NEW DEVELOPMENTS IN THERMOPLASTIC ELASTOMERS WITH IMPROVED BARRIER PERFORMANCE

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BIOGRAPHICAL NOTE

Charles Page is the European R&D manager for PolyOne's TPE product lines. He graduated from Coventry University in 1999 with a B.Eng Materials Science degree, after which he began working in AlphaGary's UK production site as their TPE-S development technologist, he remained there for three years before moving to Germany to begin working within PolyOne's international TPE team, overseeing development of TPE-S, TPE-U, TPE-O and TPE-V product ranges.

ABSTRACT

Thermoplastic elastomers (TPEs) have reached a very high level of commercial importance, resulting in numerous new products and technology developments each year. Conventional TPEs typically exhibit very poor barrier properties. Manufacturers, especially in the area of food packaging and medical industries have a performance need of TPEs with improved barrier properties. GLS and PolyOne have developed multiple TPE technologies i.e. barrier TPEs that satisfy various segments of barrier requirements. This paper covers the recent developments and properties of medium barrier, high barrier, and super high barrier TPEs, as well as their application in food and medical packaging applications.

INTRODUCTION

The growth of TPEs has been propelled by their use in many applications, including consumer (1-3), medical (4), and food packaging areas. In consumer, medical, industrial and automotive applications, TPEs have not only replaced conventional thermoset rubbers, but also created newer application opportunities. TPEs often provide design freedom at a lower system cost for designers and manufacturers. They are considered as a cleaner, less cumbersome technology and have recycling potential. A subset of TPEs is the thermoplastic vulcanizate (TPV), a blend of continuous thermoplastic with discontinuous regions of crosslinked rubber. This paper concerns TPEs that are not TPVs.

In certain applications, end users would like to combine the advantageous properties of TPE with gas barrier properties. However, traditional TPEs have rather poor barrier properties. Figure 1 compares the oxygen permeability of standard TPEs with some common thermosets and thermoplastics. It can be seen that the barrier properties of TPE are far from meeting the demanding barrier applications.

In order meet the market need, GLS, which is now part of the PolyOne Corporation, has been developing multiple barrier TPE technologies. The new barrier TPEs include medium barrier (~10,000 to 20,000 cc.mil/m².day), high barrier (4,000 to 10,000 cc.mil/m².day), and super barrier technologies (from less than 400 to ~4,000 cc.mil/m².day). These novel TPE materials not only meet or exceed the barrier provided by thermoset butyl rubber, but also demonstrate good elasticity, easy processing, and low compression set. This paper concentrates on the properties and processing as well as the potential applications of these newly developed TPE materials.

APPLICATIONS

Many foods and beverages such as beer, isotonic sport drinks, juices, and dairy products require packaging in materials providing a high barrier to oxygen. Carbonated soft drinks require a good shelf life with respect to the loss of carbon dioxide. As well as permeation through a container oxygen and carbon dioxide can also permeate through plastic closures. Generally, the transmission of gas through closures is insignificant compared to that through a bottle; however with small bottles or larger closures the loss of carbon dioxide or oxygen ingress through the closure can be important. In these cases there can be value in fitting the cap with a gas barrier (5).

The shelf life of foods sensitive to oxygen is primarily dependent upon the gas barrier performance of the packaging materials used, where higher gas barriers can extend the time period during which food maintains an acceptable quality. Gas permeation is an important consideration when packaging food with plastics because food packaging plastics are generally permeable to moisture, oxygen, carbon dioxide, nitrogen and other gasses. For metal and glass packaging gas permeation is not such an important consideration, because these materials do not have the same level of permeability, however leakage can occur at the closure point, and therefore effective sealing is often necessary (6).

Modified atmosphere packaging is used to extend the shelf life of food by preventing moisture uptake, reaction with oxygen or microbial growth. These changes can render food unpalatable and potentially unsafe for human consumption. In this technique the atmosphere in which the food product is packaged is replaced with a gas other than air, typically oxygen, carbon dioxide or nitrogen, depending upon the food product being packaged. Gas permeation occurs when there is a difference in gas concentration between different sides of a material, so permeation is a threat to the stability of modified atmosphere packages. Therefore, use of materials exhibiting good gas barrier properties can help to extend the shelf life of modified atmosphere packaging products (7).

In medical applications thermoplastic materials are sometimes specifically engineered for high barrier applications. These materials are commonly used as medical device components, and also for various types of packages such as tubes, blown containers, molded closures and sheet material (8). For medical vials, tubes and vessels either designed for delivering pharmaceuticals or collecting samples, it is sometimes necessary to provide a gas barrier either to prevent the ingress of air or to protect drugs sensitive to oxygen. In these cases it is often desirable that the stopper is manufactured from an elastomeric material that can be punctured by needle, and that will reseal once the needle is removed.

Butyl rubber is an elastomeric copolymer of isobutylene with small amounts of isoprene (hence the abbreviation “IIR”). This thermoset rubber is notable for its exceptional resistance to gas permeability, exhibiting only 10% of the air permeability of natural rubber at 65°C. Being a thermoset elastomer it is necessary to cure butyl rubber before anything useful can be produced from it. In order to do so a compound of butyl rubber must be heated to a high enough temperature for a time long enough to cause a chemical reaction known as curing (9). Once cured, thermoset rubbers such as butyl rubber cannot be remolded or reprocessed, and therefore cannot easily be recycled.

Thermoplastic elastomers, on the other hand, offer the benefits of thermoset rubbers such as flexibility and elasticity, but can be re-melted by heating above a certain temperature. This property not only means that processing thermoplastic elastomers is as simple as typical thermoplastics, it also means that this family of materials is easily recycled.

Thermoplastic elastomers are well established in multicomponent molding applications where their ease of processability and affinity for a variety of substrates lends them readily to this technique. In applications such as seals and gaskets multicomponent molding can help ensure permanence and security of a seal during the lifetime of a product, and furthermore can reduce the needs and costs associated with assembly.

EXPERIMENTAL

Material

Three classes of barrier TPEs have been developed and are discussed in this paper. The developmental materials are as follows:

Medium Barrier (10^3-20^3 cc.mil/m^2.day): LC 321-005(50A), LC 321-089 (60A);
High Barrier (4^3-10^3 cc.mil/m^2.day): LC 321-073 (50A), OnFlex™-S LP XP3 (51A), OnFlex™-S LP XP4 (53A), LC 321-106 (60A), LC 321-162(65A);
Super Barrier (4^2-4^3 cc.mil/m^2.day): LC 321-074 (40A), LC 321-004 (45A), LC 321-085 (50A), LC 321-058(70A).

All components of the compounds were mixed and then compounded using a twin screw extruder at 300-500 rpm and temperatures of 180-240°C. The extrudates were then pelletized using an under water pelletizer system.

Injection Molding Of Plaques

A Milacron injection molding machine was used to prepare plaques for the measurements of physical and gas transmission properties. The barrel temperature of the injection molding machine was set from 180°C to 235°C (360°F to 455°F) and the injection velocity from 1.27cm/s (0.5 in/sec) to 3.05cm/s (1.2 in/s). The dimensions of the plaques produced were 12.7cm (5") by 15.24cm (6"). The plaques used for physical property testing were 3.05mm (0.12") thick and those for barrier property tests are 1.65mm (0.065") thick.

Physical Properties

The barrier TPEs were characterized for Shore A hardness (ASTM D2240), specific gravity (ASTM D792), tensile strength (ASTM D412), elongation at break (ASTM D412) and tear strength (ASTM D624).

Compression Set

Compression set measures the permanent set after sample compression and was performed at 25% compression for 22hours at 22°C and also 22h at 70°C (ASTM D395).

Oxygen Transmission Rate

Oxygen transmission rate was measured using MOCON 2/21 barrier tester according ASTM D3985. Injection molded plaques were tested at 23°C and 0% humidity and the resulting permeability was recorded as cc.mil/m^2.day. The test area is normally 50 cm^2, however, if the permeability of the specimen is too high (>16,000 cc.mil/m2.da), an aluminum mask with 5 cm^2 area is used to allow for more accurate testing.

Rheology

The viscosities of the barrier TPEs at different shear rates were measured using a capillary rheometer at 200~230°C by a method prescribed in ASTM D3835.

RESULTS AND DISCUSSION

Medium Barrier TPE

Although there are presently many applications in consumer and other applications for traditional styrenic block copolymer (SBC) based TPEs, these compounds typically have very poor gas barrier properties (50,000~60,000 cc.mil/m^2.day for oxygen). At GLS and PolyOne, we developed a new medium barrier TPE technology. This novel technology has kept the benefit of traditional SBC TPEs such as excellent flexibility, flow and processability, whilst reducing the oxygen permeability by 60-80% to 10,000 to 20,000 cc.mil/m^2 day. LC 321-005 and LC 321-089 are two examples of this technology. These compounds have a Shore A hardness of 50 and 60 respectively, however a broad range of hardness of 30-90A can be achieved with this technology.

Table 1 lists the physical and mechanical properties of LC 321-005 and LC 321-089, and compares these with traditional, non barrier TPEs. It can be seen from Table 1 that the barrier TPE has very similar physical and mechanical properties, except that it has much lower oxygen permeability. Rheology is another important property for TPE. Like other type of TPEs, the barrier TPE has low viscosity at high shear rate, and high viscosity at low shear rate (Figure 2), showing a high dependency of viscosity on shear rate. The medium barrier TPE can be designed for both injection molding and extrusion processes.

High Barrier TPE

High barrier TPEs were developed at GLS and PolyOne as a material of choice when a superior barrier is required versus medium barrier TPEs. With these compounds the barrier properties are a step better than medium barrier TPE but they still retain a good cost/performance ratio. These high-barrier TPEs have oxygen transmission rates in the range of 4,000~10,000 cc.mil/m^2.day. Several examples of high barrier TPEs are listed in Table 2. For medical and food packaging applications, especially seals, gaskets, cap liners, and medical stoppers, low compression set is very important for good sealing. Table 2 shows that the compression set of some of these high barrier TPE is quite low, approaching the compression set performance of traditional TPVs (at 70°C). Figure 3 shows the viscosity curve of high barrier TPEs, however the formulation can easily be adjusted to achieve low, medium, or high viscosities based on the process requirement, allowing the high barrier TPEs to be use in a wide variety of processing methods.

Super Barrier TPE

Super barrier TPEs have also been developed for the most demanding barrier applications, where ultra low permeability is required. The barrier properties of these compounds are in the range of 400 to about 4,000 cc.mil/m^2.day. This dramatic improvement over the high barrier TPE technology is achieved through an entirely new and novel technology approach, not just different barrier numbers. Table 3 lists the properties of some super high barrier TPEs. We can see from the table that this new class of TPEs have a hardness range from 40-70A and oxygen transmission rates as low as 400 cc.mil/m^2.day. These examples show that the super high barrier TPEs are truly a unique new class of TPE which can meet the most demanding barrier applications on the market. A couple of formulations in the table have relatively high compression set at 70°C. However, the formulations of these compounds can easily be adjusted to improve compression set values without significantly affecting the super high barrier performance.

CONCLUSIONS

A range of barrier technologies have been developed at GLS and PolyOne meeting the different requirements of food packaging and medical industries. In this paper the properties of medium barrier, high barrier, and super high barrier TPEs have been discussed and compared. It can be concluded that these barrier TPEs have a broad range of barrier performance, as well as different hardnesses, flow characteristics, and elasticity. Furthermore, these technologies can be processed using different processing technology such as injection and extrusion. In comparison with existing materials used in elastomeric barrier applications these specialty TPE compounds are cost effective, clean and safe, recyclable and easy to process offering fast, rapid, low cost processing.

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Figure 1; The oxygen permeability of TPEs compared with common thermoset and thermoplastics at 22℃.

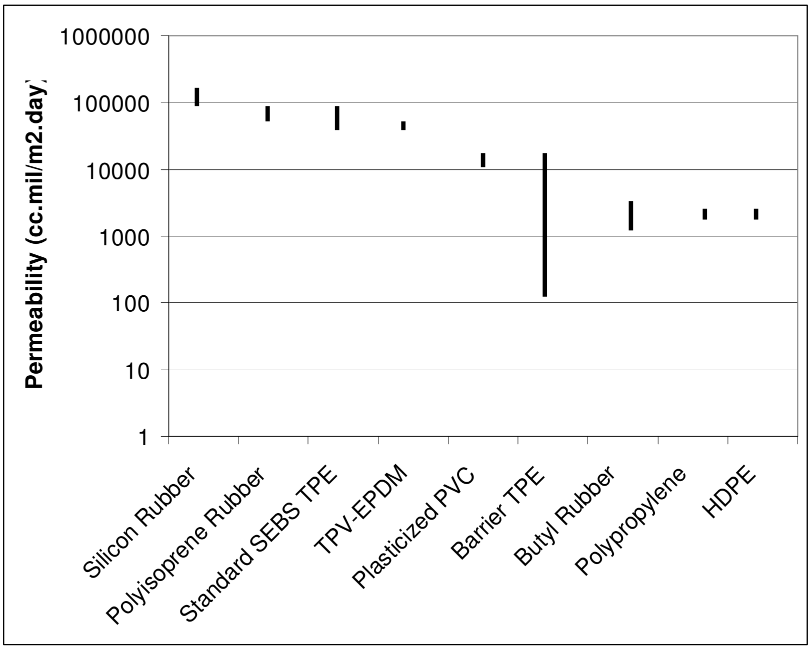

Table 1; Properties of Medium Barrier TPEs Compare with Traditional Non-Barrier TPEs

Material	LC 321-005	Non-Barrier TPE 1	LC 321-069	Non-Barrier TPE 2
Shore A Hardness	50	50	60	58
Specific Gravity (g/cm³)	0.90	0.89	0.90	0.90
Modulus at 100% (psi / MPa)	239 / 1.65	220 / 1.52	331 / 2.28	310 / 2.14
Modulus at 300% (psi / MPa)	463 / 3.19	350 / 2.41	447 / 3.08	540 / 3.72
Tensile Strength (psi / MPa)	778 / 5.36	840 / 5.79	1072 / 7.39	1160 / 8.00
Tensile Elongation (%)	745	760	777	690
Tear Strength (psi / MPa)	149 / 1.02	140 / 0.97	186 / 1.28	180 / 1.24
Oxygen Permeability (cc.mil/m².day)	15,100	50,00-60,000	14,100	50,000-60,000

Figure 2; Viscosity Curves of Medium Barrier TPE

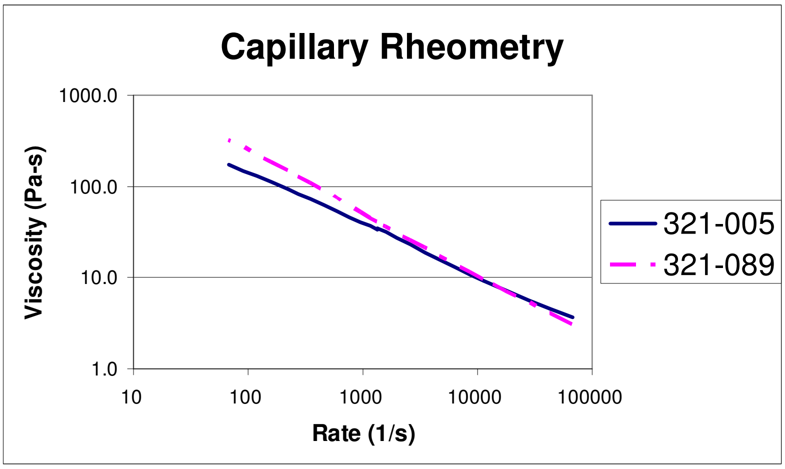

Table 2. Properties of High Barrier TPEs

Material	LC 321-073	OnFlex-S LP XP3	OnFlex-S LP XP4	LC 321-106	LC 321-162
Shore A Hardness	50	51	53	60	65
Specific Gravity (g/cm³)	0.94	0.95	0.96	0.93	0.92
Modulus at 100% (psi / MPa)	294 / 2.03			298 / 2.05	311 / 2.14
Tensile Strength (psi / MPa)	345 / 2.38	813 / 5.61	1000 / 6.89	381 / 2.63	351 / 2.42
Tensile Elongation (%)	166	269	276	228	181
Compression Set (22h @ 22°C)	27	24	22	27	29
Compression Set (22h @ 70°C)	28	76	73	33	36
Oxygen Permeability (cc.mil/m².day)	3,900	9,900	4,300	5,000	4,100

Figure 3. Viscosity Curves of High Barrier TPEs

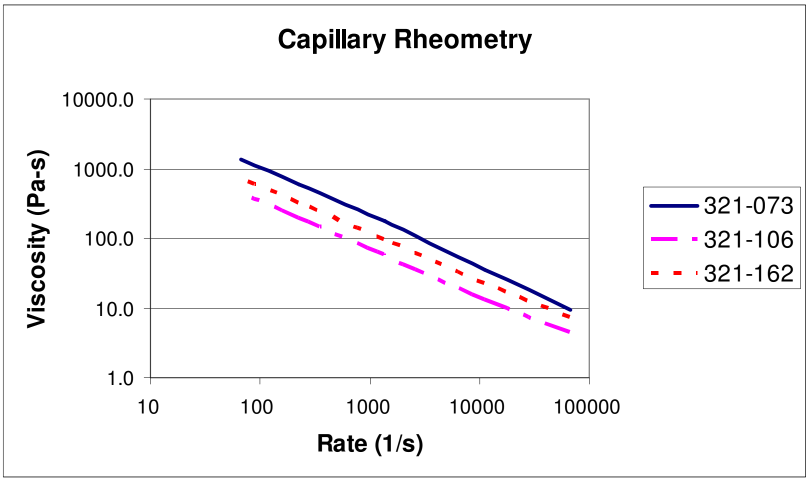

Table 3. Properties of Super Barrier TPEs

Material	LC 321-074	LC 321-004	LC 321-085	LC 321-058
Shore A Hardness	40	45	50	70
Specific Gravity (g/cm³)	0.95	0.93	0.94	0.99
Modulus at 100% (psi / MPa)	204 / 1.41	230 / 1.59	250 / 1.72	1500 / 10.34
Tensile Strength (psi / MPa)	208 / 1.43	264 / 1.82	255 / 1.76	1780 / 12.27
Tensile Elongation (%)	118	178	109	226
Compression Set (22h @ 22°C)	24	16	28	27
Compression Set (22h @ 70°C)	26	24	44	93
Oxygen Permeability (cc.mil/m².day)	2,100	3,900	2,00	400

Figure 4. Viscosity Curves of Super High Barrier TPEs.