Novel Thermoplastic Elastomers with Universal Bonding Characteristics

Dr. Liang Xu, Dr. Sehyun Kim, Dr. Krishna Venkataswamy, John Simons[1]
1. GLS International, Rilland, Netherlands

GLS Corporation, 833 Ridgeview Drive, McHenry, IL 60050
Tel: 815-385-8500 Fax: 815-385-8533 email: info@glscorp.com Web: www.glscorp.com

BIOGRAPHICAL NOTE

John Simons is currently employed by GLS International Inc. as Business Manager Europe. GLS International Inc. is part of GLS Corporation, a world-wide leader in TPEs that is located in McHenry, USA. John started his career in the adhesives industry where he worked for about 22 years in various jobs. After his chemistry study in 1979 he joined a local Dutch adhesive supplier called Verbunt Chemie. Over the years his responsibilities at Verbunt Chemie included: Product Development, Quality Management, and Purchasing.
After 12 years at Verbunt Chemie John accepted a job at Hercules Inc. as Hot melt Adhesive Chemist and was promoted over a 7-year period to Senior-Chemist, Hot Melt Department Team Leader, and Applications Manager.
In 1998 he joined Bostik Findley, the world's 2nd largest adhesive manufacturer as R&D Manager Nonwovens Europe. In this position he was responsible for managing Bostik Findley's European Hot Melt Adhesive R&D, Product Development, and QC labs for the nonwoven market. After 4 years at Bostik Findley John joined GLS in January 2002.

ABSTRACT

Overmolding thermoplastic elastomers (TPEs) on rigid substrates for consumer applications has been driven by the escalating market trends in enhanced ergonomic feel and touch, grip ability, aesthetics, cushioning against impact, vibration isolation and insulation. Polarity of the substrate dictates the chemical nature of the thermoplastic elastomer and hence the properties and the performance of the thermoplastic elastomer. This paper introduces novel developments in themoplastic elastomers which have the uniqueness of universally bonding to non-polar substrates such as polypropylene at the same time exhibiting outstanding bonding characteristics to various polar substrates.

INTRODUCTION

A hard/ soft combination of TPEs and rigid thermoplastics provides differentiations of a product in various applications (1). This hard/soft combination design has been driven by an escalating market trend pushing toward enhanced ergonomic feel and touch, gripping feel, aesthetics, cushioning against impact, vibration isolation or dampening and insulation. Overmolding technology facilitates such a combination. Although overmolding requires a new tool and sophisticated equipments, the demand in TPE materials overmoldable onto various substrates has significantly increased since the 1990s. This is because overmolding eliminates the traditional bonding process which requires adhesives and primers for bonding and instead allows the surface of an article of complicated design to be conveniently covered. As such, overmolding presents an opportunity to design articles that have not been possible with the traditional bonding process.

Over the years, many rigid thermoplastics have been utilized with this hard/soft design in order for specific performance and additional value. Rigid thermoplastics include both commodity thermoplastics and engineering thermoplastics, such as polypropylene (PP), polystyrene (PS), high impact polystyrene (HIPS), polycarbonate (PC), acrynitrile-butadiene-styrene (ABS), poly(ethylene terephthalate) (PET), poly(methylmethacrylate) (PMMA), styrene acrylonitrile (SAN), poly(phenylene oxide) (PPO), polyamide (PA), PC/ABS blend and PPO/PS blend etc..

Demands for TPEs that would bond to countless rigid thermoplastics substrates have propelled the development of numerous novel TPEs in recent years. Most of the new TPEs are designed based on the concept of matching the surface energy between the TPEs and the substrates. Figure 1 shows the surface energy match of various thermoplastic elastomers with rigid thermoplastics. These TPEs usually have good adhesion on substrates with similar surface energy. However, their adhesion on other substrates is poor. For example, a TPE that can bond to PC does not bond to PP, vice versa. Thus, one of the limitations for most of the existing TPE overmolding technology is that one needs to develop and use different TPE materials for different substrates.

Venkataswamy et al. (1) introduced a general guideline of overmolding and a choice of material with respect to the substrates employed for the applications. Novel TPE materials that can overmold onto various engineering plastics also were reported elsewhere (2-4). This paper concentrates on a new class of TPEs that can bond to a number of substrates with dissimilar surface energy or polarity, such as PP, ABS, PC and COPE, etc., called "universal overmolding TPE." This new technology opens up unprecedented opportunities for new designs where the TPEs need to bond to dissimilar substrates. Also, this new technology can reduce cost by reducing the number of TPEs needed for different applications.

EXPERIMENTAL

Material

Two classes of "universal overmolding TPEs" have been developed and used in this study. TPE-1 and TPE-2 have a hardness of 40-45 and 50-55 Shore A, respectively.

Injection molding of plaques

A Milacron injection molding machine was used to prepare plaques for the measurements of physical properties and adhesion. Plaques for the measurement of adhesion were prepared by injection molding TPE materials onto cold inserted rigid thermoplastic substrates. 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 15 mm/sec to 65 mm/sec.

Physical property

Both 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).

Adhesion

The adhesion between the TPE and rigid thermoplastics substrates was measured by a “90 degree peel test” which is a modified ASTM D903 method. Figure 2 shows a schematic diagram of the test. This test is done on overmolded plaques with TPE on top of rigid thermoplastic substrates. A 25 mm wide strip of TPE is cut and pulled at a 90^o angle toward the substrate using an Instron tensile tester. The substrate is locked in its place on wheels in order to maintain the 90^o angle as the elastomer is pulled. The adhesion strength, i.e., peel strength, is measured by the force required to pull the elastomer from the substrate and is reported as an average or a maximum strength over 50 mm of pulling. The adhesion is also categorized based on a visual observation of the failure mode, i.e., an adhesive failure if no TPE residue is left on the substrate or a cohesive failure if the failure is in TPE.

Rheology

The viscosities of both TPE-1 and TPE-2 at different shear rates were measured using a capillary rheometer at 200^oC by a method prescribed in ASTM D3835.

RESULTS AND DISCUSSION

TPE-1

TPE-1 materials have a shore A hardness at 40-45 Shore A. TPE-1A is translucent and TPE-1B is opaque. Table 1 gives the physical properties of TPE-1A and TPE-1B, including tensile strength, tear strength and elongation at break. Figure 3 shows the capillary viscosity of TPE-1A, B at 200°C, which has good flow characteristics for injection molding applications.

Table 2 lists the substrates employed for the overmolding of TPE-1A, B and the corresponding adhesion strength on the different substrates. As given in Table 2, TPE-1 demonstrates good adhesion on all ten substrates with very different surface energy and polarity; from the low like PP to the high like PC and ABS. The failure mode is cohesive on PP and adhesive on all other substrates. Good adhesions of TPE-1A, B can be achieved over a broad processing range. Figure 4 and Figure 5 shows the peel strength of TPE-1A, B on PP (D040W6), PC (Lexan 141) and ABS (Cycolac NA1000) over a broad temperature range from 190°C to 235°C. Figure 6 and Figure 7 also shows that consistent good peel strength of TPE-1A, B can be achieved over broad processing speeds from 25mm/sec to 64mm/sec.

TPE-1A, B also exhibits good aging properties at 70°C. Figure 8 shows the properties of TPE-1A, B after 7 days at 70°C compare to 7 days at room temperature. The percent of change in tensile strength, elongation, modulus and tear strength is nominal.

TPE-2

TPE-2 materials are opaque and their base chemistries are different from TPE-1. The substrates materials employed for overmolding were PP, ABS, PC/ABS, polyester, Nylon and POM. Each formulation was designed to selectively bond to a substrate based on the functionality of the substrate material. The properties of TPE-2 are given in Table 1. The bonding characteristics of TPE-2 materials to all the substrates were adhesive in nature. As the formulation was altered, bondability of TPE-2 to a substrate varied. TPE-2B exhibits a relatively strong bond to all the substrates employed in this study irrespective of surface energy and/or polarity of a TPE and a substrate. Compared to other substrates, Nylon and polyacetal, i.e., POM, appear to be difficult to bond.

CONCLUSION

Two classes of TPE formulations have been developed and studied for rigid thermoplastics overmolding applications. Their physical properties and adhesion properties were measured and compared. These TPEs have exhibited good adhesion on various substrates including PP, PS, HIPS, PMMA, PC, PET, ABS, PC/ABS and Copolyester. Both TPE-1 and TPE-2 also possess good flow properties suitable for injection molding applications. The results confirm that TPE-1A, B and TPE-2B are truly the “universal overmolding TPEs.”

ACKNOWLEDGMENT

The authors would like to thank William Pepe and Richard Means, and Jessica Stukins for preparation of TPE materials and testing.

REFERENCES

1. Krishna Venkataswarmy, Rajesh Varma and Walter Ripple, Rubber World, Vol. 227, No. 3, December, 2002.

2. Jiren Gu and Krishna Venkataswamy, “Block Copolymer Compositions for Overmolding any TPE, US patent filed, March 2004.

3. Krishna Venkataswamy, Jiren Gu and Walter Ripple, “A Novel Robust Polyamide Overmold Thermoplastic Elastomer, John Simons,” RAPRA 2005.

4. Krishna Venkataswamy, Jiren Gu, Joe Gerkhardt and John Simons, “Novel developments in thermoplastic elastomers for overmolding applications,” RAPRA2006.

Figure 1 Surface energy of various thermoplastic elastomers with rigid thermoplastics

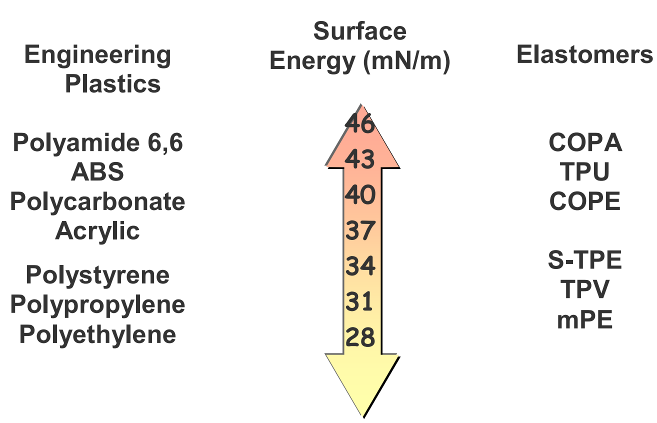

Figure 2 Schematic diagram of the peel test

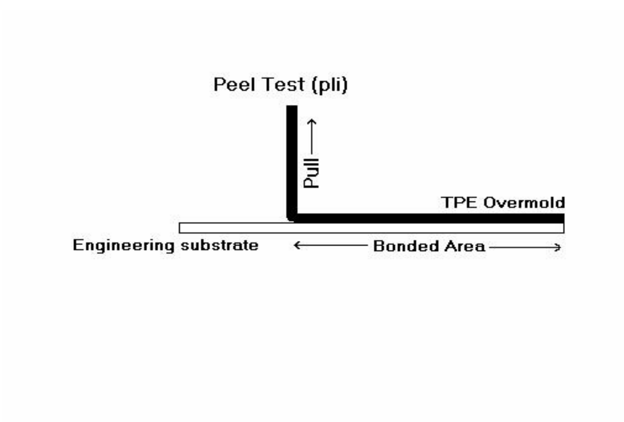

Table 1. Physical Property of TPE-1 and TPE-2

Properties	TPE-1A	TPE-1B	TPE-2A	TPE-2B
Shore A Hardness (10 second delay)	44	43	51	56
Specific Gravity (g/cm^3)	0.90	0.92	0.93	0.93
300 % Modulus (MPa)	2.4	3.2	3.0	3.6
Tensile Strength (MPa)	4.1	5.2	7.0	7.5
Elongation at Break (%)	598	500	721	713
Tear Strength (N/mm)	19	20	24.5	23

Table 2. Adhesion value of TPE-1 on different substrates

Substrate	TPE-1A		TPE-1B	
	Peel Strength (N/mm)	Failure Type	Peel Strength (N/mm)	Failure Type
PP	3.0	Cohesive	3.7	Cohesive
PS	3.2	Adhesive	2.8	Adhesive
HIPS	2.3	Adhesive	1.9	Adhesive
PPE/HIPS	3.2	Adhesive	3.5	Adhesive
PMMA	2.7	Adhesive	2.7	Adhesive
PC	3.0	Adhesive	2.9	Adhesive
PET	2.3	Adhesive	2.6	Adhesive
Copolyester	2.3	Adhesive	2.8	Adhesive
PC/ABS	2.5	Adhesive	3.1	Adhesive
ABS	2.3	Adhesive	2.6	Adhesive

Table 3. Adhesion value of TPE-2 on different substrates

Substrate	TPE-2A		TPE-2B	
	Peel Strength (N/mm)	Failure Type	Peel Strength (N/mm)	Failure Type
PP	4.9	Adhesive	3.6	Adhesive
PET	1.2	Adhesive	3.9	Adhesive
PC/ABS	3.3	Adhesive	4.0	Adhesive
ABS	-	Adhesive	4.3	Adhesive
Nylon	1.2	Adhesive	2.7	Adhesive
POM	1.1	Adhesive	1.9	Adhesive

Figure 3. Capillary viscosity of TPE-1 and -2 at 200°C

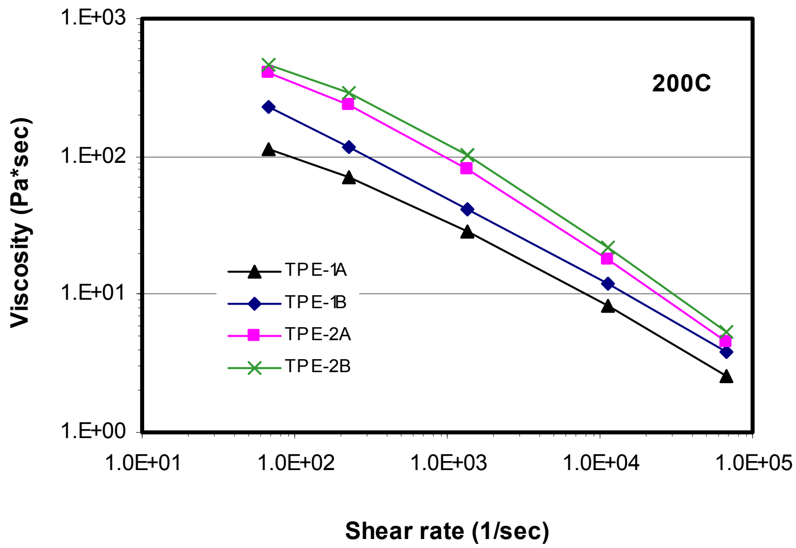

Figure 4. TPE-1A adhesion values overmolded onto PP, PC and ABS over a wide range of melt temperatures. Injection velocity at 51mm/sec.

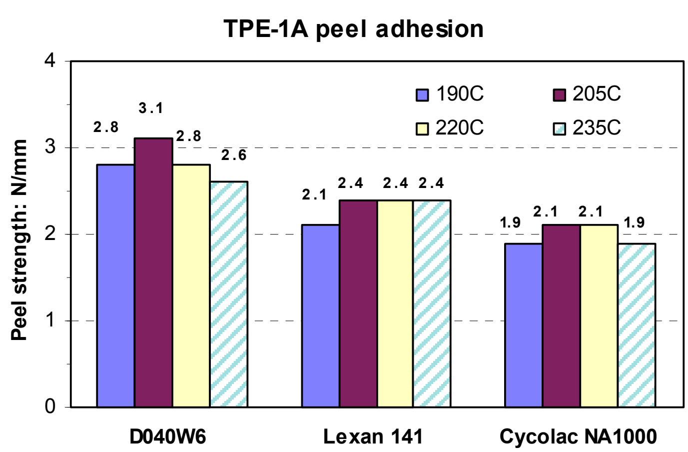

Figure 5. TPE-1B adhesion values overmolded onto PP, PC and ABS over a wide range of melt temperatures. Injection velocity at 51mm/sec.

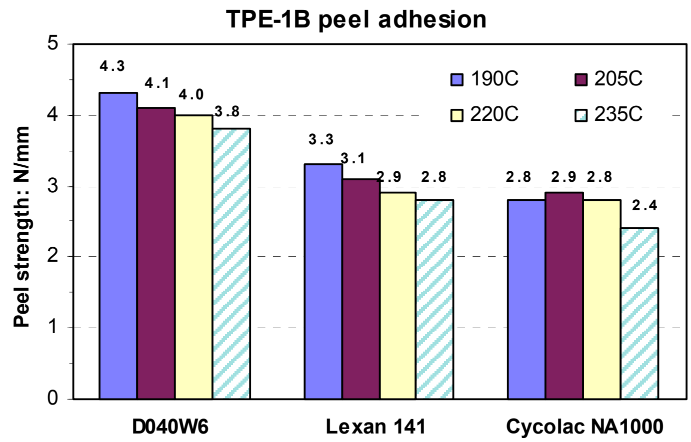

Figure 6. TPE-1A adhesion values overmolded onto PP, PC and ABS over a wide range of injection velocities. Melt temperature at 220C.

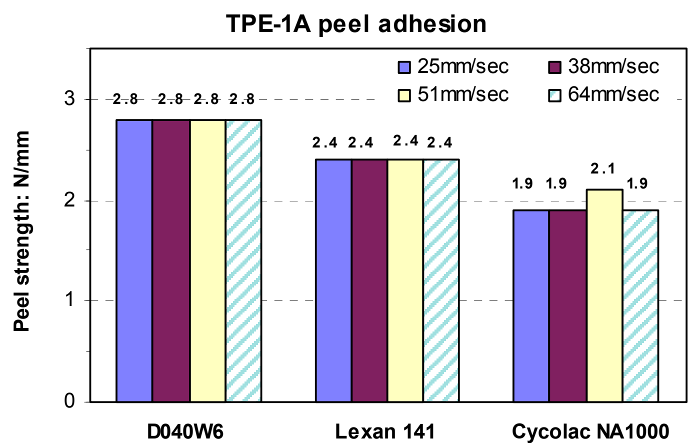

Figure 7. TPE-1B adhesion values overmolded onto PP, PC and ABS over a wide range of injection velocities. Melt temperature at 220C.

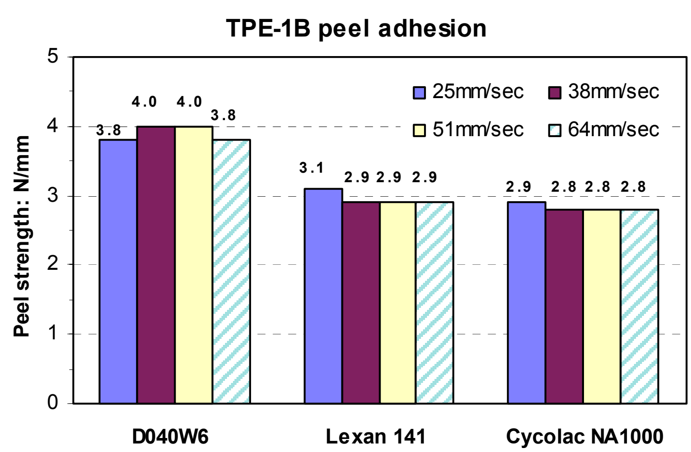

Figure 8. Physical property retention of TPE-1A and TPE-1B after 1 week at 70C.