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A New Polymer Platform for the Future — Sorona® from Corn Derived 1,3-Propanediol

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Responding to environmental, sustainability, business, and market factors, DuPont has commercialized a new polymer platform, Sorona®, based on 1,3-propanediol. The physical and chemical property advantages over other polymers are described. The diol component of this polymer, 1,3-propanediol, has been demonstrated to be manufacturable via biological (fermentation) process from corn sugar. The economic, environmental, and process/product quality advantages of bio-PDO over conventional diols are discussed.

KEY WORDS: Sorona® polymer; 1,3-propanediol; bio-process; sustainability.

INTRODUCTION: DEVELOPMENT OF SUSTAINABLE TECHNOLOGIES

Several factors arising over the last quarter of the 20th century have led to increased global interest in bio-derived materials and biotechnology:

1. Instability of price and availability of crude oil as a chemical process feedstock;
2. Increased attention to recyclability of manufactured products;
3. An added economic stimulus for emission reduction, brought about by the Kyoto protocol.

These factors influence how global manufacturing companies manage themselves for both present and future. An example is E. I. du Pont de Nemours and Company, just starting its third century.

In its latest move towards sustainability, DuPont has set ambitious goals for increased use of renewable resources for both feedstock and energy, reduction of greenhouse gas emissions, and zero growth in energy use.

The strategy to meet the first of these targets includes the use of biological processes to make products from renewable raw materials. In support of that strategy, DuPont formed the Bio-Based Materials business (BBM) unit in 2000. BBM's first commercial product is the Sorona® family of poly(trimethylene terephthalate) (PTT, or "3GT") polymers.

Other companies share the DuPont view of sustainable growth. Concurrently, Dow Chemical Company in a joint venture with Cargill has recently commercialized the NatureWorks™ family of polylactic acid (PLA) biodegradable polymers.

HISTORY AND DEVELOPMENT OF SORONA®

Polyester is the most widely used synthetic fiber in the world today, in apparel, home furnishings and industrial applications. Since its invention more than 50 years ago, the dominant polyester has been polyethylene terephthalate, also called PET or 2GT. Other varieties of the polymer have been known since the beginning. For example, instead of reacting ethylene glycol with the terephthalic acid ingredient to make 2GT, one could use 1,4-butanediol to make 4GT or 1,3-propanediol for 3GT. The unique properties and attributes of 3GT polymer and fibers have

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been known for many years. 3GT fibers were reported to have better elastic recovery and lower modulus versus PET and PBT [1]. Until recently, three factors have effectively kept 3GT polymer off the market: the relatively high cost of the 1,3-propanediol; inability to make high quality polymer for downstream end-uses; and more difficult polymer process requirements compared to 2GT.

Since the 1990s, however, significant developments have taken place to improve the business prospects for 3GT. More economical methods have been established for producing 1,3-propanediol ("PDO," also called 3G) in commercial quantities from petrochemical sources. Production of PDO has been demonstrated to be feasible from renewable resources as well, via biological processes [2–5]. Finally, continuous polymerization processes have been refined to enable commercial manufacture of 3GT polymer to "fiber-grade" standards of quality and uniformity. In the last decade, DuPont has generated over 100 patents related to the cost-effective production, processing, and applications of 3GT. A few of those patents are listed at the end of this article.

UNIQUE PROPERTIES OF SORONA®

Molecular Structure and Effects on Mechanical Properties [1,6,7]

Sorona® 3GT polymer is one member of a family of polymers based on fiber-grade 1,3-propanediol. It is a linear crystallizable polymer with a melting temperature of about 228 °C and a glass transition temperature of about 50 °C. The structure of 3GT polymer is shown in Fig. 1.

The structure of PTT has been studied extensively [3–5]. The beneficial properties of Sorona® 3GT polymer are derived from a unique, semi-crystalline molecular structure featuring a pronounced "kink," as shown in Fig. 2.

The 3GT polymer shape is a consequence of the convolutions of the bonds in the trimethylene constituent. This zigzag shape means that tensile or compressive forces translate at the molecular level to bending and twisting of bonds, rather than simply stretching. This is analogous to the tensile behavior of a coil spring compared to a straight wire.

When the polymer is cooled from a liquid state, it forms crystalline and amorphous regions. The crystalline regions contribute most significantly to the elastic properties of the solidified polymer. With 3GT, the modulus of the crystalline regions is significantly lower than that of other commercial polymers, e.g., PET (see Fig. 3). The fiber can take an appreciable level of applied strain (up to 15–20%), and recover completely, e.g., no permanent set, when forces are removed (see Fig. 4).

Table I compares properties of Sorona® 3GT with other synthetic and natural fibers (*Handbook of Fiber Chemistry*, Lewin, M., and Pearce, E.M., Eds., 2nd Edition, Marcel Dekker Inc., New York, 1998) and with polylactic acid (PLA), another bio-derived polymer.

In addition to its unique stretch-recovery characteristics, Sorona® 3GT provides all the advantages

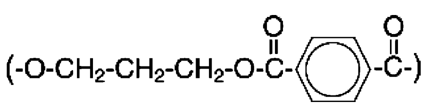


Fig. 1. Molecular structure of 3GT.

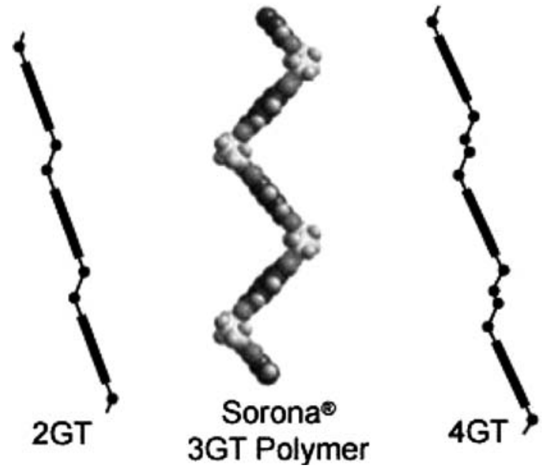


Fig. 2. Molecular shape and crystal structure of 3GT.

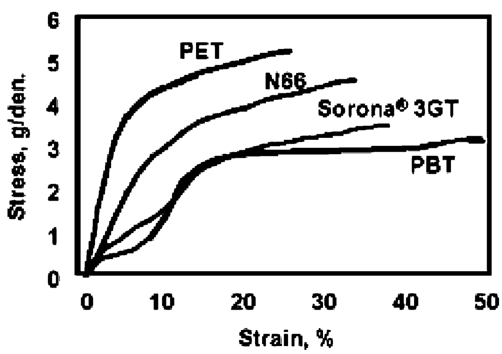


Fig. 3. Comparison of tensile characteristics.

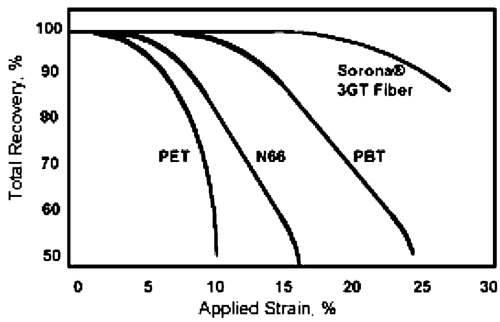


Fig. 4. Comparison of stretch recovery characteristics.

generally associated with polyesters, i.e., excellent physical and chemical properties, dimensional stability, low moisture absorption, easy care, good weather resistance, easy processability and recyclability. Sorona® polymer can be easily modified to achieve desirable functional properties as well.

Other Properties

Sorona® offers several advantages over both conventional polyester (PET) and nylon. It can be effectively disperse-dyed at 100 °C eliminating the need for carriers or pressurization in the dyeing process (see Fig. 5). Once dyed, the fabric exhibits deeper shades and superior washfastness over other products.

Other advantages of Sorona® become more evident in actual use conditions. The fiber is highly resistant to most stains without the need for surface treatment with additives or coatings. It resists UV degradation better than other fibers, and exhibits both low water absorption and low electrostatic charging.

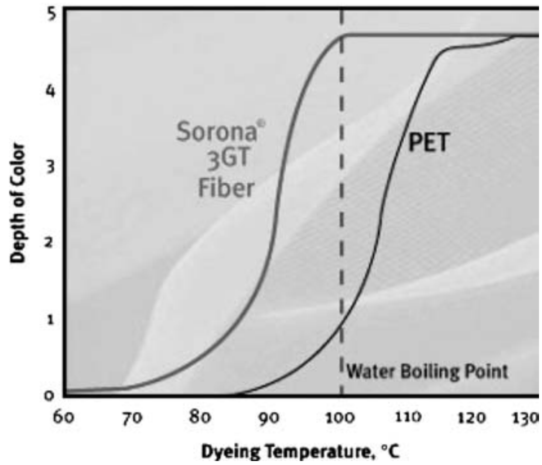


Fig. 5. Comparison of dyeing characteristics.

Environmental Footprint

The world is increasingly looking at the environmental consequences of a product throughout its life, from raw material through ultimate disposal (see Fig. 6). In this area, Sorona® has a number of advantages over other polymers.

- Greenhouse gas emission in the manufacture of bio-PDO has been demonstrated to be about 40% less than for petrochemical PDO.
- The overall 3GT polymerization process is more energy efficient than PET.
- Polymerization and downstream processing of Sorona® saves energy compared to PET due to lower temperatures required, both for processes involving remelt and for dyeing.
- Recycling of Sorona® is made much easier by the absence of heavy metals in the product, compared to PET and Nylon.

Table I. Polymer and Fiber Properties

	Synthetic fibers				Melt spinnable natural based			Natural fibers		
Fiber Property	Nylon 6,6	Nylon 6	PET	Acrylics	Sorona® 3GT[a]	PLA[b]	Rayon	Cotton	Silk	Wool
Specific gravity	1.14	1.14	1.39	1.18	1.33	1.25	1.52	1.52	1.34	1.31
T_g (°C)	40–55	40–60	70–80		45–55	55–60	–	–	–	–
T_m (°C)	265	220	260	320 (degrades)	228	130–175	None	None	None	None
Tenacity (g/d)	6–10	5.5	6.0	4.0	4-5	6.0	2.5	4.0	4.0	1.6
Moisture regain (%)	4.0	4.1	0.2–0.4	1.0–2.0	0.2–0.3	0.4–0.6	11	7.5	10	14–18
Elastic recovery (5% strain)	89	89	65	50	100	93	32	52	52	69
Refractive index	1.54	1.52	1.54	1.50	1.57	1.35–1.45	1.52	1.53	1.54	1.54

[a]Sorona® 3GT polymer is currently produced using a chemical process. Full scale commercialization of bio-derived polymer is expected by end of 2004.

[b]Data for PLA is taken from "Fibers and Fabrics Properties Comparison," downloaded 8/15/2003 from Dow/Cargill website, http://www.cargilldow.com/ingeo/applications_apparel.asp.

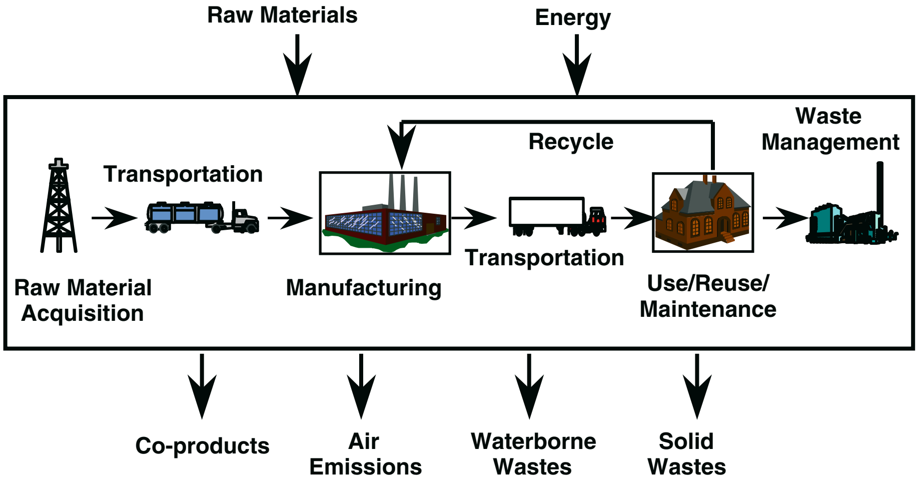


Fig. 6. Product life cycle: environmental effects.

Table II. Basic Properties of 1,3-Propanediol (PDO)

CAS number 504-63-2
Chemical structure, $HOCH_2CH_2CH_2OH$
Chemical formula $C_3H_8O_2$
Molecular weight 76.1
Viscosity at room temperature 52 cp
Specific gravity 1.05
Boiling point 214 °C
Freezing point −32 °C
Refractive index 1.4386

PDO AND BIO-PDO

Sorona® 3GT is made from 1,3-propanediol (PDO) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). Other materials used in the manufacture of 3GT include an organo titanium catalyst [8–11], and a delustrant (TiO_2).

PDO is a colorless, odorless liquid. The basic properties of PDO are summarized in Table II, and a typical product specification for polymer manufacture is shown in Table III.

PDO from Traditional (Chemical) Sources [12, 13]

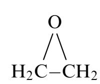
Development of Sorona® took place within a business model that requires the commercial success of a product to be established independently of environmental or sustainability considerations. Consequently, early product development and commercialization were undertaken with PDO made from conventional chemical processes, two examples of which are listed below.

A. The Degussa process consists of the following three steps:

1. Oxidation of propylene to acrolein
   $CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CHCHO$
2. Selective hydration to 3-hydroxypropionaldehyde (3-HPA)
   $CH_2{=}CHCHO + H_2O \rightarrow OCHCH_2CH_2OH$
3. Catalytic hydrogenation to 1,3-propanediol (PDO)
   $OCHCH_2CH_2OH + H_2 \rightarrow HO(CH_2)_3OH$

B. Shell Chemical uses a two-step process:

1. Hydroformylation of ethylene oxide to 3-HPA.

 $+CO + H_2 \rightarrow OCHCH_2CH_2OH$

2. Catalytic hydrogenation to 1,3-propanediol (PDO)
   $OCHCH_2CH_2OH + H_2 \rightarrow HO(CH_2)_3OH$

Bio-PDO [2–5]

The need for development of a biological source/process for PDO grew out of several factors:

- Difficulty and cost of producing "polymer and fiber-grade" PDO;

Table III. Specific Analytical Properties of 1,3-Propanediol (PDO) Used for Polymer Manufacture

Purity (GC) 99.9%
Color (APHA, ASTM D1209) < 5
Water content 0.05% max.
Ash content < 0.001% by weight.

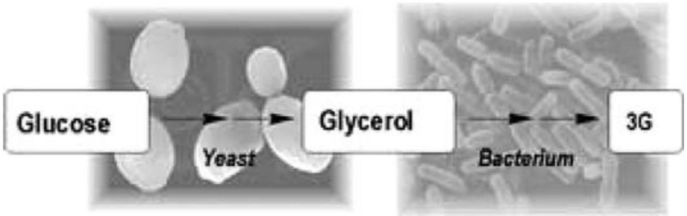


Fig. 7. Conversion of glucose to PDO occurs in two steps in nature.

- The demonstrated efficiency of early trials of bio-PDO processes, which showed the potential to be economically competitive with established processes;
- Lower levels of greenhouse gases from bio-processes;
- The commitment of DuPont to integrated science, which includes biological science and biotechnology;
- The company's unique position to integrate biotechnology with its longstanding competency in polymer and fiber technology.

Initial development of biologically manufactured PDO has been with corn sugar, well known as a plentiful and inexpensive raw material. Conversion of glucose to PDO has been known to occur in nature in two stages: first by yeast to an intermediate product, glycerol, then by bacteria to PDO or 3G (Fig. 7).

DuPont and Genencor International have jointly developed a bacterium ("biocatalyst") to do both steps in a single fermentation stage. DuPont and Tate & Lyle, a major corn based products company with expertise in fermentation processes, partnered to develop the manufacturing process based on this biocatalyst. The process is represented in Fig. 8, and the facility in Fig. 9.

The trial product was confirmed to have attributes and quality equivalent or superior to chemically produced PDO. For example, the results of purity tests of bio-based PDO and conventional (Wesseling) PDO are shown in Fig. 10. In summary, the percentage of impurities in Bio-PDO is around one-tenth the amount of impurities in chemical PDO (0.003% versus 0.032%).

POLYMER MANUFACTURE [8–10, 14, 15, 24]

The DuPont 3GT process technology was developed for retrofitting to existing 2GT facilities. One such converted facility is located at the DuPont site at Kinston, NC, USA, which has been making commercial quantities of 3GT polymer for several years. A schematic diagram of a typical Continuous Polymerization (CP) process is shown in Fig. 11.

Typical properties of CP polymer, as reflected in the current DuPont specification, are shown in Table IV.

Molecular weight analysis of a representative sample from commercial production is given below.

Number average molecular weight $M_n = 30{,}300$

Weight average molecular weight $M_w = 56{,}300$

Z average molecular weight $M_z = 85{,}900$

$M_w/M_n = 1.86$

(The analysis is by SEC triple detection, using HFIP solvent. The refractive-index detector chromatogram is shown in Fig. 12 below).

Melt Viscosity Characteristics

The behavior of Sorona® 3GT polymer in the melt state is similar to other condensation polymers.

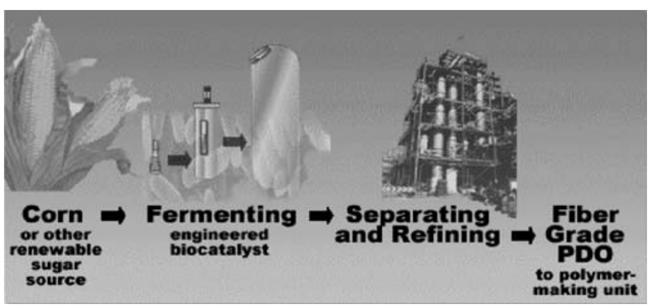


Fig. 8. Pictorial representation of process: Corn to PDO.

Fig. 9. Pilot scale fermentation facility of Tate & Lyle, Decatur IL, USA.

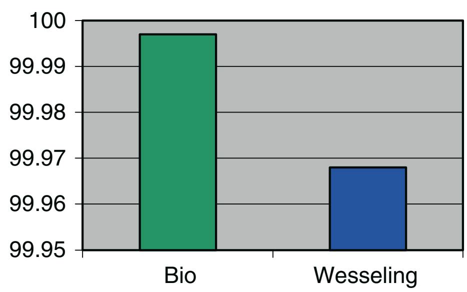


Fig. 10. Purity comparison of bio and chemical (Wesseling) PDO.

That is, at low shear rates the viscosity is nearly constant (Newtonian) and at higher shear rates viscosity decreases with increasing shear rate approaching a power-law relationship. Viscous behavior measurements for a melted production sample of Sorona® polymer are shown for several melt temperatures in Fig. 13 below.

POLYMER PROCESSING, APPLICATION AND END-USES

Sorona® 3GT polymer can be converted into a variety of products by conventional methods on existing equipment. The significant differences of Sorona® 3GT in processing are lower melt temperature (comparable to Nylon 6 or polypropylene), lower modulus, higher stretch, and better stretch recovery. In end-use performance, Sorona® polymer exhibits mechanical properties equal to or in some cases better than nylons, (e.g., Nylon 6, Nylon 6,6) in

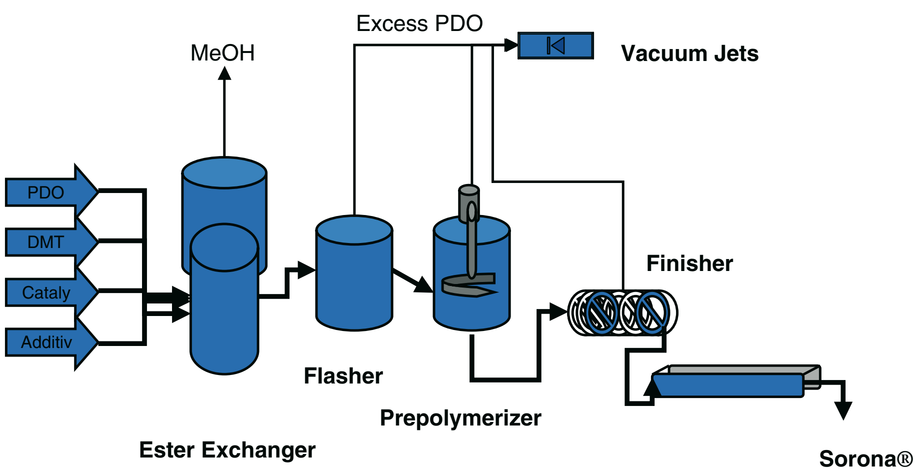


Fig. 11. Continuous polymerization process.

Table IV. Properties of Continuously Polymerized 3GT[a]

Property	Aim	Limits		Test method
		Min	Max	
Intrinsic viscosity	1.02	1.01	1.03	TM-0590-91
Color, Hunter b	–	5	8	GEN-07
Color, Hunter L	–	80	–	GEN-07
COOH, μeq/g	–	–	15	TM-1145-91
Melting Point, deg C	228	224	232	SP-509
TiO2, wt%	0.30	0.27	0.33	TM-1090-90
Moisture, ppm (as packaged)	–	–	500	SP 525
Pellet size, wt. of 50 pellets, g	1.6	1.4	1.8	GEN-08
Appearance	No foreign substances, dust, or gross particles			Visual
Package description	Lined Gaylord boxes, 1475 lbs (670 kg) nominal per box			

[a]Product: Sorona® Polymer (a trademark of E. I. du Pont de Nemours and Company).
Type: Semi-dull Homopolymer.
Process: Continuous Polymerization (CP).
Specification date: March 30, 2001.

combination with chemical properties equal to or better than PET.

Fibers for Apparels and Carpets

Lower melt temperature compared to 2GT and Nylon 6,6 allows spun-dyed yarn with a greater variety of pigments/colors. 3GT fiber can be spun on "short stack" spinning machines originally built for Nylon 6 and polypropylene bulk continuous filament (BCF) yarns. [16–18] Draw [19], windup, texturing [20], weaving, knitting, and tufting performance are comparable to PET once the equipment is properly adjusted for the mechanical properties of 3GT.

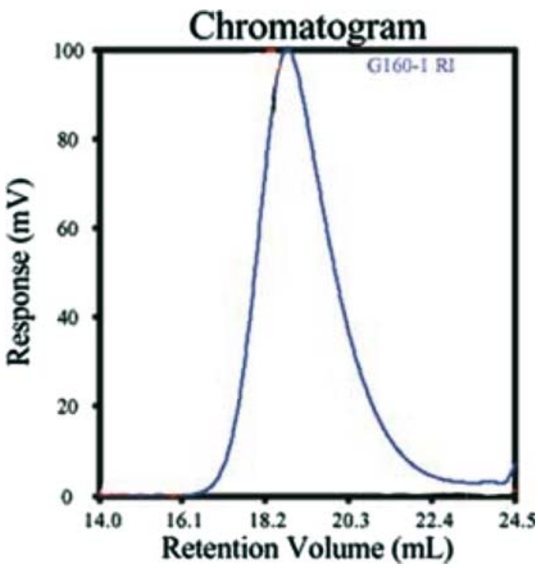


Fig. 12. Size exclusion chromatogram (SEC) of production sample of Sorona® polymer (RI detector).

The most significant advantages of Sorona® 3GT fiber for apparel are softness and natural hand, printability and easy dyeability. Additionally, resistance to chlorine and UV add value in outdoor/sport markets. 3GT fibers can be blended with other natural (e.g., cotton, wool, etc.) or synthetic (e.g., PET, acrylics, etc.) fibers for enhanced softness, stretch recovery and other functional attributes.

For floor coverings, Sorona® can be made in a variety of colors and styles with good dye uniformity. It offers superior bulk, resilience, texture retention, stain resistance, easy dry, and a softer feel. They're resistant to fading in the presence of UV or chlorine, and they have low electrostatic properties. 3GT is as easy to recycle as PET polyester.

Films

3GT can be cast into films at settings comparable to polypropylene or Nylon 6. Process optimization is required to eliminate film brittleness of cast films. Biaxially oriented films can also be prepared using 3GT. Modified 3GT polymers (e.g., copolymers with isophthalic acid, etc.) or blends of 3GT with other commercially available polymers (2GT, 4GT, etc.) can be successfully used in films to obtain desirable property advantages and increased value. For exam-

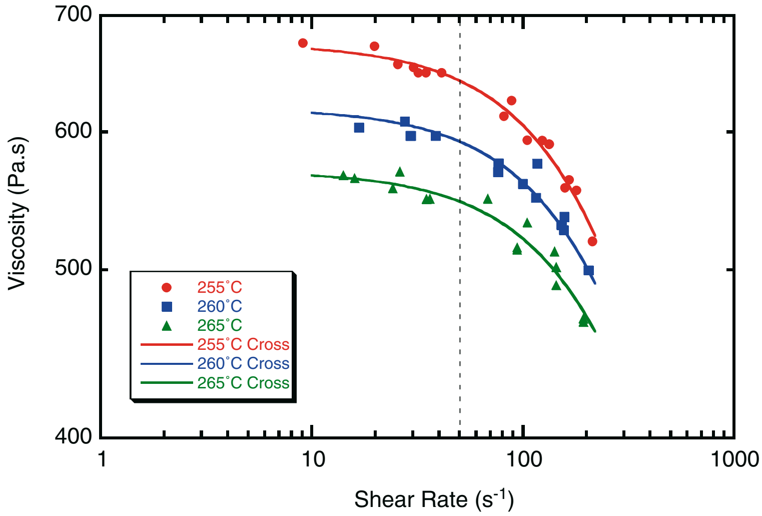


Fig. 13. Melt viscosity traces of production sample of Sorona® polymer.

ple, the combination of properties of 3GT (oxygen and water vapor barrier, printability and heat sealability) means that in many food packaging applications a single 3GT or modified 3GT layer may replace several layers of presently manufactured laminated films. [21]

Nonwovens

The suitability of Sorona® polymer has been demonstrated for various nonwoven processes including flash spinning [22] Advantages in properties over other polymers include softness, handfeel, drapability, air permeability, stretch recovery, printability, and heat fusability.

Engineering Components

All conventional thermoplastic formation techniques can be used with 3GT: injection molding, pressure molding, blow molding, casting, rotary molding, etc. with attention paid to minimize melt time. Otherwise, molding processes are comparable to Nylon 6, PBT, PET, or polypropylene[23]. 3GT molding conditions are similar to that of PBT.

As with many other plastics, the addition of glass fiber reinforcement significantly increases tensile strength, modulus of elasticity, bending strength and modulus, impact strength, and heat deflection temperature in molded parts of 3GT. In addition to glass fibers, other natural fibers can be incorporated in 3GT to take advantage of lower process temperature and to increase total bio-derived materials content in the final product.

CREATING THE FUTURE

Direction and Vision

The development and commercialization of bio-based Sorona® 3GT by DuPont is consistent with the sustainable growth objectives of the company in its third century and beyond, through

- Knowledge intensity: increased knowledge component of our products
- Productivity improvement: reduced capital, environmental footprint, energy/resource usage, waste, emissions, and social cost
- Integrated science: historically, chemistry and physics; in the future, chemistry, biology, physics, and information science

Realization

Carrying these principles forward, by DuPont and others, will lead to

- Greater use of renewable biological resources such as crop vegetation
- Further development of biological manufacturing processes, e.g., fermentation, (“biorefinery”) for intermediates and end products
- Products with integrated information technology, such as “smart” garments that automatically sense need for insulation versus cooling/ventilation and respond accordingly

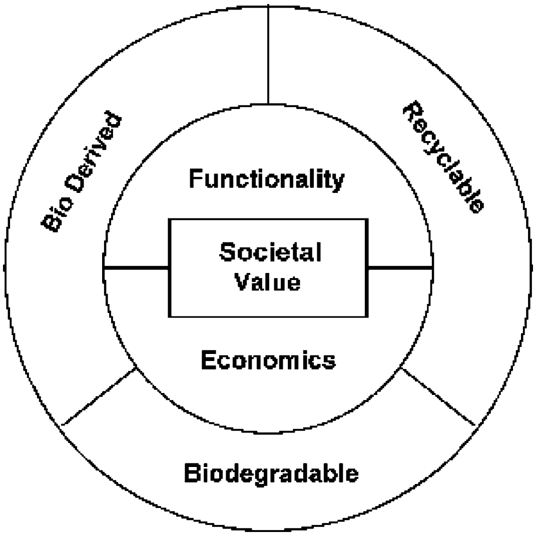


Fig. 14. Strategy for sustainable development and environmental responsibility.

CONCLUSIONS

Sorona® polymer provides functionality and attributes different from that of other polymeric materials in the market today. To be successful, in addition to being a bio-derived material, products also need to provide value and functionality. With Sorona® polymer, either alone or in conjunction with other polymers, a variety of functionalities can be developed. From the PDO based platform other similar polymers can also be developed to satisfy growing needs of society. Figure 14 represents the combination of attributes central to the DuPont product strategy for sustainable growth and environmental responsibility.

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