Vandar® High-Impact Strength Polyester for Sporting Goods

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Abstract

Vandar® 2100 is an impact modified engineering thermoplastic resin developed to deliver consistent performance over a wide range of temperature and humidity conditions, primarily in injection molded articles. Vandar 2100 provides outstanding ductility and stiffness combined with the excellent chemical and environmental resistance properties of polyesters. The unreinforced and higher flexibility Vandar grades fill the property gap between standard thermoplastic polyesters and elastomers. These plastics are easy to process including by injection molding and retain their impact strength down to -30°C.

Introduction

In the last two decades there has been an enormous growth in the application of advanced materials in sports equipment for individual use, including professional and amateur participants [1-3]. Golf clubs and tennis rackets which use to cost several dozen dollars now cost several hundred dollars, but the incurred benefits in terms of performance and achievement justifies the extra financial outlay. These areas requiring high performance demand special attention to innovation, quality and manufacturing excellence. As a consequence, they are generally highcost applications, requiring new innovative materials. This is a relatively new target area for sports equipment, which often requires impact modified plastics. New material developments are continually being sought for the property improvements of materials with structures below the micron level [4-7].

Design considerations for sports equipment include weight, energy to break, bending stiffness and torsional stiffness. Generally, to achieve maximum performance at lowest effort, the components should be as thin as possible, have a high yield stress and low elastic modulus. Such a $\sigma y/E$ index minimizes any plastic deformation by impact and maximizes elastic deformation. The plastic must be resistant to UV radiation, abrasion, moisture, creep and any chemical agents such as cleaning solutions, sweat, lotions, oils, etc. However, the major requirement is to reduce the impact force on the hand and arm and provide control and impact power. To achieve this goal, proper selection of materials is necessary. Plastics often fulfill these requirements due to lighter weight, well controlled properties with required performance and less chances of injury. For engineering plastics to be used in sports applications, the material must meet the performance requirements such as stiffness and toughness across a range of temperature and humidity. In addition, the material should have good processability and be injection moldable.

Thermoplastic polyesters can meet this need. They are fast-cycling resins with high strength, rigidity and toughness. They offer low creep even at high temperatures, as well as excellent dimensional stability, low moisture absorption and powerful insulation resistance. Polyesters also offer resistance to a wide range of chemicals, solvents, oils and cleaning agents.

These semi-crystalline resins are used in a wide variety of applications, most commonly in injection molded durable goods. PBT is a preferred polyester used for the continuous phase, which displays good solvent resistance, high heat resistance, good elongation, high strength and modulus. PBT also has low melt viscosity and very fast crystallization, hence allowing for easy processing for injection molding. PBT has good coldwater resistance, excellent electrical properties, high gloss, good inherent lubricity and wear resistance. The vast majority of PBT resins are blended with many other ingredients to give a balance of properties for different injection molding applications. In some cases, only a small amount of additive may be combined with the PBT.

In other cases, high loadings of a variety of ingredients can push the PBT content to below 30%. In all cases, the PBT is still the continuous phase. Like many crystalline resins, the low melt viscosity of PBT and its ability to "wet-out" many fillers and resins make it very amenable to the formation of blends.

Toughening semicrystalline polymers including polyester is a common practice in the plastics industry. The general approach is to create a second dispersed rubbery phase, which helps initiate matrix plastic deformation that leads to dissipation of a large amount of energy before fracture. To be effective, the rubber particle size has to be within a certain range. The optimal rubber particle size range varies from polymer to polymer. In general, for aromatic polyesters like PET and PBT or polyamides like nylon 6 and nylon 66, the optimal rubber particle size range is from 0.1 to 1 micron. To achieve such fine rubber dispersion, some kind of reactive compatibilization is usually needed since most rubbers are neither miscible nor compatible with polyesters or polyamides. Selection or design of the proper impact modifier and proper compatibilizer is the key to developing a material which has the desired properties. Moreover, using hydrophobic impact modifier is critical for maintaining property profile across temperature and humidity range.

With all above constraints in mind, innovative high-impact polyester grades, such as Vandar® 2100 were created to satisfy unmet needs of the high-performance sporting goods market. Unlike other engineering thermoplastics, Vandar 2100 polyesters are not as sensitive to dimensional change due to moisture absorption. Their mechanical and thermal properties are virtually unaffected when exposed to moist environments at wide temperature ranges. In addition to good impact strength at room temperature and subzero temperature, Vandar 2100 has excellent performance at broader temperature range and can be decorated (i.e., dye sublimation, pad printing, paint, laser marking). Since aesthetic appeal is always important for consumer goods, Vandar 2100 will also easily accept pigments for coloring and special effects (i.e., metallic, sparkle, anodized, and vivid colors). All these properties make Vandar 2100 an ideal candidate for the sports and entertainment industry where performance and appearance matter.

In this paper, we discuss the structure-property relationship of Vandar 2100 and a commercially available high-impact (HI) Nylon within the context of sport equipment requirements.

Experimental Materials and Testing:

"As received" pellets of Vandar 2100 and HI Nylon were dried at 121ºC and 80ºC respectively for four hours in a dehumidifying oven, before testing, as recommended in technical data sheet. A standard injection molding machine (Demag 661) was used to mold test bars in accordance with either ASTM or ISO standards.

Testing and evaluation of the Vandar 2100 and HI nylon was carried out via several analytical techniques. All samples were conditioned at 23°C and 50% relative humidity for 48 hours before testing. Tensile tests were performed according to ISO 527-2/1A, using a crosshead speed of 50 mm/min. Flexural tests were performed according to ISO 178 using a crosshead speed of 50 mm/min at 23ºC and -20ºC. Five specimens were tensile tested for each sample pull. Notched Charpy impact tests were performed in accordance with ISO 179/1eU at 23ºC and -20ºC; 10 bars were tested for each sample and notching was performed immediately after molding.

Results and Discussion Mechanical, Thermal and Physical Properties:

Mechanical Properties:
A comprehensive list of properties for both the materials used in this study is provided in Table 1.

Table 1. Mechanical and Physical Properties of Vandar 2100 and HI Nylon

	Vandar 2100	HI Nylon (DAM/50% RH)
Tensile modulus (MPa)	1,640	2,000/900
Tensile stress at yield (MPa)	37	50/43
Tensile strain at yield (%)	4.5	5.7/37
Tensile strain at break (%)	250	32/>50
N-Charpy impact (23°C) (kJ/m^2)	90	80/115
N-Charpy impact (-30°C) (kJ/m^2)	23	18/17
Moisture absorption (%)	0.2	2.2

The mechanical property equivalence is further illustrated by comparison of stress-strain data in tensile mode as shown in Figure 1 and multi-temperature flexural stress-strain data as shown in Figure 2. The flexural stress-strain curves were measured at -20 and 23°C, using standard ISO tensile bars. Cross-head speed was 5 mm/min.

Figure 1. Tensile Stress-Strain Curve of Vandar® 2100 and HI Nylon at Room Temperature

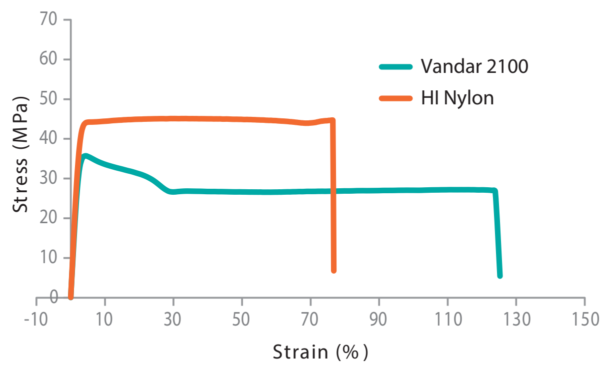
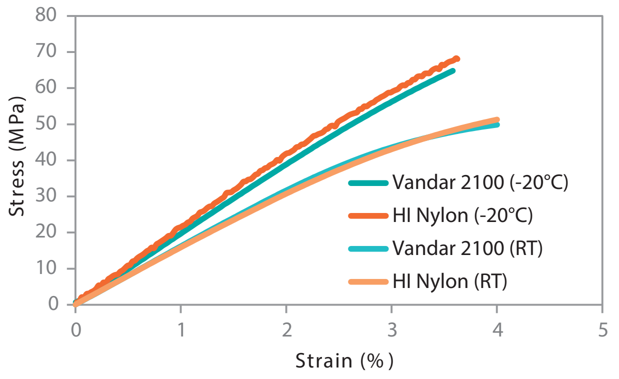


Figure 2. Flexural Stress-Strain Curve of Vandar 2100 and HI Nylon at -20°C at Room Temperature



In general, the flexural stress values observed at a given strain for the Vandar 2100 are equivalent to those observed for the HI Nylon at room temperature; however HI Nylon stiffens more than Vandar 2100 at -20ºC.

Flow

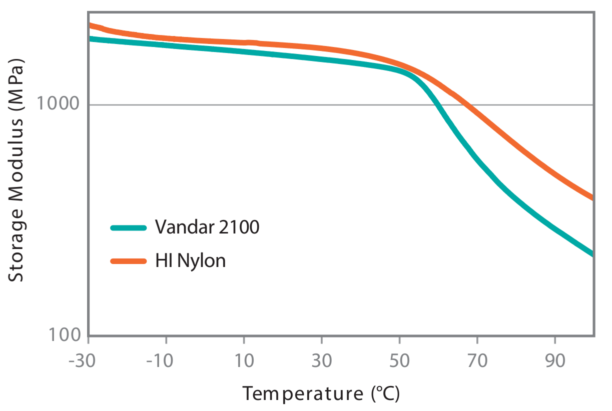
Melt flow behavior during injection molding is illustrated by spiral flow measurements for both plastics. The spiral flow measurements were made with a mold having a flat profile spiral, 1/16" deep and ½" across, at melt temperature of 250, and 270°C, respectively. Flow of the Vandar 2100 is higher than HI Nylon at melting temperature and below degradation temperature.

Figure 3. Spiral Flow Pattern for Vandar 2100 and HI Nylon

Dynamic Mechanical Properties

The mechanical performance of Vandar 2100 and HI Nylon at a wide window of temperature is studied via dynamic mechanical analysis. Dynamic flexural modulus of Vandar 2100 and HI Nylon is indicated in Fig 4. The drop in modulus value from -20ºC to 23ºC is defined as the rigidity factor. Apparently this value is higher for HI Nylon as compared to Vandar 2100 due to a more dramatic decline of the modulus for the HI Nylon.

Figure 4. Dynamic Storage Modulus for Vandar 2100 and HI Nylon in Flexural Mode



Impact Strength and Morphology

The notched charpy strength of Vandar® 2100 at room temperature is 90 kJ/m2, on the other hand, for HI Nylon it is 80 kJ/m2. At -30°C this value for Vandar 2100 is 23 kJ/m2 and for HI Nylon it is 18 kJ/m2. The new impact modifier formulation allows improved compatibility and interaction resulting in substantial improvement in impact strength at room temperature and -20°C compared to standard HI Nylon.

The morphology of both materials was evaluated by freeze fracturing a standard tensile bar in the direction of the flow and then examining the surface by SEM. The micrographs for standard impact modified nylon exhibit a non-uniform pattern causing domains of stress concentration. The micrograph for the polyester shows a much more random flow pattern, which leads to the improved impact performance. The micrographs are included in Figure 5 and 6.

Figure 5. Representative SEM/SEI Micrographs Show the Dispersion of Impact Modifier in Vandar 2100

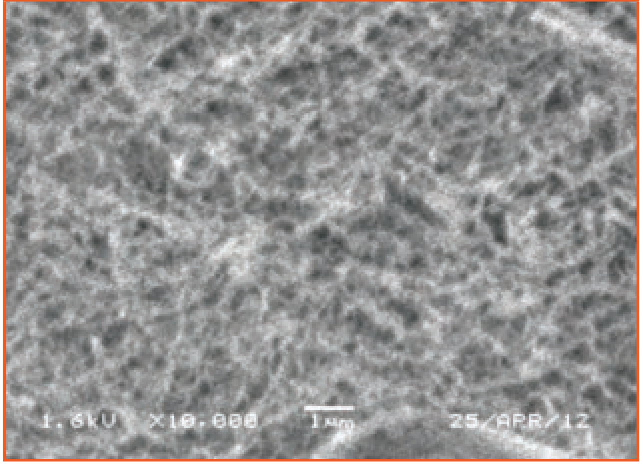
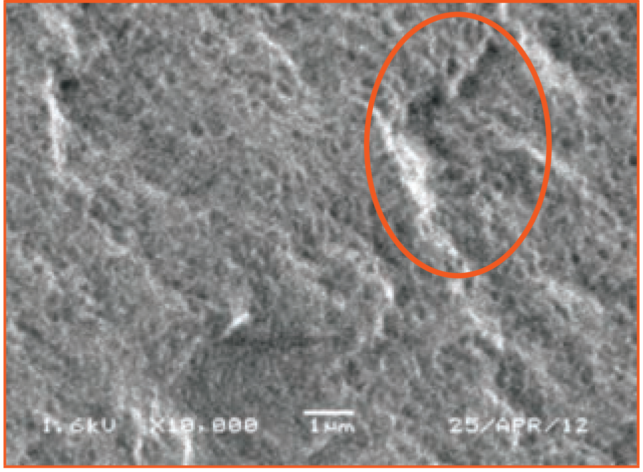


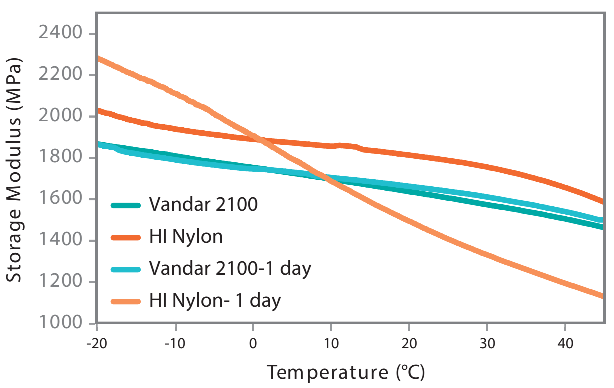
Figure 6. Representative SEM/SEI Micrographs Show the Dispersion of Impact Modifier in HI Nylon



Chemical Resistance

While the mechanical performance is critically important to functionality, maintaining thermal and chemical stability over time is equally important. Being a semicrystalline polymer, Vandar has excellent resistance to stress cracking in various chemical environments. These include dilute acids, bases and salt solutions, most organic chemicals and automotive oils and ozone. The effect of water on both Vandar 2100 and HI Nylon, was analyzed by soaking standard ISO tensile bars in water at room temperature for 24 hr. The soaked samples were subjected to DMA analysis to closely monitor the effect of water on mechanical and thermal performance.

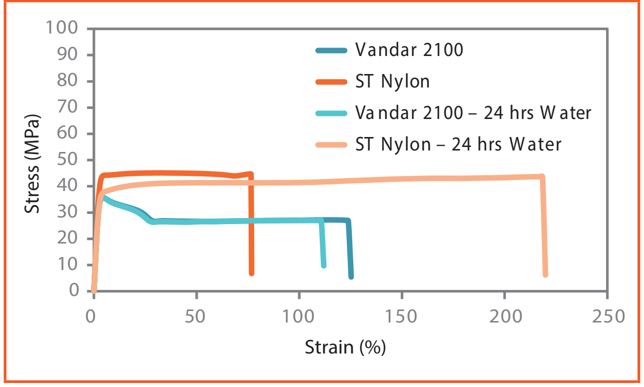
Figure 7. Dynamic Storage Modulus for Vandar 2100 and HI Nylon in Flexural Mode



Soaking HI Nylon in water resulted in the higher modulus below sub-zero temperature. On the other hand, at above sub-zero temperature, it had lower flexural modulus and strength indicating that it undergoes significant plasticization as shown in Figure 7. This can be attributed to hydrogen bond formation tendency of Nylon.

To further study the effect of water on large strain deformation, the tensile bars were soaked and tested for tensile strength (yield) and tensile modulus by the standard ISO test method – ISO 527. Bars were wiped dry and equilibrated (23 °C/50% R.H.) before testing. The results are presented in Figure 8. It should be noted that both materials failed in a ductile manner throughout the mechanical testing.

Figure 8. Tensile Stress-Strain Curve of Vandar® 2100 and HI Nylon After Soaking in Water for 24 hrs



Weathering Resistance

UV-stabilized Vandar alloys can be made available in natural, precompounded colors, and salt and pepper blends to help prevent premature degradation from exposure to UV light.

Accelerated UV weathering was performed on Atlas Weather-Ometer Ci4000 according to SAE J1960 method. Data were calculated under D65, 10° observer, specular included. Results are reported as per DE CIElab.

Figure 9. Color Change After UV Exposure for 500kJ/m^2 for Vandar 2100 and HI Nylon

Table 2. UV Weathering Data of Vandar 2100 UV and HI Nylon at 100 kJ/m^2

	DL*	Da*	Db*	DC*	DH*	DE
Vandar 2100 UV	0.14	-0.71	0.94	1.17	0.13	1.18
HI Nylon	-1.97	0.66	0.40	0.42	-0.64	2.11

Overall mechanical, physical and chemical performance of Vandar 2100, showed robust consistent behavior in terms of stiffness and mechanical and impact retention. Vandar 2100 has inherently lower tear strength and abrasion resistance, but this can be improved if needed by design modifications. Under demanding conditions, impact and flexural strength, outdoor UV, and temperature fluctuation for Vandar 2100 are not compromised.

Conclusions

This study confirms the robustness of impact modified polyester as compared to high-impact Nylon. The mechanical properties of Vandar 2100 remain consistent over a wide range of service temperature window, while HI Nylon shows significant change in stiffness with temperature. Moreover, the properties of impact modified polyester are not affected by moisture or water soaking unlike HI Nylon.

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Key Words: Polyester Alloy, Moisture Resistance, Impact Strength, Rigidity Factor

Product performance and material data values included in this publication are either based on evaluating laboratory test specimens, and represent data that fall within the normal range of properties, or were compiled from various sources. To the best of our knowledge, the information contained in this publication is accurate; however, no representation is made as to its suitability in any specific application for establishing maximum, minimum, or ranges of values for specification purposes.

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