Stable High Molecular Weight PET.

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Executive summary

We have searched the literature, spoke with resin manufacturers, contacted distributors, to select PET resin materials with higher IV numbers and this report summarizes our findings.

We have recommended and procured for you in the past a number of resins with higher IV numbers such as Merge 5054, Crystar 1994 etc., therefore we have restricted our search to other than those resins. We also found out that there is no great interest in the commercial marketplace for these type of resins (nevertheless most resin companies are willing to make them at the proper customer's request). The primary reasons for this is, that resins with higher than 1.1 IV No. tends to revert back to the much lower IV No. during "ordinary" processing. Also, because these resins require secondary so-called solid-stating polymerization process, they carry a premium price. These branched structures are achieved by proprietary additive processing which creates spikes on the backbone of the resin's molecule. This modified PET resin is a more stable tougher resin than those not treated.

PET resins like most polyester resins absorbs moisture when exposed to even a mildly humid atmosphere. This moisture hydrolyzes the polymer chains to lower molecular weight. This results in an excessive drop in IV value and an associated loss off physical properties. Therefore, it is extremely important to properly dry the PET resin. We recommended a residual moisture content of less than 40 ppm after drying.

Our recommendation is to use a PET homopolymer called MERGE 5014 made by DuPont. This resin although has only a nominal 0.980 IV No. but it is branched and therefore it is said to behave like a 20 percent higher IV number resin. In addition, this resin because it is branched is more stable during ordinary processing. We have also listed number of other PET and like resins from Du Pont and other manufacturers. We have even included a resin called MELINAR 5922C. We know that you have tried MELINAR before but we were not certain that this particular resin was the one you have tried.

We have also presented two resins called Kalidar™ made by DuPont, one is X-61 the other is X-70. They both are poly(ethylene naphthalate) resins [PEN] having IV numbers of 1.78 and 1.165. PEN is an upscale equivalent of PET. It has thermal, mechanical and dielectric properties which are superior to those of poly- ethylene terephthalate [PET] making PEN a high-performance extension of PET.

In response to your request to find high molecular weight, high IV (intrinsic viscosity) PET resins, we have contacted 13 manufacturers and/or representatives of PET manufacturers as well as an equal number of distributors and institutions. We have endeavored to find not only the commercially available resins but also those which are either new or developed for special purposes. We have summarized the information in this report.

We were not able to uncover large number of resins over the IV value of 1.0, in addition to those we recommended to you earlier. We found the reason to be that there are simply not many manufactured. The primary reason for this is that resins with an IV number higher than 1.1, if not branched, will revert back too less than 1.1 during ordinary processing. Since these resins have to be subjected to a secondary solid state polymerization process, high IV resins are selling at a higher premium price. This and other reasons discussed later in this report are the rationale why users are not very interested in purchasing them; - consequently resin manufacturers are not making them. Theoretically, most existing lower IV (0.6 -0.75) PET resins can be solid stated to increase the IV number, if a customer with large purchasing power wishes it and is willing to pay the premium for it.

INTRODUCTION

Polyethylene terephthalate (PET) thermoplastic resins are polyester materials designed to provide the clarity, processing characteristics, chemical and solvent resistance, and high strength and impact resistance required for bottles and containers. A biaxial molecular orientation can provide high strength. Directional blowing can result in axial orientation resulting in increased hoop strength.

CHEMISTRY

Polyester is a long chain polymer. During processing into some finished products, these long chains are oriented to provide the outstanding strength-to-weight ratios characteristic of polyester-based products.

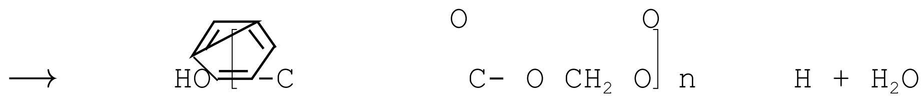
Polyesters are formed via the condensation polymerization of di-functional organic acids (or esters, or anhydrides) with di-functional organic alcohols called diols. For example, PET is manufactured by the catalyzed condensation of a glycol and an aromatic diacid such as terephthalic acid (TPA) or a derivative like dimethyl terephthalate (DMT).

PET, the most widely used polyester, is prepared by combining ethylene glycol (HO CH_2 CH_2 OH) and terephthalic acid (HOOC|O| COOH) in the presence of a catalyst and stabilizer. The reaction forms the glycol ester of terephthalic acid which is polymerized at a high temperature to form the long chain polyethylene terephthalate molecules. The molecular weight can be precisely controlled to achieve the chain length (or molecular weight) desired within limits. Unlike the chemistry of most other performance polymers, polyester chemistry can produce a wide variety of compositions.

The polymerization takes place in the molten state and when the desired molecular weight is reached, the molten polymer is cooled and converted into amorphous (transparent) pellets or cubes.

The chemical reaction is as follows:

terephthalic acid and ethylene glycol



Where n = 100 - 220

Other polyesters and copolyesters similarly can be prepared from other glycols, acids or mixtures.

To achieve the higher molecular weights that are required for improved physical properties, PET resins are further polymerized in the solid-phase, or "solid stated".

In the solid stating process, crystallized pellets of PET are heated under vacuum, or a continuous flow of inert gas to remove ethylene glycol and water. The ethylene glycol and/or water is removed from the ends of adjacent, low molecular weight PET molecules, thus condensing them into higher molecular weight PET. At high temperatures, such as those found in an extruder, this condensation reaction is reversible if water is present. Thus, all PET resins must be dried (or all water removed by other methods) prior to processing in order to retain their properties. Some manufacturers subject PET resins to a secondary solid state polymerization process, designed to yield even higher molecular weights. These high IVs are necessary for the higher strengths demanded for bottle and packaging applications. The secondary polymerization also yields a higher purity polymer. They carry however a premium of price as much as 25 - 35 ¢/lbs. Unfortunately as we said above most resins over 1.10 IV number will revert back to that level during the "ordinary" processing.

<u>ACETALDEHYDE</u>

Acetaldehyde is a harmless by-product generated during the manufacture of polyester and the production of polyester containers. It is a colorless vapor at temperatures greater than 69.4 ˚F (20.8 ˚C) and has a fruity odor. It also occurs naturally at levels greater than 1ppm in many foods.

Although the low acetaldehyde levels in foods and beverages is not considered a safety or health concern, it can affect taste. It is necessary, therefore, to minimize acetaldehyde levels during processing to ensure that the bottles will not affect taste or odor. Acetaldehyde can be minimized by processing the resin properly at the lowest possible melt temperature, residence time, and shear heating consistent with the production of quality products.

<u>DRYING</u>

Polyester readily absorbs moisture when exposed to a even a mildly humid atmosphere. The reaction of water and polyester is extremely rapid in the molten state and hydrolyzes the polymer chain to lower molecular weight. This results in an excessive drop in IV and an associated loss of physical properties.

To prevent deterioration of end product properties, it is extremely important that polyester resins be dried to a moisture content of not more than 500ppm by weight prior to processing (we recommend even less 30-50ppm) to maintain the higher IV number.

One of the best methods to dry the polymer is in a high heat dehumidifying air hopper with a regenerative desiccant bed, at a temperature range of 150-180°C for 4 (four) hours. It is very important to note, that longer is not better, PET's degradation is controlled by a rate process, it is the amount of heat which degrades it. Every four hours of additional heating will require a reduction of drying temperature by 10°C. The polymer is exposed to -20 to -40 ˚F (-29 to -40 ˚C) dew point air. Moisture content should be measured by weight control instruments available in the trade, such as Mark 2, manufactured by OMNIMARK (Tempe, AZ), capable of detecting as little as 30ppm water. Maximum of 40ppm moisture content needed to maintain original IV number.

INJECTION MOLDING

The major processing objectives in molding polyester for blow molding into shapes are:

- The production of clear, amorphous parts
- Retention of molecular weight
- Minimization of acetaldehyde generation for objects to be used in food or medical contact.

Parts clarity is directly related to mold conditions. Crystallization occurs in the 239 to 473 ˚F (115 to 245 ˚C) range. Therefore, the part must be rapidly cooled through this range.

Desired molecular weight is retained by:

- Drying the polymer adequately (30-40ppm max moisture)
- Employing low melt temperatures (max. 10-15°C over Tm)
- Minimizing shear and associated heating (well designed screw)
- Minimizing melt resistance time (i.e. no sharp curves or closed restrictor bar)

The following tables describe characteristic thermal, tensile, and barrier properties of PET resins.

THERMAL PROPERTIES OF TYPICAL PET RESINS

Property	Constants	Value
Glass Transition Temperature (T_g)		73 ˚C
Melting Point (T_m)		245-258 ˚C
Drying Temperature		60-180 ˚C
Heat of Fusion		9-16 cal/gm
Computation		
Coefficient of Thermal Expansion	Range 30-60 ˚C	1.6 x 10-4/˚C
	Range 90-190 ˚C	3.7 x 10-4/˚C
Thermal Conductivity(C)		
Cal/Gm. x ˚C	3.36 x 10-4/Cal /cm/sec x ˚C	
Heat Capacity (C)		
Cal/Gm. x ˚C		
Molten Polymer (270-290 ˚C)	Range	0.3243 +0.000565T3
Crystallized Chips	(-20 to + 60 ˚C)	0.2502 + 0.000940T3
Undrawn Film	(-5 to + 60 ˚C)	0.2469 + 0.001007T3
Drawn Film	(-10 to + 55 ˚C)	0.2482 + 0.000989T3
Heat Distortion Temperature	(65 ˚C (150 ˚F)	

TENSILE CHARACTERISTICS OF TYPICAL PET RESINS

Condition	PSI
Tensile Strengths	
Amorphous Unoriented Sheet	7,000
Uniaxially Oriented Film	
(3.75 Longitudinal Draw)	
Longitudinal Direction	36,000
Transverse Direction	10,000
Biaxially Oriented Film	
(3x3 Draw-Longitudinally and Transverse)	25,000
Tensile Modulus	
Amorphous Unoriented Sheet	400,000
Oriented Film	600,000

BARRIER PROPERTIES OF TYPICAL PET RESINS

Diffusing Substance & Conditions	Condition of Polymer	Units	Value
CO_2@ 25 ˚C, 0% Relative Humidity	Unoriented	cm3mil/ 100 in^2 day atm	20
	Oriented	cm3mil/ 100 in^2 day atm	12
O_2@ 25 ˚C, 0% Relative Humidity	Unoriented	cm3mil/ 100 in^2 day atm	10
	Oriented	cm3mil/ 100 in^2 day atm	5
Water Vapor Transmission at 100 ˚F, 100% Relative Humidity	Unoriented	gm mil/ 100 in^2 day atm	4
	Oriented	gm mil/ 100 in^2 day atm	2

GENERAL RECOMMENDATION

In addition to those PET resins we have already recommended and procured for you in the past, we are recommending the following additional resins for your trials.

From DuPont Chemicals:

MERGE 5014 (solid stated 3972) High Molecular Weight (HMV) Homopolymer having an IV number of 0.980 (clear) this is however a branched resin behaving like a 20% higher IV number resin. The advantage of this is that the branched structure will not deteriorate as rapidly during processing. Branching is achieved by a proprietary additive, which in addition to the above mentioned stabilizing effect also increase the melt strength of the resin.

MERGE 5029™ (Solid Stated 1989)having an IV number of 0.95 (white).

Melinar 6922C™ which is a homo-polymer with an IV number of 1.1

DuPont also manufactures a host of PEN products many of which have high molecular weight, although their IV number is measured differently then PETs. While this area was not in the scope of the current project please find our recommendations of Kalidar X-70/X-61™ (PEN) and their Data-Sheets those of which has a PET equivalent 1.165/1.78 "IV" numbers respectively, be mindful however that the cost of these resins are substantially higher then PET.

From Eastman Chemicals:

Eastapak 12822™ (Clear) HMV having IV number of 0.95 (homopolymer)

The following resins are copolyesters but each have high hoop strength as well as high IV numbers.

Eastar DN004™ (Copolyester)
Eastar EN058™ (Copolyester)
Eastar PETG™ 6763 (Copolyester)

From Shell Chemicals

TRAYTUF® 1006 similar to 8006, which you have used before but with an IV number of 1.040± 0.025.

Please find below the manufacturer's specifications of some of these resins.

THE DUPONT COMPANY

OLD HICKORY, TENNESSEE

PROPERTIES	AIM	MINIMUM	MAXIMUM
Intrinsic Viscosity	0.98	0.976	0.985
TiO_2, %	0	0	**0**
Diethylene Glycol,(DEG), wt%	1		0.7
Color "L"	58	54	62
Color "b"	-0.5	-2.5	1.5
Moisture, %	0.20		
Melt Point, °C	256 Nominal		

Clear

Physical Property Data Sheet
Eastapak™ Thermoplastic Polyester 12822 (Clear)

PROPERTY, UNITS	TYPICAL VALUE	TEST METHOD
Intrinsic Viscosity	0.95	ECC-A-AC-G-V-1
Molecular Weight,		
Number Average (Mn)	32,500	–
Weight Average (Mw)	65,000	–
Crystalline Density, g/cm^3	1.4	ASTM D 1505
Bulk Density, kg/m^3 (lb/ft^3)		
Poured	785 (49)	ASTM D 1895
Vibrated	850 (53)	
		ASTM D 1 238-90b
Melt Density, @ 285°C,g/cm^3		
1.2		
Acetaldehyde, ppm	<3	TEPO-A-AN-G-GC-67
Crystalline Peak		
Melting Point, °C	252	ASTM D 3418
Heat of Fusion, kJ/kg	59	ASTM E 793
Thermal Conductivity, W/m°K	0.25	ASTM C 177
Specific Heat, kJ/kg°K		
@ 230°C	1.13	
80 °C	1.42	
		DSC

100 °C	1.51	
200 °C	1.88	
280 °C	2.05	
Fines, wt %, maximum	0.1	TEPO-A-AN-G-GA-4
Pellet Size, mm (in.), and Shape	2.5 (0.1) Cubical	

[a]Unless noted otherwise, all tests are run @ 23 °C (73 °F) and 50% relative humidity. **EASTMAN**

Comments:

Tenite thermoplastic polyester 12822 is suggested for use in film and sheeting products, crystallized trays (with appropriate nucleating agent), and strapping.
Properties reported here are typical of average lots. Eastman makes no representation that the material in any particular shipment will conform exactly to the values given.

THE DUPONT COMPANY;

OLD HICKORY, TENNESSEE

MERGE 5029 (SOLID STATED 1989)

PROPERTIES	AIM	Minimum	Maximum	
Intrinsic Viscosity	0.95		0.93	0.97
TiO2 %	0.255	0.235	0.275	
Diethylene Glycol, (DEG), wt%	0.6	0.3	0.75	
Color "12"	79	74	84	
Color "h"	6.5	5.5	7.5	
Moisture, %	.020			
Melt Point, °C	258 Nominal			
White				

Physical Property Data Sheet

TRAYTUFF 1006™

Thermoplastic Polyester

Sales specifications

PROPERTY	Values	Test Methods
Intrinsic Viscosity	1.040±0.025	29A02-921
Melting Point (°C)	257.5min	29A29-921
Color Gardner b	6.0max	29A05-921
Moisture, % as packaged	0.2max	29A06-921

Shell Chemical Company

Melinar™
polyethylene terephthalate resin

Type 5922C

Product Description
Melinar™ polyethylene terephthalate (PET) resin
Type 5922C is an extrudable PET resin.

Melinar 5922C™
is designed for use in the manufacture of clear, rigid containers produced by extrusion blow molding with less than a 0.200 in (0.50 cm) wall thickness.

Typical Properties
Melinar 5922C™ is a high intrinsic viscosity (IV), extrudable PET resin designed for use in the manufacture of PET bottles on extrusion blow-molding equipment. This process is well suited for use in applications where handled containers or other special shapes are required, Melinar 5922C offers good flow properties and melt strength suitable for extrusion blow molding applications. It can be used on most existing equipment with minor modifications, Typically, modification to equipment screw design will offer additional improvement in quality and productivity.

Certification
Melinar 5922C™ is ideally suited for food packaging applications and is considered in compliance with the Food and Drug Administration (FDA) Food Additive Regulation 21 CER 177.1630, covering PET polymers.

Specifications

Property	Value	Unit	Test Method
Intrinsic Viscosity	1.12±0.04	IV	C-100a
Color "L"	77. 0 ± 7.0	Hunter	C-111
Color"b"	-2.0± 3.0	Hunter	C-111
Acetaldehyde	3.0max.	ppm	C-170b
Chip Size (nominal	40 ± 5	# of chips/g	C-185
Density. Bulk	53.4	lb/ft3	C-186
Crystallinity, %	>50		
Melting Point	251/484	(°C)/°F	C-120

Comments: Not a branched polymer

Kalidar™

polyethylene naphthalate resin (PEN)

Type X-61

Product Description

Kalidar X-61™ is a polyethylene naphthalate. (PEN) homopolymer resin produced by catalytic polymerization of dimethyl 2,6 naphthalene-dicarboxylate and ethylene glycol.
A state-of -the-art production unit was designed specifically for manufacture of our PEN resins using proprietary technology.
Kalidar X-61™ is engineered to make it ideally suited for use in industrial fiber and compounding applications.

Specifications

Property	Value	Unit	Test Method
PEN IV*	1.05±0.10	dL/g	C-100
PET- Equivalent IV	1.78± 0.24	dL/g	C-100
Color "L"	82.0± 7.0	Hunter	C111
Color "b"	6.0±3.0	Hunter	C-111
Chip Size	60±1.0	# of chips/g	C-185

*The reported intrinsic viscosities (IV) are determined by a correlation to the melt viscosity of the polymer.

Polyethylene Naphthalate (PEN)

Dimethyl-2,6-naphthalenedicarboxylate (NDC), is the dimethyl ester of 2,6-naphthalene-dicarboxylic acid (2,6-NDA). Polyethylene naphthalate (PEN) is the homopolymer of NDC with ethylene glycol. PEN resins with high molecular weight have been produced. Poly(ethylene naphthalate) (PEN) can be regarded as an upscale analogue of PET made with 2,6-naphthalene dicarboxylic acid (NDA) rather than the terephthalic acid used with PET. PEN has thermal, mechanical and dielectric properties which are generally superior to those of polyethylene terephthalate (PET), positioning PEN as a high-performance extension of PET, but currently at high premium ($4.0/lbs).

Kalidar™

polyethylene naphthalate resin (PEN)

Type X-70

Product Description

Kalidar X-70™ is a polyethylene naphthalate. (PEN) homopolymer resin produced by catalytic polymerization of dimethyl 2,6 naphthalene-dicarboxylate and ethylene glycol.
A state-of -the-art production unit was designed specifically for manufacture of our PEN resins using proprietary technology.
Kalidar X-70™ is engineered to make it ideally suited for use in rigid container applications.

Specifications

Property	Value	Unit	Test Method
PEN IV*	078 ± 0.02	dL/g	C-100
PET IV	1.165±0.03	dL/g	C-100a
Color "L"	53.0±7.0	Hunter	C-111
Color "b"	0±3.0	Hunter	C-111
Acetaldehyde	3.0 max.	ppm	C-170b
Chip Size	60±10	#of chips/g	C-185

*The reported intrinsic viscosities (IV) are determined by a correlation to the melt viscosity of the polymer.

SPECIFIC RECOMMENDATION

Our recommendation, based on the evaluation of these resins is DuPont's Merge 5014™ and DuPont's Crystar 5029™ both have an IV number around 1.0. We also based our recommendation on the fact that the 5014 is not only a solid stated Merge 3972 resin but it is a branched resin manufactured by a new reactor based TPA process using a proprietary additive to accomplish branching and is expected to be more stable at normal manufacturing methods, while the other is also solid stated, but not branched. Or some of the Kalidar (PEN) resins. Out of these, if you only want one resin, we would recommend you go with Merge 5014™. If you so desire we can help you procuring these or any other resin in our list.

DISCLAMER

The information contained in this report is believed to be reliable. However, no guaranties are made of its accuracy and neither the writer nor anyone connected with the preparation of this report assumes legal responsibility with respect to the use of information contained herein. No statement or suggestion in this report is to be considered a recommendation to use technologies described nor authorization to practice a patented invention without a license.

Limitations

The estimates, projections, assumptions and other related data presented are as accurate as possible within general scope of this report. A number of factors determine the detail and accuracy. Some of the companies contacted are subsidiaries or divisions of very large and often foreign corporations that do not break out information at the level we are interested. Difficulty also exists in obtaining details and crucial proprietary information from Corporations having strict policies to withhold information relating to their internal affairs. We have made estimates based on our knowledge of the subject in question or used information available from other sources, on a best effort basis, where necessary.

Methods

This report is primarily based on information gathered from interviews of personnel employed by organizations throughout the World, but overwhelmingly in the U.S., including interviews which may have included, marketing, production, development, purchasing, executives of major participants of resin manufacturers, as well as from in-house information and systematic search of current literature available at this time.

No Responsibility

We cannot anticipate all conditions under which data, information, suggestions, analysis and even recommendations may be used. We cannot and do not accept responsibility for results obtained by the application of information conveyed, unless specifically stated by us in writing. Users are advised to make their own evaluations and or tests regarding any information conveyed to them by us. Unless otherwise agreed in writing we sell our services without warranty and buyers and users assume all responsibility and liability for loss or damage arising from the services provided.