Universal Polyamide Overmold Thermoplastic Elastomer

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ABSTRACT

Overmolding of thermoplastic elastomers (TPEs) for consumer applications has been driven by the escalating market trends in enhanced ergonomic feel, touch, grippability, aesthetics and cushioning against impact, vibration isolation and insulation. Polyamide (i.e. nylon) is preferred plastic in many high end applications due to its crystalline structure and high melting temperature. Achieving TPE adhesion to polyamide with varied base chemistries is well regarded to be difficult. An Universal polyamide overmolding TPE technology has been developed by inventing novel compatibilization technology. These TPEs overcome the limitations of traditional polyamide overmolding TPEs exhibiting wider processing windows for overmolding over a variety of polyamides. They exhibit Universal bonding to every type of polyamide tested, unlike the earlier technologies which were very sensitive to the type of polyamide.

INTRODUCTION

In the last decade, overmolding thermoplastic elastomers (TPEs) onto rigid substrates has been a 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, asthetics, 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 will bond to various rigid substrates. Customer demands for robust overmolding elastomers have increased with global manufacturing vendors with various degrees of sophistication both in equipment, accessories and facilities.

The current paper emphasizes the science behind the adhesion principles of a soft thermoplastic elastomer onto a rigid substrate. Overmolding TPEs onto polyamide (often referred to as “Nylon”) as a rigid substrate is well regarded to be difficult. A novel TPE platform technology has been developed which has outstanding overmolding performance onto a variety of polyamide chemistries especially in insert molding which is a litmus test for overmolding. The TPE family has adhesion on any type of polyamide tested in the study, including undried materials, making them truly Universal polyamide overmold TPEs.

BACKGROUND

ADHESION MECHANISM

Adhesion principles between thermoplastic elastomer and the rigid substrate are governed by three very important molecular factors which are the foundation of science 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.

Matching 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. Polyamides represent the highest polarity in Figure 1. The current paper offers a novel robust TPE material selection for overmolding on to Polyamide.

Another important variable is wettability of TPE on substrate surface. For specific interactions to occur between the TPE and the substrate, both have to come in intimate contact to 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. Over molding compounds have relatively low viscosity. Furthermore, they are shear -sensitive and exhibit shear thinning behavior. The viscosity is in the lower end of the spectrum as shown in the figure 2 in high shear rate regimes. This helps TPE flow and fill thin walled sections commonly encountered in over molding.

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

The interface of the TPE and rigid substrate plays a vital role in determining not only the bond strength, but also the type failure; i.e. cohesive (C) or adhesive (A). The cohesive mechanism is generally regarded as the preferred mode of failure for indication 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 in the mechanism of adhesive failure.

Three types of mechanisms at the 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 is necessary between the polymeric components of the thermoplastic elastomers and the rigid substrate. Especially in insert molding, the hot thermoplastic elastomers should be capable of melting a few nanometers of the rigid surface. This implies 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^o Peel Test”. We have modified ASTM D903 method for plastics to evaluate the adhesion of soft TPE onto rigid thermoplastic. A schematic diagram of this test procedure is shown in Figure 3. The testing is done on a molded substrate with a TPE skin insert molded on it. 25 mm wide strip of TPE is cut and pulled at 90^o to the substrate using an Instron tensile tester. The substrate is locked in its place on a moving plate in order to maintain the 90^o angle while the elastomer is being pulled. The adhesion strength is measured by the force required to pull the elastomer from the substrate and 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 is in TPE.

POLYAMIDE TYPE

Polyamides are a family of semi-crystalline engineering polymers with variations in chemistries, melting point and crystallinity. It is more difficult for a TPE to form a melt bond with a semi-crystalline polymer, such as polyamide, than with an amorphous polymer like polycarbonate. There are various types of polyamides, such as Nylon 6, Nylon 66, Nylon 12, Nylon 6, 12 and their copolymers.

Nylon crystallinity has a major role in bond strength. Nylon 66 has the highest melt temperature, i.e. 265 ^oC which would require a TPE with good, high temperature melt stability. Bonding of TPE with a particular polyamide chemistry is also affected by the additives packages, such as heat stabilizers, glass fibers, flow modifiers, impact modifiers and pigments. As an example, most TPEs do not bond effectively to heat stabilized grade polyamide 6 (HS).

AGING OF NYLON

Nylon is extremely hygroscopic and it also goes through post molding crystallization. Both of these factors adversely affect bonding with a TPE.

For these reasons, it is often required to over mold TPE immediately after molding the nylon substrate. This manufacturing practice reduces operational efficiency and flexibility.

NYLON MOLDING PROCESS

Bonding is also affected by mold design and nylon molding conditions. Conditions that would increase nylon crystallinity adversely affect the TPE bonding.

There has been a technical and a market need for a TPE which can bond to different types of polyamide chemistries from various sources which includes variables such as polyamide chemistries, additive packages, moisture content, post molding aging history and processing conditions.

NYLON OVERMOLDING TECHNOLOGIES

Relying on the presence of the polyamide structure in the TPE composition to generate a strong bond when the molten blend comes into contact with a nylon substrate, US patents 5,843,577 (2) and 5,750,268 (3) disclose TPE blends for nylon overmold. However, TPEs based on this technology can only be reliably used in two-shot over molding and very often do not work universally on different polyamides.

NEW POLYAMIDE OVERMOLD TECHNOLOGY

We have developed a universal polyamide OM TPE technology platform(4). Specific TPE grades were evaluated with different types of polyamides with various aging conditions. The material properties data of 60A (I), 60 A (II) and 75A of Universal TPEs are presented in Table 1. 60 A (II) is the latest development based on the technology platform to improve the adhesion behavior over 60 A(1) for certain specific polyamides.

The adhesion between TPE and polyamide was measured by the force required to pull the elastomer from the substrate. The data is reported as average force over 2 inch (5.08mm) of pulling at speed of 2"/min (5.08mm/min).

Universal polyamide overmold TPEs exhibit exceptional bond strength on different polyamide substrates. Table 2 summerizes the data of different polyamide systems; polyamide 6, polyamide 66, glass filled, fiber reinforced , impact modified and heat stabilized. Also included are the nylons at three aging conditions. As seen in Table 2, chemistry, types and aging have no effect on bonding strength. These novel TPEs have no flow marks and showed fast cycle times, which are important commercial considerations.

COMPARISON WITH OTHER COMMERCIAL NYLON OVERMOLD TECHNOLOGIES

The novel universal nylon overmolding TPEs are compared with several commercial nylon overmolding TPEs. Insert molding at three barrel temperatures was employed. Actual melt temperature is about $5^oC(10^oF)$ lower than barrel setup. Three universal polyamide overmolding TPEs are comparatively evaluated with two commercial SEBS nylon OM TPEs and two commercial TPVs. They are designated as below:

Universal Polyamide OM TPEs: 60A (I), 60A (II) and 75A (III),
Commercial SEBS based TPE: 55A (III) and 65A (IV),
Commercial EPDM based TPE: 50A (V) and 70A (VI).

INSERT MOLDING

Insert molding data is reported in Table 3 and Figures 4 through 9. Insert molding is the most severe test for the TPE as it has to bond to a cold substrate. It is apparent that the new universal polyamide overmold TPEs can be processed at lower temperatures and have a strong adhesion with various types of nylon substrates. Other advantages include fast setup, good mold release and a wide processing window. Other commercial TPEs do not perform well in comparison, to various polyamide types considered in this study.

TWO-SHOT MOLDING

Data is reported in Table 4. All TPEs provide bonding as two molten surfaces come together. Universal polyamide TPEs can be processed at the lowest temperature and have the highest bond strength in two-shot molding compared to other commercially available TPEs.

SUMMERY

Universal overmold TPEs provide excellent bonding on various types of polyamide substrates for insert molding application. This new technology provides a universal nylon overmold solution for polyamides and offer superior performance over other commercially available TPEs.

REFERENCES

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

2. Trazollah Ouhadi and Jacques Horrion, U.S. patent 5,843,577.

3. Mace Jean-Michel and Jacques Moerenhout, U.S. patent 5,750,268.

4. Jiren Gu and Krishna Venkataswamy, “Block Copolymer Compositions for Overmolding any type of polyamide,US patent filed , March 2004

Table 1: Material properties of 60A and 75A TPE.

	60A (I)	60A (II)	75A (III)
Hardness, A	60	60	75
Tensile MPa (psi)	3.54 (514)	2.75 (400)	3.36 (488)
Elongation, %	450	395	280

Table 2: Universal polyamide OM with different types of polyamides and aging conditions.

No	Nylon Type	Nylon description	TPE Hardness	Aging condition	Peel, N/mm / lb / in
1	Capron 8333GHI	Glass and impact	60A(1)	Aging A	3.7 / 21
2	Capron 8333GHI	Glass and impact	60A(1)	Aging B	3.2 / 20
3	Capron 8333GHI	Glass and impact	60A(1)	Aging C	3.3 / 19
4	Capron 8333GHIHS	Glass, impact and heat stabilized	60A(1)	Aging A	3.2 / 20
5	Capron 8333GHIHS	Glass, impact and heat stabilized	75A	Aging A	3.0 / 17
6	Ultramid B3ZG6	Glass and impact	60A(1)	Aging A	3.2 / 18
7	Zytel 70G33L	Glass	60A(1)	Aging A	3.9 / 22
8	Zytel 408AHS	Heat stabilized and flow aid	60A(1)	Aging A	3.7 / 21
9	Zytel 409AHS	Heat stabilized and flow aid	60A(1)	Aging A	3.2 / 20

Aging A: nylon substrate conditioned at room temperature and humidity for 4 weeks before TPE overmolding.

Aging B: nylon substrate conditioned (1) at room condition for 4 weeks, (2) immersion in water for 24 hours and (3) dry 12 hour at room condition before TPE overmolding.

Aging C: nylon substrate conditioned (1) at room condition for 4 weeks, (2) immersion in water for 24 hours and (3) dry with tissue paper immediately before TPE overmolding.

Molding condition:
Barrel temperature (from feed and nozzle) C (F):182, 249, 260, 260 (360, 480, 500, 500F)
Injection speed: 5.08 mm/min
TPE thickness: 1.5 mm.

Tabel 3: Inserting molding comparison.

Capron 8333GHI							
N/mm (lb/in)	60A-I	60A-II	75A-III	55A-IV	65A-V	50A-VI	70A-VII
260C/500F	3.7 / 21	N/A	3.2 / 18	No	No	No	No
276C/530F	3.7 / 21	3.7 / 21	3.2 / 18	2.1 / 12	No	No	No
288C/550F	N/A	N/A	N/A	2.5 / 14	2.5 / 14	No	No

Capron 8333GHIHS							
N/mm (lb/in)	60A-I	60A-II	75A-III	55A-IV	65A-IV	50A-VI	70A-VII
260C/500F	3.9 / 22	N/A	3.3 / 19	No	No	No	No
276C/530F	3.5 / 20	N/A	3.3 / 19	No	No	No	No
288C/550F	N/A	N/A	N/A	2.5 / 14	2.6 / 15	No	No

Ultramid B3ZG6							
N/mm (lb/in)	60A-I	60A-II	75A-III	55A-IV	65A-IV	50A-VI	70A-VII
260C/500F	3.0 / 17	3.3 / 19	3.2 / 18	No	No	No	No
276C/530F	3.2 / 18	3.3 / 19	3.2 / 18	No	No	No	No
288C/550F	3.3 / 19	N/A	3.0 / 17	2.1 / 12	2.1 / 12	No	No

Zytel 70G33L							
N/mm (lb/in)	60A-I	60A-II	75A-III	55A-IV	65A-IV	50A-VI	70A-VII
260C/500F	3.7 / 21	N/A	3.3 / 19	No	No	No	No
276C/530F	3.7 / 21	3.7 / 21	3.3 / 19	2.3 / 13	No	No	No
288C/550F	N/A	N/A	N/A	2.1 / 12	2.5 / 14	No	No

Zytel 408HS							
N/mm (lb/in)	60A-I	60A-II	75A-III	55A-IV	65A-IV	50A-VI	70A-VII
260C/500F	3.0 / 17	N/A	3.2 / 18	No	No	No	No
276C/530F	3.2 / 18	4 / 23	3.0 / 17	No	No	No	No
288C/550F	N/A	N/A	N/A	2.5 / 14	2.5 / 14	No	No

Zytel 409AHS							
N/mm (lb/in)	60A-I	60A-II	75A-III	55A-IV	65A-IV	50A-VI	70A-VII
260C/500F	3.2 / 18	N/A	3.0 / 17	No	No	No	No
276C/530F	3.3 / 19	4.2 / 24	2.8/ 16	No	No	No	No
288C/550F	N/A	N/A	N/A	2.1 / 12	2.1 / 12	No	No

Table 4: Two-shot molding comparison

TPE	60A-I	75A-III	55A-IV	65A-IV	50A-VI	70A-VII
Barrel temp C/F	260/500	260/500	288/550	288/550	288/550	288/550
Peel Values N/mm or Pli						
Capron 8333GHI	4.2 / 24	3.5 / 20	3.3 / 19	3.0 / 17	2.3 / 13	3.0 / 17
Capron 8333GHIHS	4.0 / 23	3.9 / 22	2.8 / 16	3.0 / 17	2.3 / 13	3.2 / 18
Zytel 70G33L	4.2 / 24	3.3 / 19	2.8 / 16	3.3 / 18	1.9 / 11	3.3 / 19
Zytel 408AHS	4.0 / 23	4.0 / 23	3.5 / 20	3.7 / 21	1.9 / 11	3.9 / 22
Zytel 409AHS	4.2 / 24	4.0 / 23	3.2 / 18	3.3 / 19	1.6 / 9	3.3 / 19

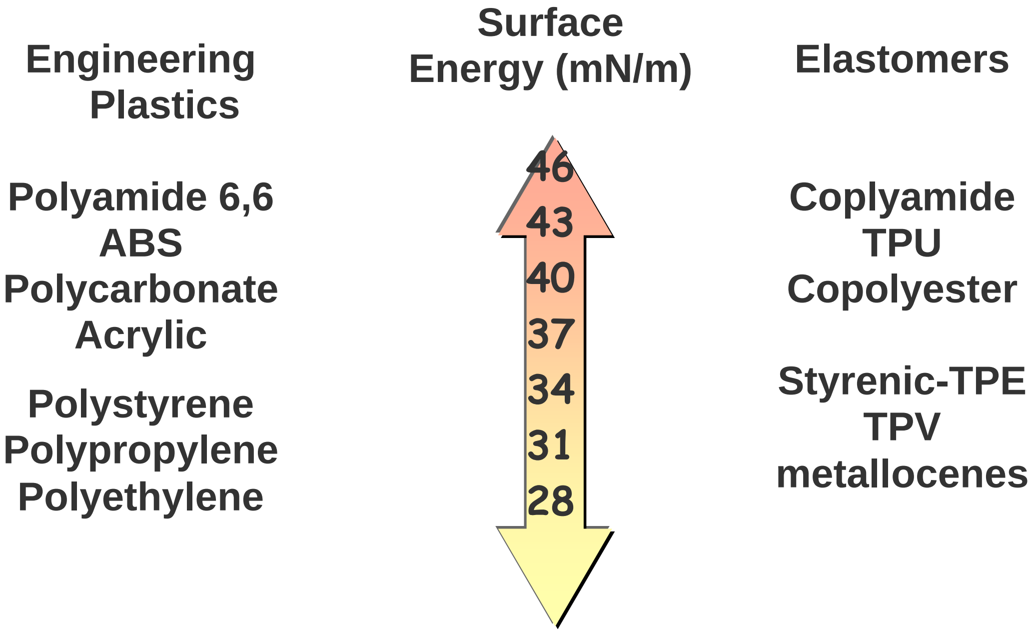

Figure1. Surface energy match of various thermoplastic elastomers with rigid thermoplastics

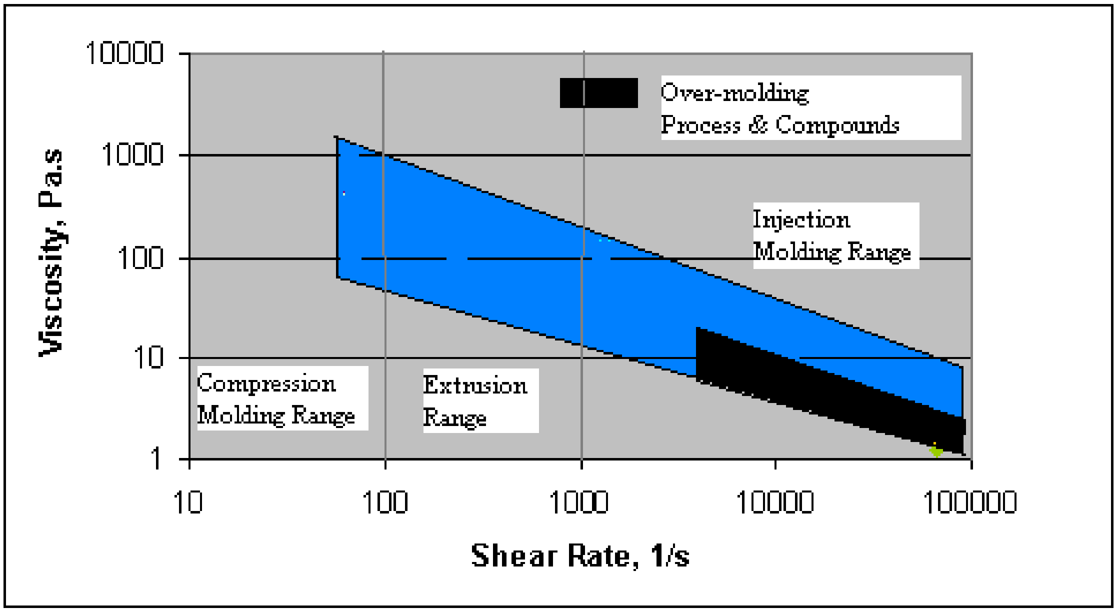

Figure 2. Rheological behavior of the thermoplastic elastomer which are shear sensitive. Shaded area represents rheological range most suitable for overmolding.

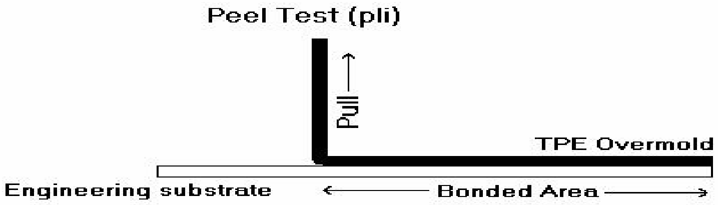

Figure 3. Schematic Diagram of the peel test.

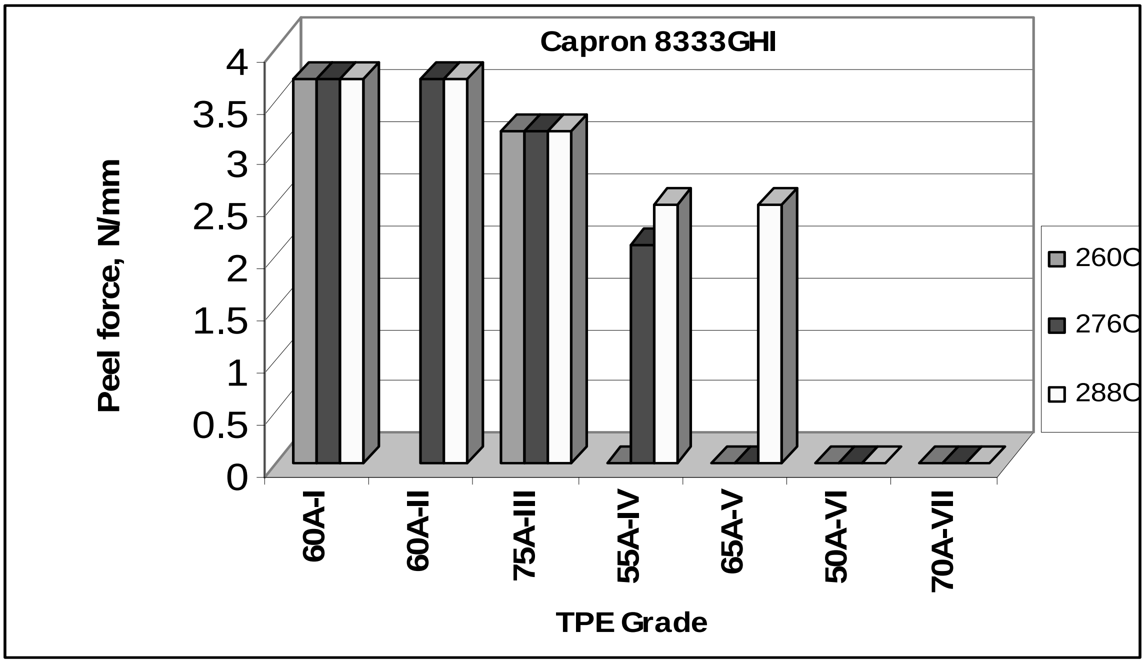

Figure4. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Capron 8333 GHI

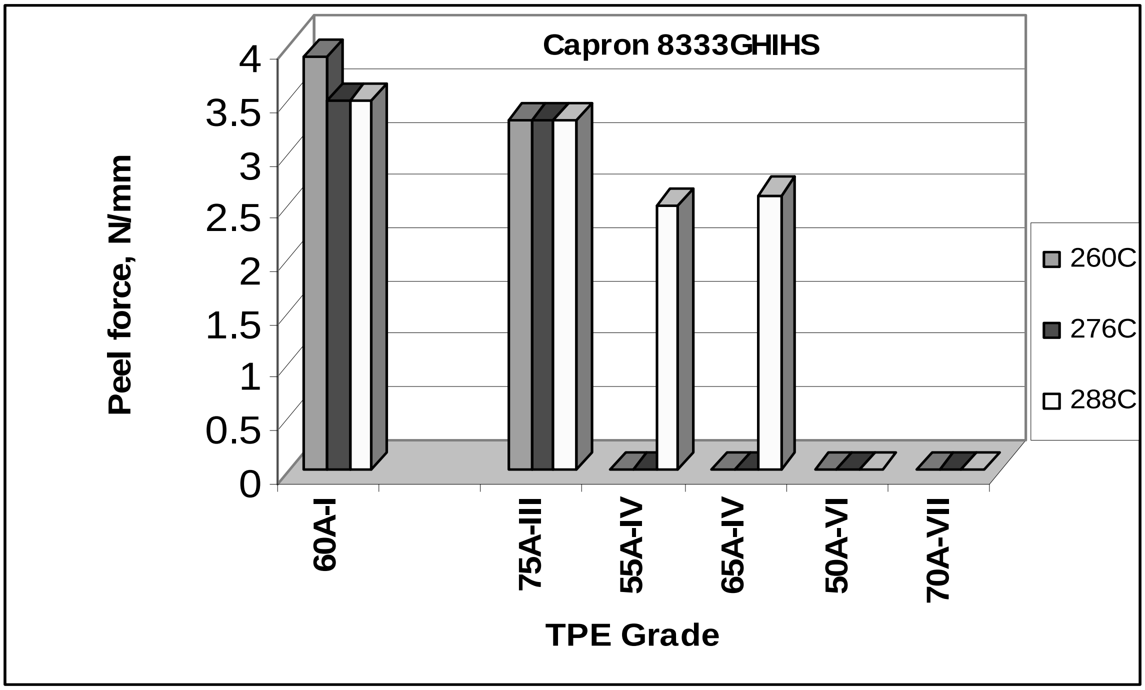

Figure 5. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Capron 8333 GHIHS**.**

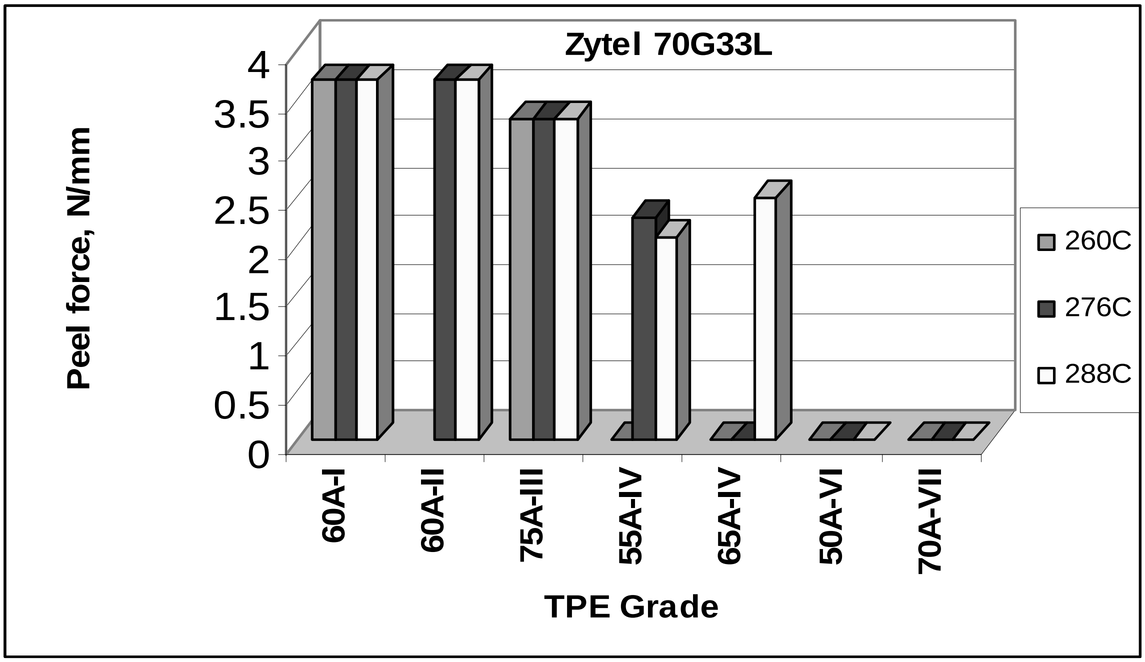

Figure 6. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Zytel 70G33L.

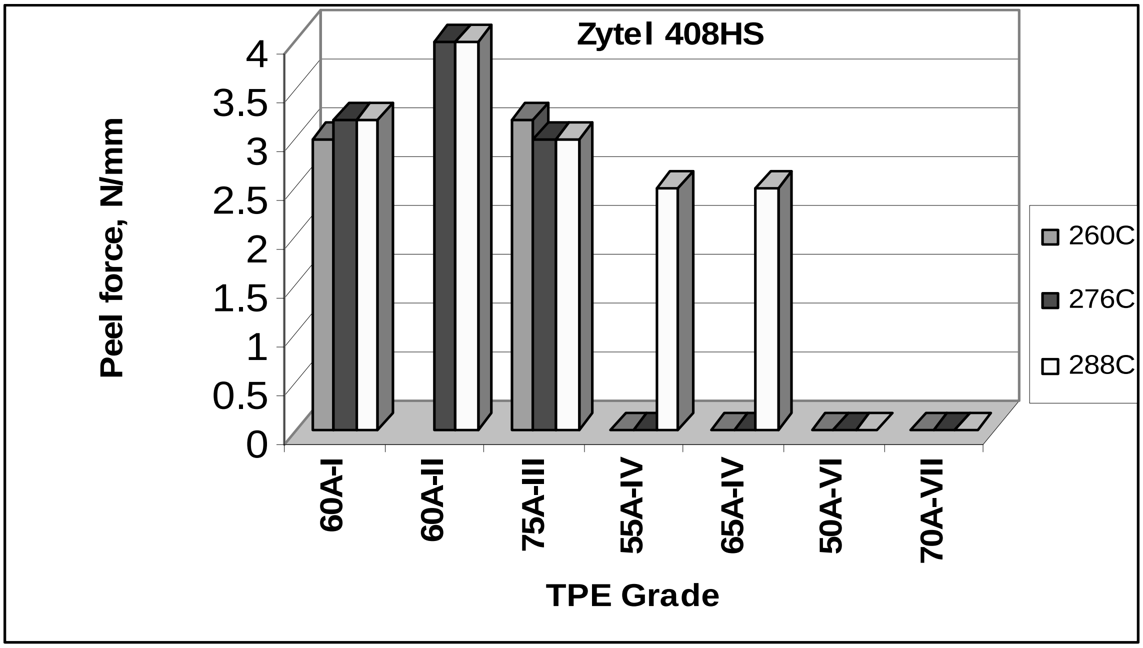

Figure 7. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Zytel 408AHS.

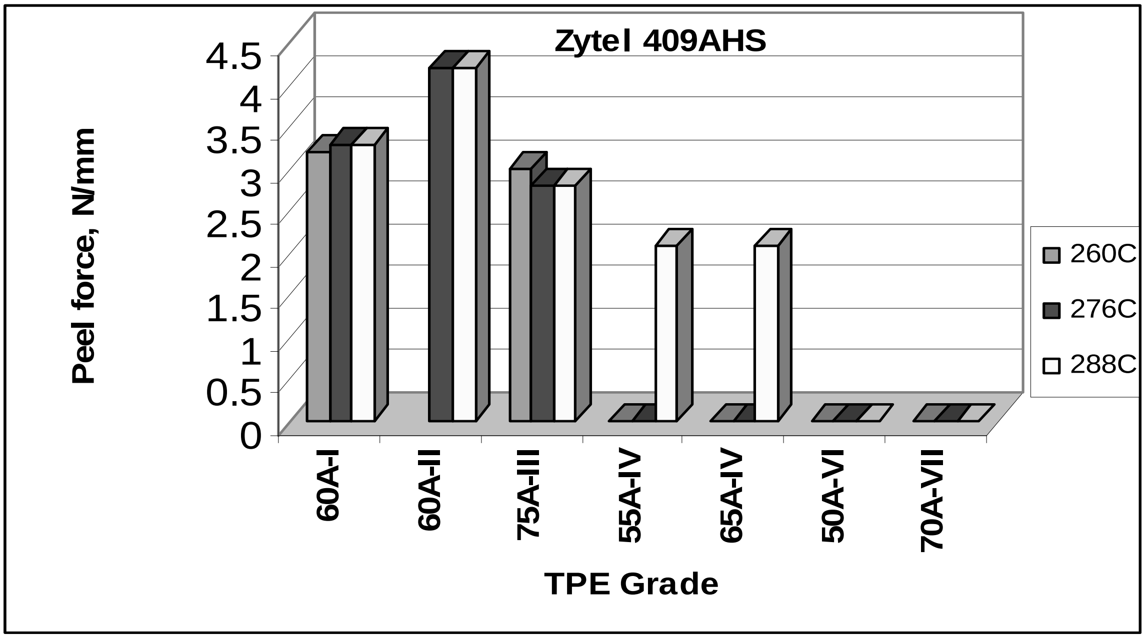

Figure 8. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Zytel 409AHS.

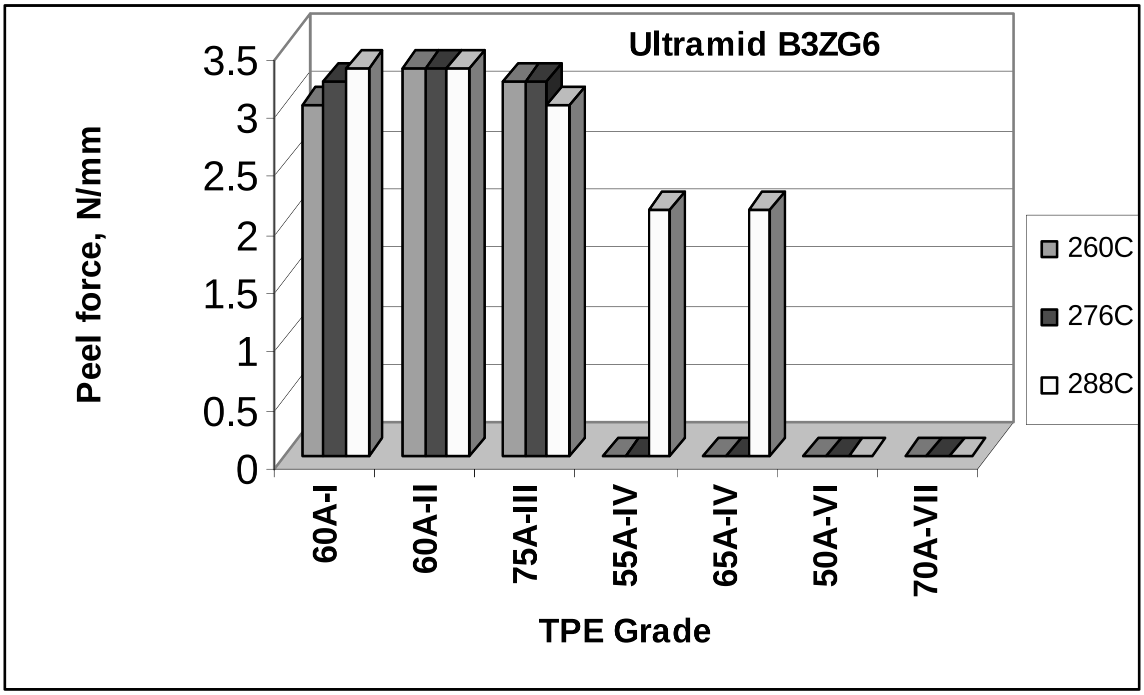

Figure 9. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Ultramid B3ZG6.