

Novel Thermoplastic elastomers for overmolding applications

Dr. Krishna Venkataswamy, Dr. Jiren Gu, Maria Furtak¹ and Dr. Sehyun Kim

1. Business Manager, Asia Pacific, GLS International

GLS Corporation, 833 Ridgeview Drive, McHenry, IL 60050

Tel: 815-385-8500 Fax: 815-385-8533 email: info@glscorp.com Web: www.glscorp.com

ABSTRACT

Market trends and consumer demands for enhanced ergonomic feel and touch, grippability, aesthetics, cushioning against impact, vibration isolation and insulation have driven novel developments in thermoplastic elastomers for overmolding applications. Principles of adhering soft elastomer to a rigid substrate as well as utilizing novel thermoplastic elastomers for various overmolding applications are detailed in this paper.

INTRODUCTION

In the last decade, overmolding thermoplastic elastomers (TPEs) onto rigid substrates has been an exploding trend in product differentiation in various consumer applications⁽¹⁾. Overmolding eliminates the need for adhesives and primers to bond TPEs to rigid substrates. Design, functionality, aesthetics, performance needs and value addition have opened the rigid substrate selection from commodity plastics to various engineering thermoplastics and their alloys. This demand has propelled the development of novel thermoplastic elastomers that have the ability to bond to various rigid substrates. Customer demands for foolproof overmolding elastomers have increased with various degrees of sophistication both in equipment, accessories and facilities from global manufacturing vendors.

The current paper emphasizes the science behind the adhesion principles of a soft thermoplastic elastomer onto a rigid substrate. The main focus of this paper is to introduce novel developments in adhering thermoplastic elastomers onto rigid thermoplastics such as polycarbonate, ABS and their alloys, polyacetal and polyamide. These novel thermoplastic elastomers neither require drying nor any pre-molding preparation such as preheating which is employed especially during insert molding.

ADHESION MECHANISM

Adhesion principles between thermoplastic elastomer and the rigid substrate are governed by three very important molecular factors which are the scientific foundation behind good adhesive behavior.

1. Surface energy match between the thermoplastic elastomers and the rigid thermoplastic substrate
2. Wetting and flow behavior of the soft thermoplastic elastomer and
3. Molecular interaction between the thermoplastic elastomer and the rigid thermoplastic.

The matching of the surface energy of the known thermoplastic elastomers chemistries with various rigid thermoplastics is illustrated in Figure 1. Novel developments in thermoplastic elastomers have been driven by application demands that far exceed the TPE chemistry material selection space illustrated in this figure. The current paper introduces novel developments in this area.

Another important variable is the wettability of the TPE on the substrate surface. For specific interactions to occur between the TPE and the substrate both must come in intimate contact with each other on a molecular level and wet-out the surface. The wet-out characteristic is determined by the rheology of the TPEs as shown in Figure 2. Overmolding TPE compounds have a relatively low viscosity. Furthermore, they are shear-sensitive and exhibit shear thinning behavior. As shown in figure 2, in high shear rate regimes, the viscosity is at the lower end of the spectrum which helps the TPE to flow into and fill the thin-walled sections commonly encountered during overmolding.

TPE chemistry and the type of engineering plastic play a critical role in influencing wettability. In addition to the diffusion, viscoelastic properties of the elastomer have an influence on the adhesion properties.

The interface of the TPE and rigid substrate play a vital role in determining not only the bond strength, but also the type of bond-failure: i.e. cohesive (C) or adhesive (A). The cohesive mechanism is generally regarded as the indicator of good bond strength. However, a weak TPE with marginal bond strength can create an illusion of good bonding. In some instances, good bonding exists even to the mechanism of adhesive failure.

Three types of mechanisms at the substrate interface can facilitate bonding of the soft thermoplastic elastomer and the rigid substrate: i.e. mechanical interlock, chemical compatibility and specific reaction or interaction at the interface. In order for any of these interactions to occur, molecular level interaction must precede between the polymeric components of the thermoplastic elastomers and the rigid substrate. Especially with insert molding, the hot thermoplastic elastomer should be capable of melting a few nanometers of the rigid surface implying efficient heat transfer between the molten TPE to the rigid substrate.

ADHESION MEASUREMENT OF THE OVERMOLD TPE

The bond strength between the TPE and the engineering plastic can be measured by performing a "90° Peel Test". We have modified the existing ASTM D903 method for plastics in order to evaluate the adhesion of soft TPEs onto rigid thermoplastic. A schematic diagram of this test procedure is shown in Figure 3. The testing is conducted on a molded substrate with a TPE skin insert molded onto it. A 25 mm wide strip of TPE is cut and pulled at a 90° angle to the substrate using an Instron tensile tester. The substrate is locked in its place on wheels in order to maintain the 90° angle while the elastomer is pulled. The adhesion strength is measured by the force required to pull the elastomer from the substrate which is reported as an average over 50 mm of pulling. The adhesion is categorized based on adhesive failure (A) if no TPE residue is left on the substrate or cohesive failure (C) if the failure exists in the TPE.

ENGINEERING PLASTIC SUBSTRATES

There are a number of plastic substrates that are used for various consumer applications. These include semi crystalline and amorphous polymers such as polypropylene, high impact polystyrene (HIPS), polycarbonate (PC), polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polymethyl methacrylate (PMMA), styrene acrylonitrile (SAN), polyphylene oxide (PPO), polyoxymethylene (POM) and polyamide (PA). In addition, several blends of the above polymers such as PC/ABS, PC/PETG, PC/PBT and PPO/PS have great commercial importance for several applications.

Apart from the degree of crystallinity, these polymers vary in their base chemistry, which dictates the surface energy or cohesive energy density. The amorphous content of the polymer, which varies from polymer to polymer, provides the anchor for the interactions occurring at the interface between the rigid plastic substrate and the TPE. As an example, POM (acetal) exhibits 98% crystallinity and is very difficult to bond to. In addition, various rigid thermoplastics can have reinforcements and/or additives, such as fillers and fibers or color masterbatches, which not only can alter the resultant properties of the substrate, but also the surface chemistry. Moreover, polar engineering thermoplastics have a propensity to absorb moisture which hinders the bonding of the TPE. Polyamide is an extreme case example of such an occurrence. The chemistry variations of a few of these polymers are illustrated in Figure 4.

The development of specific TPEs for a given substrate is driven by the specific consumer application that will set the targets of performance and processability. A single TPE chemistry can not bond to all the rigid plastic substrates as evidenced by the surface energies demonstrated in Figure 1. The balance of rheology and surface chemistry along with cost and performance requirements dictates the TPE developments to bond to various engineering plastic substrates. GLS has focused its R&D efforts on the chemistry and technology of developing overmolding compounds to virtually any substrate. In short, this paper focuses on the development of novel thermoplastic elastomers and the leading ability of GLS TPEs to bond to any substrate used in a multitude of applications and markets.

NOVEL TPE DEVELOPMENTS:

Non-Drying TPEs for PC, ABS, PBT and their alloys

Novel classes of non-drying TPEs which can overmold onto a variety of engineering thermoplastics have been developed. These TPEs are inherently non-hygroscopic and do not require drying, making them cost-efficient. Table 1 below illustrates an example of this class of novel TPEs.

Table 1: Novel Non-Drying Overmold TPE

Shore A Hardness(10 second delay)	57
Specific Gravity(g/cm ³)	1.05
Color	Natural
300% Modulus(MPa)	2.87
Tensile Strength(MPa)	3.24
Elongation at Break (%)	400
90° Deg., Peel ASA (N/mm)	2.72
90° Deg., Peel SAN (N/mm)	2.72
90° Deg. Peel ABS (N/mm)	2.72
Type of Failure	C/A

GLS285-085 is an overmold TPE which requires no drying and bonds to ABS, SAN and ASA with very good adhesion after insert molding as measured by the 90° peel test and illustrated in Figure 3. The failure mode is dual meaning both adhesive and cohesive on these substrates. Optimal adhesion values are also obtained for overmolds onto PC (Lexan), ABS (Cycloy), PC/ABS(Cycolac) and PC/PBT (Xenoy) as demonstrated in Figure 5. This good bonding performance was observed within a wide range of melt processing temperatures as shown in Figure 5. Broad processing speeds from 25 mm/sec to 75 mm/sec result in outstanding adhesion as shown in Figure 6. The new non-hygroscopic TPE is very forgiving in terms of substrate chemistries as well as processing conditions.

GLS 285-056 exhibits good aging properties at 70°C for at least one week. This is illustrated by the initial and final properties after aging shown in Figure 7 indicate that GLS 285-056 exhibits good aging properties at 70°C for at least one week. The percent of change in tensile strength, elongation, modulus, and tear strength after heat aging is nominal.

Overmolding TPE for Acetal and their Copolymers:

Acetal is an abrasion resistant high performance polymer with a high degree of crystallinity (>98%). It is very difficult to overmold a TPE onto an acetal due to a low level of amorphous content which is essential to anchor TPE onto the substrate via surface melting during the overmolding process. GLS271-051 is a novelty TPE material that overcomes such an inherent difficulty. Table 2 demonstrates the outstanding adhesion values of GLS TPE onto Delrin and Hostaform.

Table 2: GLS 271-051 overmolded to polyacetal (Delrin511P) and its copolymer (Hostaform 9021)

LC 271-051 to Delrin 511P			
Average, N/mm	Maximum,N/mm	Mode of failure	Melt temperature
1.65	1.95	Adhesive	220°C
1.84	1.98	Adhesive	220°C

LC 271-051 to Hostaform 9021			
Average, N/mm	Maximum,N/mm	Mode of failure	Melt temperature
2.12	2.22	Adhesive	220°C
2.14	2.33	Adhesive	220°C

Universal Polyamide Overmold Update:

In earlier studies, robust universal polyamide overmolding materials and their benefits were introduced,^{2,3} where overmoldability of a 60 shore A and a 75 shore A material to Nylon was demonstrated. In this presentation, the development of new 40 shore A and 60 shore A versions with prime adhesion properties and universality of overmolding to various polyamides has been introduced.

The initial and final tensile strength and modulus results of Versaflex OM6240 (40 shore A universal polyamide OM TPE) and Versaflex OM6258 (60 shore A) after aging at 70°C for one week have been recorded. Figure 8 and Figure 9 show that the retention in properties is excellent. Furthermore, the material has outstanding adhesion to Ultramid B3G6 (glass reinforced polyamide 6) as demonstrated in Figure 10 and 11.

Summary:

In order to effectively address a range of market needs and applications involving varied rigid substrates novel TPE materials have been developed at GLS. Thus far, the insert molding data presented here is very encouraging and it is determined that these novel TPEs will exceed expectations in two-shot molding environments as well. Finally, these novel TPEs for engineering thermoplastics contribute valuably to our ever-expanding portfolio of technologies that offer our customers differentiated solutions for various applications in the consumer market.

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

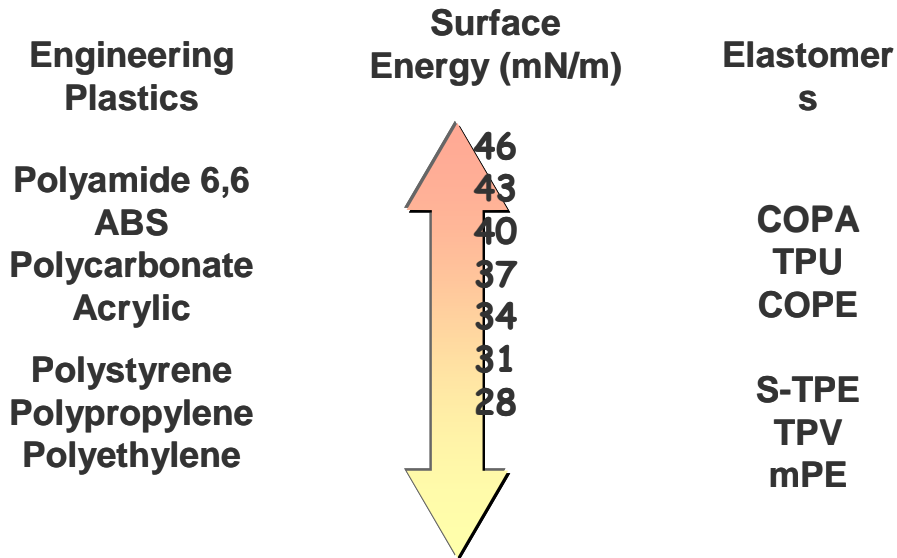


Figure1. Surface energy match of various thermoplastic elastomers with rigid thermoplastics

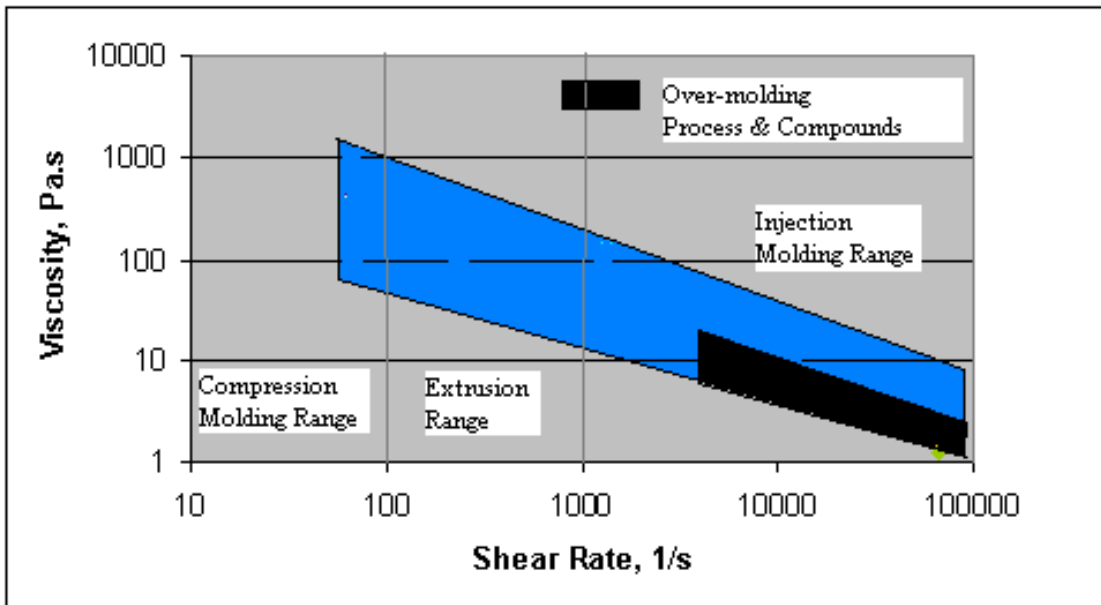


Figure 2. Rheological behavior of the thermoplastic elastomer which are shear sensitive. Shaded area represents rheological range most suitable for overmolding.

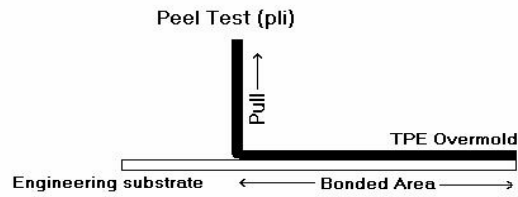
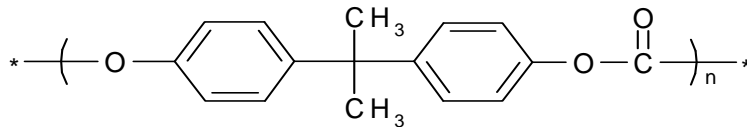
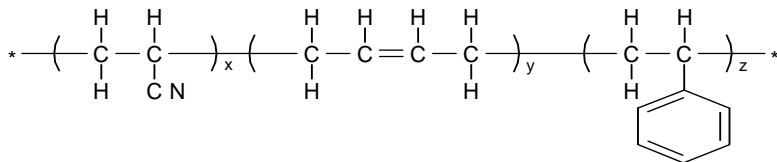


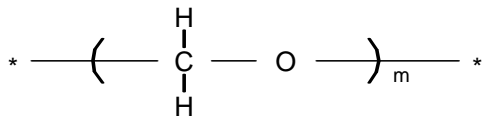
Figure 3. Schematic Diagram of the peel test.



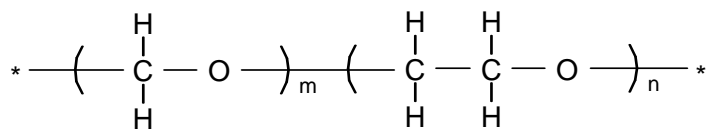
Polycarbonate derived from Bisphenol A (PC) - Totally Amorphous



Poly(acrylonitrile-co-butadiene-styrene) (ABS – 15%-35%AN,5-30%BD,40-60%ST) – Totally amorphous



Acetal Homopolymer – 98% crystalline



Acetal Copolymer

Figure 4. Some examples of the chemistries of the engineering thermoplastics.

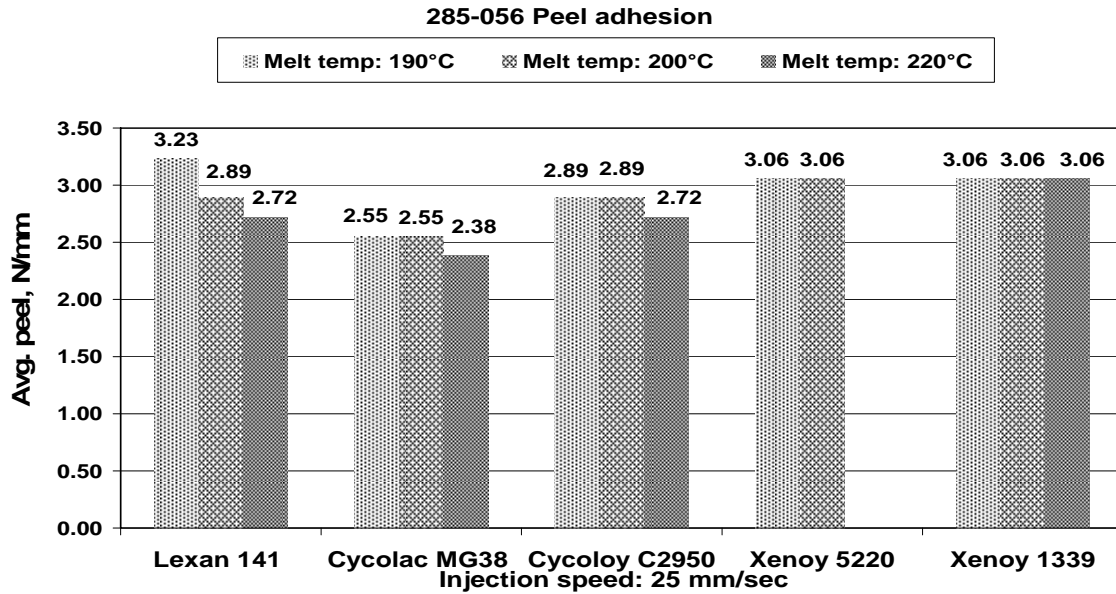


Figure 5: GLS 285-056 adhesion values overmolded onto PC, ABS, PC/ABS and PC/PBT over a wide range of melt temperatures of the TPE.

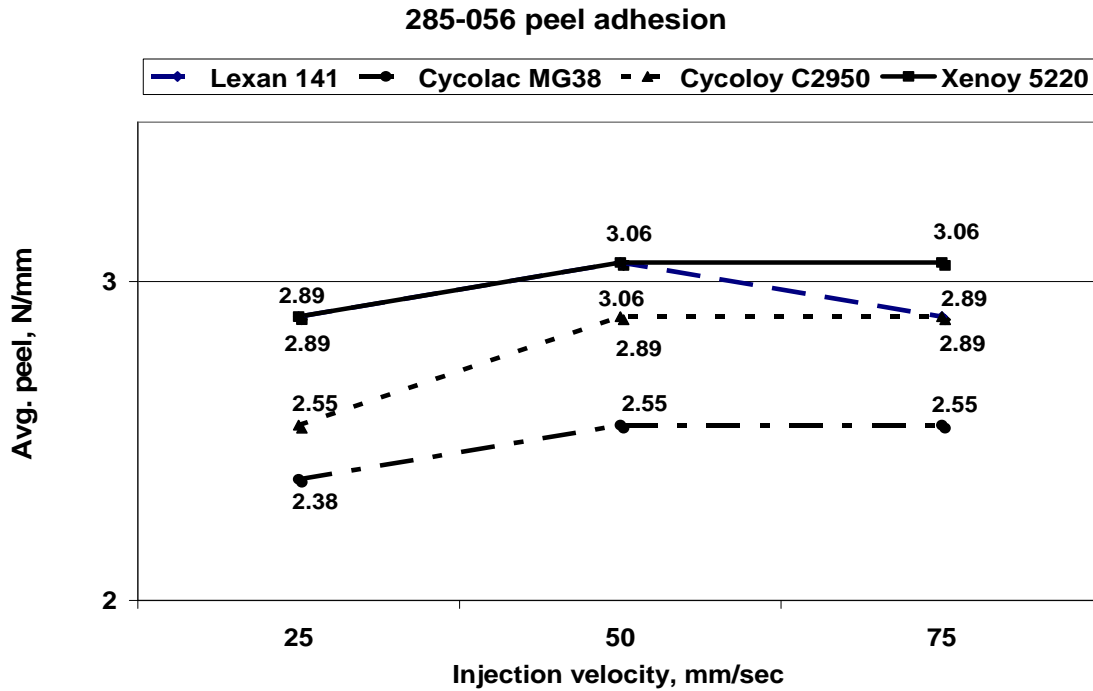


Figure 6: GLS 285-056 adhesion values overmolded onto PC, ABS, PC/ABS and PC/PBT over a wide range of injection speeds.

285-056 tensile properties: initial & aged after 1 week at 70°C.

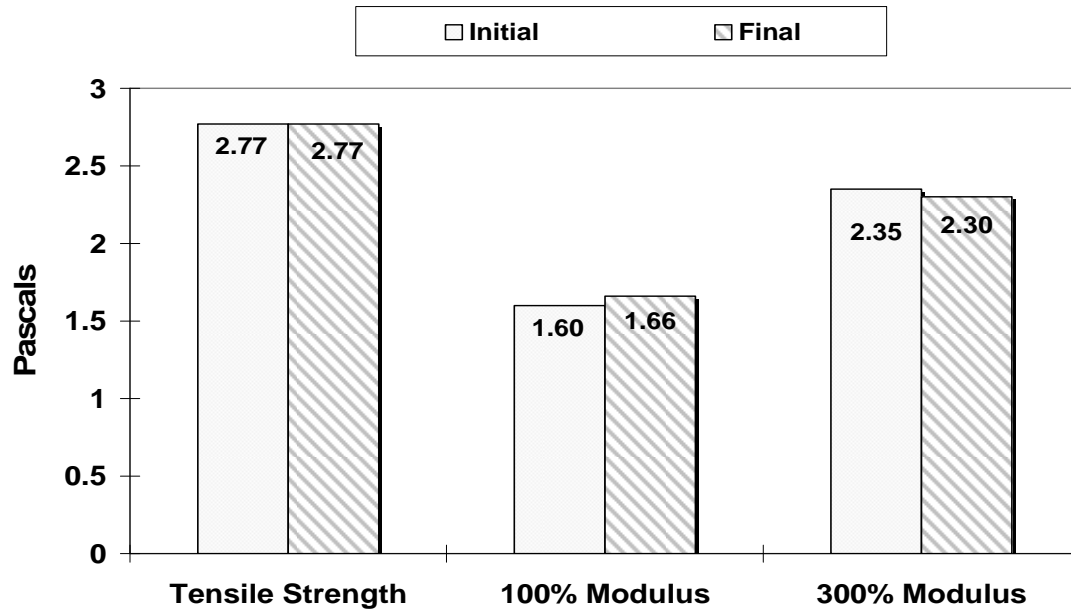


Figure 7: Physical property retention of GLS 285-056 after 1 week at 70°C.

OM6240 tensile properties: initial and final after 1 week at 70°C

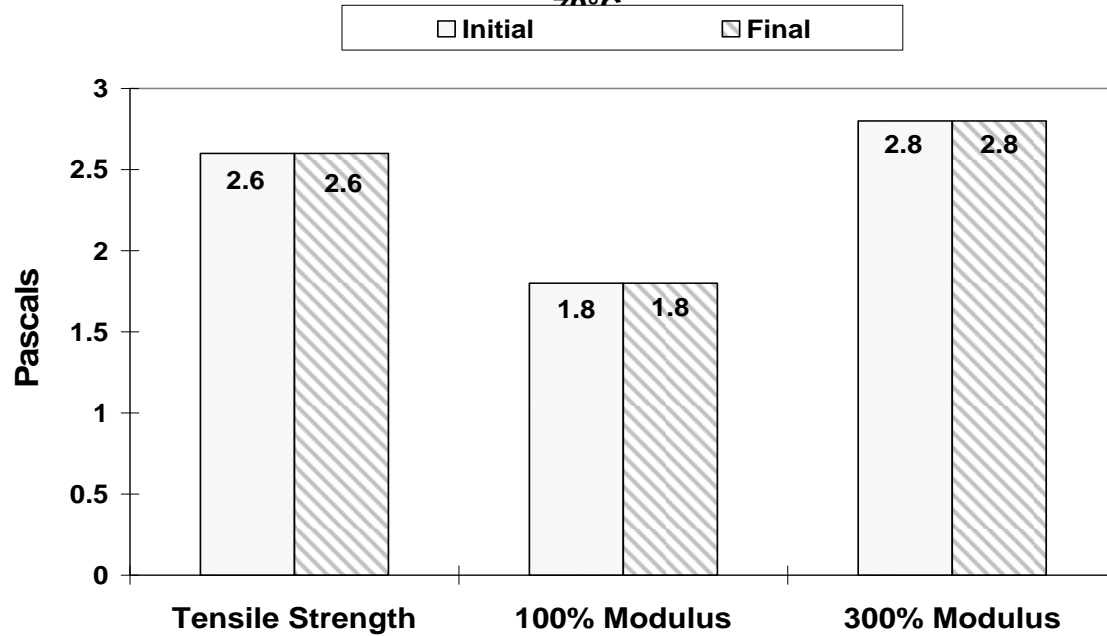


Figure 8: Physical property retention of Versaflex OM 6240 after 1 week at 70°C.

OM6258 tensile properties after 1 week at 70°C

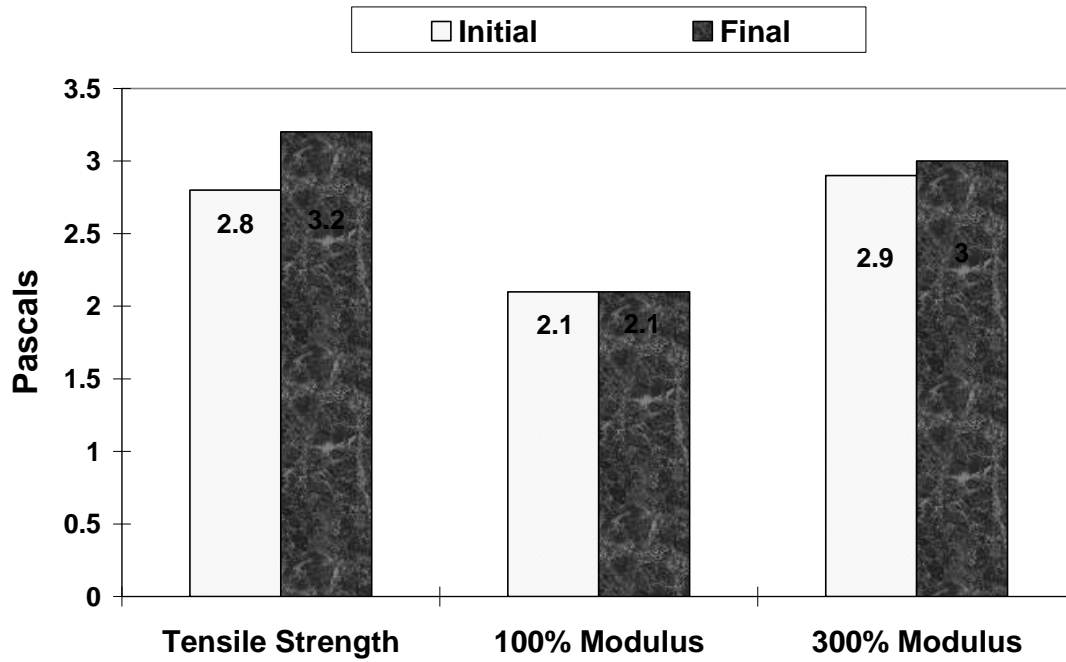


Figure 9: Physical Property retention of OM 6258 after 1 week at 70°C.

OM6240 adhesion to Ultramid B3ZG6

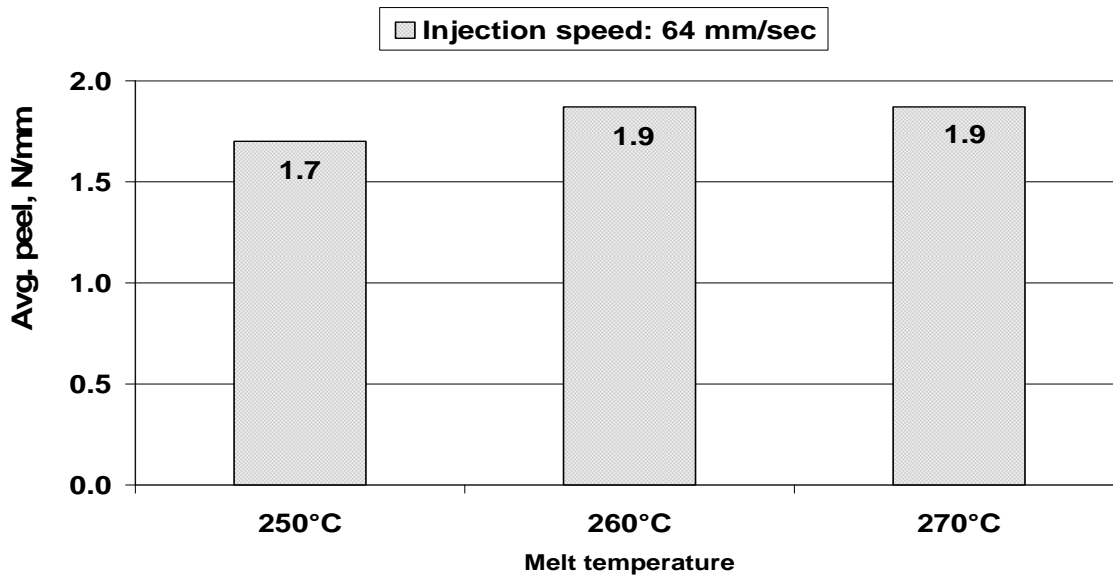


Figure 10: Versaflex OM 6240 adhesion values to polyamide Ultramid B3ZG6

OM6240 adhesion to Ultramid B3ZG6

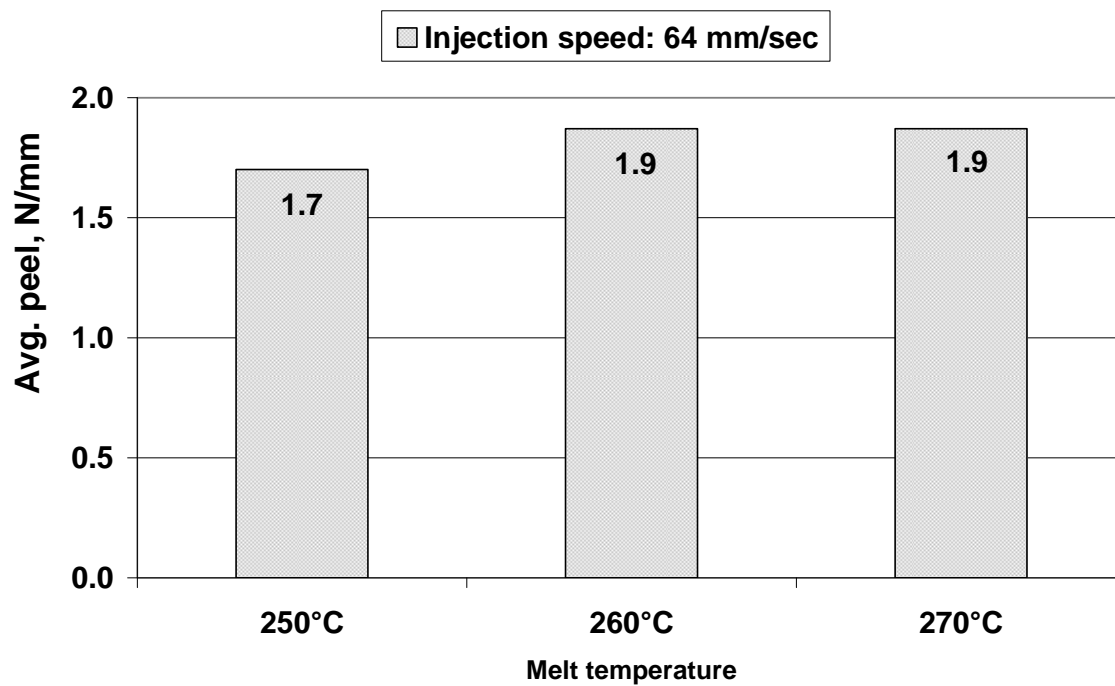


Figure 11: Versaflex OM 6258 adhesion values to polyamide Ultramid B3ZG6