

Synthesis and Investigation of Polypropylene Random Copolymers Yarn with High Flexibility and Changeable Length

Akram Shabani¹

¹Master of Science in Chemical-Polymer Engineering

Abstract

Structure of yarn has been investigated and base textures have been presented. Yarns have been improved by adding propylene to it. Propylene has many properties. Propylene yarn has good tensile strength and flexibility. Polypropylene random copolymers hardness and temperature stability. Here flexibility of polypropylene random copolymer has been investigated. Also, Commercial grades are available in a variety of molecular weight distributions, and co-monomer types as well as contents and additives. Enhanced physical properties allow polypropylene to be the core material in most demanding applications such as films, fibers, tapes, sheets, thermoforming, injections, and blow molding.

Key words: Polypropylene, Synthesis, Flexibility, Copolymers Yarn, Changeable Length.



1- Introduction

In our daily life we are surrounded by more and more articles produced of synthetic polymers rather than traditional materials such as wood, metals or ceramics. For instance, approximately 20 years ago, most car bumpers were made of steel, and nowadays, almost every new car is equipped with plastic bumpers. One of the main drivers contributing to the popularization of polymers is their ease of processing into complexly shaped parts at high speeds and low costs via relatively simple processes, such as extrusion, injection- and compression molding. Other advantages of polymers are their low density and large range of specific properties, from soft rubbers to fibers stronger than steel. Generally, the improvement of stiffness and impact strength is a main driver in the polymer industry, since enhanced properties offer more design freedom. Increased material stiffness allows producing thinner products while maintaining a similar rigidity of the final article, being an important means of reducing material consumption and hence costs. Moreover, down gauging lowers the impact of waste management concerns. In Western Europe, close to 20 million tons of synthetic polymers have been produced in the year 2000. Among these materials, the Standard or Commodity Thermoplastics, viz polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), and polyethylene terephthalate (PET) constitute the major fraction (Rault et al, 2010).

In contrast to other polymers like polystyrene or polyvinyl chloride, PP is widely used in producing engineering plastics. Its price varies according to three elements, i.e., its alkylation value, its netback depending on the parity between high-density polyethylene and resins such as PS. Polypropylene has replaced other polymers in the production of a wide range of fibrous materials in household textiles (carpet backing and yarns, upholstery fabrics, rugs, and others), in health and medicine for care materials or disposable diapers, in protective clothing, in geo and/or agro textiles, nonwovens, and others. Thus, the production of PP fibers represented 10% of the volume of fibers manufactured in 2007 globally (Maddah, 2016).



The needs of consumer protection, coupled with the new regulations and environmental concerns, require the development of more eco-friendly flame-retardant treatments for PP fibers. Improvements in flame retardancy of the fiber-forming polymers, including PP, have become increasingly important in recent years, to comply with the safety requirements of textile products for automotive and home furnishing. Flammability of PP fibers represents one of the main drawbacks for the use of this polymer, due to its aliphatic hydrocarbon structure. This combustible material ignites spontaneously and can be ignited at about 360 and 380 °C, respectively. Since the burning leads to the formation of droplets spreading the fire, the reduction of flammability of PP is needed for safety consideration. Furthermore, polypropylene has a high heat of combustion, about 46,8 kJ·g⁻¹, and no char-forming character with a limiting oxygen index (LOI) of about 18%. Its ignition time is relatively low compared with some other thermoplastics, and even if it may be classified as a polymer with low smoke emission, its high peak of heat release and its rapid production of smoke constitutes a hazard in real fire situations. To prevent the burning and to enhance the fire retardant (FR) properties of textile structures, various solutions have been studied. One of them introduces a single additive or a mixture of additives to provide a synergistic effect and/or to reduce cost, into the polymer by melt mixing processes or onto the surface by finishing treatments. One way recognized to develop effective in tumescent systems is the use of metal hydroxides such as magnesium and aluminum. Nevertheless, a high amount of additive is required, about 60 wt. % and 20 wt. % to 30 wt. % for single or mixture of FR, respectively. This loading content is not suitable to manufacture fiber with conventional textile processes, since the addition of such a high content of additive into the fibers decreases their mechanical properties, which limits their use in conventional spinning textile process. The use of high loadings of additives can be only achieved by surface coating processes, which can impair properties of the substrate such as softness, drivability, etc. Typically, the amount of additives within a fiber should not exceed 10 wt. % and more generally should be restricted to 5 wt. % or 6 wt. % for a flame

retardant polypropylene fiber produced by melt-spinning. Furthermore, the additives have to be thermally stable during the manufacturing process and compatible with the polymer matrix. They should have particle sizes that will not affect the fiber spinning process; they should not change the color of the final substrate, and should have no leaching properties. Furthermore, they should retain their flame retardant properties after textile processing. They should function at a lower temperature than the degradation temperature of the PP and should reduce the toxicity of gases and smoke produced during burning to an acceptable level (Blum et al, 2008).

2- Propylene Properties and Types

There are three different types of polypropylene. First, polypropylene containing only propylene monomer in a semi-crystalline solid form; which is called a homo-polymer PP (HPP). Second, polypropylene containing ethylene as a co-monomer in the PP chains at levels in the range of 1-8% and this is referred to as a random copolymer (RCP). Third, HPP containing a co-mixed RCP phase that has an ethylene content of 5-10% is referred to as an impact copolymer (ICP). In general, polymers consisting of identical monomers are called homo-polymers where polymeric compounds with more than one type of monomer in their chains are known as co-polymers.

Homo-polymer PP (HPP) is the most widely used polypropylene material in industry. HPP is a two-phase system contains both crystalline and non-crystalline regions. The non-crystalline (amorphous) regions have both isotactic PP and a tactic PP. The isotactic PP in the amorphous regions is crystallizable and crystallizes slowly over time. In other words, HPP consists of only one propylene unit along the chain with mostly isotactic propylene units and that give us a crystalline structure to the polymer. Therefore, HPP exhibits a high level of stiffness at room temperature and a high melting point but lower transparency as well as diminished impact strength. Random copolymers (RCP) are ethylene/propylene copolymers that are produced in a single reactor by copolymerizing propylene and small amounts of ethylene (usually 1% or lower). Ethylene disrupts

the regular structure of polypropylene and results in a reduction of crystalline uniformity in the polymer. The relation between ethylene and crystalline thickness is inversely proportional which means that as the ethylene content increases the crystalline thickness gradually decreases and resulting in reaching lower melting point. Co-polymers usually have slightly better impact properties, decreased melting point and enhanced flexibility. Impact copolymers (ICP) are physical mixtures of HPP and RCP with an overall ethylene contents approximately 1-10% weight. Impact polymers are optimal at low temperatures with higher impact resistance. The RCP part of the mixture is designed to have ethylene contents in the order of 4-6% ethylene and it is called the rubber phase. The rubber-like reinforcement greatly improves impact strength particularly at low temperatures (below -20°C). However, stiffness is retained resulting in excellent stiffness/impact balance. ICP product as well as the impact resistance varies with respect to size, shape and distribution of the rubber particles (Table 1).

Table 1: Mechanical & Thermal Properties of polypropylene

Property	Homo-polymer			Copolymer	
Melt flow index	3	0.7	0.2	3	0.2
Tensile strength (MPa)	34	30	29	29	25
Elongation at break (%)	350	115	175	40	240
Flexural modulus (MPa)	1310	1170	1100	1290	1030
Brittleness temp. ($^{\circ}\text{C}$)	+15	.	.	-15	-20

Vicat softening point (°C)	154-	148	148	148	147
	15.				
Rockwell hardness (R-scale)	95	90	90	95	88,5
Impact strength (ft lb)	10	25	34	34	42,5

3 - The properties of propylene yarn

Nowadays polypropylene (PP) fiber is one of the most popular synthetic fibers due to its low cost and a set of valuable properties. During last decades the growth rate of its production is higher than of such distinguished fibers as PES, PA and PAN. Production of PP multifilament yarns in 2003 comprised 1,7 mln. t and it was by 13 % higher than in 2002. The range of PP fiber and yarn application fields depends on the product mechanical properties, which in turn are mostly determined by the fiber spinning and drawing parameters because during spinning, drawing and heat setting the proper supramolecular structure of the fiber is formed.

Among such usual properties as strength and extensibility, one of distinct features of PP fiber is a well-marked viscoelasticity, manifesting in a high time-dependency of their mechanical behavior. A study of materials viscoelastic behavior is a subject of great importance from viewpoint of the material processing or its usage according to the specific purpose as well as of the theory of viscoelasticity originated from the material structure. To provide information about the viscoelastic behavior of a polymeric material various experimental techniques have been used, among which stress relaxation is in common use. A number of studies on stress relaxation in textile fibers and other polymeric materials, published during last decade, should be mentioned (Behera et al, 2001).

3-1 - Tensile properties



The increase in percentage of propylene up to 20% initially decreases the yarn strength and subsequently the strength increase with the further addition of PP. However, the extension at break continuously increases with the increase in polypropylene proportion. This is due to the more extensibility of the polypropylene fiber. The initial fall in single yarn strength is due to the differential loading of the fibers in cross-section. Beyond 30% PP, the increase in the yarn structure is in accordance with the Hamburger's model for blended yarn. Similarly, the count strength product (CSP) value first decreases from 2320 to 2192 and then increases to 2347. The reason for this trend is also attributed to the Hamburger's model. Therefore, to achieve any improvement in the yarn strength, at least 20% of polypropylene should be added.

3-2- Unevenness and Imperfections

The absolute unevenness appears to be at higher side. There is slight improvement in the User CV% of yarn with, the addition of polypropylene, but the improvement is not statistically significant. The reduction in the value is due to evenness of polypropylene staple fiber. The result of tests does not show any definite trend in the thick places, thin places and naps in the yarn with the change in PP proportion in the blends.

3-3- Flexural rigidity

The flexural rigidity increases with the increase in polypropylene proportion which is quite obvious. As the polypropylene is a coarse and stiffer fiber, its presence increases the yarn flexural rigidity (Behera et al, 2011).

4- Polypropylene random copolymer synthesis

The production and synthesis of polypropylene (PP) copolymers resulted from a natural development of polyolefin technology from

the manufacturing of PP photopolymer. Two main types of propylene-ethylene copolymers are available in the market today, which are usually prepared using heterogeneous catalysts. These are block and random copolymers. The introduction of random copolymers expanded the range of properties available depending on ethylene content. Low ethylene content copolymers are interesting lower crystalline materials because the insertion of a second monomer into the propylene backbone would inhibit the crystallization and produce a copolymer with lower melting point and higher impact strength than the photopolymer. For these PP copolymers, the structure and crystallization behavior depend on molecular weight and molecular weight distribution as well as tacticity, comonomer content and comonomer sequence distribution. It is worth mentioning that the actual copolymerization technique used has not been disclosed and there is also little information about dynamic mechanical properties, structure and morphology of these copolymers. Isotactic polypropylene (i-PP) is readily crystallized and the polymer chain exists in the crystal as a 3_1 helix with 3 monomer units per turn of the helix. Four different chain conformations exist which have identical intermolecular interaction energies. However, their intermolecular interactions with each other in the crystal depend on packing geometry. When the nearest neighbors of left-handed helices are enantiometric

Right-handed helices and vice versa the best packing is achieved. From different packing geometries four well-known crystallographic forms have been observed for PP. These are monoclinic (α), hexagonal (β), triclinic (γ) as well as a quenched form. A less common δ - form structure has also been proposed. Among these crystalline structures the α -form is the most common (Razavi Nouri, 2005).

o- Propylene random copolymer yarn flexibility

Because of the development of the Fourth Generation Catalysts, it has become possible to prepare a new family of high alloy copolymers, which include soft copolymers, stiff copolymers and low melting

copolymers. These materials show a great degree of flexibility in terms of degree of crystallinity, comonomer selection and molecular weight (Kumar, 2001).

3- Propylene yarn length variability

The tensile behavior and ultimate mechanical properties are very important characteristics of semi-crystalline polymers. These macroscopic properties are known to very closely depend on the strain rate, thus an understanding of strain rate dependence of their deformation behavior is important for encouraging their wide use in engineering and structural applications. Strain rate has a complicated and dramatic effect on materials deformation processes because the energy expended during plastic deformation is largely dissipated as heat. This process was observed to be more prominent at higher loading rates that are associated with adiabatic drawing than during lower loading rates where isothermal drawing occurred. In general, three stages of plastic deformation were suggested in tensile tests of semi-crystalline polymers: (1) pre-neck deformation of micro-spherulitic structure that proceeds in the whole sample, (2) large deformation in the neck, which transforms the micro-spherulitic structure to fibrillar structure, and lastly (3) post-neck deformation of the fibrillar structure. In general, in the neck, the polymeric material softens drastically for a very short period, which is associated with a decrease of plastic modulus. However, as the neck develops and exceeds a limiting zone, the morphology changes to that of a fibrillar structure with increase in plastic modulus, termed as strain-hardening.

Typical stress-strain curves of the PP-R samples tested at different crosshead speeds are given in Fig 3. The test samples were not broken at 200% elongation at crosshead speeds up to 20 mm/min, but for the higher test speeds, the samples were ruptured at lower % elongation and had a value of about 150% at crosshead speed of 1000 mm/min. At lower test speeds, the PP-R samples formed a very marked and stable neck with a wide stress-whitening zone; as the test proceeded, the necked zone extended throughout the whole test gauge to the point of rupture at very large deformation values. At this stage, due to strain-

hardening there was a gradual increase in the stress as the test proceeded up to rupture. As the test speed increased, the stress-whitening zone narrowed and, at very high crosshead speeds, the remainder of the gauge length was not plastically deformed (Shahin and Yayla, 2005).

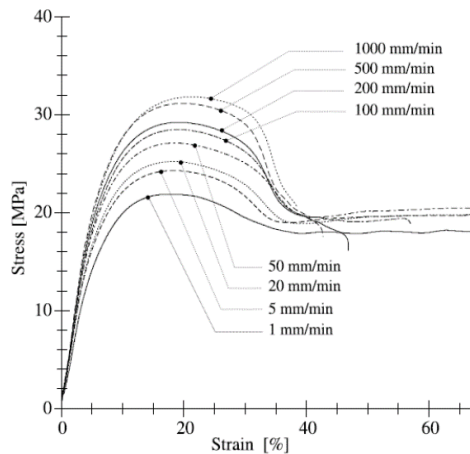


Fig 1. Variation of stress-strain response with respect to crosshead speed for natural PP-R material (Shahin and Yayla, 2005)

V- Conclusion

Propylene is an elastomer that improves yarn properties. It increases flexibility and tensile strength. Properties of propylene depend on both the molecular properties of the polymer used and the processing conditions applied during fabrication. Not only mechanical properties depend on crystal structures, but also properties, like dimensional stability and transparency.



References

- Rault. F, Giraud. S, Salaun. F, Almeras. X, (۲۰۱۵), Development of a Halogen Free Flame Retardant Master batch for Polypropylene Fibers, Polymers, No ۷.
- Maddah. H, (۲۰۱۶), Polypropylene as a Promising Plastic: A Review, American Journal of Polymer Science, ۶(۱۱).
- Blum. R, Bogner. H, Nemoz. G, (۲۰۰۴), Material Properties and Testing, European Design Guide for Tensile surface structures, Brussels
- Behera. B. K, Sardana A, Verma. B. C, (۲۰۰۱), Studies on Polypropylene-Cotton Spun Yarns and their Fabrics, Indian Journal of Fiber & Textile Research, Vol. ۲۶.
- Razavi Nouri. P, (۲۰۰۵), Thermal and Dynamic Mechanical Properties of a polypropylene Random Copolymer, Iranian Polymer Journal ۱۴ (۵).
- Kumar. A, (۲۰۰۱), Morphology, Crystallization and Melting Behavior of Statistical Copolymers of Propylene with Ethylene, ۱-Butene, ۱-Hexene and ۱-Octene, Thesis Submitted to the Faculty of the Virginia Polytechnic Institute and State University, United States.
- Shahin. S, Yayla. P, (۲۰۰۵), Effects of Testing Parameters on the Mechanical Properties of Polypropylene Random Copolymer, Polymer Testing ۲۴.

