# Adhesion Control for Injection Overmolding of Polypropylene With Elastomeric Ethylene Copolymers

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Two types of random semicrystalline copolymers (ethylene-octene and ethylene-butene) were overmolded on a core polypropylene. Maximum solid-liquid interface temperature achieved for the overmolding injection process is used as the key parameter for adhesion control. The main bonding process is shown to be a Rouse-type fingering mechanism that develops in short time scales. Normalized peel tests were conducted on overmolded samples to measure the resulting polypropylene copolymers' bonding strength. All the ethylene random copolymers used for this study give good adhesion to polypropylene in overmolding processes, provided the right range of interface temperature is reached. Adhesion strength can be easily controlled for efficient debonding and recycling of used overmolded parts. POLYM. ENG. SCI., 49:1886-1893, 2009. © 2009 Society of Plastics Engineers

## INTRODUCTION

Sequential injection overmolding, also called two-stage sequential overmolding, is the process by which a rigid substrate is overmolded with a more flexible material. The final product is a single piece, made out of polymers with very different mechanical properties that must be safe and permanently bonded together throughout its useful life.

This type of process is used for manufacturing parts where the rigid polymer is used for structural purposes, and the softer materials are expected to take care of the user comfort or to repeatedly admit larger deformations without noticeable damage. Examples of such applications can be seen in telephone keypads, toothbrushes, shaving hardware, household appliances, hand tools, automotive interiors, and medical devices [1, 2].

Thermoplastic polyolefins (TPOs) are rapidly replacing traditional engineering thermoplastics (ETPs) in exterior and interior automotive applications on a global basis. Polypropylene (PP) is a preferred material for use in automotive applications, because of mechanical properties, reasonable cost, easy processing, and recyclability. PP parts can be overmolded with selected types of elastomers that are also often required to be recyclable at reasonable cost. In this work, we explore the convenience of using several types of ethylene copolymers as elastomers for overmolding recyclable PP cores.

Using always polypropylene (PP) as the rigid polymer, a whole family of elastomers has been used for overmolding. Dynamically vulcanized blends of PP with ethylenepropylene-diene copolymers (EPDM), usually labelled as thermoplastic vulcanized elastomers (TPE or TPV), show good adhesion arising from their PP continuous phase that can be easily bonded to the PP substrate by melting and recrystallization, and also show good mechanical properties. Detailed procedures for optimization of processing parameters have been developed and published [3, 4]. These TPV share the common drawback of undesirable oil content in their formulations, needed to plasticize the rigid continuous PP phase. Also, PP parts overmolded with TPV are very hard to recycle and reprocess. The TPV-PP interface adhesion is hard to control and often the elastomer cannot be easily separated from the PP because the PP recrystallization produces too strong adhesion.

Ethylene-octene random copolymers look as a more attractive alternative for PP overmolding, because of

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lower costs and no oil content. Parts could be easily recyclable if the interface adhesion were controlled to the point of resisting proper use and being easily peelable when parts are discarded, thus obtaining pure PP on one side and pure elastomer on the other.

Earlier work done on one ethylene-octene copolymers (EOC) (Engage 8411, Dow, with 11 mol% octene) overmolded on a PP homopolymer surface explored the influence of the overmolding interface temperature on the peeling force needed to separate the EOC strips from the PP surface. As no cocrystallization of the EOC is expected to occur on the PP surface, elucidation of the bonding mechanism becomes then crucial for its adhesion control. The temperature of the PP-copolymer interface evolves from copolymer melt-solid PP contact temperature toward higher temperatures, because of the heat conducted from the melt core and through the solid PP to a cold mold surface. Therefore, as molecular penetration mechanisms are activated by temperature, the maximum interface temperature is taken as the important parameter to characterize adhesion strength [5]. It was found that this liquid EOC adheres well to the PP surface even at low temperatures, well below the PP melting range. The bonding mechanism was claimed to be dominated by Rouse-type fingering cooperative relaxation movements, and therefore the penetration depth would be in the range of the longest Rouse chain length, producing some adhesion but not efficient entanglements. Adhesion was found to be acceptable for normal mechanical requirements. Diffusion of EOC into the PP core did not seem to play an important role at the interface temperatures range used and in the time scale of the overmolding process. This type of surface adhesion, without much efficient entanglements production, ought to be much easier to control for later debonding.

Bonding efficiency between a PP core and different overmolded ethylene copolymer elastomers was studied in this work, to explore the feasibility of using other newer and less expensive ethylene copolymers,. Two types of random semicrystalline copolymers [ethylene–octene (EOC) and ethylene–butene (EBC)] were overmolded on a core PP, using wide ranges of melt injection temperatures. The chemical composition range used is as wide as available. The mold was cooled to maintain the temperature well below the copolymers' melting range, to quickly lower the interface molding temperature below the ethylene copolymers' melting range. Normalized peel tests were conducted on overmolded samples to measure the resulting PP–copolymers' bonding strength. Other overmolded samples were heat-treated after the cooling stage to explore longer PP–copolymers' melt contact times and higher PP–copolymers' interface temperatures, to further learn about the bonding mechanism. Normalized 180 degrees peeling test (ASTM D 903-93) was used to evaluate the adhesion strength. The maximum interface temperature—calculated via a commercial injection simulator—is also used as the correlation parameter for adhesion strength.

#### **EXPERIMENTAL**

#### Materials Used

A commercial PP homopolymer (Cuyolen 1100 N, made by Petroquímica Cuyo, Mendoza, República Argentina). A set of four random EOC and two random EBC, produced by Dow Chemical, was used for this work. The physical properties of copolymers are presented in Table 1. Density, melt index, and modulus data were taken from the manufacturer data sheets. Comonomer content (wt%) for the EOC was also taken from manufacturer data sheets. Comonomer content values for the EBC were estimated from the solid density data published by the manufacturer and random ethylene copolymers' data published by Alamo et al. [6, 7].

## Samples Preparation

A Multiplas (Model HM-10T) conventional injection molding machine was used to make the sequentially overmolded specimens, using two separate molds. At the first stage, PP substrate plates were injected at 200°C in the form of 40 mm  $\times$  70 mm  $\times$  3 mm pieces and stored. At the second stage, the already injected PP plates were placed as inserts in a second mold that contains extra cavities to overmold the ethylene copolymers, and EOC or

TABLE 1. Physical properties of used materials.

Properties	Copolymer (commercial designation)						
	Octene				Butene		
	8401	8411	8407	8130	7256	7447	PP
Density (g/cm <sup>3</sup> )	0.885	0.88	0.87	0.864	0.885	0.865	0.91
Melt index (dg/min)	30	18	30	13	2	5	11
Comonomer content (wt%)	31	33	40	42	18 <sup>a</sup>	28	_
Comonomer content (mole%)	10	11	14	16	10	16	—
Flexural modulus (MPa)	25.8	21.9	12.1	6.9	27.2	6.2	1450

<sup>a</sup> Estimated values.

EBC strips were overmolded. The dimensions of the overmolded strips are 160 mm  $\times$  20 mm  $\times$  2 mm. Six different melt injection temperatures (between 120 and 220°C) were used. Mold temperature was always 10°C to obtain a short molding sequence time. Samples made by overmolding PP with EOC are named as PP–EOC. Samples made by overmolding PP with EBC are named as PP– EBC. The melt index data in Table 1 shows that the EOC are injection grade polymers, while the EBC are not, and this circumstance severely limited the usable range of injection parameters that were used for the PP–EBC samples. Higher injection temperatures were needed for adequate mold filling.

PP–copolymer interface overmolding maximum temperatures were calculated using commercial simulation software (MoldFlow). Also the time evolution of the interface temperature was calculated from the same commercial software. Overmolding injection machine parameters were selected to minimize temperature gradients along the melt flow path, via calculations followed by design modifications.

## Thermal Treatment

EOC samples overmolded at a melt temperature of 140°C were heat-treated for time periods of 30 min, at constant temperatures ranging between 140 and 180°C. EBC samples overmolded at a melt temperature of 180°C were heat-treated for time periods of 30 min, at 180°C. To avoid samples' deformation and flow at temperatures close to and above melting temperatures, specially designed and constructed demountable aluminum molds were used with the inner surface covered with PTFE tape. Temperatures were controlled by individual heaters and measured inside the aluminum mold plates. The purpose of this thermal treatment is to further explore the effects of time and temperature on the adhesion process, for times much longer than the longest Rouse relaxation time for each copolymer. Five samples were treated at each mold temperature.

## Peeling Tests

An Instron Testing Machine (Model 4467) was used to measure PP–EOC and PP–EBC peeling force in a normalized 180 degrees peeling test (ASTM D 903-93). The peeling rate was 0.025 m/min, and the tests were all conducted at room temperature.

To minimize the EOC or EBC deformation during the peeling test, a 25- $\mu$ m-thick bioriented polypropylene film (BOPP) was glued over the EOC or EBC surfaces using a cyanocrylate adhesive (Loctite 770 primer and Loctite 406 adhesive). Preventing elongation of the EOC or EBC keeps the peeling speed essentially constant, and the elastomer energy storage is thus neglected. Other authors have also used a different approach, where the elastomer

is allowed to stretch and store elastic energy that is later calculated from separate stress-strain tests [8].

#### Amorphous Phase Free Volume Calculations

Published PP density data [9] was used to calculate PP specific volume. PP crystalline unit cell volume was calculated from cell dimensions published by Isasi et al. [10]. Using the DSC-measured PP crystallinity, the amorphous phase specific volume ratio was calculated for several temperatures.

## **RESULTS AND DISCUSSION**

Figure 1 shows a typical overmolded sample undergoing the peeling test. The aluminum plate tools provide a safe and rigid grip for the PP base, while the overmolded strip end is pulled by the machine standard elastomers grips. The typical force versus crosshead displacement graphs display a common pattern shown below in Fig. 2, as the peeling force measured in this kind of test is strongly dependent on geometric details—strip radius of curvature—that depend on the overmolded strip thickness, modulus, and adhesion strength. The curvature and the local deformation of the strip being pulled away from the PP surface affect the force applied on the load



FIG. 1. Typical PP–EOC overmolded sample undergoing the peeling test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



FIG. 2. Force-crosshead displacement graph for (A) PP–EOC Engage 8407. (B, C) PP-EOC Engage 8401. Interface temperatures achieved along the melt pathway are shown at three selected points.

cell. At the test start, for some of the samples, a pronounced maximum is observed due to geometric details at the mold that caused a slightly larger and curved adhesion surface. After reaching the debonding level, for constant interface molding temperature, the peeling force is almost constant along the whole peeling process, with rather large random oscillations that are typical for elastomers' debonding process. The thick solid line corresponds to the average peeling force, used for the results analysis. At the end of the peeling test curve, sometimes another maximum is observed, which is due to mold entrance effects that cause a local melt overheating and thus a local maximum of interface temperature.

Figure 2A–C shows typical peeling graphs for different PP–EOC samples, included for the sake of showing the effect of local differences of the interface maximum temperature. Peeling forces increase with this temperature, and the effect is larger at higher average temperatures.

Figure 3 shows typical data calculated with the Mold-Flow simulator for selected PP-EOC samples, in the form of local PP-copolymer interface temperatures versus total elapsed time, for several points along the melt path in the mold. The mold temperature was 10°C. The time scale displayed starts at the beginning of the injection process. The interface temperature calculation starts from the time when the melt flow front arrives at the particular point along the PP surface, denoted by the first point for each curve. For this sample, the maximum interface temperature increases slightly along the melt path. The temperature data correspond to the injection conditions used to make the samples used for the peeling force experiments shown in Fig. 2C. The small slope of the peeling force curve along the debonding length is caused by the difference of maximum interface temperature along the melt path, as is also shown in the Fig. 2C. Total injection time lengths for all PP-EOC samples are in the range of 2 s. Maximum interface temperature values are obtained at short time lengths after molding is completed and last for about 2 s. A similar pattern is also observed for the EBC samples.

Figure 4 shows the average peeling forces for all PP– EOC samples, shown as functions of octene comonomer content (wt%) for several maximum interface temperatures calculated with the MoldFlow simulator. Error bars



FIG. 3. Calculated interface temperature evolution for several points along the overmolding interface. Runs correspond to the samples shown at Fig. 2C. Points a, b, and c are identified at the peeling force curves.



FIG. 4. Average peeling forces as functions of octene comonomer content (wt%) for several calculated maximum interface temperatures.

shown are estimated from the original (not smoothed) graphs. For constant maximum interface temperatures, in the interface temperature range between 96 and 120°C, peeling forces show well-defined maxima for samples made with Engage 8407 (40 wt% octene), suggesting an optimum chemical composition for maximum adhesion after an injection overmolding process (short contact times for the hot melt on the solid PP surface).

The Engage 8130 (42 wt% octene) is the only EOC that could be injected at interface temperatures lower than 90°C, and it shows poor adhesion for samples injected at 86°C. All other EOC displayed virtually no adhesion when injected at an interface temperature of 86°C, and thus the measured peeling force was extremely low. For all EOC chemical compositions, the average peeling forces for constant chemical composition increase with maximum interface temperature in the range between 86 and 120°C. Peeling forces for all samples injected with an interface temperature of 132°C is almost independent of EOC chemical composition, and the peeling force result graphs show very large oscillations. These peeling tests are very difficult to carry on, because the stress applied to the elastomer is very close to its tearing stress. Then the elastomer strips alternate peeling and tearing along the test, showing large force oscillations because of the geometric changes at the peeling front, caused by the different deformation modes.

In summary, (a) for injection of liquid copolymer over a solid PP phase, adhesion at low temperatures is very poor for any copolymer composition; (b) despite the indication for an optimum copolymer composition, adhesion is best and independent of chemical composition at high temperatures These results suggest that adhesion for these copolymers depends strongly on the free volume of the amorphous (liquid) phase at the PP surface.

Figure 4 presents results on a basis (comonomer wt%) commonly used by the copolymer manufacturer for technical data sheets. Figure 5 is used to display the measured

peeling force results for all used ethylene copolymers on a common basis (comonomer mole%), because it scales well with the branching frequency along the linear random copolymer chain. Branching frequency has been established as the adequate basis for properties correlation for random semicrystalline ethylene copolymers [5, 6].

Data for all PP–EBC samples show that these EBC need higher interface temperature than EOC copolymers to attain similar adhesion levels. Also, for PP–EBC samples, the adhesion increases with interface temperature. As only two copolymers were available, the existence of an optimal EBC chemical composition cannot be evaluated. For the composition range used, adhesion increases with butene content. All copolymers with high branching content share the common feature of very good adhesion at high overmolding temperatures. As for Engage 8130 samples, adhesion for Engage 7447 (28 wt% butene) overmolded at interface temperatures higher than 139°C was very strong, and the copolymer alternate peeling and tearing during the test, with very large force oscillations, making measurements extremely imprecise.

Other authors have conducted similar adhesion tests for EOC on PP, with different sample preparation and testing procedures [8]. First, PP was compression-molded in the form of flat plates, and then EOC with several chemical compositions were compression-molded on top of the PP plates, in a range of temperatures. No action was taken to minimize the EOC deformation during the peeling test. Energy stored by the EOC was calculated for every test. Separate tests were conducted to quantify the EOC stress-strain behavior. Peeling tests were conducted at an angle of 90°, at room temperature, and results were shown in the form of calculated peel energy per unit area. For constant sample preparation temperature, also a maximum in the peel energy was reported for a chemical composition in the range used for our study. Nevertheless, the effects of preparation interface temperature on peel energy results reported by Godail and Packham [8] are



FIG. 5. Average peeling forces as functions of comonomer content (as mole%). Full symbols denote EOC, and hollow ones denote EBC.

somewhat different to our findings. Their reported peel energy results increase abruptly with preparation temperature in the range between 140 and 160°C and decrease markedly for temperatures above 160°C [8]. An explanation is advanced for this peel energy decrease above the PP melting temperature, as PP crystallization is claimed to cause rejection of interpenetrated copolymers chains.

Other studies have been recently conducted for adhesion of ethylene copolymers to PP homopolymer [11]. Statistical and block copolymers were used, and we refer here only to results published for the statistical copolymers. Samples were made by coextrusion of thin layers; thus, only liquid-liquid interface contact was used for samples preparation, for time lengths longer than Rousetype relaxation times but shorter than characteristic diffusion times. Peeling energy was shown to depend on the ethylene copolymers layer thickness, due to the energy invested on this layer deformation during the peeling process. Peeling was shown to take place at the PP-elastomer interface. Mechanical interlocking mechanisms, maintained at the solidification stage, are claimed to control the adhesion strength. Mechanically interlocked Rouse chain lengths are expected to be large enough for the adhesion strengths reported.

For all overmolded samples used in the present study, adhesion increases with the maximum interface temperature attained during injection. Some experiments were conducted to shed more light on the true adhesion process.

Two main differences exist between the samples preparation mode used by Godail and Packham [8] and also by Dias et al. [11], and the injection overmolding used for this study: (a) samples prepared with either the compression-molding procedure or the coextrusion process have relatively long EOC-PP contact time lengths, while samples prepared for our study have a relatively short EOC-PP contact time at the higher overmolding interface temperature: (b) PP melts crystallize slowly. Compression-molded samples have a long time for crystallization, and the PP surface semicrystalline morphology will not be much different to the inner layers. PP samples injected in cold molds show a relatively thick frozen skin layer (about 20-30 µm) with molecular orientation different to the inner layers [12]. Annealing at 160°C has been shown to homogenize the molecular superstructure throughout the PP plate thickness [12].

Expecting to check for contact time or PP frozen skin effects on copolymers adhesion strength, a selected number of our samples was thermally treated as described earlier, in a range of temperatures below and above the PP melting temperature. Results are shown in Fig. 6A and B. As a general rule, thermal treatments at temperatures higher than the injection temperature increase adhesion for samples injected at lower interface temperatures, and the adhesion increases with temperature, even above the PP melting temperature. For samples injected at the higher interface temperatures, thermal treatments at temperatures higher than the PP melting temperature do not change appreciably the adhesion strength.

The differences found between the adhesion strength measured in this study and in others [8] are not large, but still meaningful. Some causes may be found in the used PP chain statistics, which affect the PP crystallization rate, suggested by Packham as the reason for the adhesion decrease above the PP melting point because of rejection of the interpenetrated copolymers chains during PP crystallization. Also, the copolymer chain statistics must play an important role in liquid miscibility [13–15] that modifies the copolymer rejection process rate at the PP crystallization stage. Quantitative studies focused to elucidate these details are well beyond the scope of this article.

Figure 7 shows data from three sources, all of them on the same temperature basis. DSC melting data in arbitrary vertical scales are shown for an EOC (Engage 8411, dashed line) and for the PP (solid line). These data show



FIG. 6. Measured average peeling forces for (A) PP–EOC samples after thermal treatment, as functions of octene comonomer content (mole%), for several treatment temperatures. Heat-treated samples were injected with an interface temperature of 96°C. (B) Same data for PP–EBC samples as functions of butene comonomer content (mole%), for several treatment temperatures. Heat-treated samples were injected with an interface temperature of 139°C.



FIG. 7. DSC data for an EOC (Engage 8411, dashed line) and for the PP (solid line). Peeling force values for the corresponding EOC–PP samples—without thermal treatments—as a function of the injection interface temperature as solid circles. Calculated specific volume ratio for the PP amorphous (liquid) phase as hollow circles.

the wide temperature range where the hot liquid EOC contacts the solid PP surface, where some liquid molecule segments can penetrate hollow interstitial volume in the amorphous PP phase. Peeling force values for the corresponding EOC-PP samples-without thermal treatments-are shown as a function of the injection interface temperature as solid circles. Calculated specific volume ratio for the PP amorphous (liquid) phase is shown as hollow circles. The adhesion strength increase with temperature closely parallels the PP amorphous phase specific volume increase, suggesting that adhesion depends strongly on the temperature-controlled excess free volume available for the copolymer chain fingering process (Rouse-type relaxation process) to occur. Increasing the number of the copolymer chains that are linked to the PP increases the peeling force linearly. The longest Rouse relaxation times for these elastomers can be estimated from the viscosity-shear rate curve or from the ratio of the plateau modulus to the zero-shear rate viscosity, and it was always found to be in the order of fractions of a second. Thus, the calculated overmolding maximum interface temperatures last for time periods that are just longer than the longest Rouse relaxation times, giving enough time for fingering, but not for diffusion. Calculated characteristic times for diffusion for the used elastomers is in the order of 3 h.

Details considered to arrive at a conclusion on the main mechanism for adhesion in the overmolding process can be summarized: (a) adhesion depends strongly on temperature-activated excess free volume for the PP phase; (b) Rouse relaxation times are not expected to change much at liquid temperatures about 150°C above its  $T_g$ . Therefore, changes are mostly due to PP volume changes; (c) major changes for adhesion strength are obtained without thermal treatments, thus for short liquid–solid contact time lengths, and (d) long-time thermal treatments produce only minor changes in adhesion

strength, thus supporting the Rouse-type fingering process as the main cause for copolymer adhesion in the overmolding process.

## CONCLUSIONS

All the ethylene–octene and ethylene–butene random copolymers used for this study can give good adhesion to polypropylene homopolymer in overmolding processes, provided the right range of interface temperature is reached.

PP–copolymers adhesion is produced by a Rouse-type fingering mechanism that develops in a short time of the order of less than 2 s. Adhesion strength closely correlates with the PP amorphous phase excess free volume. Thus, longer time thermal treatments do not modify adhesion strength in a significant way, unless its temperature is different to the maximum interface temperature used for overmolding.

Some ethylene–octene copolymer chemical compositions cause more efficient adhesion, and the peeling force values for these compositions are higher than for others, for the same interface maximum temperature.

Adhesion can be then safely controlled via the maximum interface temperature, which can be modeled with a commercial simulator. It can be inferred that preferential adhesion can also be produced in selected parts of the overmolding piece, for easier later separation for recycling, by careful design of the injection mold and injection points. Overmolding of large surfaces, as found for cars' doors and dashboards, will require a careful mold design, including multiple injection ports sequentially open and closed to obtain controlled maximum interface temperature for the whole PP–copolymer interface.

Interface temperature changes cause the larger changes for final values of peeling force for copolymers with comonomer content in the range of 10 mol%. Therefore, these copolymers will allow the wider selection of adhesion strength to be attained.

Adhesion of copolymers with 14 mol% octene will allow easier adhesion control, in a somewhat narrower adhesion strength value range, as these compositions show less temperature sensitivity.

Simple piece design will allow easier recycling when copolymers with comonomer content in the range of 10 mol% are used. Intricate designs will be more easily overmolded with copolymers with octene content in the range of 14 mol%, and recycling may become more difficult.

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