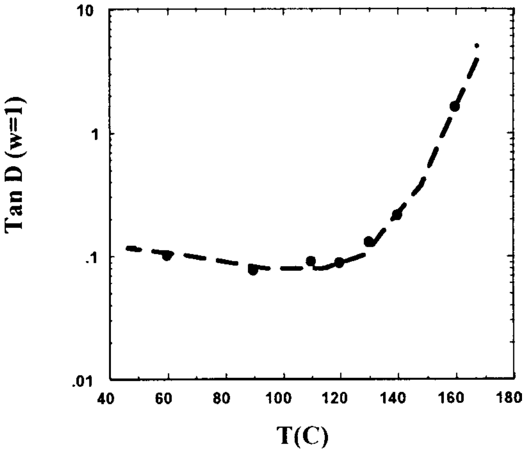

Fig. 3. Flexible PP tan δ.

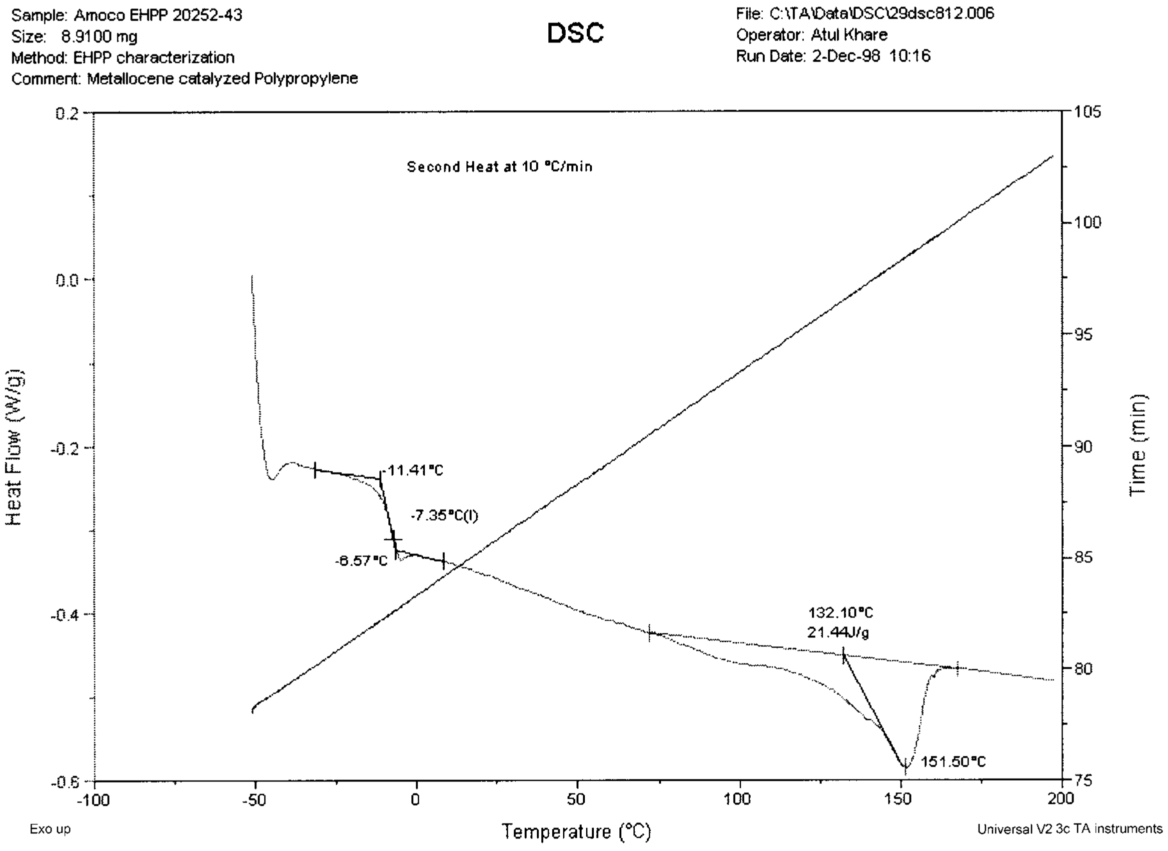

Fig. 4. Typical thermogram of the experimental PP.

extending to beyond 120°C (Fig. 2), indicating that this material will be able to withstand steam sterilization conditions. The tan δ (ratio of dynamic loss modulus versus elastic modulus) indicates that the material demonstrates fluid-like behavior about 140°C (Fig. 3).

Thermal analysis of a typical experimental elastomeric PP showed a glass transition temperature at about -7°C and a broad melting peak with a maximum at 150–160°C (Fig. 4). The melting endotherm, which is a reflection of the crystallinity, is quite small and based on that the calculated degree of crystallinity is of the order 5–20% (ΔH for 100% crystalline PP $= 209$ J/g). The thermogram of an extruded sample showed small melting peaks at 41 and about 70°C (Fig. 5). To confirm the origin of these melting peaks, the samples were melted at 200°C and then step-annealed at 120, 90, 60 and 30°C for 1 h at each temperature. The subsequent heating of the sample showed small melting peaks at 43, 67, 97 and 125°C (Fig. 6). So the small melting peaks observed at 41 and 75°C were due to annealing of these extruded samples during cooling and are attributed to the low isotacticity fraction. The fact that the sample can be fractionated into clearly separable fractions indicates that the isotactic sequence length distribution (which leads to distinct lamellae thickness populations) is quite broad.

When the crystallinity data were plotted against the ^{13}C NMR isotactic sequence content, a roughly straight line dependence is seen (Fig. 7). However, the modulus exhibited a much stronger and steeper dependence (Fig. 8), possibly indicating that the morphological features between the crystalline domains and the amorphous phase are gradually changing from a series to a parallel configuration.

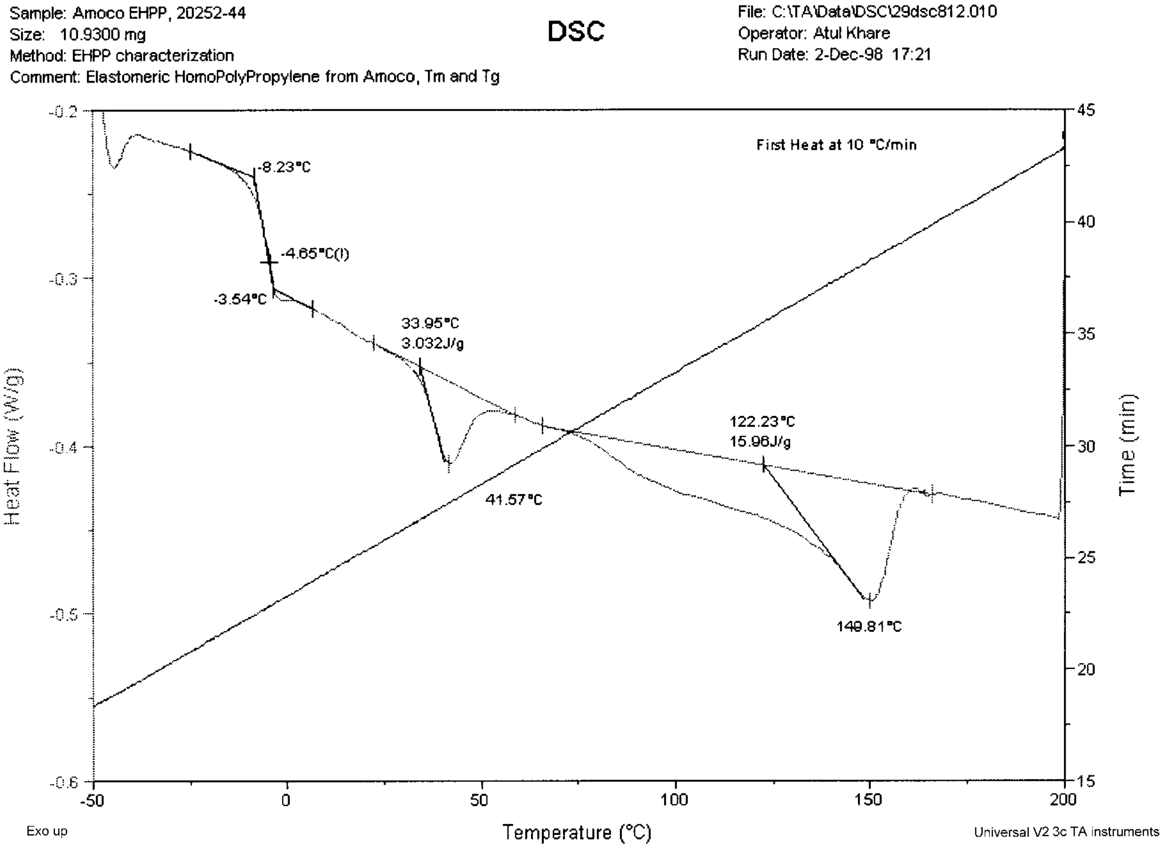

Fig. 5. First heat of extruded sample.

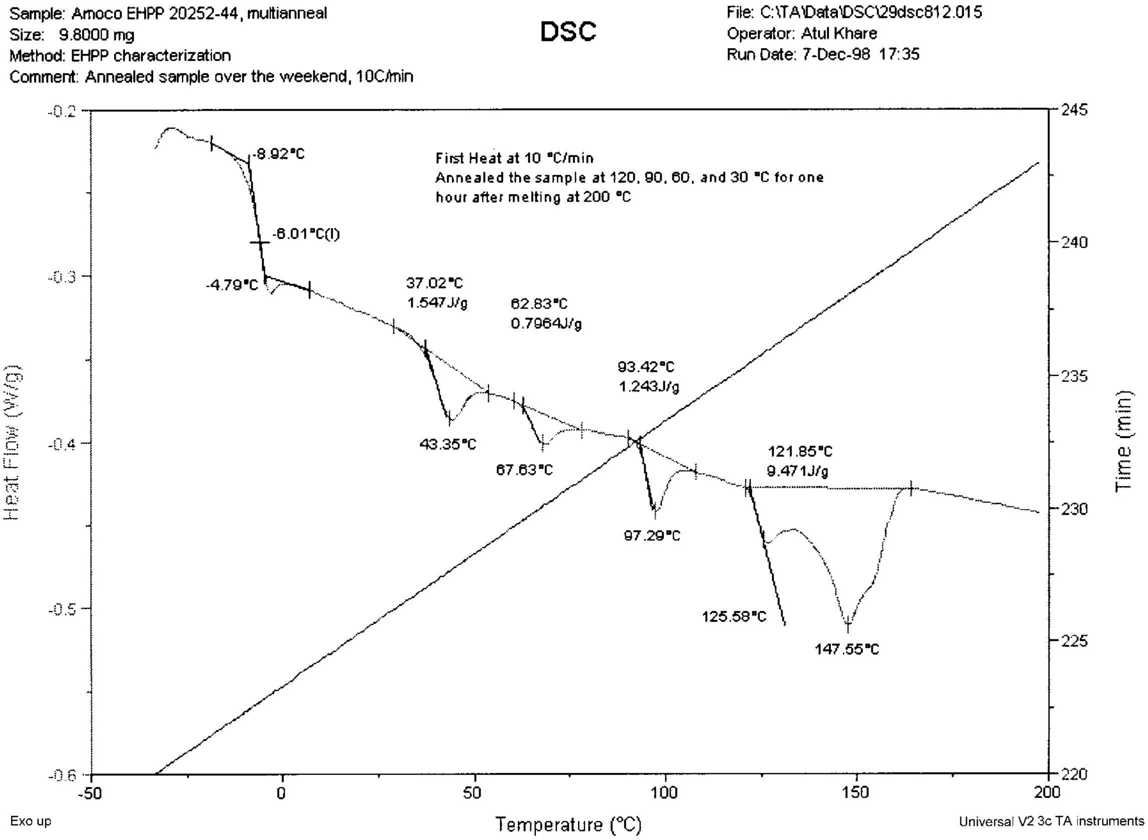

Fig. 6. Step-cooled sample.

The rheological behavior (Fig. 9) is quite similar to other typical polyolefins, exhibiting a shear-thinning behavior. Numerical ordering of the viscosities was found to be a direct consequence of the melt flow or molecular weight of the samples. The processing of these polymers showed that the melt strength was good. The formed parts from these elastomeric PP samples showed excellent surface finish and clarity. The parts were flexible and were found to be autoclavable. However, upon autoclaving, surface tackiness, a reflection of low molecular weight oligomer

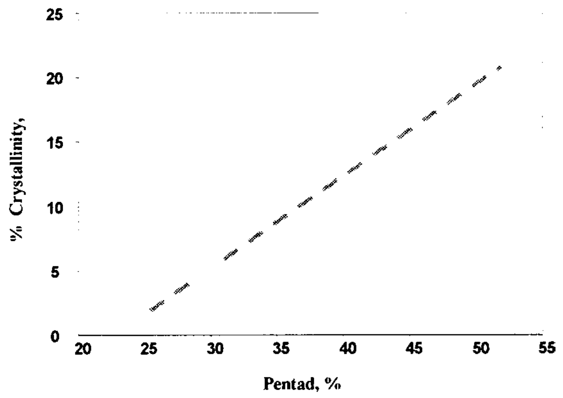

Fig. 7. Crystallinity dependence.

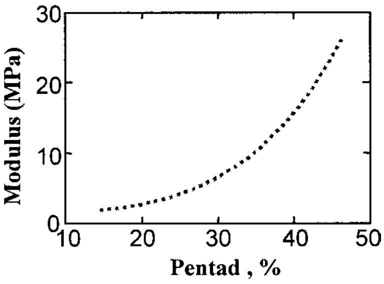

Fig. 8. Modulus behavior.

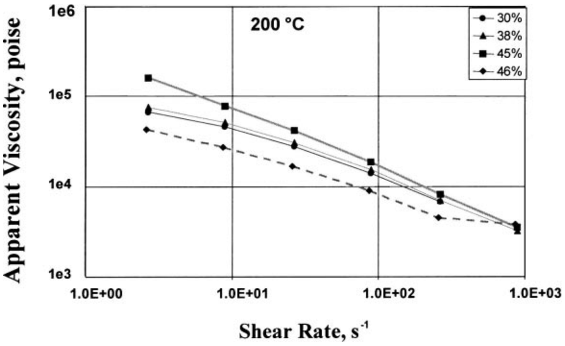

Fig. 9. Capillary rheology data.

fractions, was still evident, pointing to areas for further optimization efforts.

4. Summary

A preliminary characterization study was carried out on some recently commercialized and experimental elastic polypropylenes. All samples exhibit a rather high melting point typical of isotactic propylene sequences, and low overall crystallinity. The blocky arrangement between the crystalline sequences and the elastomeric amorphous sequences along the main chain gave rise to the thermoplastic elastomeric behavior. When the isotactic content goes beyond a certain limit, samples were found to be capable of surviving autoclaving without significant distortion. However, the isotactic sequence length distribution was found to be quite broad, and significant low molecular weight oligomer fractions still existed in the bulk samples.

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