Two-component injection moulding of thermoset rubber and thermoplastics: Absolute interface strength prediction

W. Six, F. Desplentere
Materials Technology TC, KU Leuven, Bruges Campus, Belgium

G-J. Bex and A. Van Bael
Materials Technology TC, KU Leuven, Diepenbeek Campus, Belgium

J. De Keyzer
Sustainable Chemical Process Technology TC, KU Leuven, Diepenbeek Campus, Belgium

ABSTRACT: Polymer products which combine two different materials, for their specific properties, are often produced via the two component injection moulding technique. An optimal adhesion between the two components is a critical quality parameter for this kind of products. This property for the combination of two thermoplastic materials is well known and extensively described in literature. For thermoset rubbers combined with thermoplastic materials, almost no information is available on the adhesion between the two components and how to predict its strength. From earlier research, it is known that curing of the thermoset rubber combined with the interface temperature influences the interfacial strength, however, until now, no absolute value prediction is given. This paper presents the necessary insight to predict the absolute interfacial strength, based on the melting trajectory of the semi-crystalline thermoplastic material and the degree of cure of the thermoset rubber. Results show that this method makes it possible to predict the manner of interface failure (adhesive, cohesive or mixed), estimates the interfacial strength and correlates well with experiments on a simple geometry.

1 INTRODUCTION

Two component injection moulding is a process where a first material is injected into a cavity, cooled down and afterwards a second equal or different material is injected on the first component to form a finished product. In this product, adhesion between the two components is one of the most important quality parameters. For all kind of 'thermoplastics' and 'thermoplastic elastomers' (TPE's), studies have been performed to predict the influence of local parameters on the interfacial strength between the two components, Prager et al (1981) and Neogi (1996) state that amorphous polymers can heal as soon as temperature rises above T_g and Brownian montion can occur. Also Huang et al (1999) found that interfacial temperature mainly determines the interfacial strength for a two-component injection molding product produced of polystyrene (amorphous) as it influences the interpenetration depth of the overmoulded material. They present an exponential function which gives the relation between interpenetration depth and degree of bonding. In their publication, it is assumed that overmoulded amorphous polymers are healed completely if the interpenetration depth of this materials is equal to ½ of the radius of gyration. For semi-crystalline polymers, crystals prohibit healing, and thus it is assumed that these kind of polymers have to exceed melting temperature to heal. (J. Lamèthe et al. 2005) In the cooling phase of a semi-crystalline material, literature states that healing is possible until the polymer starts to crystallize. (A. Levy et al, 2012). M. Bouwman et al. (2017) presented a method based on the latter, predicting the adhesive strength between a semi-crystalline polymer and an organosheet having the same semi-crystalline matrix.

For the combination thermoplastic material, amorphous or semi-crystalline, and thermoset rubbers in overmoulded product, no in-depth studies have been performed on the prediction of adhesion. Bex et al (2018), however, presented a paper showing the results of a DOE, determining the influencing injection molding parameters for this material combination. Tests showed that interfacial temperature, determined by mold temperature has the largest influence on the bonding strength between the two components. Bex et al (2017) also showed that the order of injection is important for this kind of material combination. The thermoplastic material should be injected first, and must be overmoulded with the thermoset material afterwards. In that specific order, the thermoplastic material can heal to the thermoset rubber before the rubber itself cures. If rubber is cured first, almost no chain mobility is left to heal towards the thermoplastic material.

The use of numerical simulations for all kind of processes, including injection molding is very common. For thermoplastic, thermoplastic overmoulding many simulation tools are available, however, as far as known by the authors, no real simulation tools are available to predict adhesion between those two components. Furthermore, until now, for two component thermoset rubber - thermoplastic injection molding, there is even no straight way to simulate the overmoulding process. (Shoemaker 2006). Six et al (2016), presented a method to overcome this issue by using the simple reactive solver and implementing the first component as a part insert with specified initial conditions.

2 METHOD

2.1 *Mold and material*

To investigate the adhesion between a thermoset rubber and a thermoplastic material, a specialized mold has been developed by Bex et al (2017), to produce a two component plate product. The plate product exists of two components, a thermoplastic part and a thermoset part. The procedure for the production of these products is shown Figure 1. To produce this kind of products the mold has two thermally insulated cavities where temperature can be controlled separately. This temperature regulation is needed to avoid melting of the thermoplastic part while curing the thermoset part.

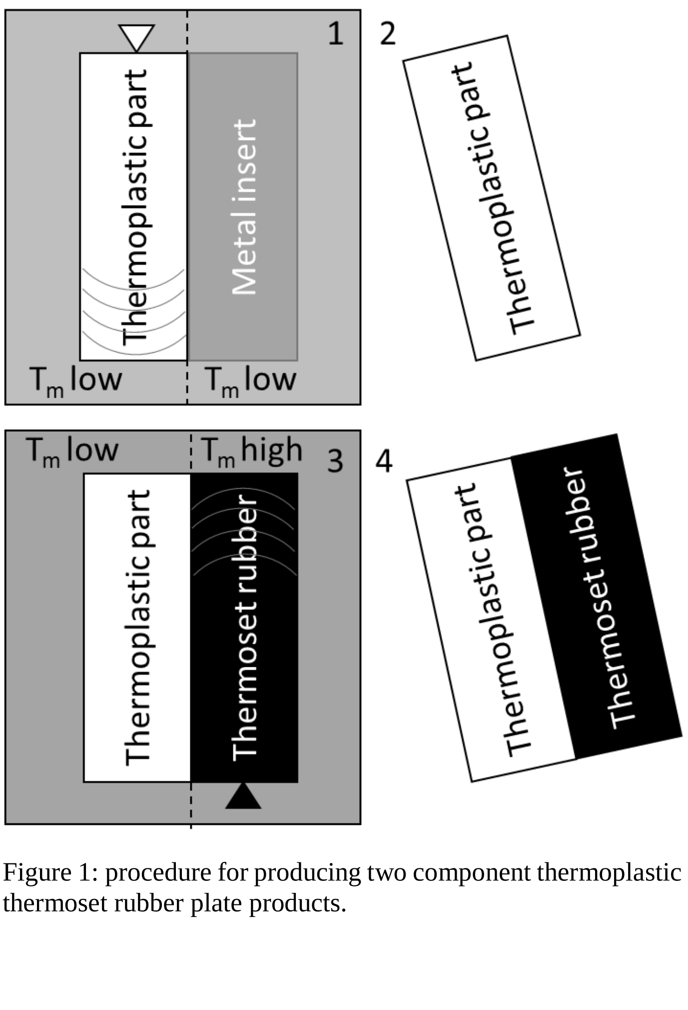

Figure 1: procedure for producing two component thermoplastic thermoset rubber plate products.

The materials used for the study, discussed in this paper are the following:

- Sabic HDPE M80064S
- Hercorub EPDM 005K

The used curing temperature for the thermoset rubber (T_m high), for all test will be 180°C, curing time and temperature for the thermoplastic cavity will vary during the presented study.

2.2 *Influence of interfacial temperature*

Interfacial temperature has been proven to have a major influence on the interfacial strength by Bex et al (2018). Modeling temperature influence on healing is mainly done by the reptation theory (Neogi 1996). This theory describes the movement polymer chains, in melt material, restricted by neighboring, entangled polymer chain. The chains are only allowed to move back and forward within an idealized tube. This theory is often used for predicting diffusion of macromolecules across the interface between the two materials (Tierney et al. 2005). The amount of healing is defined as 'healing degree' D_h. which is the ratio between instantaneous and ultimate interfacial bond strength Lee et al. (1987) stated that this D_h can be modeled by using a (t_w) or welding time by the use of equation 1

$$\frac{\partial D_h}{\partial t} = \left(\frac{1}{t_w(T)}\right)^{\frac{1}{4}} \quad (1)$$

For high molecular weight polymers, reptation times, the time to achieve complete healing, have been found to be smaller than welding times, the time where polymer chains can move freely across the interface. Furthermore, for semi-crystalline materials, it has been observed that reptation times are very short above melting temperature ($T_{m.}$). The transition is almost instantaneous, thus binary, However, instead of using a binary, using the melting trajectory is considered of greater importance. (Bouwman et al.2017)

The melting trajectory of the semi-crystalline, High Density Poly-Ethylene (HDPE) is shown in Figure 2. This curve has been defined by a DSC analysis.

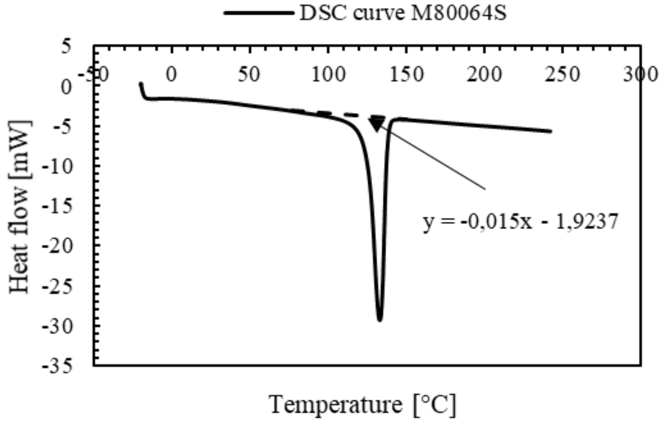

Figure 2: Melting trajectory of HDPE (Sabic M80064S); heating rate 20K/min

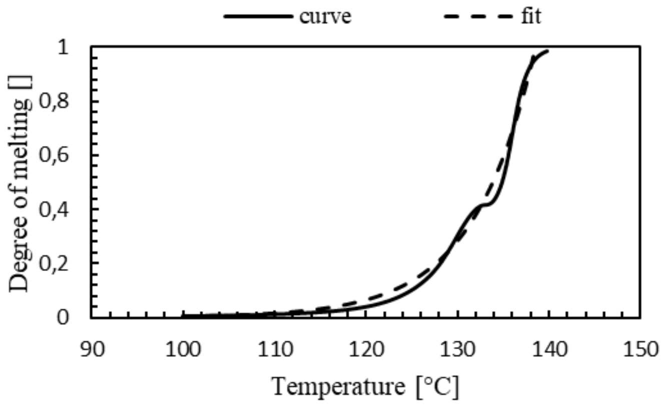

Figure 3: Degree of melting D_m in function of temperature for HDPE Sabic M80064S

The base line is added on the first heating curve and the cumulative area of the melting peak is normalized. Figure 3 shows this cumulative curve of the used HDPE material. The curve shows the ratio of crystallites which are molten relative to the original state at room temperature. The given curve has been fitted with an exponential model, for numerical modeling reasons. The result of this fit is shown in Equation 7. M. Bauwman et al. (2017) state that the degree of melting (D_m) is correlated to the degree of healing.

At a value of zero for the D_m, no healing can occur as the chain movement is completely blocked by the crystallites. At a D_m of one, a complete healing is possible as no crystallites are left and chains have maximum mobility. For the ease of the model, a simple, time independent relation between degree of melting D_m and D_h is used for $0 < D_m < 1$. This is valid as reptation times are smaller than the welding times for semi-crystalline materials. (Lee et al 1987)

Determination of the adhesive strength can be done by mechanical testing samples with a predefined interfacial temperature. The thermoset rubber must be cured completely. By testing the samples, the adhesive strength can be determined. After testing a pure adhesive failure is essential, otherwise, the given data

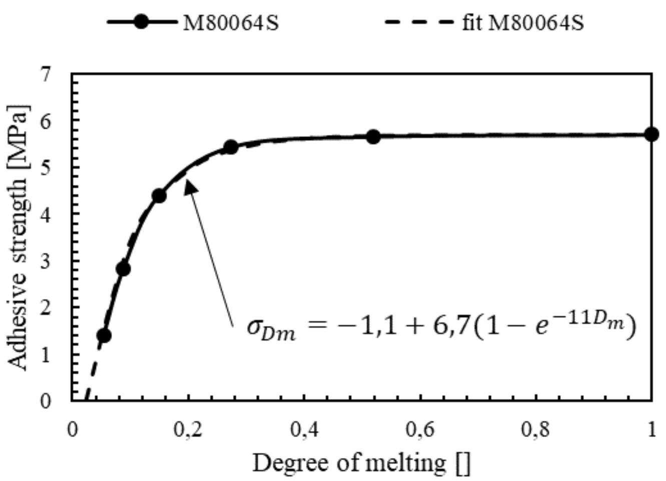

Figure 4: Measured adhesive strength of Sabic HDPE M80064S to Hercorub EPDM 005K

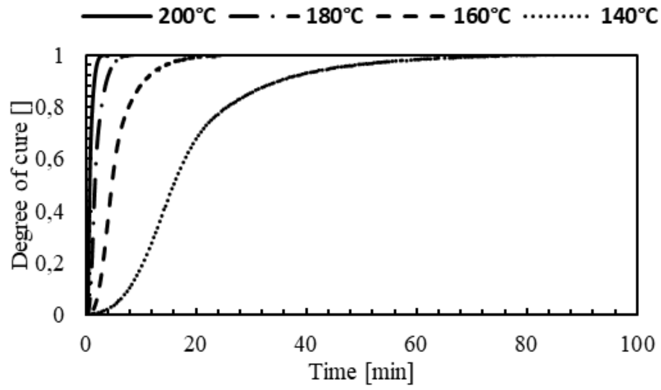

Figure 5: Curing behavior of Hercorub EPDM 005K measured by MDR. Curing degree in function of time and temperature

cannot be used to define adhesive strength in function of degree of melting. This strength is material combination dependent

The result of this data is defined by an asymptotic regression function, defined by equation 2:

$$\sigma_{Dm} = \theta_1 + \theta_2(1 - e^{-\theta_3 D_m}) \tag{2}$$

The result of this test, combined with the fit given by equation 2, is given in for the HDPE materials injection molded in combination with the Hercorub EPDM 005K.

2.3 *Influence of curing*

The second main influencing parameter is the degree of cure of the thermoset rubber in the adhesive zone. Previous studies performed by Bex et al (2018). showed an optimal adhesive strength if curing of the thermoset material is complete. This is not surprising as strength of rubber is correlating with the degree of cure. Uncured thermoset material has much chain mobility and cannot fixate the diffused thermoplastic polymer chains. By characterizing the curing behavior with a moving die rheometer (MDR) and fitting the data by the Kamal model, given in equation 3 (Kamal et al. 1973), the resulting degree of cure can be predicted for specified temperatures and curing times

$$\frac{d\alpha}{dt} = \left(K_1 + K_2 \cdot \alpha^m\right)(1-\alpha)^n \tag{3}$$

The value of K_1 and K_2 are given by equation 4

$$K_i = A_i \cdot \exp\left(-\frac{E_i}{T}\right) \tag{4}$$

where α = the degree of cure, T = the temperature and t = time, i= 1, 2. The other variables, A_i, E_i, m and n are data fitted variablesFigure 5 shows the curing behavior of the used EPDM 005K material.

To determine the local rubber strength, determination of the green rubber strength ($\sigma_{\alpha=0}$) and of the full cured strength ($\sigma_{\alpha=1}$) is necessary. Afterwards a linear relation can be created between degree of cure and the rubber strength. This relation is shown in equation 5

$$\sigma_\alpha = \sigma_{\alpha=0} + \frac{\sigma_{\alpha=0}}{\sigma_{\alpha=1}}\alpha \tag{5}$$

According to Figure 5, curing time at high T_m, should be below 5 min, and full curing should not be a prob

the two component product, temperatures in the adhesive zone are much lower. This will consequently affect the final rubber strength.

2.4 *Prediction of interfacial strength*

Interfacial strength depends on two major properties, strength of the interface itself and the strength of the materials near the interface. If the interface itself fails, the failure mode is defined as an adhesive failure, on the other hand, if the material near the interface fails it is defined as an cohesive failure. In the given 2K situation, and as stated in section 2.2 and section 2.3 local temperature at the interface will mainly determine the interfacial strength. It influences the cohesive strength by defining the degree of cure of the thermoset rubber and determines the degree of healing of the thermoplastic material towards the thermoset rubber.

By producing samples with a defined interface temperature, combined with a full cured thermoset rubber, the adhesive strength versus degree of healing can be determined by tensile testing these predefined samples.

Determination of the local interface strength (σ_I) can be done by comparing the local rubber strength and the expected healing strength at the interface. This is given in equation 6

$$\sigma_I = \begin{cases} \sigma_\alpha, & \sigma_\alpha < \sigma_{Dm} \\ \sigma_{Dm}, & \sigma_\alpha \geq \sigma_{Dm} \end{cases} \tag{6}$$

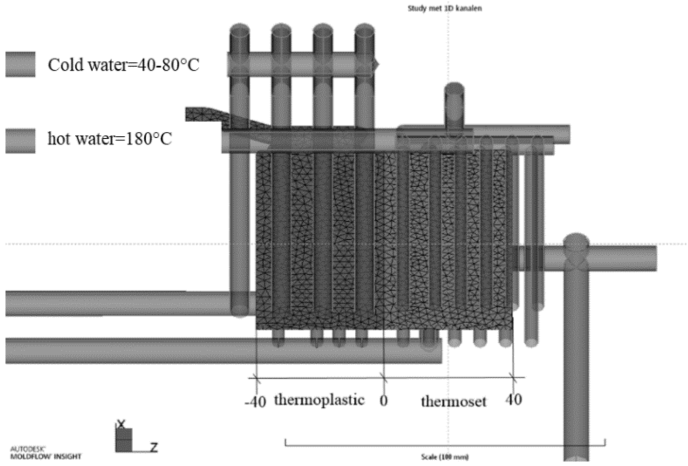

Figure 6: Simulation model for plate product

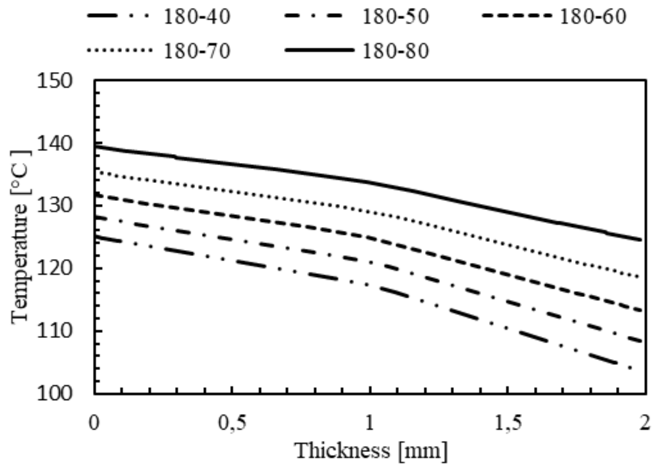

Figure 7: Temperature through thickness at the interface of the plate product for various temperature combinations

3 SIMULATIONS AND RESULTS

3.1 *Simulation model*

To predict the adhesive strength of the unknown products, numerical simulations have to be performed to determine the local temperature during the injection moulding phase. The simulation model of the plate product is shown in Figure 6. In the simulation model, cooling channels are represented by 1D Channels and the product is represented by 3D elements. The curing temperature for the thermoset material is set at 180°C. In the presented study temperatures for cooling the thermoplastic part are set between 40 and 80°C in steps of 10°C. The thermoplastic part is inserted in the reactive solver as a part insert with the properties of the M80064S HDPE material. The thermoset EPDM rubber Hercorub 005K is injected at 80°C in 0.5s. Injection time has to be short to avoid curing of the thermoset material during the injection phase.

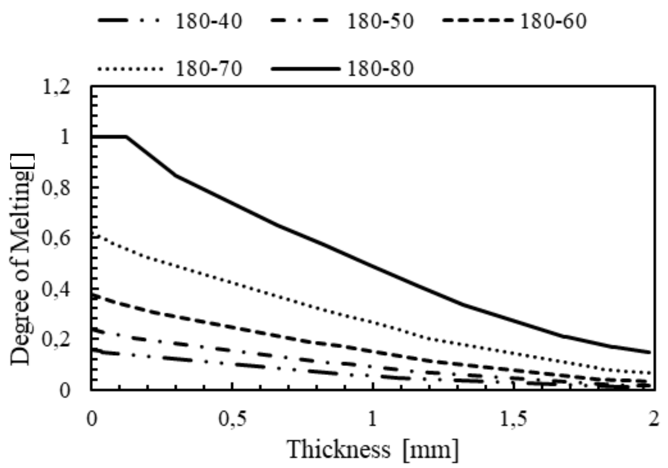

Figure 8: Degree of melting trough thickness for various temperature settings.

3.2 *Results*

By performing a Cool(FEM) Fill Pack simulation, the local interface temperature of the product can be determined for various temperature settings. The result of this interface temperature is given in Figure 7.

In Figure 7 and further results, 180-60 complies with a thermoset water temperature of 180°C and a thermoplastic water temperature of 60°C

The figure shows the interface temperature trough thickness. This temperature is not constant, as result of this variation of temperature, degree of melting will also vary through thickness. By using the exponential fit, given in Figure 6, defined by equation 7, the local effective degree of melting can be calculated

$$D_m = 1{,}1 \cdot 10^{-9} e^{0.149T} \quad (7)$$

The resulting degree of melting for the various temperature settings is shown in Figure 8. As shown, the resulting degree of melting varies from 0 to 0.2 for the lowest temperature setting (180-40) and increases towards a value between 0.2 and 1 for the highest temperature setting (180-80). Increasing the temperature towards higher values would result in higher degree of melting at the interface. However, surpassing the D_m of 1, the material will get low viscous and the stiffness of the material at the interface will drop dramatically and, as a result, the interface would deform while over moulding.

Next to the degree of melting, the local degree of cure of the thermoset rubber can be determined by these simulations. As stated in section 2.3, the local degree of cure determines the resulting strength of the rubber. This strength is given in Figure 9 for three curing times. The average curing degree is given as the third value in the nomenclature. As can be noted, also the strength of this rubber varies through thickness due to the temperature variation shown in Figure 7. Next to

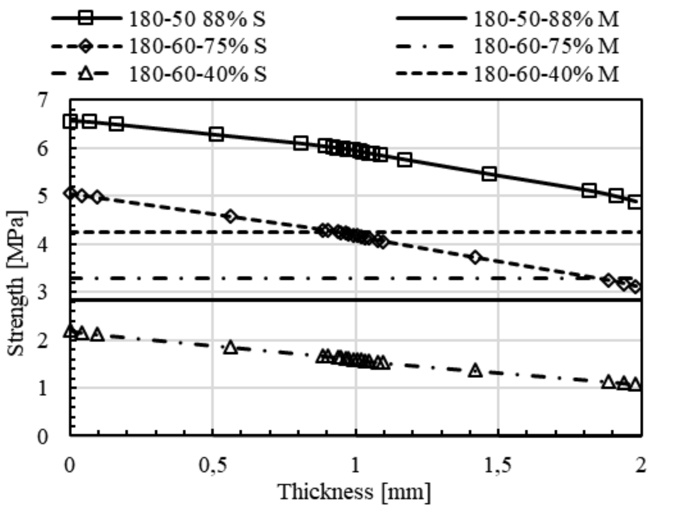

Figure 9: Strength of thermoset rubber Hercorub EPDM 005K at the interface of various test samples (inclined lines) combined with the real interface strength in combination with Sabic HDPE M80064S (horizontal line) S in the connotations stands for simulation, M for measurement.

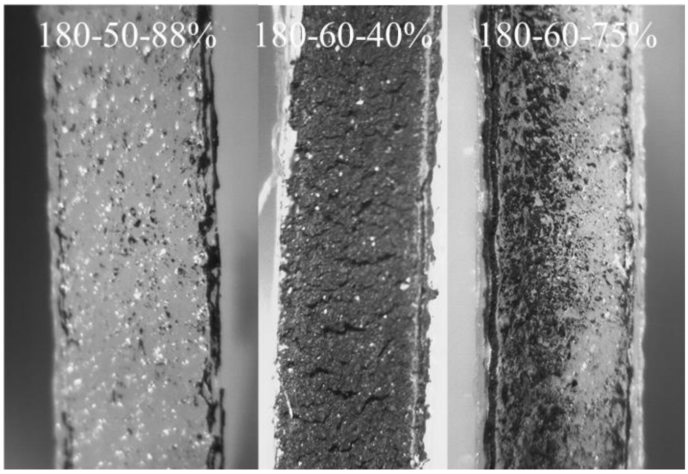

Figure 10: Interface of three samples after testing

the rubber strength, the horizontal lines on Figure 9 show the measured tensile strength at the interface. Three possible situations are given, the measured strength is higher, lower or crosses the line of the rubber strength. The interface of these three situations is given in Figure 10. If the rubber strength is higher in comparison to the real interface strength, the sample will fail at the interface and resulting in an adhesive failure (180-50-88%). In this case, the sample will fail due to the degree of melting at the interface. In a second situation, if the rubber has a lower strength, compared with the measured strength, the rubber has to fail, and a cohesive failure will be the result (180-60-40%). The last case where lines cross, one part of the interface should have an adhesive failure while the other half should have a cohesive failure. As can be seen in Figure 10, this is the case in the 180-60-75% sample.

4 CONCLUSIONS

It can be concluded that combining the data for adhesive strength, determined by the degree of melting for HDPE, and the rubber strength, determined by the degree of cure, enables to predict the failure behavior of the interface. The described method predicts the adhesional strength, since there is a good correlation with experimental values

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