High-performance films from new technology polypropylene

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ABSTRACT

New-generation bulk process polypropylene resins can be produced with tacticity and resulting crystalline order that are higher than slurry process resins. Since the process operating window in biaxial film orientation, whether double-bubble or tenter, is strongly dependent on resin crystallizability, both resin and processing parameters must be optimized for desired film properties. This paper presents a correlation between resin tacticity, as measured by polymer solubility in xylene, as a function of temperature and orientability, as measured by biaxial draw stress on a T. M. Long laboratory film stretcher. These laboratory screening tests and a process model were used to develop a packaging film with improved thermal dimensional stability.

Application

This work presents a new approach to optimizing polymer and processing conditions for superior physical properties of oriented films.

ISOTACTIC POLYPROPYLENE, COMMERcially introduced in the late 1950s, was made by a slurry process with low-activity Ziegler-Natta catalyst and hydrocarbon diluent. The resulting polymer was traditionally washed to eliminate spent catalyst and low-molecular-weight fractions. Whole product washing remained as a typical step in slurry polymer production through catalyst advancements including high-activity and low-ash catalysts. In the early 1980s, the production of polypropylene shifted to bulk process by development of a super-higher-activity catalyst and hydrocarbon diluent replaced by a monomer in either liquid or gas phase. With catalyst and diluent removal and recovery greatly simplified or eliminated, resin process economics alone assured the exit of slurry product film-grade resin. From the perspective of the biaxially oriented polypropylene (BOPP) film producer, it was imperative that a bulk process resin replacement be identified with both processing and end-use properties of existing resins. As new-technology resin presented opportunities for significantly changing molecular architecture in terms of tacticity and molecular weight, the need arose for a better understanding of the role of polymer tacticity on deformation in the partially molten crystalline state in the time and temperature regime characteristic of the BOPP film process. The objective of this work was to apply various polypropylene characterization techniques in developing the polymer architecture that will allow production of a biaxially oriented film with significantly improved thermal dimensional stability. Included is the application of laboratory stretching data directly to a tubular film process model.

DISCUSSION

Polypropylene can be considered in two levels of order: tacticity, which is a measure of the ordering of specific monomer units within the polymer chain, and crystallinity, which is a measure of the ordering of polymer chains with respect to themselves and their neighboring polymer chains. Tacticity is determined by the polymerization conditions. Crystallinity is determined in part by molecular structure as well as by the time-temperature profile of the fabrication process. In BOPP film manufacture, much of the thermal profile is dictated by limitations of heat transfer and process economics; a smaller component can be considered truly as process variables. A third level of order related to degree of ordering among crystalline and noncrystalline components in BOPP film is an important differentiation among orientation processes, and some properties, including thermal dimensional stability, are influenced by the noncrystalline component, which is typically on the order of 40 vol. %.

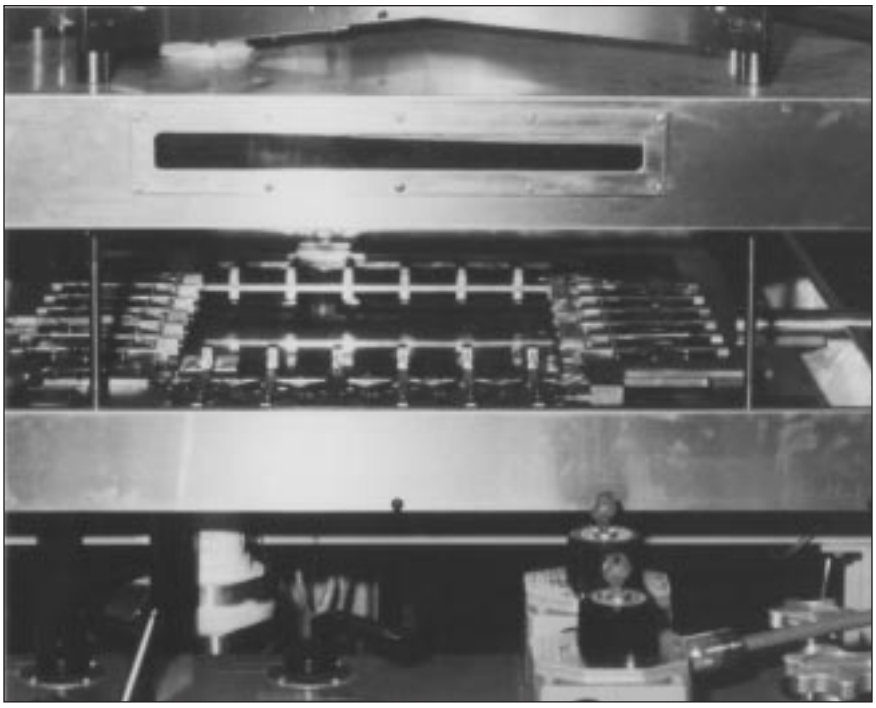
Polypropylene tacticity

Polypropylene tacticity in this work is defined in Natta's terms *(1): atactic,* random stearic order that precludes crystallization; *isotactic,* high steric order that allows proximity of polymer chains for crystallization to occur; and *stereoblock,* which can be considered as a copolymer of the two. While tacticity is now routinely characterized by spectroscopic methods, e.g., nuclear magnetic resonance, polymerization processes are controlled on the basis of room temperature solubility in hydrocarbons, typically xylene. The weight fraction of room temperature xylene solubles, on the order of 1–4 wt. % of the total product, consists primarily of low-molecular-weight crystallizable waxes as well as atactic species, which are important to control from the viewpoint of additive migration and block of film surface but of minor significance to orientability in the film process. The higher-molecular-weight stereoblock component has a more decisive impact on orientability, since these species are capable of melting and recrystalliza-

tion in the normal operating temperature window of the film process. In this work, tacticity is defined in terms of hydrocarbon solubility/insolubility as a function of temperature after Natta *(1)* as follows:

- Atactic: soluble at 0°C
- Stereoblock: insoluble at 0°C, soluble at 98.5°C
- Isotactic: insoluble at 98.5°C.

The Natta procedure was refined to improve reproducibility of results by changing solvent from heptane to xylene and by introducing a conditioning or recrystallization step to sharpen the fractions *(2)*. Even so, this conditioned fractional extraction (CFE) technique remains labor intensive, and more recently, temperature rising elution fractionation (TREF) shows promise as a way of providing a fingerprint of the stereoblock component *(3)*. It is understood that any of these fractionation methods are arbitrary and applicable to the extent that they are informative as a characterization tool.



1. T.M. Long film stretcher clip assembly

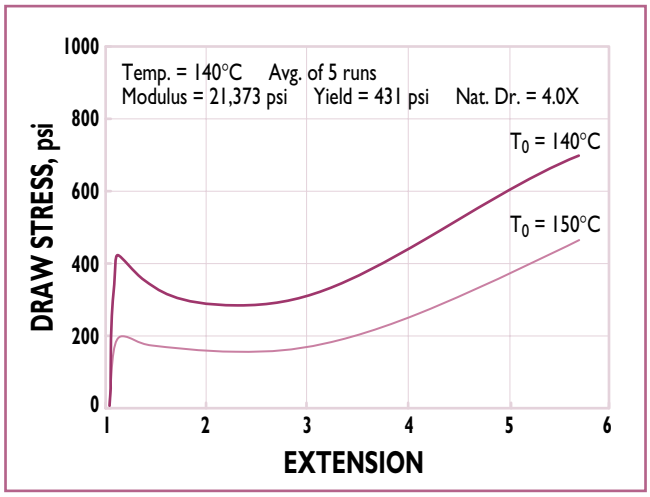
Polypropylene crystallinity

Polypropylene crystallinity is based on a two-phase model of perfect crystalline and amorphous (noncrystalline) species derived by X-ray diffraction and density, respectively. In our experience, this model is of limited value in predicting and understanding BOPP film properties, which are critically dependent on the interface between oriented crystalline and less crystalline domains *(4, 5)*. More informative from a film process standpoint is the heat of crystallization as measured by differential scanning calorimetry (DSC) at relatively rapid cooling rates. The initial morphology of the quenched tube or sheet is determined in part by the inherent crystallization as well as by quench efficiency, which for most of the polymer volume, is limited by thermal conductivity of the outer quench layers. On average, the cooling rate experienced by the bulk of the quenched product is on the order of 800°C/min, which can adequately be approximated in a conventional DSC by noting the breadth of the crystallization isotherm and the heat of crystallization.

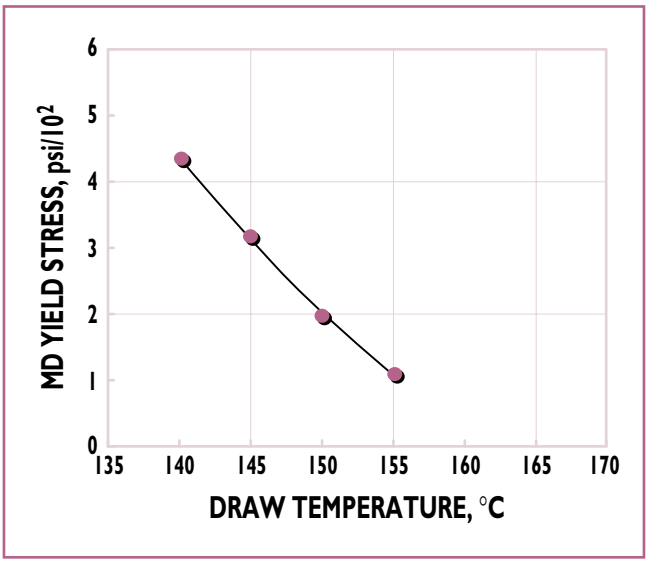
Polypropylene orientability

Polypropylene orientability and final film properties are very much dependent on both the starting polymer tacticity and the film processing used. To effect specific changes in film shrinkage, specific correlations between this film property and the starting polypropylene molecular architecture need to be developed through the polymer orientation step. In simplest form, yield stress as a function of preheat temperature can be determined in a conventional tensile tester fitted with a thermostatted oven and cast sheet morphology correlated with polymer type. Where the material is partially oriented, relaxation and annealing of the material to be characterized occurs within the preheat time needed for consistent results. Therefore, a more sophisticated approach, with more realistic preheat rates and specimen clamping, was required.

We have developed a laboratory evaluation protocol that correlates polypropylene tacticity to film processing conditions by measuring film orientation stress as a function of web extension using a T.M. Long (TML) laboratory stretcher, (T.M. Long Co., Somerville, NJ). It was instrumented by the manufacturer to allow development of the orientation stress as a function of extension for biaxial film stretching at a specific temperature and strain rate. The mechanism by which clip force is developed as the clips separate and a strain is imposed on the web is shown in **Fig. 1**. By varying the orientation temperature, the shape of the resulting stress-strain curve changes, as shown in **Fig. 2**. Increasing the orientation temperature



2. Effect of orientation temperature on TML draw stress



3. TML yield stress vs. orientation temperature

results in lower orientation stress at any given strain, and a less pronounced yield stress is observed at low strain. The yield stress (S_y), a maximum in the early portion of the stress-strain curve, was found to decrease linearly with increasing draw temperature. A plot of yield stress vs. draw temperature, as shown in **Fig. 3,** can be used to compare polymers at constant strain rate as a function of temperature.

For example, the effects of polymer nucleation and tacticity level were compared. In changing from slurry to bulk process polypropylene, tacticity increased from about 82% isotactic to a range of 86–94% isotactic, depending on catalyst, as measured by CFE. This tacticity change caused the yield stress vs. temperature curve to shift upward in temperature by about 3°C for each 4% increase in isotactic content (see **Fig. 4**). Nucleation with sodium benzoate allows more rapid crystallization, which caused an additional shift of the yield stress vs. temperature curve by 2–3°C, as shown in Fig. 4. Combining the effect of nucleation and high isotactic character in the polypropylene, the orientation temperature needed to stretch this polymer at any given stress is increased significantly. The orientation temperature is then a direct function of polypropylene tacticity/crystallinity and the process temperature used on the film production line.

Prediction of polypropylene processability

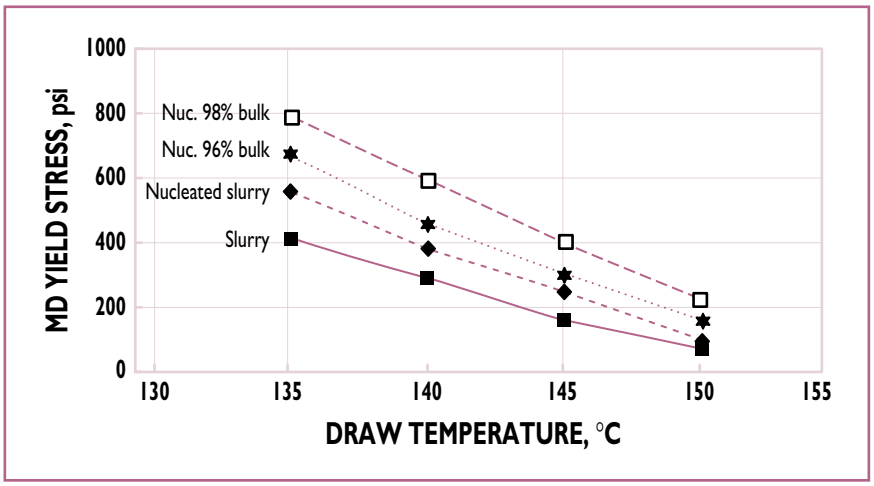
Prediction of polypropylene processability by theoretical process modeling has been attempted over the years by several groups involved with double-bubble BOPP process technology. Difficulty in getting the equations for the geometry and stress development to converge in the limit have prevented a rigorous solution, yet modeling by comparison has provided useful results for guiding film polymer and process improvements. A control polymer is characterized in the laboratory for orientability and process performance documented in commercial operation. By knowing how relative laboratory data correlate with required process conditions, bubble process operating parameters can be predicted. Bubble operating conditions can readily be predicted from the yield stress values developed on the instrumented TML by noting the orientation temperature required to achieve a yield stress equivalent to the control. As the yield stress curves in Fig. 4 are shifted to higher temperature with higher tacticity, higher orientation temperatures are required for any internal bubble pressure and polymer draw ratio.

These predictions can be made, knowing that at the point of maximum bubble size (fixed point in terms of bubble geometry), the horizontal and longitudinal stress components are approximately equal (Eh = E^L), as shown in **Fig. 5**. At this fixed point, there are no geometric considerations, and the internal bubble pressure as defined by the hoop stress is related to the motor loads required to draw the film in the machine direction. Since the hoop stress is proportional to the bubble pressure, and the hoop stress corresponds to the stress at a specific strain as measured on the TML, stress-strain data can be used to predict film orientation conditions. The power of this comparative model is in allowing the comparison of very

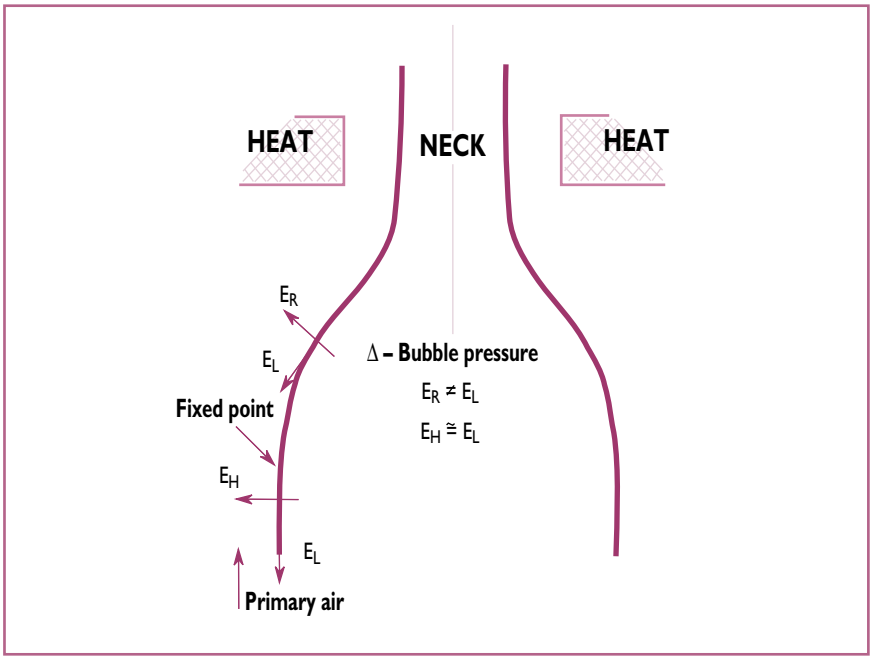
KEYWORDS
Addition polymers, biaxially oriented films, models, oriented films, packaging films, packaging materials, plastic films, polyhydrocarbons, polyolefins, polypropylene, product development, test methods, thermal properties, thermal stability, thermoplastics.

different polymers in the laboratory and predicting not only processability, but also allowing the estimation of actual process conditions.

Using this type of analysis, moving to higher tacticity and with the addition of nucleation, the higher orientation temperature necessary for processing this polymer results in film with higher thermal dimensional stability, i.e., lower shrinkage in both the machine and cross directions. Moving to higher tacticity and higher crystallinity, which requires higher orientation temperature, results in a film with improved thermal dimensional stability, but the higher crystallinity should also marginally improve barrier properties; the use of nucleation improves optical properties, as shown in **Table I**. The cost of these film property improvements lies in the increased temperature, and therefore power costs, required for processing and the narrower film process operating window, as predicted by the slope of the laboratory yield stress vs. temperature curve (Fig. 4).



4. Effect of tacticity and nucleation on draw stress



5. Bubble blowing

CONCLUSIONS

The molecular architecture of new bulk process polypropylene can be measured in the laboratory using various fractionation techniques to determine polymer tacticity. Correlations between polymer tacticity and the orientation stress-temperature relationship allow prediction of film process conditions needed to successfully orient the various types of bulk process polypropylene to biaxially oriented film. Using these laboratory characterization techniques, a target polypropylene film was specified for producing a more thermally stable oriented polypropylene film on the tubular film process. With the continued expansion of polypropylene catalyst technology, the laboratory characterization methods are used to predict changes needed in processing the resulting new polymers under optimum conditions. **TJ**

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Property	POLYMER/FILM PROCESS Slurry/ bubble	Bulk/ bubble	Bulk/ tenter
Tensile properties			
Strength (MD), psi	30,000	31,000	22,000
Strength (TD), psi	30,000	31,000	43,000
Elongation (MD), %	90	90	180
Elongation (TD), %	90	90	65
Shrinkage, %			
At 140°C (MD)	11	4	5
At 140°C (TD)	15	4	4
At 120°C (MD)	3	1	2
At 120°C (TD)	4	0	0
Opticals, %			
Haze	1.0	0.8	1.5
Gloss	92.5	91.1	90.0

I. Comparison of commercial slip film properties

Kolpak for his work on CFE and TREF, and Ruth Bruner for the many improvements to data collection and reduction on the AET Windows version of TML stress/strain. Ted Long of T. M. Long Co. Inc. has been a source of encouragement and instrument expertise in developing our laboratory stretching approach to polymer process modeling. Special thanks to Roland Saxton of our laboratory for many years of dedication to the experimental aspects of film polymer processing and evaluation on the TML.

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LITERATURE CITED

1. Natta, G., Mazzanti, G., Crespi, G., et al., in *Stereospecific Polymers* (G. Natta and F. Danusso, Eds.), Pergamon Press, New York, 1967, pp. 212-231.
2. Cox, W. W. and Bullock, E. K., "Effect of Tacticity on Deformation of Isotactic Polypropylene," in press.
3. Kolpak, F. J. and Brady, J. K., *Proceedings of the International GPC Symposium '94,* Waters, Milford, MA, 1994, p. 491.
4. Peterlin, A., *J. Materials Sci.* 6: 490(1971).
5. Peterlin, A., *Intern. J. Polymeric Mater.* 8: 285(1980).