INNOVATIVE BIORENEWABLE THERMOPLASTIC ELASTOMERS

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BIOGRAPHICAL NOTE

Dr. Krishna Venkataswamy is the Senior Director, Global Research and Development for GLS Thermoplastic Elastomers, PolyOne Corporation. He has been active in the TPE industry for the past 22 years and at GLS since 2001. He has held technology leadership positions at GAF Materials Corporation, Advanced Elastomer Systems (ExxonMobil) and Monsanto. He has developed many commercially successful products in the consumer, medical, automotive and industrial applications. Krishna has authored more than 50 technical papers and patents. He has received "SPE Fellow" award in 2006 for his technical and leadership contributions in Thermoplastic Elastomers. In addition, he has received SPEs "Outstanding Achievement Award for Leadership" in 1999. He has been the recipient of "Sherwin-Williams" award in Applied Polymer Science from the American Chemical Society in 1986 for a paper from his Ph.D work. Krishna has been very active in SPE; Current Chairman of New Technology Forum, Past Chair of EPSDIV and Board member Akron Section, Past Chair of SPE TPE Topical conferences including the first two-day International Symposium on TPEs during ANTEC during mid-90s. He has a BS in Chemical Engineering from the Indian Institute of Technology, Madras, an MS in Materials Science & Engineering from University of Florida and a PhD in Polymer Science and Engineering from Case Western Reserve University.

ABSTRACT

Thermoplastics elastomers (TPEs) have been traditionally compounded and manufactured from raw materials based on fossil fuels. In PolyOne's GLS Thermoplastic Elastomers business, we have focused our innovative developments to meet market needs by creating a suite of new TPE technologies based on biorenewable resources. In this paper we introduce our innovative biorenewable TPE technologies OnFlex™ BIO and Versaflex™ BIO, which have been recently launched as commercial products. Versaflex™ BIO is based on our latest invention in thermoplastic elastomers with very high renewable content, a broad hardness and performance range. Our novel compounded TPEs are the softest in their class with highest biorenewable contents up to 80%. Our latest biorenewable TPE technology offers our customers the broadest range of useful performance compared to other commercially available traditional reactor produced biorenewable TPEs.

DEFINING SUSTAINABILITY

The report of the Brundtland Commission (formerly the World Commission on Environment and Development, WCED), "Our Common Future" was published in 1987 and deals with the political changes necessary for sustainable development. This report contains a definition of sustainability which is often quoted:

> *"Sustainable development meets the needs of the present without compromising the ability of future generations to meet their own needs."*[1]

The responsibility of businesses in sustainability has evolved since 1987 and an expanded view of the values and criteria concerning sustainability is the "triple bottom line", i.e., people, planet and profit. This concept suggests that three broad elements, societal, environmental and financial, need to be balanced for a company to be viable in the long-term. Any element that is ignored for short-term results will lead to long-term consequences. This concept also recognizes that sustainable solutions also need to provide economic value in order to be viable and those economic incentives which neglect environmental or societal needs are not sustainable.[2]

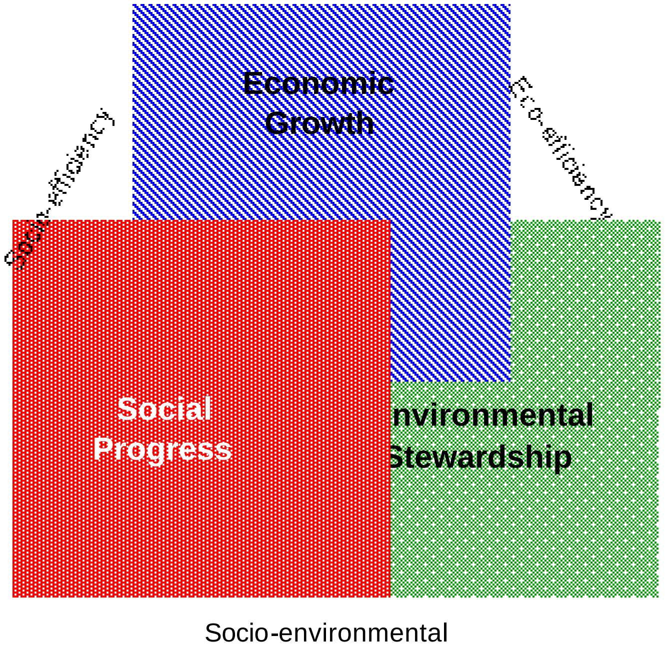

Figure 1. "Triple Bottom Line" of People, Planet and Profit

In the triple bottom line model “People” relates to the responsibility of a company towards its labour force, communities and the regions in which it conducts its business. For example, a company adopting the triple bottom line model would seek to benefit the groups in which it is involved. In practice this is difficult to quantify and can be subjective, but new initiatives are being developed which standardize reports on the social impact of a business.[3]

The term “Planet” refers to the sustainability of environmental practices. Companies adopting this model seek to limit environmental impact as much as their business practices. This may be achieved by various means including energy management, material sourcing, waste management and life cycle management of products.

The third term, “Profit” not only captures the monetary viability of business practices but also the economic benefit of societies affected by a business.

SUSTAINABLE SOLUTIONS

We have established the “PolyOne Sustainable Solutions” certification to denote those products or services that meet defined standards for sustainability in areas such as renewability, recyclability, reusability, eco-friendly composition or resource efficiency. Each of these categories has been detailed in the proceeding sections. Our new TPEs provide sustainable solutions in each of these categories.

Reusable

Reusability considers packaging and other logistics related systems which are easily returned or reused. We have worked with customers to develop packaging & logistical solutions which help reduce waste and save costs. Furthermore, PolyOne has pioneered novel, proprietary dusting systems which allow bulk packaging of TPEs that might otherwise have required more wasteful and costly packaging.

Recyclable

Recyclability considers solutions which incorporate post-consumer or post-industrial recycled content or which lend themselves to recycling such as our PlanetPak™ packaging system. Our TPE solutions are used in many cases to replace thermoset rubber when applications are re-designed and updated. Among the various other advantages that come from processing thermoplastic materials, recyclability is a key factor for many processors when specifying TPE in place of thermoset rubber. Not only can scrap produced during production (i.e. sprues) be ground and re-introduced with the virgin material, but finished articles can be reprocessed and recycled as well.

TPEs can also make use of recycled products as a component of their formulation, for example employing post-consumer waste such as recycled tyres, or post-industrial waste such as rubber dust or leather fibres. Not only can these compound components provide sustainable solutions they can also reduce cost and provide functionality.

Eco-Conscious Composition

Eco-conscious compositions are those solutions which respond to the ever-changing market needs by offering alternatives to traditional ingredients such as lead, bisphenol-A (BPA), phthalates and halogens. In many of the markets served by TPEs, there are compounds available which address current concerns. For the healthcare market, TPEs are designed to be phthalate free, plasticizer free and with low extractables, thereby meeting toughening regulations and addressing real or perceived patient safety concerns[4]. TPEs typically employ medical quality mineral oils which are much less scrutinized, but for the most sensitive applications plasticizer free TPEs offer the lowest level of extractables and leachables. Combined with careful component selection and specialized compounding techniques, TPE compounds can offer a very high level of purity and safety.

Renewable

Renewable solutions are those which employ or support the use of renewable, compostable or biodegradable resources. TPE compounds based on renewable substances help sustainable development by reducing the carbon footprint of plastic usage. Managing carbon in a sustainable manner is a central issue of sustainable development. It is generally accepted that a continued increase in the levels of CO_2 in the atmosphere will hasten climate change with dramatic effects on people and the planet in the long term. Traditional polymers are based on fossil feed stocks whose rate of carbon fixation is in millions of years, whilst their rate of release of carbon into the environment is 1-10 years. Clearly this is unsustainable. On the other hand polymers which are produced from plant based, renewable feed stocks have their end-of-life CO_2 release absorbed during the next planting season, thus balancing the CO_2 release and trending towards a zero carbon footprint.[4]

Photoautotroph such as plants fixes carbon from CO_2 in the atmosphere by reacting with water during the process of photosynthesis. This process produces organic compounds such as sugar for food and produces oxygen as a by-product. Plant materials are fossilized over millions of years providing the oil, gas and coal which today we use for fuel, chemicals and plastics. The use of fossil fuels creates an imbalance between the rate at which carbon is fixated and the rate at which it is released, clearly an unsustainable process.

$$\mathrm{CO_2} + \mathrm{H_2O} \xrightarrow{\textbf{Sunlight}} (\mathrm{CH_2O})_n + \mathrm{O_2}$$

Figure 2. Reaction of Photosynthesis

Polymers produced from bio based materials may be derived from renewable resources by chemical methods, mechanical methods or produced directly by biological processes.

TYPES OF RENEWABLE TPE POLYMERS

A number of different reactor produced TPE polymers have been commercialized by various manufacturers over the last few years.

Arkema's Pebax Rnew is a polyether-block-amide (PEBA) block copolymer consisting of segments of amino-11 and polyether. Since amino-11, is a derivative of castor oil, it is a biorenewable polymer with low environmental impact. Arkema's biorenewable TPEs contain 26-90% renewable content and have hardnesses from 35 to 72 Shore D. The higher renewable content (>60%) is for products greater than 60 Shore D which are not useful as elastomers. They are promoted for various applications including electronics, shoes and automotive.[5,6]

DuPont's renewable Hytrel RS thermoplastic polyester elastomers are based on their Cerenol polyols derived from bio-propanediol produced from corn sugar using a patented bacterial fermentation process. They contain 20 to 60% renewable based material. Hytrel RS thermoplastic elastomers have hardnesses in the range of 30 to 83 Shore D and are promoted for use in applications such as hoses, tubing boots, energy dampers and airbag doors in automotive and industrial markets.[7]

Merquinsa's Pearlthane ECO TPUs are produced from specially derived vegetable based polyols reacted with isocyanates in a novel patent pending process. Whilst polyurethane foams using plant based polyols have been around for some time, difficulty reacting these polyols has restricted their use in thermoplastic applications, until now. Merquinsa's Pearlthane ECO TPUs contain from 30 to 90% renewable content according to ASTM D6866 and offer performance at least as good as traditional, high performance PCL based TPUs. Products are available in hardnesses from 85 to 95 Shore A.[8]

BIO-SOURCED, BIODEGRADABLE OR COMPOSTABLE

Bio-plastics may be produced from renewable resources, biodegradable, or both. Synthetic polymers either naturally or by virtue of chemical modification or the addition of certain additives can biodegrade making waste handling simpler. Polycaprolactone (PCL) is one such example.[9] Certain bio plastics may be sourced from renewable resources but are not biodegradable, as are the main subjects of this paper, OnFlex™ BIO and Versaflex™ BIO.

The term biodegradation is not consistently used or clearly defined. It may be used to mean fragmentation, loss of mechanical properties or degradation through the action of living organisms. Sometimes deterioration or loss of integrity is mistakenly considered to be biodegradation. Even the speed of degradation has to be taken into account. For example LDPE has been shown to biodegrade slowly to produce carbon dioxide (0.35% over 2.5 years).[10]

Compostable means that materials will biodegrade in a composting situation, that is, together with plant material in an aerobic environment. Compostable plastics will biodegrade completely in the industrial compositing facilities. Not all biodegradable plastics are suitable for composting, as degradation may take too long or require higher temperatures to biodegrade completely. The European standard EN13432 and the American standard ASTM D6400-04 helps to determine which plastics are compostable.[11]

In any case biodegradation of a material concerns only one aspect of its environmental impact and whilst it can be considered as part of an integrated waste management plan, it must be considered along with other issues such as the material source and carbon footprint. In durable applications such as industrial and automotive markets biodegradation is undesirable. In this case alternative methods of disposal must be investigated.[4]

INNOVATIVE BIORENEWABLE TPEs AND THEIR PHYSICAL PROPERTIES:

We have developed innovative thermoplastic TPE compounds based on two different reactor based TPE polymer chemistries to offer a wide range of hardness, physical properties, functionality and end use performance.

OnFlex™ BIO

In 2008, we launched two ranges of OnFlex™ BIO renewable based thermoplastic elastomers. These product lines extended the functionality and performance of renewable thermoplastic elastomers available on the market opening up a wider range of applications and options for sustainable solutions. Based on Merquinsa's patent-pending Pearlthane® ECO technology these products feature at least 20% renewable material as certified by ASTM-D6866, meeting global market needs for sustainable and environmentally-friendly products.

The OnFlex™ BIO 5100 series as in Table 1 are glass fiber reinforced compounds which offer high stiffness in combination with excellent abrasion and impact resistance, a low coefficient of thermal expansion and excellent mechanical properties.

Table 1. Physical Properties of OnFlex™ BIO 5100 series

	Hardness (Shore)	Density (g/cm^3)	Tensile Strength (MPa)	Elongation at Break (%)	E-Modulus (N/mm^2)	Impact Resistance (Unnotched)		Renewable Content (%)
						Charpy (+23°C) (kJ/m^2)	Charpy (-40°C) (kJ/m^2)	
Grade	DIN 53 505	DIN EN ISO 1183	DIN 53 504	DIN 53 504	DIN EN ISO 178	DIN EN ISO 179-1	DIN EN ISO 179-1	ASTM D6866
OnFlex™ BIO 5170D-E0010	**70D**	1.34	65	15	1200	NB	30.0	34
OnFlex™ BIO 5180D-E0014	**80D**	1.45	75	15	2500	97.0	34.0	30

Typical applications for OnFlex™ BIO 5100 are industrial applications in demanding environments, sports equipment components such as ski bindings and caster wheels.

The OnFlex™ BIO 5300 series compounds (Table 2) are designed to offer the performance of traditional TPUs but with a wider range of hardness and easier processability. These compounds have been designed to process well in injection molding, extrusion and calendaring processes. Moreover these compounds offer exceptional abrasion, scratch and impact resistance, excellent tensile and tear performance, and adhesion to a wide range of substrates. OnFlex™ BIO compounds are available from hardnesses of 70 Shore A upwards. Typical applications for OnFlex™ BIO 5300 compounds include automotive instrument panel skins, door panel skins, interior trim, gear knobs, shoe soles and grips on sports equipment.

Table 2. Physical Properties of OnFlex™ BIO 5300 series

	Hardness (Shore)	Density (g/cm^3)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at Break (%)	Tear Resistance (N/mm)	Abrasion Resistance (mm^3)	Renewable Content (%)
Grade	DIN 53 505	DIN EN ISO 1183	DIN 53 504	DIN 53 504	DIN 53 504	DIN 53 504	DIN 53516	ASTM D6866
OnFlex™ BIO 5370A-E0004	**70A**	1.05	11.9	8.5	410	45.1	63	21
OnFlex™ BIO 5380A-E0006	**80A**	1.07	19.9	10.2	507	63.7	38	25

Versaflex™ BIO

Versaflex™ BIO series in Table 3 consists of a range of unique, patent pending renewable TPE compounds with some very special aspects. These are based on novel and innovative compatible blends of a reactor produced TPE polymer, cross-linked elastomer and additives. These are the newest and most advanced renewable TPE solutions available globally. They were launched in 2009 at the NPE exhibition in Chicago. Versaflex™ BIO compounds are unique for their highest renewable content (up to 80%) for the hardness range of 20 Shore A to 90 Shore A with lowest specific gravity. They are the softest renewable products on the market today, achieving performance currently unattainable with reactor polymer technologies.

Table 3. Physical Properties of Versaflex™ BIO series

	Hardness (Shore)	Specific Gravity	Tensile Strength (MPa)	Modulus @ 100% (MPa)	Elongation at Break (%)	Tear Resistance (kN/m)	Compression Set (%, 22h@22°C)	Renewable Content (%)
Grade	ASTM D2240	ASTM D792	ASTM D412	ASTM D412	ASTM D412	ASTM D624	ASTM 395B	ASTM D6866
LC 343-060	**22A**	0.99	1.57	0.66	300	2.41	--	64
Versaflex™ BIO 5550-40	**42A**	1.00	2.71	1.54	240	13.6	17	70
Versaflex™ BIO 5550-50	**52A**	1.00	4.18	2.12	300	19.1	20	68
Versaflex™ BIO 5550-60	**62A**	1.00	5.76	2.90	315	29.1	20	65
Versaflex™ BIO 5550-70	**68A**	1.00	7.34	3.42	450	47.1	21	66
LC 359-079B	**81A**	1.00	10.78	6.81	200	48.9	34	78
LC 359-079C	**88A**	1.01	11.78	7.94	215	62.7	31	79

Not only do Versaflex™ BIO compounds offer very high levels of renewable content, they also help to reduce environmental impact through their low specific gravity, recyclability and ease of processability.

DYNAMIC MECHANICAL ANALYSIS (DMA): Viscoelastic and Phase behaviour

DMA is particularly useful for determining viscoelastic behavior and phase transitions of a material, such as glass transition temperature(T_g) which can usually be easily identified by the peak of tan d. However, the peak location depends on the heating-rate and the frequency which may lead to different results than those obtained by differential scanning calorimetry (DSC).[12] DMA was conducted on samples of Versaflex™ BIO in order to understand the phase behaviour of these novel complex blends and to predict the performance of these compounds at different temperatures.

Figure 3 illustrates the storage modulus G' and loss modulus G'' curves for two Versaflex™ BIO compounds across a range of temperatures. These curves indicates that these Versaflex™ BIO compounds have good flexibility between -30°C and above 100°C. TPEs show a single transition as seen by the data.

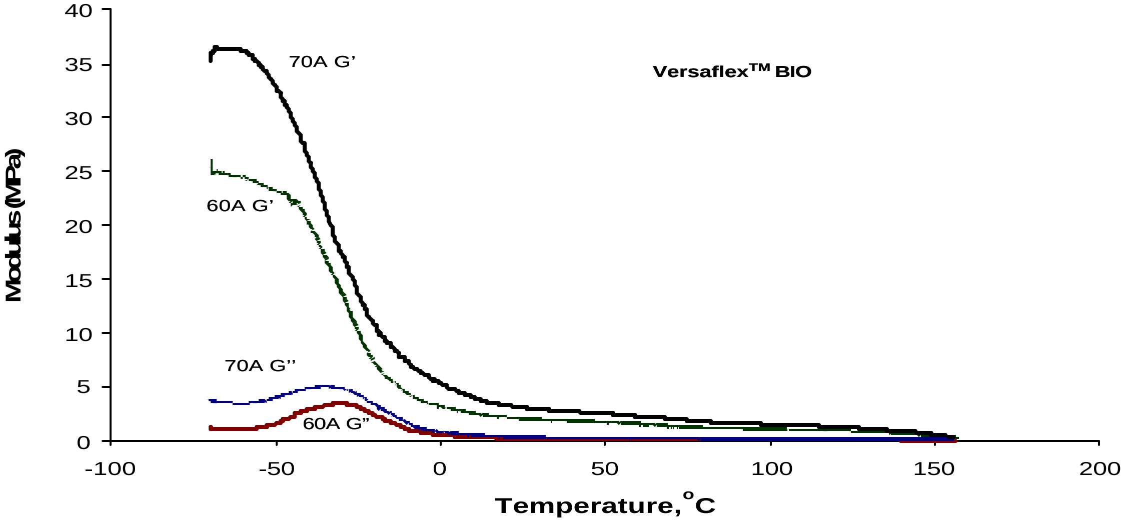

Figure 3. Storage Modulus, G' and Loss Modulus. G'' of Versaflex™ BIO at 1 Hz

Tan d is another measure of the mobility which is the ratio of the storage modulus and loss modulus as shown below:

Tan d = G"/G'

Figure 4, shows tan d curves for two Versaflex™ BIO compounds across a range of temperatures and indicates good flexibility and toughness of the TPEs in functional performance.

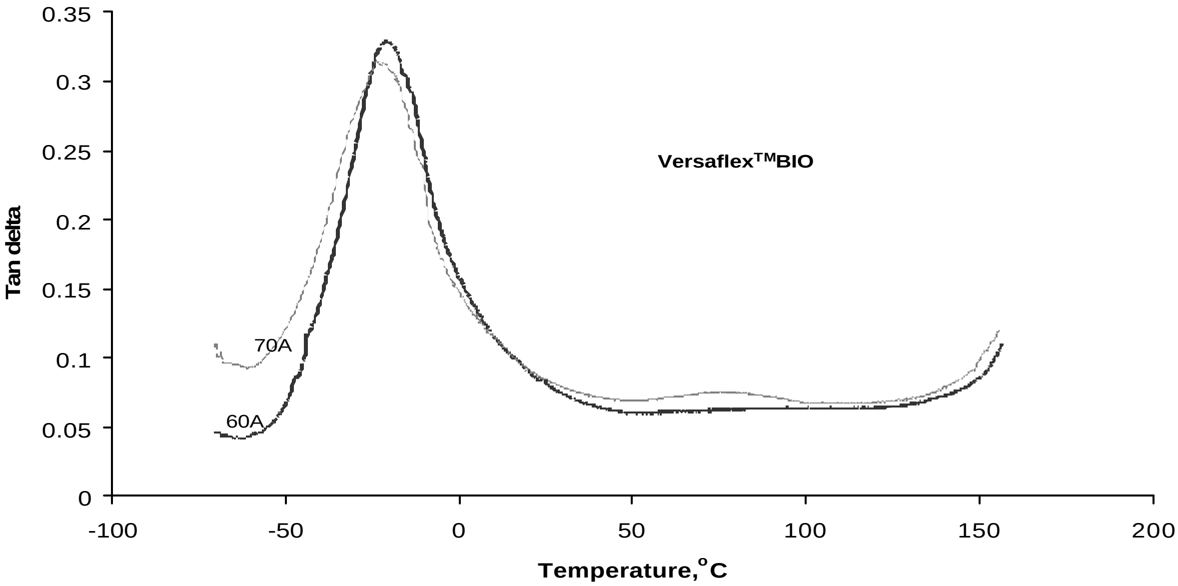

Figure 4. DMA Tan d curves for Versaflex™ BIO at 1 Hz

The unique ingredients employed in Versaflex™ BIO provide a wide range of hardnesses, flexibility across a wide temperature range and a high renewable content. A single T_g at low temperatures clearly indicates the miscibility of the softer segment of the reactor based polymer TPE with the cross-linked elastomer. There is a little shoulder around 75 °C which is a T_g of the amorphous phase of the reactor produced TPE elastomer in the compounded TPE.

MORPHOLOGY

A number of microscopic techniques are available to understand the morphology of multiphase polymer blends. Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) are the most commonly used methods. AFM technique is the most user friendly technique requiring minimum sample preparation.

For TPEs, AFM is usually conducted in the tapping mode, meaning the cantilever is oscillated by Peizo motion and brought into a light contact with the surface. As the oscillating cantilever taps the surface, energy is lost due to the contact of the tip with the surface. By measuring the cantilever amplitude information about surface morphology can be obtained. AFM characterizes hard and soft phases, based on the effect of the modulus of these regions on the cantilever.[13] This is particularly interesting for TPE blends which are typically composed of multiple ingredients of different hardness, crystallinity and other features.

Information collected in an AFM scan is quantitative in three dimensions. A micrograph can be presented as a topographical image with the elevation of each point encoded with a false color scale. A 3D image can be manipulated with a software, viewed from different angles, and measurements may be made on horizontal and vertical distances. Surface roughness can be calculated along lines or over planes.

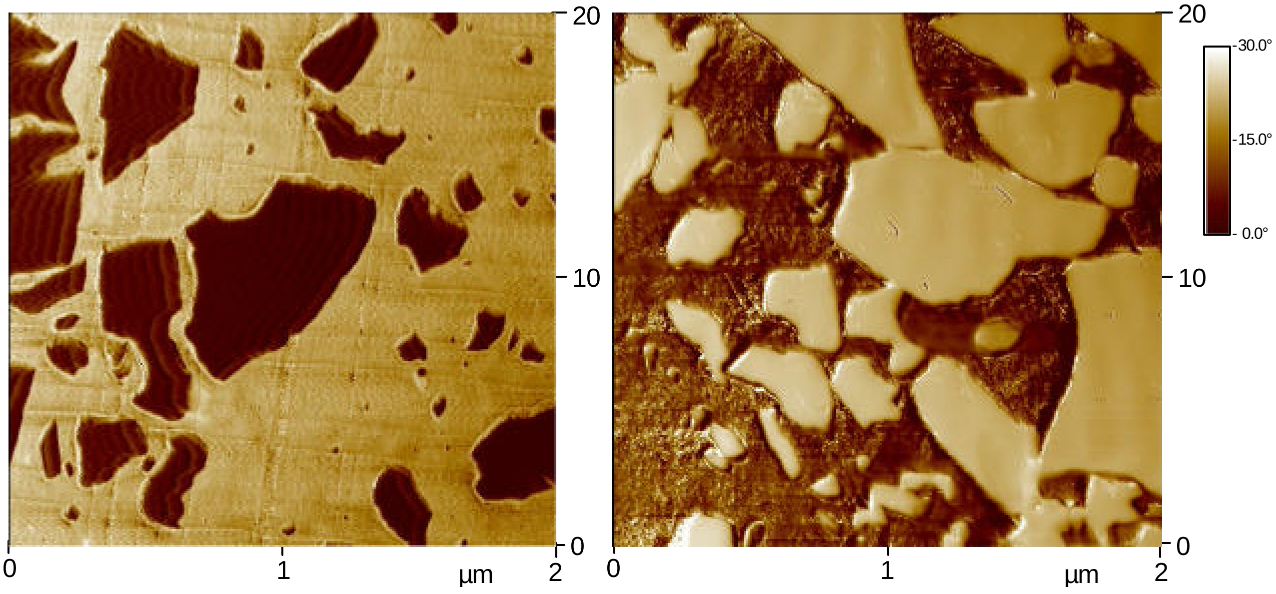

Figure 5. Atomic Force Micrographs (AFM) of Versaflex BIO™ 70A and 80A Morphology

Figure 5 shows AFM micrographs from two different Versaflex™BIO compounds. These micrographs clearly show phase separation on the µm scale. Interestingly, there is a phase change between 70 and 80 Shore A compounds; the co-continuous cross-linked elastomer (light) phase becomes dispersed into particles in a continuous reactor produced TPE matrix shown by the dark phase. These micrographs explain the improved elastic behavior and compression set for the 70 Shore A TPE compared to 80 Shore A with a penalty in tensile strength and 100% modulus.

FUNCTIONAL PERFORMANCE: Oil Resistance

Sebum oil and Skin So Soft™ exposure simulates functional performance in consumer applications, where as IRM- 903 Oil reflects the functional performance in demanding industrial and automotive applications.

We have compared test data from Versaflex™ BIO compounds with a typical TPE-S and TPE-V to benchmark their performance in Figure 6. We have looked at the % tensile change and % weight change after immersing samples in each oil at specified temperatures for two weeks.

We have chosen a 40 Shore A and 60 Shore A versions of the Versaflex™ BIO compounds for these evaluations and 60 Shore A for the TPE-S and TPE-V. The sebum resistance of Versaflex™ BIO is compared against typical TPE-S and TPE-V Compounds. Versaflex™BIO 5500-60 shows outstanding sebum resistance and is comparable to TPE-V.

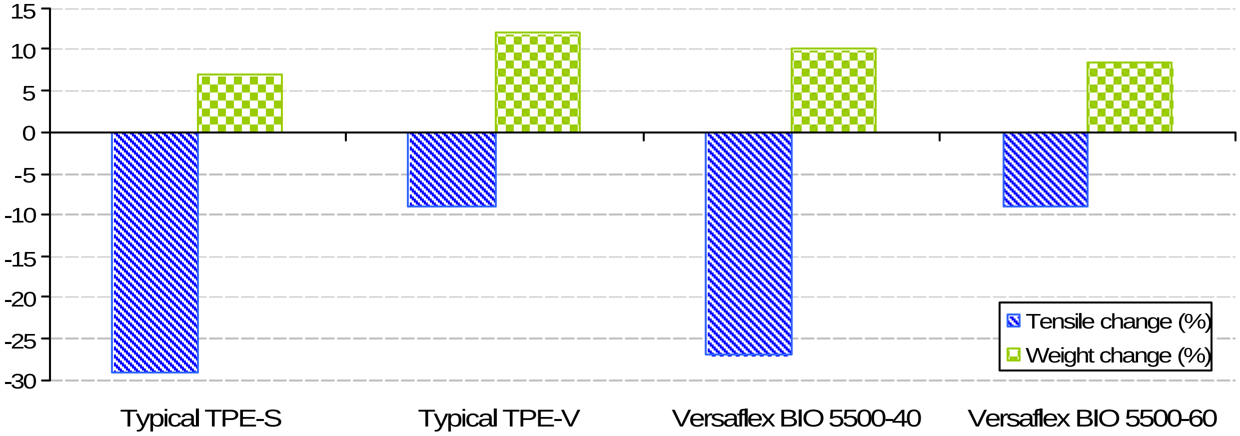

Figure 6. Sebum Resistance of Versaflex BIO™, TPE-S and TPE-V (2 weeks @ 40°C)

The soft, grippy nature of TPEs makes them attractive for use in grip applications. Among all renewable TPEs available Versaflex™ BIO is particularly appropriate for soft-touch grips due to its wide hardness range. In grip applications contact with various moisturizers and hand oils can lead to deterioration of performance, so Versaflex™ BIO was tested in contact with well known body oil, Skin So Soft™ lotion, a product of Avon Products Inc, and compared to traditional TPEs as a reference (Figure 7).

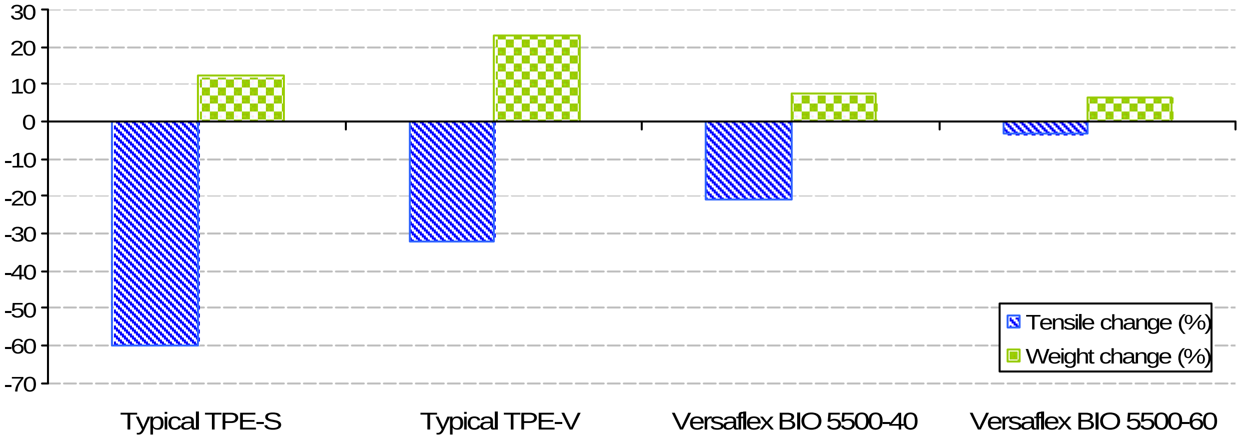

Figure 7. Skin So Soft™ Lotion Resistance of Versaflex™ BIO, TPE-S and TPE-V (2 weeks @ 23°C)

In Figure 8 performance of Versaflex™ BIO compounds in IRM 903 oil are compared to a traditional TPE-S and a TPE-V compound. Despite the highly aggressive nature of IRM 903 oil, Versaflex™ BIO performs very well, with almost no weight gain and very little change in tensile performance over the testing period. Not only does this corroborate the performance in contact with sebum and hand oils to which it might be exposed in consumer applications, but it also demonstrates performance that might be useful in industrial and automotive applications.

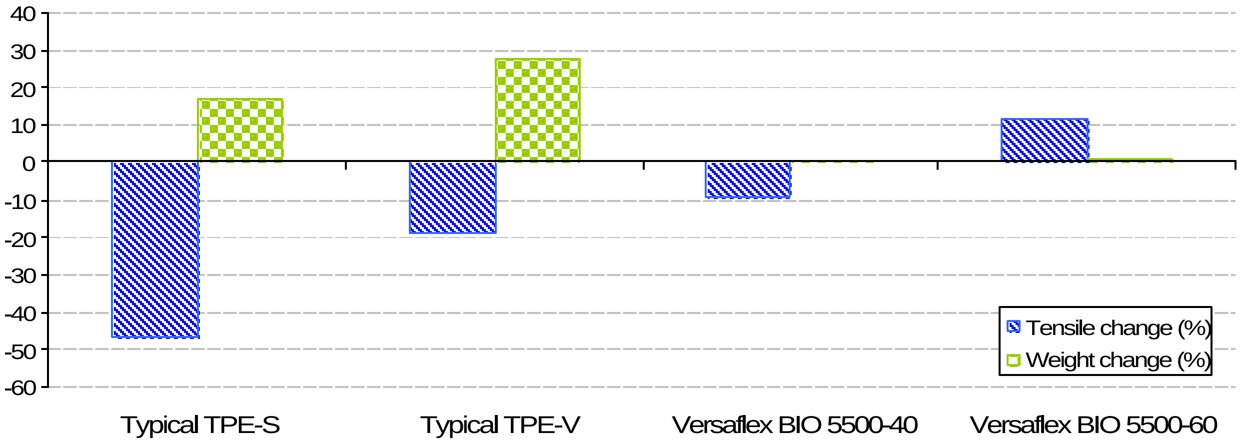

Figure 8. IRM 903 Oil Resistance of Versaflex^{TM} BIO, TPE-S and TPE-V (2 weeks @ 23°C)

RHEOLOGY, PROCESSING AND APPLICATIONS

The hardness range and novel combination of properties make Versaflex™ BIO suitable for a very wide range of applications. The capillary rheologies of Versaflex™ BIO TPEs are shown in Figure 9. The viscosity shows shear thinning behavior and is very similar to a typical robust TPE grade which has fabrication versatility. The capillary viscosities are nearly invariant for different hardness compounds at the measured range of shear rates.

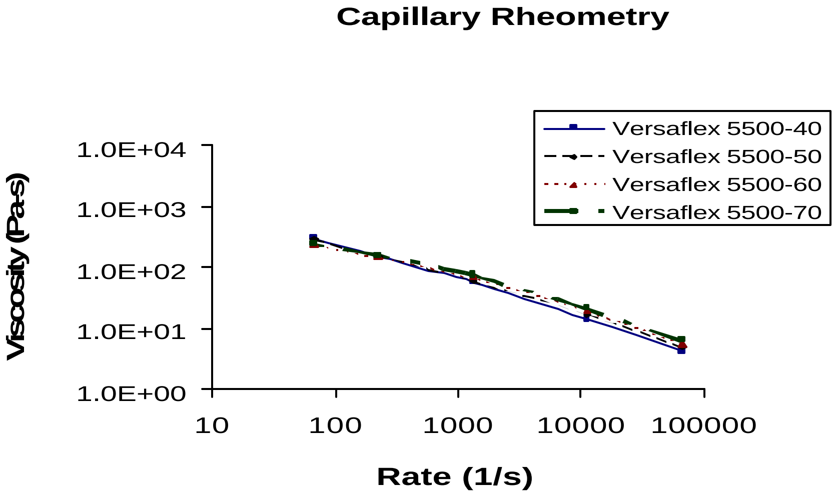

Figure 9. Capillary Rheology @ 200^{o}C of Versaflex^{TM} BIO

Versaflex^{TM} BIO exhibit very robust processing using multiple fabrication methods. Figure 10 shows three different fabricated forms produced from Versa flex™ BIO compounds. Figure 10 a) shows stepped plaques injection molded from Versaflex™ BIO. Differing thicknesses demonstrate the translucency of the compound.

A limited overmolding evaluation performed on these compounds indicates that they do not bond to polyolefins and have poor bonding to engineering plastics such as ABS and polycarbonate. Furher evaluations for other substrates are underway. At this time, Versaflex™ BIO is not recommended for overmolding applications.

Figure 10 b) shows a cast film extruded from Versaflex™ BIO, and Figure 10 c) shows a tube or hose extruded from Versaflex™ BIO.

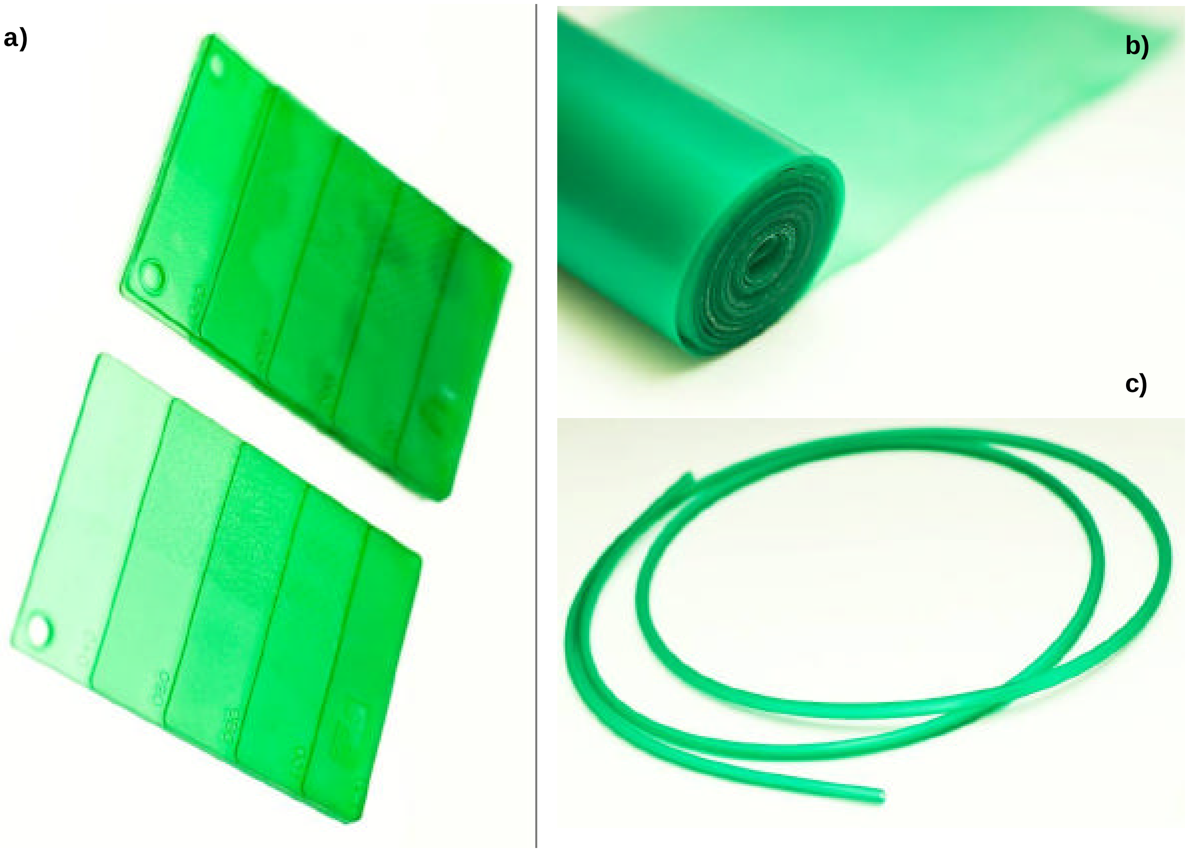

Figure 10. 70 Shore A Versaflex™ BIO a) Molded Plaques, b) Extruded Sheet , c) Extruded Hose

Figure 11 shows a blow-molded bottle produced from Versaflex™ BIO. This can provide durability, toughness and flexibility for demanding applications with limited environmental impact. Furthermore, Versaflex™ BIO can be processed by multiple fabrication methods and can be colored to suit desired economics and æsthetics.

Figure 11. 80 Shore A Versaflex™ BIO Blow-Molded Bottle

SUMMARY

A number of different renewable TPEs have been launched over the past several years. These have mostly been restricted to industrial applications due to their high hardnesses. In addition, they have fairly low biorenewable content. There has been little choice for designers and product manufacturers wishing to use soft or flexible products with a high renewable content.

The launch of OnFlex™ BIO in 2008 extended the range of renewable TPEs available by providing better flexibility and functionality than the available products. However, while OnFlex™ BIO provides outstanding mechanical and tribological performance, it has limited flexibility often required in consumer applications.

With the introduction of Versaflex™ BIO, converters are no longer limited in using soft TPEs with high renewable contents in the most demanding applications. This development has shown that Versaflex™ BIO compounds not only provide excellent flexibility but even expand the performance range. Versaflex™ BIO exhibits good Sebum, Skin So Soft™ and IRM 903 oil resistance making it suitable for consumer as well as industrial applications. Versaflex™ BIO TPEs have robust rheology, wide processing window and provide a wealth of fabrication opportunities for environmentally conscious designers

OnFlex™ BIO and Versaflex™ BIO can help TPE customers achieve their sustainability goals and reduce their environmental impact without compromising performance.

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