A Novel Polyamide Overmold Thermoplastic Elastomer

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INTRODUCTION

Overmolding thermoplastic elastomers (TPEs) onto rigid substrates is an emerging trend [(1)]. Overmolding eliminates the need for adhesives and primers to bond TPEs to rigid substrates.

Overmolding TPEs on to 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. The current paper deals with the performance attributes of these novel thermoplastic elastomers.

BACKGROUND

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.

Polyamide Type

There are various types of polyamides, such as Nylon 6, Nylon 66, Nylon12, 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 ^{o}C 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 be 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 additive packages, moisture content, post nylon molding aging history and nylon processing conditions.

Thickness of the TPE Overmold

Bonding TPE at low melt temperature is preferred for process efficiency and melt stability. L/D (Length over thickness) ratio is often used in the mold design from a design consideration. However, as shown below , it is not a proper parameter to describe the heat transfer process.

Heat transfer in injection molding can be described by two steps i.e. mold filling and cooling. Mold filling is a dynamic process and is approximated by:

$$\frac{\partial T}{\partial X} = (\frac{kL}{UD^2})\frac{\partial^2 T}{\partial Y^2}$$

A dimensionless group which indicates that the heat transfer can be correlated by L/D^2. For a 75% reduction of flow length ,L, one needs to reduce the thickness by 50% to match the heat transfer .

Mold cooling can be described by:

$$\frac{\partial T}{\partial t} = (\frac{kTm}{D^2})\frac{\partial^2 T}{\partial Y^2}$$

A dimensionless group indicates that heat transfer is proportional to Tm/D^2. A reduction of 50% of thickness leads to the reduction of 75% cooling time. Higher temperatures are needed for thinner designs.

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 reliablely used in two-shot over-mold and very often do not work universally in different situations.

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. As seen in Table 2, aging has no effect on bonding strength. These novel TPEs have no flow marks and showed fast cycle times, which is an important consideration.

Comparison with other commercial nylon over-mold technologies

The novel universal nylon overmolding TPEs are compared with several commercial nylon over molding 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 1 through 5. 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 SEBS TPEs became tacky and adhered to the mold at high processing temperature.

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.

Summary

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 TPE solutions.

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 TPE,US patent filed , March 2004

Nomenclature

k: heat transfer coefficient
t: dimensionless time
D: thickness
L: flow length
T: dimensionless temperature
Tm: time unit
U: injection velocity
X: dimensionless unit in flow direction
Y: dimensionless unit in thickness direction

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

Max peel force is reported here.

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
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

Max peel force is reported here.

Figure1. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Capron 8333 GHI

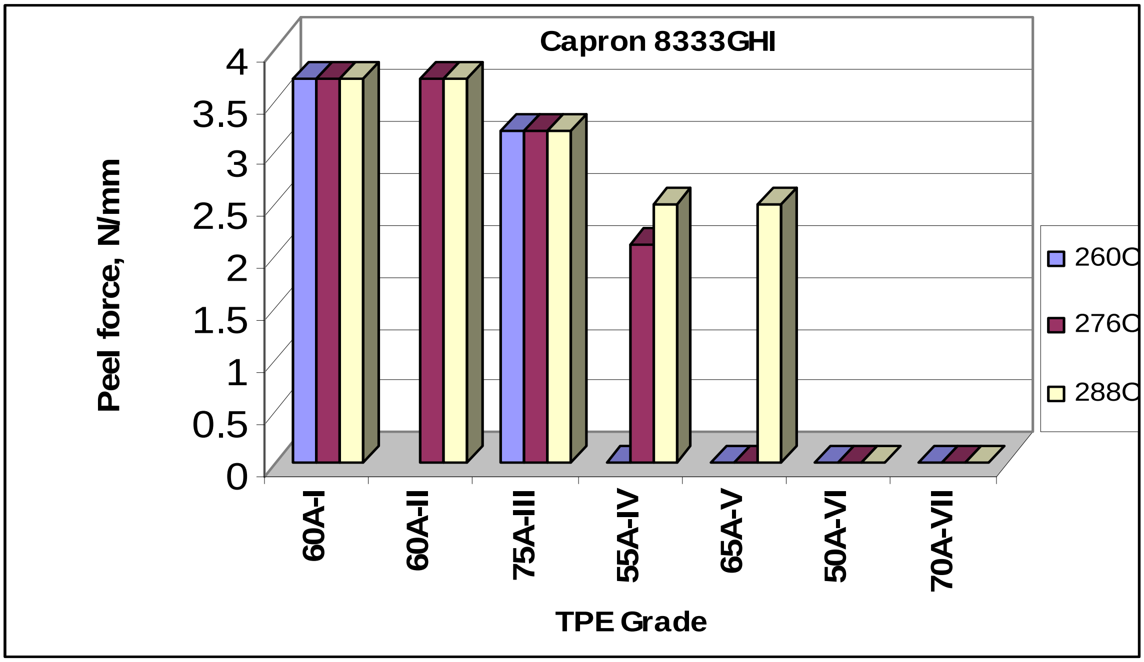

Figure 2. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Capron 8333 GHIHS

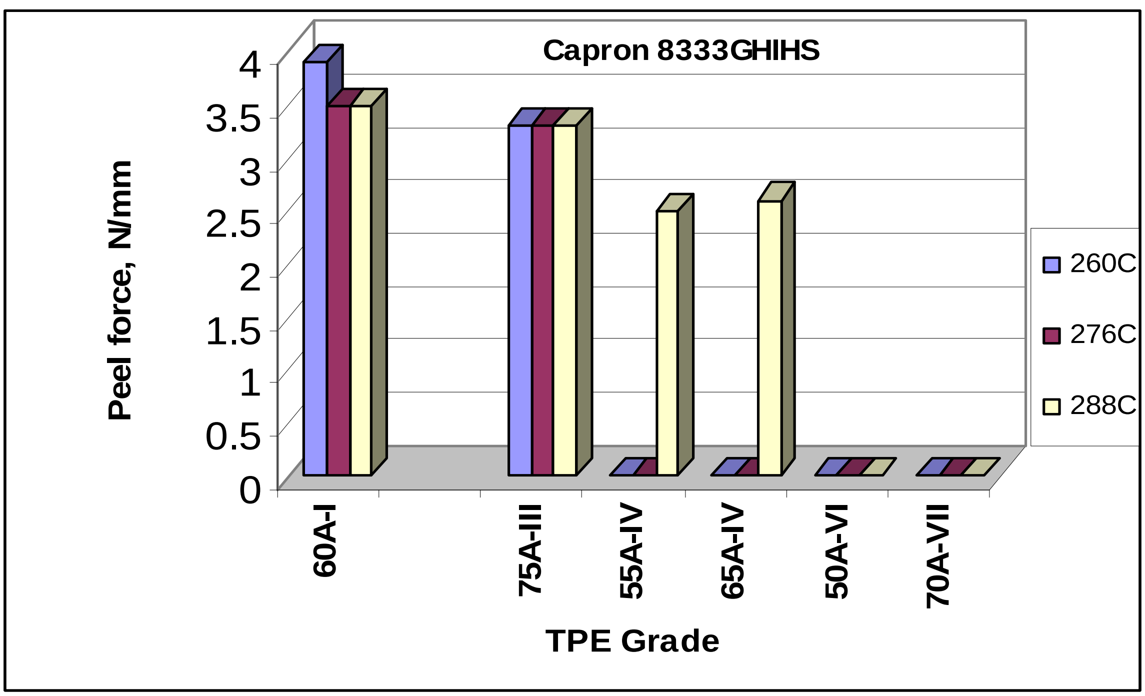

Figure 3. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Zytel 70G33L

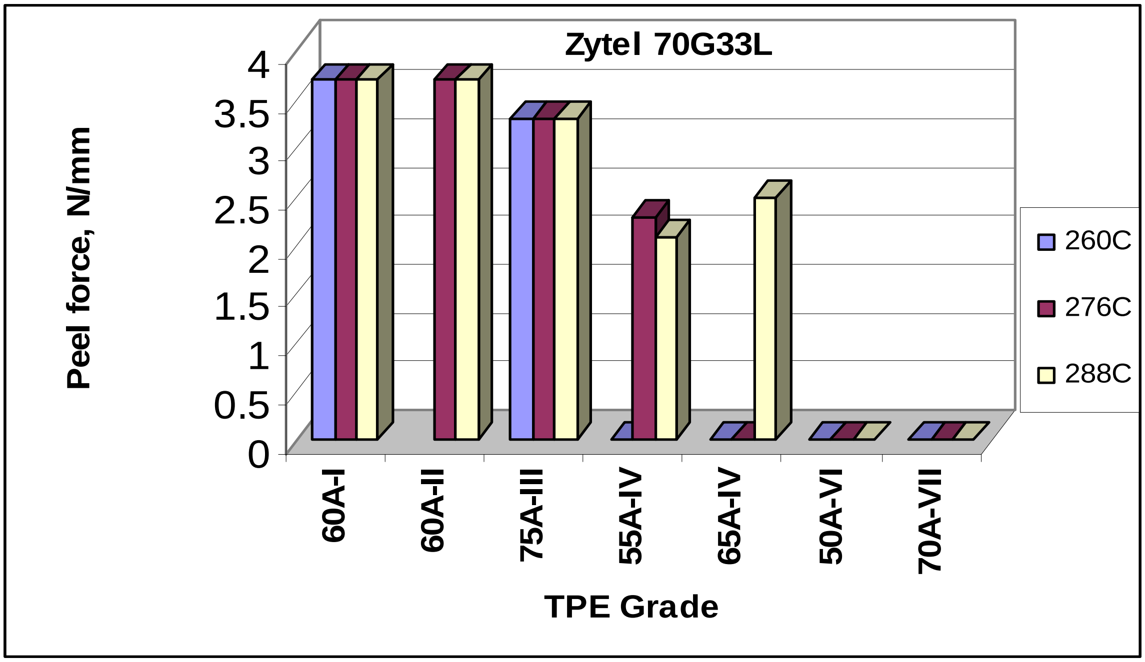

Figure 4. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Zytel 408AHS

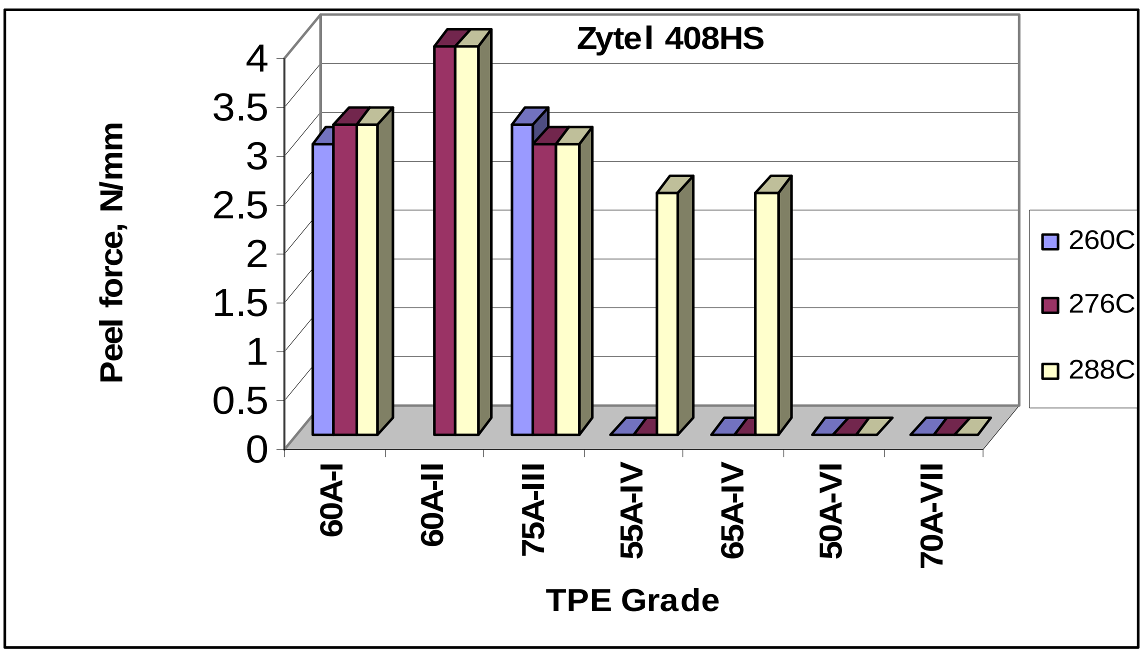

Figure 5. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Zytel 409AHS

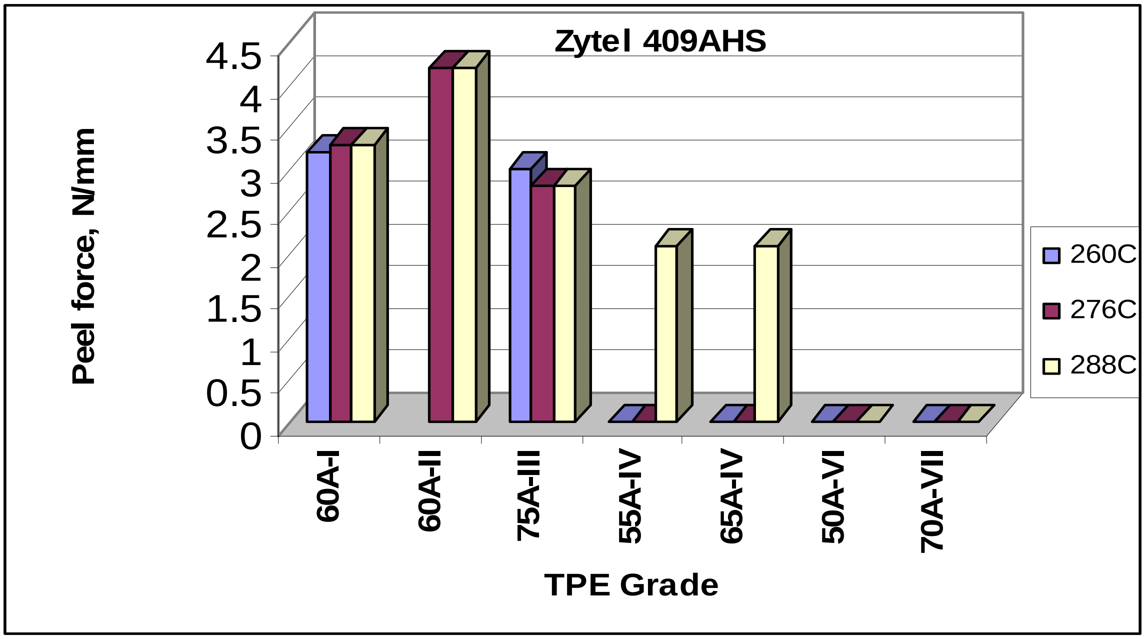

Figure 6. Adhesion comparison of commercially available TPEs and TPVs with Universal TPEs: Ultramid B3ZG6