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AGEING EFFECTS ON TWO-COMPONENT INJECTION MOLDED THERMOPLASTIC ELASTOMERS ON POLYAMIDE-12

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Abstract

The effect of ageing on the adhesion between thermoplastic elastomer materials and glass fiber reinforced polyamide-12 materials was evaluated. Test specimens were made by two-component injection molding, and the melt temperatures and the glass fiber fraction were varied. Adhesion before and after ageing was assessed via peel tests. Ageing (11-22 weeks at 70 °C with 62% relative humidity) severely reduced the adhesion strength. This could be explained by broken covalent bonds and/or disentanglement in the interphase. The individual materials were not severely affected by the ageing.

Introduction

Two-component (2C) injection molding is an important process for mass production of multi-material parts. It is a technique where one material is overmolded with another in an integrated production process. The adhesion between the two materials is often crucial for the part's performance.

Adhesion mechanisms in 2C parts range from macroscopic scale mechanical interlocking to mechanisms on a molecular level: Interdiffusion of polymer chains allows for entangling of molecules, dipolar interaction and hydrogen bonds, but also the opportunity for creating covalent bonds between the two materials. The kinetics of molecular diffusion and chemical reactions are influenced by the temperature.

The literature has analyzed many factors affecting the interaction between dissimilar polymers. The topics have been diverse, such as compatibilization of polymer blends, analysis of joining techniques, and analysis of multi-material processing methods such as co-extrusion and 2C molding. For 2C molding, the importance of the interface temperature (affected by melt and mold temperatures) has been highlighted. The interface temperature is key for diffusion-controlled adhesion mechanisms involving chain segments with some chemical compatibility and the formation of entanglements. The interface temperature will also govern reaction kinetics for material pairs where one material is modified for forming covalent bonds with the other. Adhesion modifiers or compatibilizers in thermoplastic elastomers (TPEs), for improved adhesion to polyamides, may be based on forming covalent bonds, in

which case annealing has proven beneficial to improve adhesion.

Most studies on adhesion of 2C parts have focused on the influence of process parameters on specific material pairs, or the effect of an adhesion promoter (e.g. grafted to a polymer chain in the TPE). The adhesion is typically measured soon after the specimen was molded. The aim of this study is to investigate how ageing under moderately hot and humid conditions affects the adhesion strength in the long term, as this determines the performance of a part throughout its lifetime.

Materials

Two TPE materials were acquired from Kraiburg, Germany: A dynamically vulcanized TPE (TPV) and a styrenic TPE (TPS), both with shore A hardness 57. Both were modified for adhesion to polyamide by the supplier. The details of the modification were not disclosed, but IR spectroscopy of the TPS give evidence of C-O bonds. The TPS is based on a styrene-(ethylene-butadiene)-styrene (SEBS) block copolymer. The TPV is based on crosslinked SEBS (xSEBS) in a matrix of polypropylene (PP). Four heat stabilized polyamide-12 (PA12) materials were acquired from EMS-Grivory, Switzerland. They contained 0 to 50 weight percent (wt%) short glass fibres (GF), see Table 1. The PA12 fraction in these materials had similar viscosities. The PA12 has a melting temperature (T_m) of 176-177 °C and a glass transition temperature (T_g) around 40-43 °C.

Table 1. Properties of the polyamides. The moisture absorption at 23 °C and 50% relative humidity (RH).

	PA12	PA12-GF30	PA12-GF50
<i>E</i> , MPa	1100	6000	11500
<i>Moisture</i>	0.7%	0.6%	0.4%
<i>Color</i>	natural	blue	black

Experimental

2C specimens (Figure 1), based on the ISO 527 type 1A tensile test specimen, were produced in a 110 ton injection molding machine from Engel, equipped with two screws (diameter 30 and 22 mm, used for the PA12 and TPE respectively). The PA12 and TPE parts were both 2 mm thick, and 10 mm wide in the narrow section of the specimen. The tool surface for the interface of PA12 to

TPE was sandblasted to an Ra value of 4.5 μm . Molding parameters were adjusted to achieve parts of good quality. The melt temperature of the materials was varied (T_{melt} , denoted T_{PA} and T_{TPE} when referring to a specific material), see Table 2. Some specimens were aged for 11 and 22 weeks at 70 °C in 62% RH, which after about 1 week should lead to similar moisture content as saturation at 23 °C in 50 % RH [1]. The exposure time was selected based upon an Arrhenius estimation: 10 weeks at 70 °C corresponds to five years at 23°C, if the ageing processes are similar at the two temperatures. The ageing was prolonged with the week required to achieve the moisture content for saturation at 23 °C in 50 % RH. The 22 weeks exposure is a doubled ageing cycle.

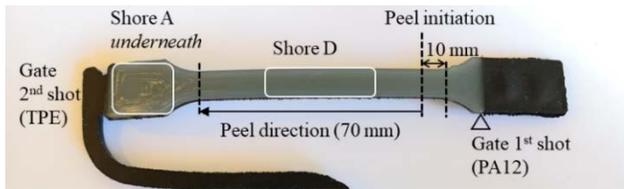


Figure 1. 2C specimen of PA12 and TPE (black). The gate locations are indicated. The peel direction was opposite to the flow direction of the TPE.

Table 2. Study variables. The mold temperature was 40 °C.

	PA12-GFx	TPE
<i>GF</i> , wt%	$x = 0-50$	-
<i>Material type</i>	-	TPV or TPS
$t_{\text{injection}}$, s	0.5	1.6
T_{melt} , °C	255, 285	250, 270

Prior to mechanical testing, the 2C specimens were conditioned at 23 °C and 50% RH for minimum 24 h. The adhesion between the materials was assessed with a 90° peel test at 23 °C in a universal testing machine (UTM) from Zwick. The procedure followed ref. [2], except for the shape of the test specimen. The crosshead speed was 50 mm/min. The peel was initialized prior to the test by cutting a lip of TPE from the PA12 with a knife, see Figure 1.

The hardness of the materials was measured; Shore A for TPE specimens (hold time 15 s), and Shore D for the hard specimens (hold time 3 s). Eight measurements were performed for each material. Note that the measurements were performed after peeling, but the TPE measurement was done on an unstretched segment, see Figure 1.

The viscosity number of the PA12 fraction (i.e. the polymer fraction) in aged and unaged hard materials was measured using a rotational rheometer (Physica MCR300, with 50 mm cone and plate fixture). The solvent was m-cresol and the polymer concentration was 0.5 g/dL.

Results

The adhesion strengths are presented via force-displacement curves, see Figure 2 for TPV on PA12 and PA12-GF, and Figures 5 for TPS on PA12 and PA12-GF. The melt temperatures are given in each figure.

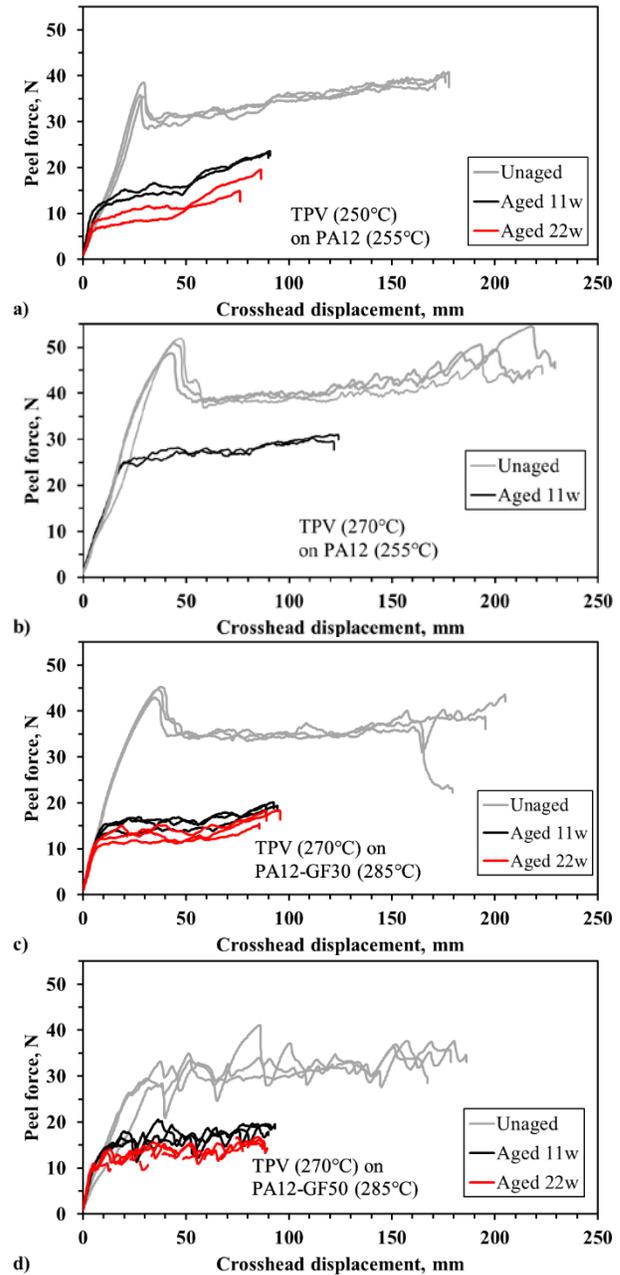


Figure 2. Peel force vs. crosshead displacement for material combinations and melt temperatures as denoted in the respective diagrams. The peeling distance for aged/unaged material was 50/70 mm.

The adhesion strength of the TPV increased with increasing T_{TPV} , and the strength after ageing was also better for higher T_{TPV} , see Figure 2a and 2b. Increasing the

ageing time from 11 to 22 weeks led to a further decrease of the strength for the TPV on PA12 (Figure 2a), while the TPV on PA12-GF strength remained almost the same, at a very low level (Figure 2c and 2d). Prior to ageing, the mode of failure was mixed adhesive and cohesive, with more of the cohesive mode at the higher T_{TPV} , as indicated by TPV residues on the PA12. Ageing reduced the adhesive strength as seen in Figure 2. An initial peak in the force curve was no longer present and the mode of failure was mainly adhesive, see Figure 3.

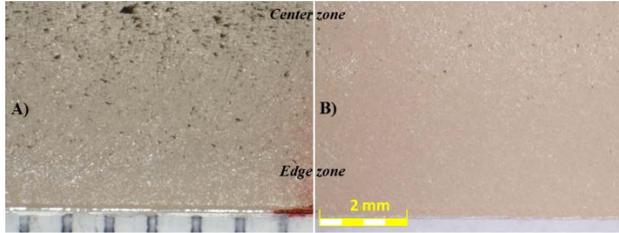


Figure 3. Peel surface of TPV (black) on PA12 (natural), T_{melt} : 250 and 255 °C. a) Unaged. b) Aged 11 weeks.

For unaged specimens, the adhesive strength generally decreased with increasing glass fiber fraction in the hard material, see Figure 2c and 2d. Comparing materials with 30 and 50 wt% GF revealed that the peel force was more unsteady in the latter case, indicating uneven adhesion over the surface for PA12-GF50. After ageing, the adhesive strength was on a very low level for both materials with glass fiber reinforcement (Figure 2c and 2d).

The natural (unpigmented) PA12 parts were slightly yellowed after ageing, see Figure 4. All other materials were pigmented and did not change hue after ageing.

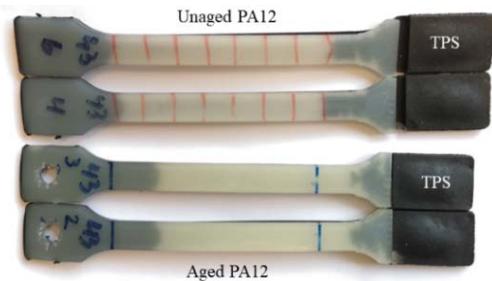


Figure 4. Peeled 2C specimens of PA12 (natural) and TPE (black). The aged PA12 (11 weeks) has a yellowish tint.

Figure 5 show the force-displacement curves for TPS on PA12 and PA12-GF. The peel strength prior to ageing was again improved by increasing T_{TPE} , see Figure 5b and 5c. Ageing (11 weeks) lowered the peel force and less residues of TPS were found on the hard surface after peeling, see Figure 6. Doubling the ageing time led to further reduction of the peel force, but when the force level was already low after 11 weeks the level was almost the same after 22 weeks (Figure 5a and 5b). As for the TPV, the adhesion decreased with increasing glass fiber content in the hard material.

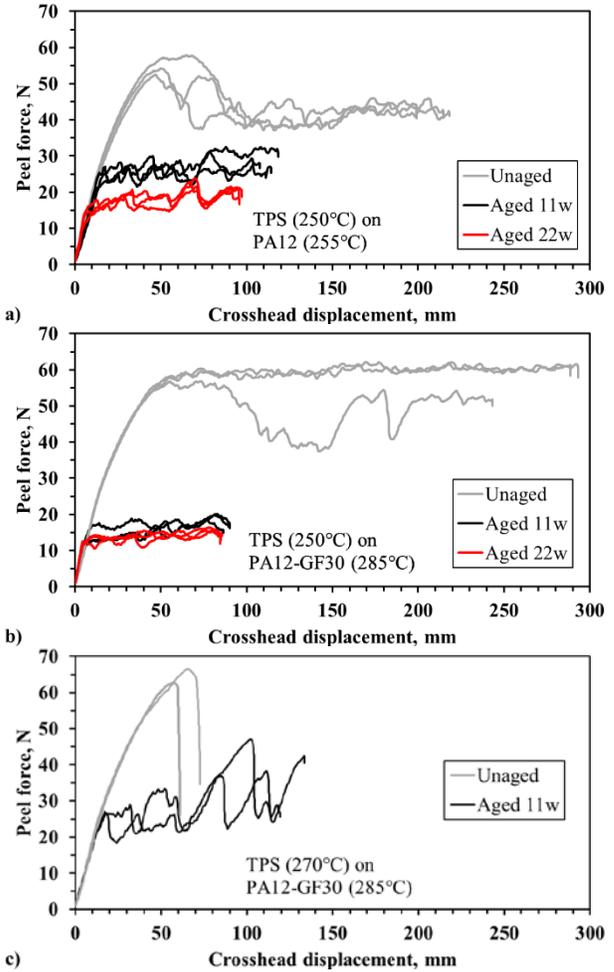


Figure 5. TPS on a) PA12 and b, c) PA12-GF30. The melt temperature T_{TPS} was a, b) 250 °C and c) 270 °C. The T_{PA12} was a) 255 °C and b, c) 285 °C.

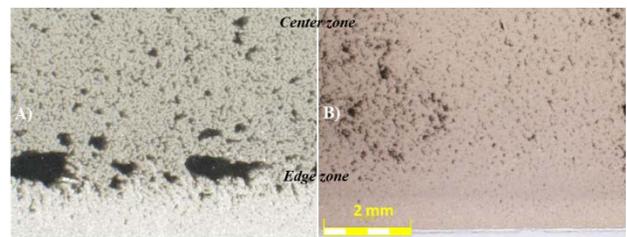


Figure 6. Peel surface of TPS (black) on PA12 (natural), T_{melt} : 250 and 255 °C. a) Unaged. b) Aged 11 weeks.

An average peel force was calculated for each peel test, for the region corresponding to steady peeling. This corresponds to the plateau in Figures 2 and 5. If the plateau has a slope, this indicates that the adhesive strength was stronger closer to the gate position of the TPE (temperature and pressure varies along the flow path). The initial peak was not included in the average. The average peel forces for all series are shown in Figure 7. TPV on PA12 experienced a 30-32% reduction in average peel force upon 11 weeks ageing, while the reduction for TPV on PA12-GF30 and PA12-GF50 was 56 and 48%, respectively. For

TPS on PA12 and PA12-GF30 the reductions were 38% and 60-75 %, respectively. After 22 weeks the total reduction of adhesion strength ranged from 58-70 % and 57-79% for TPV and TPS respectively. The data set in Figure 7 was small, but there is a correlation between the peel force before ageing and the reduction upon ageing.

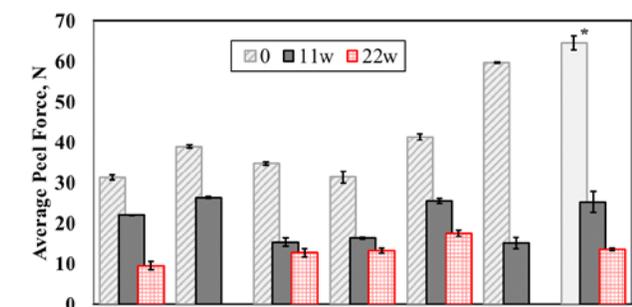


Figure 7. Average peel force of unaged and aged specimens. Note that, the highest registered force, was a tensile failure of the TPS (denoted with *).

The Shore A hardness of the TPV was unaffected by ageing, but the TPS experienced 2-4% increase. The Shore D hardness of the PA12 was unaffected by ageing.

The viscosity number of PA12 and PA12-GF50 increased upon ageing by 2.6 % and 8.9 %, respectively, see Table 3. Hence, ageing increased the viscosity average molecular weight for these materials.

Table 3. Viscosity number (VN) before and after 11 weeks of ageing. Analysis on injection molded materials.

	PA12	PA12-GF50
VN, unaged, dL/g	154 ± 1.7	146 ± 0.7
VN, aged, dL/g	158 ± 0.8	159 ± 1.3

Discussion

The TPEs in this study are modified for improved adhesion to polyamide, and the mechanism for this may be a chemical reaction between a group in a modified TPE chain added to the TPE material, and the amide group of PA12. Such a chemical group in the TPE, may be grafted to SEBS chains (in the TPE) or to PP chains (in the TPV). The TPV morphology schematically consists of soft elastomeric particles in a PP matrix, while the TPS is based on a copolymer with soft blocks (elastomeric) and hard blocks (physical cross-links). Other possible sources of adhesion for a modified TPE are dipole-dipole interactions and hydrogen bonding.

The ageing of the injection molded 2C specimens (11 weeks at 70 °C and 62% RH) had a strong negative effect on the adhesion, with a large reduction in peel force values. 22 weeks of ageing resulted in further decrease of adhesion

strength, particularly if the reduction of strength had been more moderate after 11 weeks of ageing.

Some possible causes are listed, addressing potential changes of the materials and the interphase:

1) Effects of ageing on the PA12: Moisture absorption and hydrolysis, and associated effects such as increased mobility of molecular chains and reduction of molecular weight, but also physical ageing (increased crystallinity).

2) Effects of ageing on the TPS and the TPV: The ageing could affect the main constituents (the polymers) or migration of additives, oils etc.

3) Ageing effects in the interphase: a) Moisture in the interphase may break the covalent bonds between the materials. b) The lack of chemical compatibility between the materials may lead to disentanglement of dissimilar chains and segregation.

Ageing of the individual materials

The unpigmented PA12 specimens turned slightly yellow and experienced an increase in viscosity, but there was no change in hardness. At elevated temperatures such as in the ageing in this study, the polymer may undergo several competing reactions. Which reaction that dominates would depend on temperature, humidity level, oxygen level and the time span. In our study, the small changes in color and viscosity suggest that the ageing of the PA12 caused limited chemical degradation, and, in fact, the viscosity increased. Small changes in the interphase, such as some PA12 chain scission, may have a large effect on the adhesion. For reference, in a study of heat stabilized PA12, ageing at 140 °C in circulating air led to much reduced viscosity, increased crystallinity and discolored specimens [3]. Arguably, the premises of ageing at 140 °C differs from our 70 °C, even though both are between the T_g and T_m of PA12. Another difference is the higher humidity in our ageing. In summary, it is likely that, in this study, annealing is the main process in the PA12 during ageing.

Neither of the studied TPE materials are known to be vulnerable to moisture uptake, there are few indications that they would be significantly affected by the ageing. Migration of additives can, however, not be refuted. A slight increase in hardness was measured for the TPS. A study on the influence of steam sterilization (100% RH at 121 °C for 0.5 h) of materials for medical applications, including SEBS, found no evidence suggesting changes to the chemistry or the mechanical properties [4].

Ageing effects in the interphase

In order to understand the ageing effects, it is beneficiary to start considering how the adhesion was formed during the injection molding. The interphase

between TPE and PA12 was created in the injection molding process under a specific thermo-mechanical history, including a temperature gradient through the interface between the materials, and a contact pressure. The non-equilibrium conditions inside the mold allowed for some interdiffusion of dissimilar chains (but adhesion modifiers are needed and present). The aim of [5] was to understand interdiffusion between dissimilar polymer films, one at a temperature high above melting temperature and the other around its melt temperature. These conditions resemble the situation in a 2C mold, except for time frame and distances. It was found that the temperature difference at the interface, could increase or reduce diffusion lengths [5]. Whether this effect is relevant for our study can be discussed, the interphase structure in injection molding solidifies quickly, at rates dependent on for instance mold temperature and melt temperature distributions.

During ageing, also the interphase gets exposed to the higher temperature and moisture. So, the question is what these conditions will do to a) covalent bonds likely present via the adhesion modifier and b) non-covalent interactions such as hydrogen bonds and dipole interactions. The nature of the adhesion modifier is proprietary information, but it is likely that there is a chemical reaction involved. Dry annealing (220 °C for 10 min) generated an improvement of adhesion strength between PA6 and PE/PE-g-MAH but prolonged exposure (up to 30 min) gave no additional benefit (the adhesion strength remained the same) [6]. Affects in the interphase developing over time are likely different than in a short annealing at high temperature. It is expected that the introduction of moisture and oxygen in the interphase gives room for additional reactions, which could break covalent bonds between chains in the TPE compound and PA12 chains.

The temperature during ageing (above T_g of the PA12) will increase the mobility of the polymer chains. The lack of chemical compatibility between chains would then drive disentangling of dissimilar chains, and segregation of the materials, thereby also reducing the number of non-covalent bonds. Segregation could also be promoted by cold crystallization of PA12, since the injection molding process quenched the material in the skin layer. An increase in hardness was not measured, as an indication of increased bulk crystallinity, but the crystallization referred to is thought to occur near the interphase.

The large reduction in adhesive strength due to this ageing could be explained by breaking of covalent bonds (an effect assumed to be driven by moisture, but accelerated by temperature), or by disentanglement and reduction in non-covalent interactions (an effect mainly driven/accelerated by temperature). There could also be a combination of these two causes. In order to determine if one effect is dominating, further experiments would be

valuable, such as ageing at dry conditions and at other temperatures.

As a final remark, this study has evoked new questions. What are the individual effects of humidity and temperature on the reduction in adhesion? How does the adhesion develop over time, in humid and dry conditions? Elaborating on these questions would require an expansion of the experimental scope, with ageing performed at both humid and dry conditions, and with more frequent sampling (e.g. after 1, 2, 4, 8 and 16 weeks). Adding a control material pair of compatible hard and soft materials (e.g. PP as the hard material and a PP-based TPE without adhesion promoter) could improve insight on the role of the adhesion promoter in the TPEs in this study (for adhesion to PA), and the possible breaking of covalent bonds formed by this promoter.

Conclusions

It was found that ageing significantly reduced the adhesive strength between PA12 materials (with and without GF) and TPE materials (a TPV and a TPS, both modified for adhesion to polyamides). The relative reduction was larger for glass reinforced PA12 than for unreinforced PA12. There seems to be a correlation between the adhesion before ageing and the magnitude of the reduction upon ageing.

This study does not find evidence that ageing affects the bulk properties of the individual materials to such an extent that it would explain the strong reduction in adhesion strength. However, ageing effect may be explained by changes in the interphase region, and two effects are supposed: a) Disentangling of chains in the TPE and PA12, and reduction in non-covalent interactions, driven by chemical incompatibility and possibly recrystallization of the PA12. b) Breakage of covalent bonds between chains in the TPE and PA12 chains.

Acknowledgements

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