

Quantification of the Self-healing Behaviour of a Supramolecular Elastomer by means of a Peel Testing Procedure

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Abstract

A method for testing and quantifying the self-healing behaviour of an elastomer was investigated at the NovAM (Novel Aerospace Materials) group at the Delft University of Technology (the Netherlands).

A testing plan was devised using design of experiments, aiming at optimising sample production for studying the influence of temperature, pressure and time on the healing response exhibited by the supramolecular elastomer. The production method was investigated through experimenting alternative strategies for processing the polymer.

Several samples were produced, fractured and healed. The data analysis of the results revealed significant inconsistencies in the peeling curves obtained in the testing of the virgin samples, hindering the suitability for a statistical model of the phenomenon of self-healing.

Some of the issues related to the scatter of results were further explored, aiming at understanding and improving the production procedure and obtaining reproducible samples.

It can be concluded that an adhesive is required to prevent failure of the polymer-aluminium bond. Adhesion promoted simply by curing of the material on top of the aluminium revealed to be insufficient. The last samples produced resorting to adhesive display consistent results in what comes to both the stable peeling curves and the homogeneous fracture mode (suitable for healing).

Keywords: self-healing, elastomer, supramolecular, peel-test, adhesion

1. Introduction

The classical approach for material design is one that aims at avoiding external loading damage and its effects by providing the best initial mechanical characteristics. On the other hand, the design of self-healing materials accepts the inevitable damage and proposes a commitment between the original properties and the capability of their autonomous recovery, hence extending its work life and of the product it is part of.

A healable rubber which can withstand large deformations has different potential applications such as adhesives, coatings, dynamic seals, shock absorbers, anti-vibration systems or even tissue engineering. In addition, its usage as a matrix in composites further extends this range to fields like smart electronics.

The present work concerns the study of Reverlink[®] HR, a self-healing polymer created and developed following a cooperation between Ecole Supérieure de Physique et Chimie Industrielles (ES-PCI) and the chemical producer Arkema, currently being commercialized by the latter. It consists of an elastomer that makes use of non-covalent bonds

(supramolecular network) in order to obtain its healing properties. The self-healing behaviour has already been studied [1, 2] up to some extent, but the specific effect of the temperature, pressure and time of the healing process is still to be investigated.

The aim of this project is the development and analysis of a test method for quantifying the healing efficiency of self-healing elastomers, in particular of the Reverlink[®] HR system, and the influence of the healing conditions in what concerns to temperature, pressure and time.

Among the different self-healing approaches in the design of new polymeric materials, one can distinguish between the concepts of intrinsic and extrinsic healing, depending on whether the regenerative properties are enabled by a temporary increase in the mobility of the polymeric chains or, on the other hand, if they are provided by an external agent added to it, respectively [3, 4]. The former strategy can also be divided according to the chemistry used to assemble the constitutive molecules, namely covalent bonds or supramolecular interactions - of which hydrogen bonding is perhaps one of the most studied and developed healing designs

[3, 4].

The two main healing mechanisms for this system are hydrogen bonding and polymer chain interdiffusion, although only the former has been addressed in the publications of ESPCI. This one relies basically on the reversibility of the hydrogen connections, which can re-associate after de-bonding caused by physical separation. The diffusion theory, on the other hand, states that the re-attachment of the separated interfaces results from the migration of the molecules over the polymer-polymer interface and following entanglement of the chain ends with the new surrounding ones [4, 5, 6].

The healing capacity of the material was presented in the article [7] by simply cutting the samples and then manually bringing them together for different short times at room temperature. This means there was no record of the exact pressure applied and also no variation of the temperature at which it was done. From these tests it was concluded that the healed samples were able to support large deformations and retrieve their original shape without any heat or strong pressure applied.

The research done so far on the processing and properties of Reverlink[®] already reveals some insights on its self-healing mechanisms. Essentially, it relies on small polymeric chains (oligomers) and strong long-lived yet reversible supramolecular associations between them. This chemical composition allows for a low fraction of non-associated groups in equilibrium, so that when there is breakage of the hydrogen bonds, they naturally seek equilibrium by re-connecting. Shorter healing times mean less bridging across the interface and so lower elongation and strength at break result in the mechanical tests [7].

A more comprehensive investigation on the relation and influence of temperature, pressure and healing time on the recovery of mechanical properties of this self-healing system is still to be done.

The present document describes the different tasks performed: design of experiments, processing of the samples of Reverlink[®], fracture of the samples with the peel-test, healing and analysis of the data obtained from the samples.

2. Background

A hydrogen bond is an electromagnetic interaction between polar groups or molecules in which H is bound to strong a electronegative atom. It is a special type of dipole-dipole force which is stronger than usual but still considerably weaker than covalent and ionic bonds. For this reason, adding to the thermal reversibility, the assembly of several of these bonds together provides potential for healing while still preserving acceptable mechanical properties.

The first paper published by ESPCI [7] introduced this system and concept as well as demonstrated the rubber behaviour of such network. For this purpose, several techniques were used, such as DSC (Differential Scanning Calorimetry), X-ray scattering, tensile stress, relaxation and creep experiments.

Several papers of the same authors focused on the chemistry of this elastomer [1, 8, 9, 10]. Recently the authors also focused on the mechanical properties and healing [2], addressing specifically the activation and deactivation phenomena and the definition of adhesion in opposition to healing.

Basically, the concept of self-healing requires localized temporary mobility of the molecules next to the damage. For Reverlink[®], this freedom of movement is allowed by the network structure of small oligomers connected between each other through the reversible hydrogen bonds. Both the re-association of these bonds and the migration of the polymer chains provide the reconstitution over the interface of two fractured surfaces put together.

2.1. Surface Activation and Deactivation

A phenomenon already explored is the effect of varying the waiting time that two pieces cut apart are kept before reattaching them [7]. After some time, their ability to heal is found to decrease. This is thought to be due to the reaction of free non-associated groups within the broken part.

This requirement for non-equilibrated free groups on both contact surfaces in order to make healing possible was confirmed by trying to assemble a freshly cut one with another from a non-broken specimen. No adhesion resulted from this, which indicates that there should also be a trigger for enabling the healing capability and to "activate" the surface.

Surface deactivation was further investigated in the 2012 publication [2], with the storage of fractured surfaces at room temperature and controlled atmosphere¹ prior to the healing. The recovery capacity appeared to be preserved for up to around 12 hours at the temperature of 23°C, which can be observed in the force-displacement curves of two specimens tested for this purpose, showing only a slight difference between two samples healed during 1 minute but with one being cured right after fracture and the other after 12 hours of storage time.

2.2. Adhesion vs Healing

This subject was addressed in the paper of 2012 [2], where the difference between the concepts of adhesion and healing was explored in two experiments based on the tackiness testing method. Millimeter thick films were prepared in order to produce quali-

¹18±5%Relative Humidity

tative measurements to establish the distinction between weak self-adhesion of melt-pressed surfaces and strong self-healing of fractured ones, leading to the conclusion that self-adhesive strength is in fact enhanced by the damaging process.

The self-healing experiment differed from the adhesive in the fact that the two surfaces on the metal holders were now fused together to create a bulk sample to break. A brittle fracture was made in order to obtain clean and smooth fracture surfaces with the least bulk deformation possible. It was performed at the speed of 1.5 mm/s. Right after this, the two surfaces were brought back to the testing temperature (33°C) and put together to heal. The separation stage was then analogous to the adhesion experiment, with measurements of force and displacement done at constant opening speed.

These two distinct fracture behaviours observed show that after around 5 minutes of healing there was a turning point where the interface polymer-polymer got considerably stronger. This might be an indicator of the transition from adhesion to healing, with enough hydrogen bonds re-associated to provide a strength closer to the one of the original bulk material.

Furthermore, for contact times between 10 and 100 minutes, quasi-full recovery was achieved. This might be a suitable reference for the time frames of the healing process for further experiments.

Additionally, sensitivity to humidity was found, presumably due to the large content in polar moieties. This means that water absorbed acts as a plasticizer and modifies the mechanical properties of the system – water uptake decreases the glass-transition temperature, T_g . For this reason, the samples should be stored in a desiccator under controlled conditions for 12h minimum prior to testing for insuring reproducibility of the tests². Furthermore, the humidity effect might also be related to the deactivation, which is something that requires further investigation.

Other studies have also been made on Reverlink[®], but not so focused on the mechanical properties after healing nor on its dependence on temperature, pressure and time [11, 12, 13, 14]

3. Experimental Procedure

3.1. Design of Experiments

Given the three different variables to be studied (healing time, temperature and pressure) and their effects on the healing capability, there is a need for a complete set of tests, namely a factorial experiment one that considers all possible combinations of the levels chosen of the factors. This is indicated for the case in which there is no prior knowledge about the exact type of influence of each parameter

in the response of the system.

For reliable results, each of them has to be analysed in a suitable range and values. Therefore, the time of healing of the samples was chosen to be in the domain [0,2] hours; the temperature in [20, 90] degrees Celsius and the pressure in [0.1, 6] bar. This means that a full factorial experimental procedure for 6 steps of each variable would result in 216 samples. In order to optimize this process and provide feasibility, the well established Response Surface Method(RSM) will be employed, enabling a considerable reduction in the number of samples to be tested.

RSM makes use of mathematical and statistical tools to approximate the behaviour of a desired response of interest as a function of several variables. Due to the fact that the relationship between the response and the independent variables is unknown, a second order model will be used.

After having considered different design options for devising the experiment points, the selected model was the Inscribed Central Composite Design. The reasons for the choice were: suitability for a limited variable space; rotatable design – assuring a consistent and stable variance of the predicted response; 5 levels per factor; total of 24 runs.

Since at room temperature the healing shows to be already considerably fast, with increasing temperatures the recovery is expected to be even faster, which means most of the relevant response data will be in the first hour of healing. For this reason, additional test points were added to the ones dictated by the central composite design. These were chosen to be for the lower boundaries of the ranges of temperature and pressure, so for around 23°C and for 0.1 bar. All together, this means there are 43 different healing conditions, which leads to 86 samples to be produced in order to test 2 specimens for each one, excluding the repetitions of the central point.

3.2. Sample preparation

In order to investigate the self-healing behaviour of this elastomer considering both the fracture and the healing stages, a suitable test and specimen geometry are required. So far, dog-bone samples are usually the preferred choice for their ease of testing in the tensile machine. They are simply cut with a razor, put together and tested again, which is an effective way for comparing the strength after healing with the one of the virgin samples but does not allow for a controlled coupling of the two separated parts.

Therefore, a new approach to this matter has been followed by designing the specimens to be fractured in a T-shape peel test, providing a larger rupture area and enabling the healing to be done in a mould convenient to be closed under different pres-

²According to what has been done in [2]

tures and temperatures.

The evaluation of the healing capability of this material includes a fracture of a virgin sample, healing according to the planned schedule, and fracturing it again, as illustrated in Figure 1

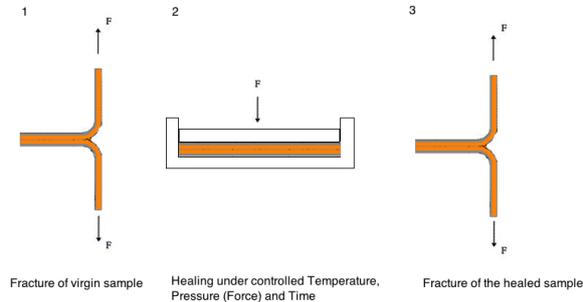


Figure 1: Scheme of the fracturing and healing course of action

For the purpose of the peel test, the samples were designed as two 1 mm rectangular layers of the elastomer cured together in half of the contact area (40×20 mm) and with an outer coat of 0.2 mm aluminium foil, as depicted in Figure 2. The closed part is to be fractured and healed while the open one provides the support for clamping in the tensile machine. Moreover, the aluminium layers are essential to prevent viscoelastic behaviour of the material during the test and ensure that only the adhesion force is being measured.

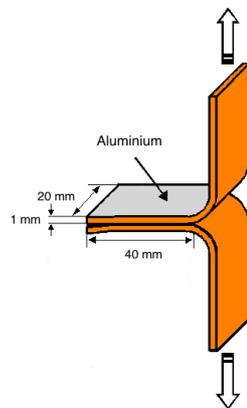
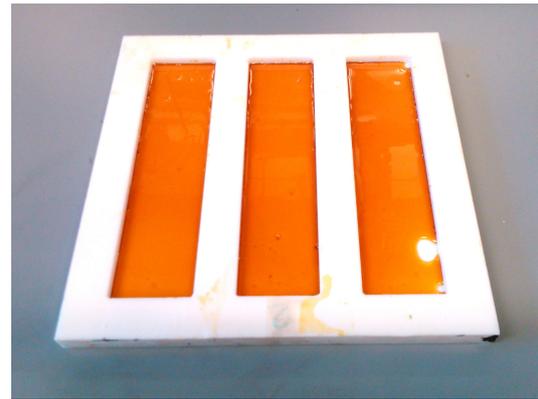
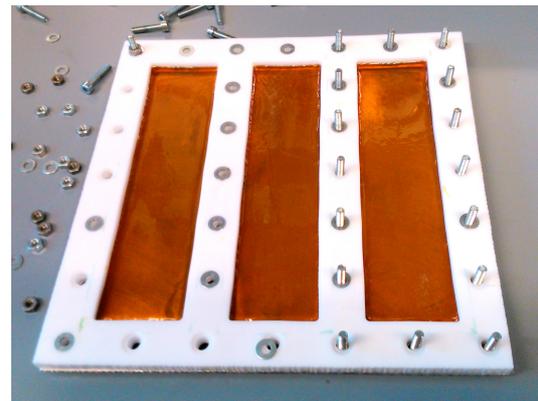


Figure 2: Peel-test specimen geometry

The batches of Reverlink[®] HR come directly from Arkema ready to be cross-linked at the recommended temperature of 130°C for 24 hours. Due to its high viscosity and adhesiveness, the curing of the samples has to be performed in a Teflon mould, given its excellent anti-adherence properties. To prevent spontaneous cross-linking, the material has to be preserved at low temperature (under 5°C), in which it is in the solid state. As it is taken out from



(a) Samples after first 18h of the curing in mould 1



(b) Samples after first 18h of curing being taken out of mould 2

Figure 3: Teflon moulds used for sample production

storage and weighted for sample production, it acquires a sticky and difficult-to-handle state. This is how it is put in the pre-heated oven for the curing cycle. As soon as there is a more homogeneous spread of the material, vacuum is applied during around 1 hour to release any air that might be entrapped.

Essentially, two types of Teflon moulds were used for processing this polymer:

- Mould 1 – One piece Teflon square with three compartments of $160 \times 40 \times 7$ mm each and a cover (Figure 3(a))
- Mould 2 – Teflon plate with three slots of $160 \times 40 \times 7$ mm each to be placed on top of aluminium plate attached with screw system, for tightening the aluminium foil in between the two (Figure 3(b))

The established curing cycle was then set to be 18 hours of curing after which the samples were cut in halves (80×40 mm) and the correspondent parts were overlapped to cure again, but now with a Teflon film of 40×40 mm in between the layers to be peeled apart. At the end the specimens were once

more cut in two (80×20 mm) and so a total of 6 is obtained out of the production cycle of one mould.

Mould 1 was used in the first trials but flowing of the elastomer constituted an obstacle to the proper attachment of the aluminium foil during the curing stage. On the other hand, mould 2 allowed the crosslinking of the polymer to promote its adhesion to the foil, as well as homogeneous displacement in its surface. For this reason, mould 2 was used further on for producing the samples to be tested.

Additionally, a parallel approach for the attachment of the aluminium foil to the elastomer was also performed by application of a strong adhesive after the first 18 hours of curing in mould 1. When tested, these samples displayed a clean homogeneous surface failure on the polymer-polymer interface instead of adhesive failure. This procedure has potential to be used with different self-healing elastomers to be studied, since it is independent of the processing method of the samples and can easily be done afterwards. However, since the method of curing the material directly on top of the aluminium proved to work and avoid one more step in the process where irregularities could arise (the application of the adhesive), this alternative was set aside for the production of the required samples for the model.

3.3. Peel test

The evaluation of self-healing properties of elastomeric materials poses several practical issues related to its mechanical behaviour. The high plasticity and elasticity of rubbers lead to considerable deformations of the test specimens and so alter the original bulk characteristics of the material. For this reason, the comparison of virgin samples with the healed ones might be compromised, since not only the fractured interface has changed, but also the surrounding bulk material in the sample. Thus, a natural approach for circumventing this problem is the resort to adhesion experiments, of which the peel test is a well established method. In addition, the attachment of a 2 mm thick aluminium foil on the outer part of the samples prevents viscoelastic behaviour.

The fracture of the samples was performed according to the geometry of the T-Peel test, as illustrated in Figure 2. It was done using an Instron tensile machine. As explained, half of the area of the samples is kept open with a Teflon film during the last stage of curing. These parts provide the surface ends to clamp in the experimental setup. So, the sample dimensions of 80×20 mm have a contact area to be tested of 40×20 mm.

After clamping the samples in place, the peel test consists on the application of tension at the displacement rate of 1 mm/second and programmed to stop when a decrease of force of 80 % is detected.

The samples were peeled apart until complete separation.

3.4. Healing

The healing stage follows the first fracture by subjecting the two separated parts together at the desired conditions of temperature, pressure and time. It was decided to proceed for the healing right after fracture in order to circumvent the surface deactivation phenomenon and leave out its contribution. For this end, the fractured surfaces are carefully put together and inserted in a tight fitting Teflon mould in order to be healed. The same procedure is done for 2 samples that are healed on top of each other inside the mould. For every sample fractured, healed and re-fractured there were two files with the force-displacement data to be further analysed.

4. Results and Discussion

4.1. Fracture of virgin samples

An example of the peel curve of a virgin sample and the resultant healed one is depicted in Figure 4. The force builds up as the sample is stretched, the T-shape is attained and the test interface starts opening. Then there is a maximum of the force followed by a plateau around the value of 100 N. At the end the two parts separate completely. The displacement goes until around 80 mm since the interface of 40 mm long is being split in two parts.

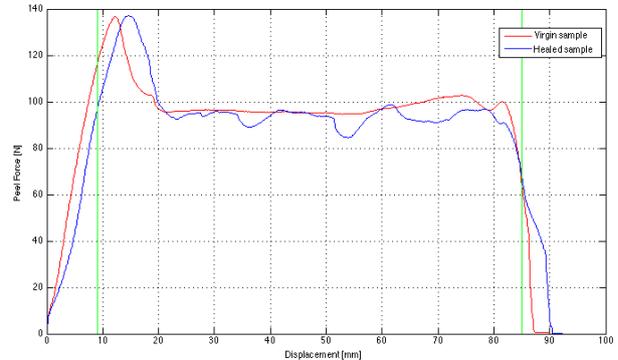


Figure 4: Optimal force-displacement peel curve – healing at 76° and 0.1 bar for 24 minutes

However, the plots obtained did not always follow this clear trend. Moreover, there were cases of samples from the same exact production displaying distinct behaviours, such as the ones in Figure 5. Despite the equal heat treatment during the processing, there are obvious differences between the two, such as the maximum force reached, and the absence of a plateau such as the one in Figure 4. Furthermore, the irregular pattern of sample Q25 (in green) and the pronounced depression in sample Q26 (Fig 5) point out to different mechanical characteristics of the specimens.

In spite of the fact that a significant part of the

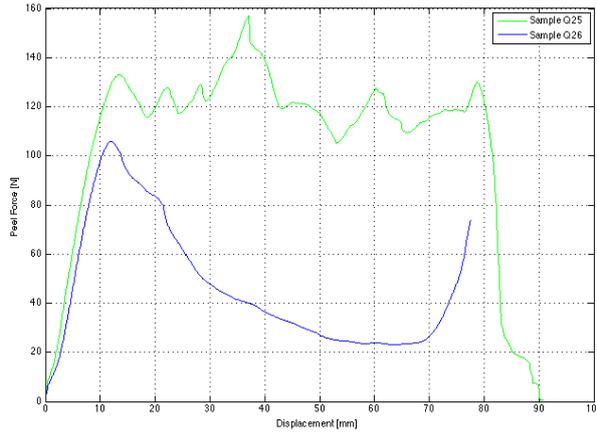


Figure 5: Plots of the force-displacement curves of two virgin samples produced under the same conditions with different behaviours

samples produced proved to be inappropriate for healing, mainly because of air bubbles or irregular fracture surfaces to be healed, there were 40 samples (out of 80 produced) considered suitable to proceed for the healing stage. The healings completed almost all the design points with different combinations for the lowest pressure (0.1 bar) and (23°C).

After the analysis of the data collected from the peel-tests performed to the specimens fractured, healed and fractured again, the comparison of the force curves of all the virgin samples (even the ones that were suitable for healing) in the same plot demonstrated a substantial scatter.

Clearly, the differences between these curves revealed to be too prominent for being disregarded. Several values for the initial peak force were obtained, in the range of 80 N to 170 N. Furthermore, not only there are almost no samples displaying a constant plateau for the peeling force, but also the average of these values fluctuates in an unacceptable range, from around 70 N to 140 N. Therefore, there is a lack of consistency which is required for establishing the basis for a model.

Moreover, even samples from the same production batch, subjected to exactly equal processing conditions, showed markedly different peel curves, such as the specimens in Figure 6. These 12 samples were actually some of the last ones to be produced before the testing phase, so they include already more experience and consistency in the manufacturing process, as well as more attention in the stage of overlapping the samples for the creation of the test interface by preventing air entrapment and applying a similar closure pressure in each sample. Despite this, different initial maximum values and average peel forces were obtained. Furthermore, a stabilization of the mechanical properties with the storage time is suggested by the greater resemblance among

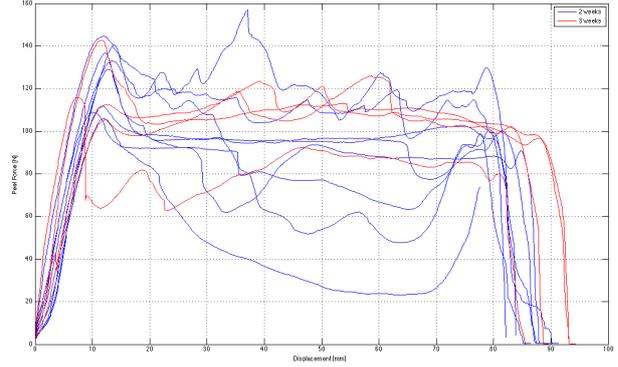


Figure 6: Scatter of force-displacement curves of samples from the same production batch – identical processing conditions (colour scheme according to time between production and testing)

the samples stored for 3 weeks before testing (red curves).

Additionally, not only the force-displacement curves displayed deviations in the sample production process, but also the fracture modes. These results point out to irregularities in the processing of the material, and some possible explanations ought to be discussed.

4.2. Different failure modes

In the first trials made with mould 2 (with screw system), the peel-tests done led to clean homogeneous fracture surfaces, as the ones in Figure 7(b). However, the testing of the specimens produced later on revealed a different kind of failure: irregular surfaces with adhesive failure at the polymer-aluminium interface, as in Figure 7(c). In addition, also the force-displacement curves differed considerably from the first ones and from each other, as already explained.

These results have two crucial implications for what concerns to the healing of the samples and its validity. One is the lack of consistency in the initial peel curves that are meant to be taken as the reference for each healing to be performed. If the mechanical behaviour of the virgin samples is not standardized, assumptions on the characteristics of the healed samples might not be generalizable enough for modelling the system. The second one is the presence of homogeneous fracture surfaces allowing for good contact when put together and thus suitable for healing. Clearly, an irregular surface with tear-out of material does not provide acceptable contact for the healing mechanisms to take place efficiently.

In order to overcome this dispersion of results and reach consistency, one should investigate the compromise between the two critical interfaces that are responsible for this: the polymer-polymer and

the polymer-aluminium interfaces.

Basically, the types of failure can be summarized as follows:

- Adhesive failure – weak polymer-aluminium interface (Figure 7(a))
- Two types of cohesive failure – irregularity of polymer-polymer interface
 - Homogeneous with smooth surface (Figure 7(b))
 - Uneven with tearing process (Figure 7(c))



(a) Adhesive failure – peel of aluminium foil (b) Cohesive failure – homogenous surface (c) Adhesive and cohesive failure – tearing process

Figure 7: Surface appearance of different failure modes

From the analysis of the force-displacement plots, turns out that the samples with uneven rupture of material in the test surfaces and peel off the aluminium correspond to the ones reaching highest force levels. This indicates that for these samples the polymer-polymer interface was stronger than the polymer-aluminium one, and so there is uneven rupture of material until adhesive failure and peel-off of the aluminium. On the other hand, when the interface polymer-aluminium is considerably stronger than the polymer-polymer one, the failure happens on the surfaces that were put together in the last curing stage and so a clean homogeneous cut results. This kind of failure is the most adequate for assuring appropriate surface contact for healing.

In what concerns to the polymer-adhesive interface it is of importance to recognize that during the whole production of samples no change was made that could actually have influenced its features. The bonding between the two different materials was solely promoted by the crosslinking of the elastomer on top of the foil. In addition, the only treatment given to the aluminium was degreasing with acetone, which had shown evidence of being enough during the first peel-test trials.

Consequentially, the fact that there was a change in the behaviour of this interface, sustained by the occurrence of adhesive failure and peel out of the aluminium foil, leads to the conclusion that the failure mode is dependent on the coupling of the two critical interfaces – polymer-polymer and polymer-aluminium. A stronger polymer-polymer interface

takes more energy to be fractured, changing the failure from a clean plane (where the samples had been put together) to an irregular tear out of material reaching the aluminium. This goes in accordance with the higher peaks of peel force measured in the tensile machine.

4.3. Proposed solutions from a processing point a view

Given the various processing issues encountered during the experimental work, additional experiments were done regarding the adhesion between polymer and aluminium.

Following the discussion on the different failure modes, the key determinant factor appears to be the difference in cohesive strength between the polymer-polymer and the polymer-aluminium interfaces. In the first trials the former was considerably low, leading to a clean homogeneous fracture surface on this interface. On the other hand, when a stronger inner interface is produced, the failure might change to a tearing process ultimately promoting adhesive failure.

Therefore, enhanced adhesion with the aluminium would in principle prevent adhesive and disruptive failure in spite of how strong is the interface elastomer-elastomer and the creation of bulk material. For this purpose, the use of an adhesive and/or the resort to surface treatment of the aluminium constitute possible strategies.

Apart from using an adhesive, surface treatment of the aluminium foil might influence greatly the quality of the adhesion. Thus, aluminium stripes were roughened with sandpaper and then exposed to Ultra Violet (UV) light treatment to produce samples in mould 2 (thus without adhesive). Testing of this samples revealed the same kind of irregular cohesive failure coupled with adhesive failure, meaning that the strength of the bonding did not improve sufficiently.

In order to further investigate the use of an adhesive, 8 samples were prepared for this purpose. Only after fully curing the polymer was attached to the surface treated aluminium foil, by applying the adhesive and taking the final samples to 120°C for 6 hours. Furthermore, for each of these samples the double of the usual weight of material was used, i.e., 20 grams per specimen. This was to ensure even spread on the Teflon mould and increased cohesive strength in each layer of the elastomer.

The effect of using different surfaces for the creation of the polymer-polymer interface was explored (the top part in contact with air or the bottom with the Teflon). Additionally, the treatment with UV light and the resort to two types of adhesive was also investigated.

From these experiments, it can be concluded that the quality of the adhesive bond between the elas-

tomers and the aluminium foil plays a key role in the outcome of the peel-test, influencing the force-displacement curves and the failure modes. This might be explained by a modification in the stress distribution along the sample promoted by a weaker (or just irregular) polymer-aluminium interface. So, depending on the conditions of the adhesive bond, the force applied to the specimen promotes a process of stretching (hence the tearing and irregular rupture) of the elastomer instead of peeling (clean fractured surfaces). UV treatment appeared to enhance the adhesion with the aluminium. In particular, samples with a strong industrial adhesive display comparable results and seem to reveal improvement into reaching conformity in production.

Regarding the quality of this polymer-polymer interface, the question remains if indeed bulk material is being produced and the original surfaces disappear during the last curing stage. The fact that the resulting fractured areas display a clear regular appearance, such as the one of Figure 7(b), might suggest the opposite. However, this could be related to the increased difference between the strengths of the two critical interfaces: a remarkably strong adhesion between polymer and aluminium may promote uniform rupture of the interface polymer-polymer. This would mean correlation between adhesive failure and disruptive tearing process, which goes in accordance with the fractured samples that were not considered suitable for healing.

Additionally, despite the fact that the scatter of the initial peel curves hinders the validation of a model for the healing capability, the methods and tools to do it have been developed and some results obtained from the healings performed to the samples were discussed.

5. Conclusions

The main purpose of this thesis was to develop a test method for quantifying the self-healing behaviour of a supramolecular elastomer, Reverlink® HR. For this end, samples of the polymer were produced and tested adopting a T-peel test procedure.

Initially, a testing plan was devised using design of experiments, aiming at optimising sample production for studying the influence of temperature, pressure and time on the healing response exhibited by the supramolecular elastomer. The production method was investigated through experimenting alternative strategies for processing the polymer.

Several samples were produced, fractured and healed. The data analysis of the results revealed significant inconsistencies in the peeling curves obtained in the testing of the virgin samples, hindering the suitability for a statistical model of the phenomenon of self-healing.

Some of the issues related to the scatter of results

were further explored, aiming at understanding and improving the production procedure and obtaining reproducible samples.

Despite the complexity of the whole production procedure, in the sense that many different factors play a role in the processing step, one can at this stage suggest that the fundamental issue is the trade-off between the strength of the polymer-polymer and the polymer-adhesive interfaces.

Defining the cohesive strength between two interfaces as σ , it is possible to relate the three following scenarios with the failure modes described, respectively:

1. $\sigma_{pol-pol} \gg \sigma_{pol-al}$ – adhesive failure
2. $\sigma_{pol-pol} \ll \sigma_{pol-al}$ – cohesive failure (homogeneous surface)
3. $\sigma_{pol-pol} \approx \sigma_{pol-al}$ – adhesive and cohesive failures (tearing process)

The different types of failure might be promoted by a variation in the stress distribution along the sample and acting on the breakage area. This would mean that when the adhesive bond with the aluminium is not strong enough, its failure possibly leads to a stretching process of the elastomer instead of peeling. Hence a coupling of adhesive and cohesive failure with irregular tear of material. This alternative stretching process constitutes a different type of force application in the test interface, thus explaining the higher force levels measured.

Finally, following the experiments regarding the polymer-aluminium interface, it can be concluded that a strong adhesive is required to prevent failure of this bond. Adhesion promoted simply by curing of the material on top of the aluminium, even with UV treatment, revealed to be insufficient. Conversely, the last samples produced resorting to adhesive display consistent results in what comes to both the stable peeling curves and the homogeneous fracture mode (suitable for healing).

In addition, in spite of the lack of consistency for modelling obtained with the samples healed, some insight into the testing procedures and results was provided.

5.1. Recommendations for Future Work

Given the last positive experiments towards reaching consistency in sample processing, further attempts of productions resorting to a strong adhesive might definitely lead to results suitable for validating the healing stage and so for modelling this phenomenon.

However, if unacceptable scatter of results appears and the adhesive proves to be insufficient, there are diverse options to be considered in the processing procedure. These include different kinds of

surface treatment of the aluminium foil, like plasma activation, or using anodized aluminium for improved adherence.

Additionally, more investigation into the quality of the polymer-polymer interface created is key to understand the behaviour of this elastomer.

Once the appropriate quality of the polymer-aluminium interface is established and adhesive failure is prevented, supplementary tests for evaluating the influence of the thickness of the samples in the results should be performed in order to determine the ideal amount of material to be used for each specimen.

To conclude, it should be regarded that, ideally, the development of this test method should enable its use for exploring the self-healing behaviour of different polymers. Hence, once a methodology is established and reproducible results are obtained, attempts with other self-healing elastomers are crucial.

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