



Characterization of the ethylene-vinyl acetate copolymer and the influencing parameters of the weld in intravaginal rings

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Characterization of the ethylene-vinyl acetate copolymer and the influencing parameters of the weld in intravaginal rings

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Abbreviations

API	Active pharmaceutical ingredient
DSC	Differential scanning calorimetry
EVA	Ethylene vinyl-acetate
EVA9	EVA with 9% VAc content
EVA28	EVA with 28% VAc content
EVA40	EVA with 40% VAc content
IVR	Intravaginal ring
T _c	Temperature when re-crystallization of the polymer starts
T _g	Temperature for the glass transition state
T _m	Melting temperature when all crystalline regions are melted
VAc	Vinyl-acetate

Abstract

The aim of this thesis was to characterize the mechanical and thermal properties of three different ethylene vinyl acetate (EVA) polymers with varying vinyl acetate (VAc) content and to investigate the influential parameters when welding the polymer into intravaginal rings. A second purpose in this study was to compare two different produced EVA polymers with the same VAc content to find thermal and structural differences. Since the weld is a crucial part of the production of a thermoplastic based IVR it is of high interest to gain knowledge and experience on how the material behave upon a second heating and what parameters affect the strength and robustness of the rings. The study was made by first investigating the properties of the EVA polymers with 9, 28 and 40% VAc content by running samples in a DSC. A modelling study was then made to get knowledge and to find interesting temperatures and times for the welding part of the thesis. The polymeric fibers were welded into IVRs while alternating the important parameters time, temperature and VAc content. To evaluate the welding, tensile testing was carried out and the stress and elongation at break were analyzed. The analysis and results showed clear trends where the elongation and stress at break increased with the welding time for the EVA9 and EVA28 IVRs. For EVA40 the trends in the results were not as clear. Conclusions made in this thesis are that the VAc content parameter has a large effect on the weld strength where the elongation at break will increase with increasing amount of VAc content. The stress at break will increase with a decreasing amount of VAc content. For IVRs made of EVA28 welded at 100°C the time needs to reach at least 20 seconds to result in a good weld. EVA9 IVRs need to be welded at a higher temperature than 110°C but the material shows a clear trend with increasing elongation and stress at break with increasing time, thus it can be concluded that the time is an important parameter for the welding process.

Sammanfattning

Målet med denna studie var att karaktärisera de mekaniska och termiska egenskaperna hos tre olika etylen-vinylacetat (EVA) polymerer med varierande halter av vinylacetat och de betydande parametrarna när man svetsar ihop polymeren till intravaginala ringar. Även en jämförelse av två olika producerade EVA polymerer med samma halt av vinyl-acetat för att hitta skillnader i termiska egenskaper och struktur gjordes. Eftersom svetsningen är en väldigt avgörande del av produktionen av termoplastiskt baserade IVR så är det av största intresse att få kunskap och erfarenhet om hur detta material beter sig vid en andra värmning och vilka parametrar som påverkar styrkan och robustheten i ringarna. Studien startade med att först undersöka egenskaperna av EVA polymererna med 9, 28 och 40 viktprocent vinylacetat genom att köra proverna i en DSC. Sedan gjordes en modelleringsstudie för att få kunskap och hitta intressanta temperaturer och tider för svetsdelen av arbetet. Polymerfiberna svetsades sedan till IVRs samtidigt som viktiga parametrar så som tid, temperatur och andel vinylacetat varierades. För att utvärdera svetsningen så gjordes dragtester där elongationen och spänningskraften vid ringens brytpunkt analyserades. Analysen och resultaten visade tydliga trender där elongationen och spänningskrafter ökade med svetsningstiden för ringarna gjorda av EVA9 och EVA28. För EVA40 så var inte trenderna i resultaten lika klara. Slutsatser som dragits i detta arbete är att vinylacetatsinnehållet är en parameter som har en stor effekt på svetsstyrkan där elongationen ökar med en ökande andel av vinylacetat. Spänningskraften ökar med en minskande andel av vinylacetat. För IVRs gjorda av EVA28 och svetsade vid 100°C så behöver tiden nå minst 20 sekunder för att resultera i en bra svets. IVRs gjorda av EVA9 måste svetsas vid temperaturer högre än 110°C även om materialet visar en tydlig trend med ökande elongation och spänningskraft med ökande tid. Detta innebär också att man kan dra slutsatsen att tid är en väldigt viktig parameter för svetsningsprocessen.

Populärvetenskaplig sammanfattning

Karaktärisering av polymermaterial för produktion av säkra och hållbara vaginala ringar

Vaginala ringar är en läkemedelsformulering som är väldigt användarvänlig och som kan vara ett alternativ till traditionella preventivmedel som ofta kan anses vara tabu i U-länder. Därför är det av största intresse och vikt att få kunskap om hur man producerar säkra och hållbara vaginala ringar för att kunna hjälpa fler människor världen över.

Den huvudsakliga frågeställningen i denna studie har varit hur man producerar vaginala ringar med en stark svets. Detta för att lösa problemen med ringar som går sönder eller får andra defekter vid produktionen. Eftersom vaginala ringar är en läkemedelsformulering som dels sätts in av användaren själv men som också befinner sig i en människas kropp så är det av största vikt att få kunskap om produktionsprocessen för att kunna producera vaginala ringar som inte kan gå sönder när de används.

I denna studie har ringar med polymeren etylen-vinylacetat (EVA) studerats, EVA9 med 9% vinylacetat, EVA28 med 28% vinylacetat och EVA40 med 40% vinylacetat. Parametrar som studerades i svetsningsprocessen av ringarna var tid, temperatur och halten vinylacetat uttryckt i viktprocent.



Figur 1. Illustrerar hur de vaginala ringarna ser ut efter svetsning.

Studien visade hur polymererna beter sig under en andra uppvärmning. Ringarna testades i ett dragningsstest där man fäster ringarna i en rigg som sedan drar isär ringen och mäter spänningskraft och elongation vid brytpunkten av ringarna.

Resultatet visade tydligt att andelen vinylacetat spelade stor roll på både elongationen och spänningskraften vid ringens brytpunkt. En minskande halt av vinylacetat ökade spänningskraften hos svetsen i ringen och en minskande halt av vinylacetat minskade elongationen av svetsen. Resultaten visade även att för ringarna som var gjorda av EVA9 och EVA28 så påverkade parametern tid hur bra svetsen i ringen blev. För EVA28 som svetsades vid 100°C så såg man en stigande trend med tiden. EVA9 som svetsades vid 110°C visade en liknande trend som EVA28 gjorde vilket innebär att tiden har en tydlig påverkan för de båda polymerringarna där det vid dessa givna svetsstemperaturer är tydligt att ju längre ringarna svetsas desto bättre svetsresultat. För temperaturen går det inte att tolka ett entydigt resultat eftersom problem uppstod under svetsningen där en hel del material istället fastnade i utrustningen och därför kommer temperaturparametern behöva studeras ytterligare i framtida studier.

Tack vare denna studie så har man nu fått klara slutsatser på hur några parametrar påverkar svetsningen och i slutändan kvalitén på de vaginala ringarna. Man vet att halten vinylacetat spelar en stor roll för hur starka ringar man kan producera och även att vid givna temperaturer för EVA28 och EVA9 så är tiden en mycket viktig faktor. Denna kunskap kan användas för att driva vidare utvecklingsarbetet av denna läkemedelsformulering för att i slutändan kunna leverera en säker, effektiv och hållbar produkt.

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1 Introduction

Intravaginal rings are used for different formulations, for example as a contraceptive or to treat vaginal atrophy by releasing hormones. The IVR investigated in this thesis consists of the ethylene-vinyl acetate (EVA) copolymer and two different dimensions on the rings will be used, 4 mm and 5 mm in interface diameter. In this study placebo rings without the API will be used due to the a highly potent hormone. The polymeric fibers are first produced by extrusion followed by the final step in the production where the IVR is welded into a ring. This weld might be more fragile than the rest of the ring due to the material properties of the polymer and the second heating of the polymer.

To investigate the thermal properties of the polymers the method Differential Scanning Calorimetry (DSC) were used. This method gives information about melting temperatures, recrystallization temperatures, the heat of fusion and the heat of recrystallization. These are all very interesting and important thermal properties to have knowledge about when an experiment where polymers are heated is made. The DSC provides information about what temperatures the welding needs to be done at for each of the three polymers in order for the polymers to fully melt.

For the investigation of the welding there are three major parameters that are known to have an effect: time, temperature and pressure to hold the two fiber ends together. For this thesis EVA polymers with different VAc content will be tested to find its tensile strength while alternating the time and temperature in the welding process. The pressure will be held the same at all tries and will not be investigated further due to lack of time. This study will provide knowledge about which EVA polymer of the three different investigated ones that provides the strongest weld and how the parameters mentioned affect the strength of the weld.

To find the most interesting and optimal parameters for the welding study, COMSOL Multiphysics[®] was used. In the multifunctional software time and temperature profiles of the welding process were studied to find what temperatures and times that should be investigated. The temperatures 90, 100 and 110°C and the times 10, 20 and 30 seconds were decided since this interval has temperatures close to the three polymers melting points.

For studying the strength of the vaginal rings a tensile test were made to get information about the elongation and stress at break. To compare the weld strength of each weld, the ring values were compared to polymeric fibers in order to see the quality of the welds. The stress at break will tell how big the stress force over the interface of the weld is and comparing this to the reference fibers it can show how well the polymers chain segments have entangled over the weld interface. For the elongation at break, which also is compared to the reference fiber, this will also show how well the polymers chain segments have entangled over the welding interface.

This information will be useful knowledge in the welding process of IVRs and contribute to further understanding about the influential welding parameters and the polymeric materials.

2 Aim

The aim of this thesis was to characterize the thermal properties of three different EVA polymers with varying VAc content and to investigate the influential parameters during the welding of the polymer into intravaginal rings. The influential welding parameters investigated in this thesis are the welding time, welding temperature and the VAc content of the polymeric fiber.

The second aim of this thesis was to compare two different produced EVA polymers with the same VAc content to find thermal and structural differences. This in order to illustrate the importance of fully knowing the properties of a polymer before changing supplier even if the name of the polymer is the same.

3 Theory and background

3.1 Ethylene vinyl acetate

EVA is a random copolymer which is synthesized from the ethylene monomer and the co-monomer of vinyl acetate. The copolymer is mainly produced in a continuous process polymerization where it is easy to adjust the properties of the polymer by adjusting the vinyl acetate ratio [1]. It is also possible to produce the polymer in a batch process by using a batch reactor with solvent and vinyl acetate in the bottom of the reactor and a feed of ethylene entering the reactor.

Research has been performed on the EVA polymer in the past and it is stated that the more vinyl acetate the polymer contains the lower the melting point temperature will be of the polymer [2]. This is in theory not surprising since the vinyl acetate content will create more amorphous regions in the polymer and thus decrease the melting temperature and the possibility for the ethylene chains to form crystals [1]. By using a heat flow differential scanning calorimetry (DSC), thermal properties for the polymer can be studied. The melting point temperature will not give a single clear peak in the DSC thermogram according to other studies [2]. Instead it is expected to get a broad range and several peaks or deformations of the curve. The reason for this is when the forming of the crystals in the polymer takes place both large and small crystals will form. Less energy will be needed to melt the smaller crystals and an endothermic deformation at a low melting temperature will occur showing the melting for the small crystals. When the smaller crystals are fully melted another clear endothermic deformation will occur to show the melting of the larger crystals.

Regarding the glass transition state, studies have shown that the glass transition temperature (T_g) for the EVA polymer occur in the range of -40°C to -20°C and that the glass transition is not shifted significantly by the crosslinking, i.e. the amount of vinyl acetate (VAc) in the polymer does not affect the glass transition state perceptibly [2, 3]. Literature have also shown that the glass transition is nearly constant and occur at -25°C for the EVA polymer which is the assumed T_g for this work since it is very hard to determine an exact T_g with DSC equipment [2].

Storing conditions is a parameter that will affect the thermogram of the DSC [4]. Though even if the thermogram shifts, the enthalpy of the melting area will remain the same showing that the crystallinity of the polymer is not affected by the storing condition [4]. In this study the storage condition is not a parameter that will be investigated further since it is already concluded that the crystallinity for the EVA polymer is not affected by this [4].

3.2 Modelling

COMSOL Multiphysics[®] was used for modelling the welding process of the IVRs. The modelling was done in an already existing model and assumptions made for the modelling are shown in Table 1 and are based on knowledge, calculations and experience from professionals in the field through internal Certificates of Analysis (COAs) and supplier product information. It was also assumed that there was no heat transfer from the equipment to the surroundings.

Table 1. The assumptions made in the modelling including density, heat capacity and thermal conductivity of the polymer.

Density	0.95[g/cm ³]	kg/m ³
Heat capacity at constant pressure	C _p = 3139	J/(kg·K)
Thermal conductivity	k = 0.25	W/(m·K)

Figure 1 shows how the actual mold used for welding looks like in the model. The cylinder shaped part is the polymeric fiber with the fiber ends inside the mold, the two rectangles encapsulating the fiber ends is a plastic material and the more quadratic area on top, which is located at the bottom as well but not seen in the image here, is the heating area made of aluminum.

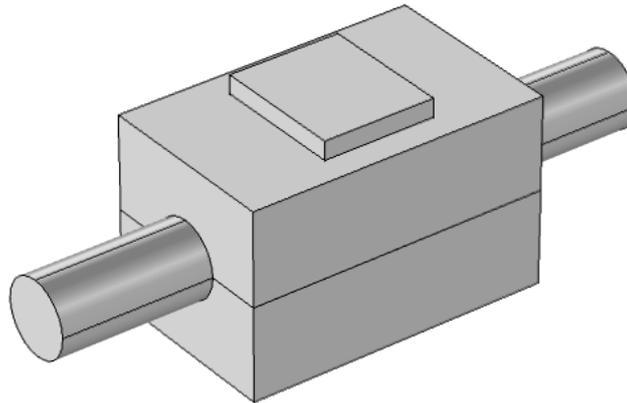


Figure 1. Image of how the mold for the welding of the polymeric fiber look.

The modelling in this work was made to see how the welding temperature and welding time would affect the heating of the polymer fibers and to get an understanding of what welding temperatures and welding times would be suitable for the welding of different polymers in this study.

3.3 Welding

Welding of polymers is a very complex process. With two polymer surfaces it is of high importance to create a weld with a symmetric interface where the chain segments can diffuse over both sides of the interface. By using heat to melt the polymers, diffusion and entanglement of the polymers chains over the interface will occur. The degree of entanglements of the polymer chains and the diffusion are the parameters that will decide the strength of the weld [5]. When the two heated and molten surfaces are brought together the phenomena wetting, which is a liquids ability to have contact with a solid surface, will occur followed by diffusion of the polymers chain segments. The wetting has a large impact on the diffusion since the longer the time is, the more the polymers chains can diffuse and entangle over the interface. Figure 2 presents a schematic image showing how the chain segments in the polymer diffuse over the interface when welded and how the chains entangle over the interface during welding.

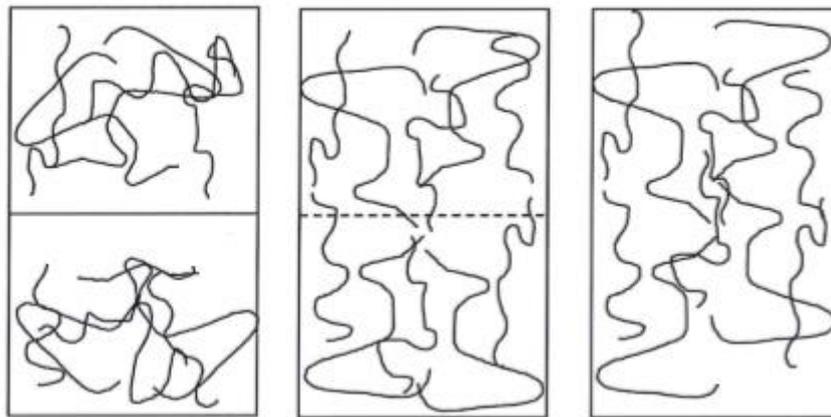


Figure 2. Image of how the polymeric chains diffuse over the interface during welding.

Time is one of the major parameters affecting the weld strength. This is because the time must be enough for the wetting between the polymers surfaces to occur so the diffusion and entanglement over the interface can take place. If the time is not enough the chains may not have enough time to entangle and diffuse over the interface and therefore not sufficient time to create a strong weld.

Temperature is also of high importance for the welding where a temperature above the polymers melting temperature should be used. This is to ensure that the desired mobility of the polymers chains is achieved to make it possible for entanglement over the interface. If the temperature is too low or not high enough the chains will not be able to move enough to diffuse and entangle over the interface.

Pressure is another parameter of importance. The pressure needs to be high enough to create contact and wetting between the polymer's surfaces. It is of high importance that the pressure is not too high since this can cause deformations and leakage of material in the weld. The effect of pressure will not be investigated in this thesis as mentioned before.

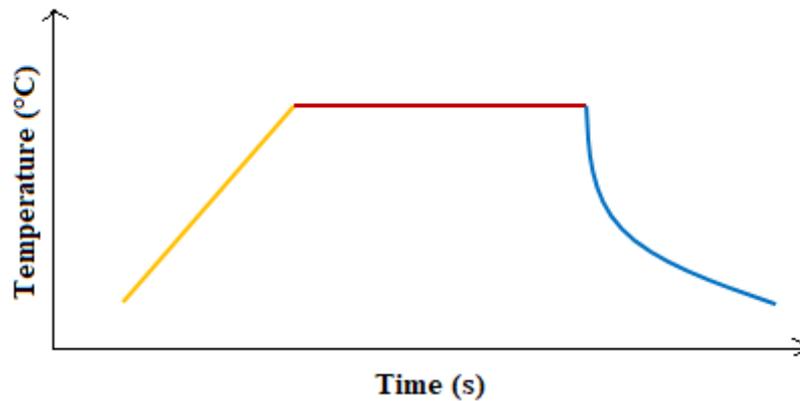


Figure 3. Schematic image of the time and temperature cycle during the welding process.

Figure 3 shows a schematic image of the temperature cycle in the welding process. The yellow line represents the first part where the two heating tools will increase in temperature in order to reach the set welding temperature. This part can manually be modified by changing the temperature of the two heating elements, which are automatically moving back and forth to create contact with the welding tools to reach the set welding temperature. If the temperature is set too high, it will create a risk that the pre-set welding temperature will get too high since the temperature will rise too fast and go past the set goal temperature. If the temperature of the heaters is too low, it will instead prolong the entire heat cycle where the yellow line will become longer but not increase at the same speed. This will inflict a risk that for example if the goal temperature is 100°C, the heating can be very slowly and almost increase only 0,1°C/s at the end, thereby increasing the cycle time drastically. If the welding time is set to 20 seconds and 100°C, then if the equipment stay between 99°C and 100°C for 10 seconds this will have a major impact on the welding result.

The red part of the cycle in Figure 3 is where the actual welding occur. For example, if a fiber is supposed to be welded for 20 seconds, the red part is 20 seconds long while the entire cycle can be 50 seconds. The welding start when the heating tools have reached the set desired welding temperature.

The blue part of the cycle in Figure 3 is the cooling of the tools which is made by the flow of pressurised air through small channels in the equipment. In this method, the tools are cooled down to 25°C and when this temperature is reached for both the top and bottom tools the equipment will release and push out the ring.

To fully understand the welding method it is important to have the cycle in Figure 3 in mind. It starts by the fiber gets locked into the equipment and the heating elements starting to heat up the welding equipment, this is the yellow part of the cycle. When the welding equipment has reached the desired welding temperature the heating elements will release from the metal part of the equipment and start the off-time which is the time the heating elements is off the welding equipment. This off-time is set to 3 seconds in the method. During this off-time the temperature of the weld will start to decrease, though not too many degrees. When the off-time is completed the heating elements will again push down against the metal part of the equipment and heat until the pre-set desired welding temperature is reached. The amount of times the heating elements will heat up the weld after the off-time is decided by the amount of cycles that is set in the method. In this thesis 3, 6 and 9 cycles were set since these cycles equals to approximately 10, 20 and 30 seconds. When the heating in the red part is completed the pressurised air will be released into the system, cooling the tools down to 25°C and end the entire welding cycle.

4 Analytical methods

4.1 Differential scanning calorimetry (DSC)

DSC was carried out using a Seiko Instruments Inc. EXSTAR6000 Differential Scanning Calorimeter. All polymer samples were stored at room temperature (~20°C) for 2-4 days. The sample, approximately 3-5 mg, was put into an aluminum pan (10μl). Another empty aluminum pan (10μl) was used as reference pan. The pans were sealed with an aluminum lid by using a sealing device and a hole was punched at the top of the lid with a puncher device in order to remove any pressure that might build up inside the pans. Both pans were then placed into the chamber of the DSC equipment. First the equipment was stabilized a few minutes at the starting temperature -50°C before the run started. The sample were then measured in three steps: first a melting step from -50°C to 135°C. Secondly a cooling step from 135°C to -50°C and finally another melting step from -50°C to 135°C. The temperature gradient was 10°C/min for both the heating and cooling steps. These temperature intervals were decided by knowledge from other studies on the EVA polymer [2, 3].

The degree of crystallinity of the polymer is calculated by an already known equation [6]:

$$C = \frac{\Delta H_f}{\Delta H_{f,100\%}} \times 100\% \quad \text{Equation 1}$$

Where:

C = Degree of Crystallinity (%)

ΔH_f = Heat of fusion for the polymer (J/g)

$\Delta H_{f,100\%}$ = Heat of fusion of 100% for the crystalline polyethylene (J/g)

The $\Delta H_{f,100\%}$ is known to be 293.6 J/g [4].

4.2 Tensile strength testing

In the method for the tensile testing the gauge length was set to 50 mm and the test speed to 500 mm/min. To avoid slippage of the fibers, hydraulic clamps were used holding the fiber ends with a pressure of 1-1.5 bar. The pressure is of high importance because a too low pressure will cause the fibers to slip out of the clamps, but a too high pressure will cause too large deformations of the fiber ends in the clamps. Fibers were then pulled until breakage and the tensile strength and elongation at break were measured with digital equipment.

For the mechanical weld strength test, the clamps where changed into a jig. The rings were then placed on the jig and the clamps were separated with a speed of 5 mm/min until a force of 0.2 N was reached. The speed was then increased to 500 mm/min until breakage of the ring and the stress and elongation at the breakage point were recorded.

5 Results and discussion

5.1 Thermal properties and degree of crystallization of EVA

By measuring the thermal properties of the polymers with a DSC, characterization of the material's thermal properties and the degree of crystallization were made.

5.1.1 EVA40

Figure 4 shows the first curve for melting of the EVA40 polymer from Supplier 1 which indicates that the polymer is totally melted at approximately 73°C. The heat of fusion for the melting was calculated by the equipment software "Muse Jobs" and was decided to 42.7 mJ/mg.

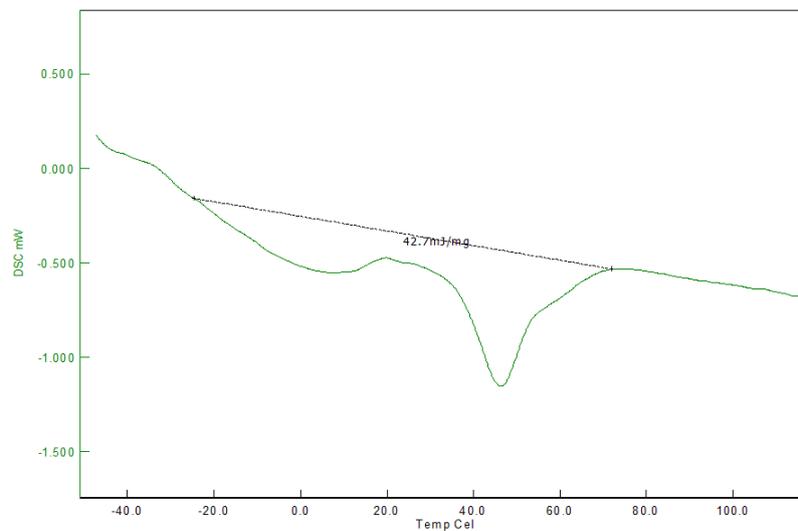


Figure 4. Thermogram of the first melting stage for the EVA40 copolymer supplied by Supplier 1.

The second melting curve is presented in Figure 5, where the polymer is totally melted at approximately 75°C, similar to what was observed in the first melting curve. This is not surprising since the melting point is expected to be the same. Regarding the heat of fusion of the melting phase, it is here 40.7 mJ/mg which also is similar to the first melting curve. This is also expected to be the same even if the thermograms indeed look different.

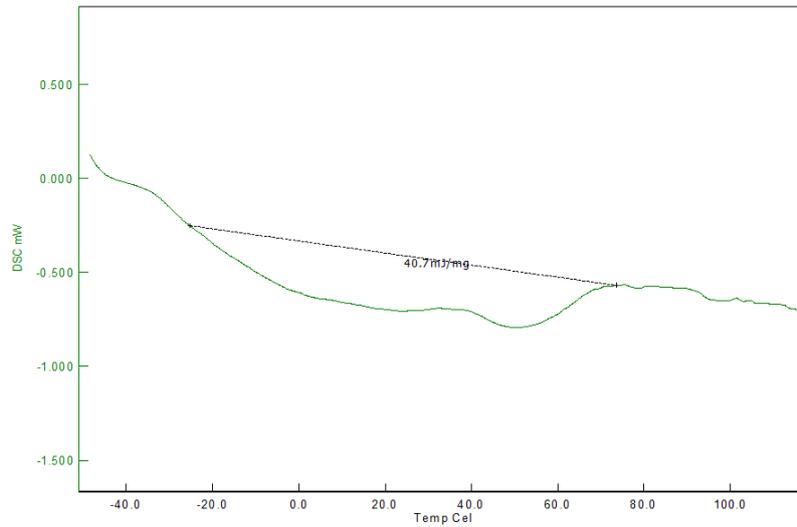


Figure 5. Thermogram of the second melting stage for the EVA40 copolymer supplied by Supplier 1.

Figure 6 presents the first melting curve for the EVA40 polymer from Supplier 2. The melting of all polymer is achieved at approximately 84°C and the heat of fusion is 43.0 mJ/mg.

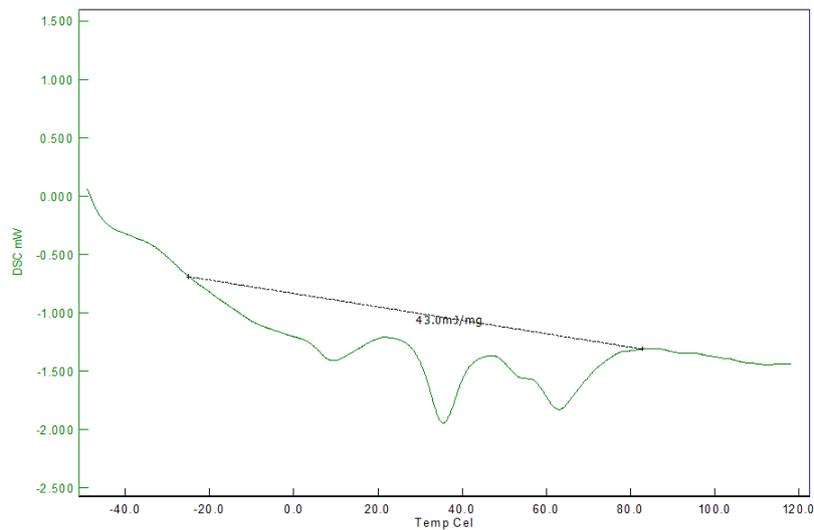


Figure 6. Thermogram of the first melting stage for the EVA40 copolymer supplied by Supplier 2.

The second melting curve is shown in Figure 7 where the melting temperature is approximately 84°C and the heat of fusion is 43.9 mJ/mg. The difference in melting temperature and heat of fusion is very small as expected.

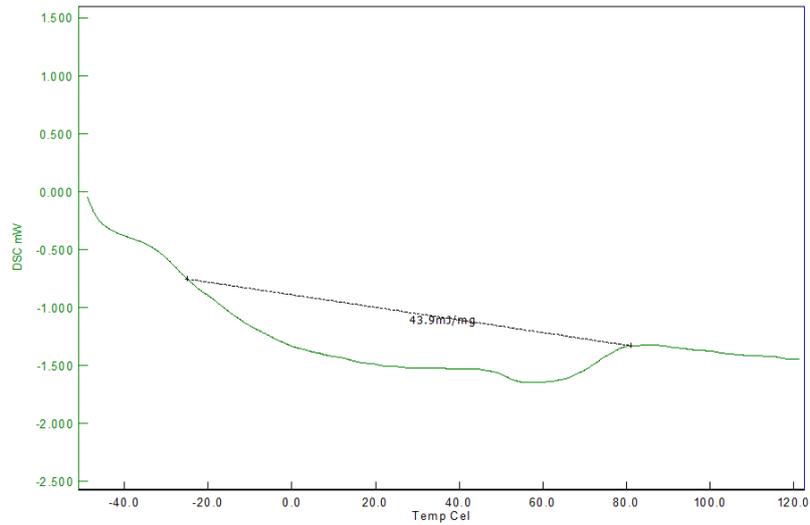


Figure 7. Thermogram of the second melting stage for the EVA40 copolymer supplied by Supplier 2.

Seen in Figure 8 is the crystallization stage for EVA40 from Supplier 1. The polymer is cooled down from the melted state and gain enough energy to form ordered arrangements i.e. crystals. The crystallization starts at approximately 45°C giving a clear and sharp peak. The heat of crystallization is -35.6 mJ/mg which means this is an exothermic process releasing energy to the surrounding.

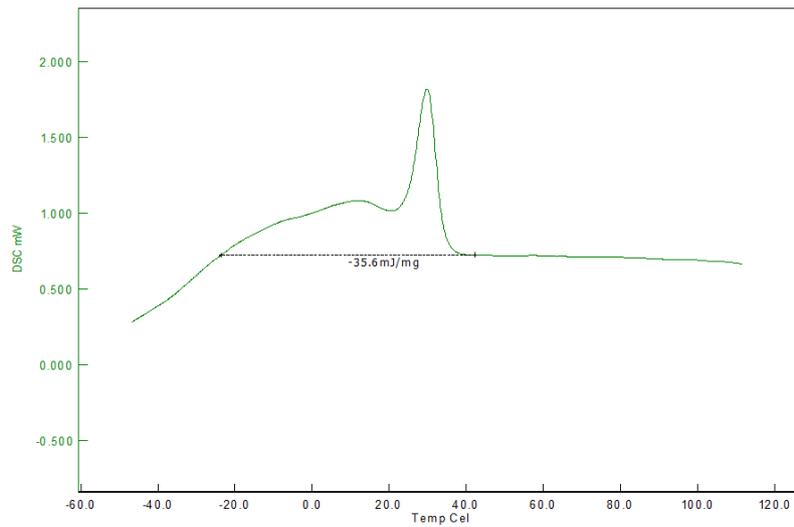


Figure 8. Thermogram of the crystallization stage for the EVA40 copolymer supplied by Supplier 1.

In Figure 9 the crystallization stage for the EVA40 polymer supplied by Supplier 2 is presented. It has a starting temperature at approximately 63°C showing that this polymer starts to recrystallize earlier than the polymer from Supplier 1. The heat of crystallization for this step is measured to be -37.9 mJ/mg.

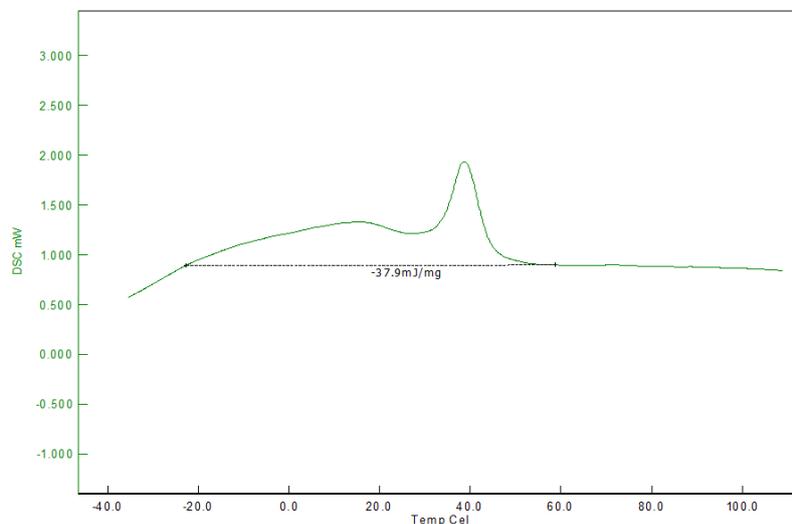


Figure 9. Thermogram of the crystallization stage for the EVA40 polymer supplied by Supplier 2.

By using the statistical Grubbs test, see equation B 1 and B 2 in the appendix, the data set were concluded to not include any outliers and therefore all the data will be used to calculate an interval for the degree of crystallinity from the different values of the heat of fusion. This includes the replicate DSC thermograms found in part A in the appendix.

Table 2. Data of the EVA40 polymers from the DSC experiments of the two different suppliers.

Supplier of EVA40	Supplier 1	Supplier 2
T _c onset	45°C	63°C
T _m offset	74°C	84°C
Heat of fusion	39.4-42.7 mJ/mg	43.0-43.9 mJ/mg
Degree of crystallinity	13.4-14.5%	14.7-15.0%

The difference between the EVA40 polymers from the two different suppliers is presented in Table 2. The biggest differences are seen in the T_c onset, which is where the polymer starts recrystallizing from the melted state, and the melting temperature offset T_m where the polymer is fully melted. This suggests that the EVA40 supplied by Supplier 2 has more large crystalline regions which makes the melting temperature to increase compared to the polymer from Supplier 1 since more energy is needed to melt the larger crystal regions. The difference in melting temperature also affects the recrystallization since larger crystals will again start to recrystallize earlier than the smaller ones in the polymer from Supplier 1.

To explain this, you will have to look at how the polymers are produced. In Supplier 1's case it is a continuous process where an even amount of VAc and ethylene are used to produce a fully random copolymer of EVA40 with the help of an extruder. That means the polymeric chains will have the same amount of ethylene and VAc in the whole polymer resulting in a random copolymer. In Supplier 2's case the polymer is produced in a batch process where the entire VAc is already in the solvent in the bottom of a batch reactor tank. This will provide the incoming ethylene with an excessive amount of VAc which will give rise to polymeric chains with a very high amount of VAc content in the

beginning of the process while in the end of the process chains with a very low amount of VAc content will form. This will result in a less random copolymer compared to Supplier 1's polymer, where you instead have large amorphous areas with a high content of VAc and other areas with a very low content of VAc. This will in turn be the reason for the larger crystals since the ethylene, which are the chains forming the crystal regions, will be able to form very big and perfect crystals in the areas where VAc is not highly present to disturb this process. That is most likely the reason for the different results of the DSC for the two EVA40 polymers where a big difference in T_c and T_m is observed.

5.1.2 EVA28

In Figure 10 the first melting curve for the EVA28 polymer is presented. The thermogram shows that the polymer is completely melted at approximately 87°C, i.e. T_m is 87°C. The heat of fusion for the first melting curve is 70.3 mJ/mg. Both the T_m and the heat of fusion are higher than the EVA40 polymer which was an expected result since less VAc content will give rise to more and larger crystalline regions.

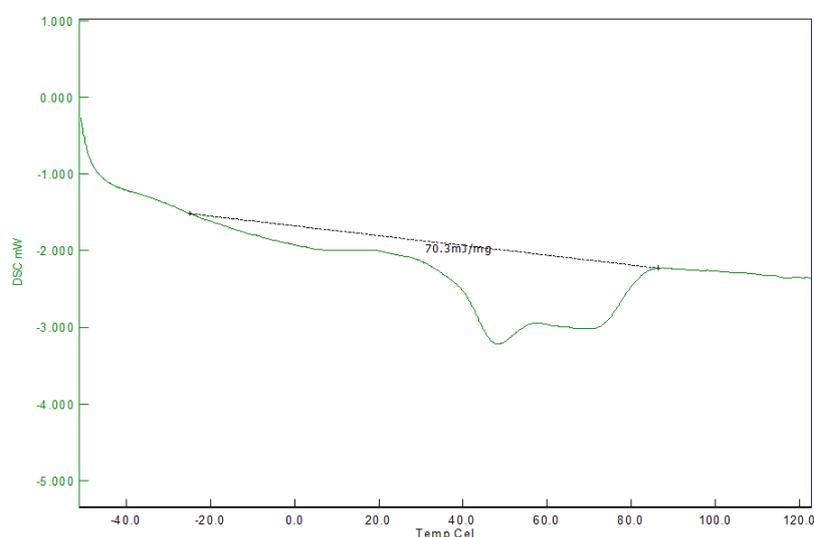


Figure 10. Thermogram of the first melting stage for the EVA28 copolymer supplied by Supplier 1.

In Figure 11 the thermogram for the second melting for EVA28 is presented. Compared to the thermogram in Figure 10 this thermogram do not show clear melting peaks. Instead it is a long pocket-like melting phase suggesting a big variation of crystal sizes. Though the largest melting takes place for the large crystals at somewhere around 73°C. T_m here is the same as the first melting stage in Figure 10, 87°C, and the heat of fusion a bit lower 67.4 mJ/mg.

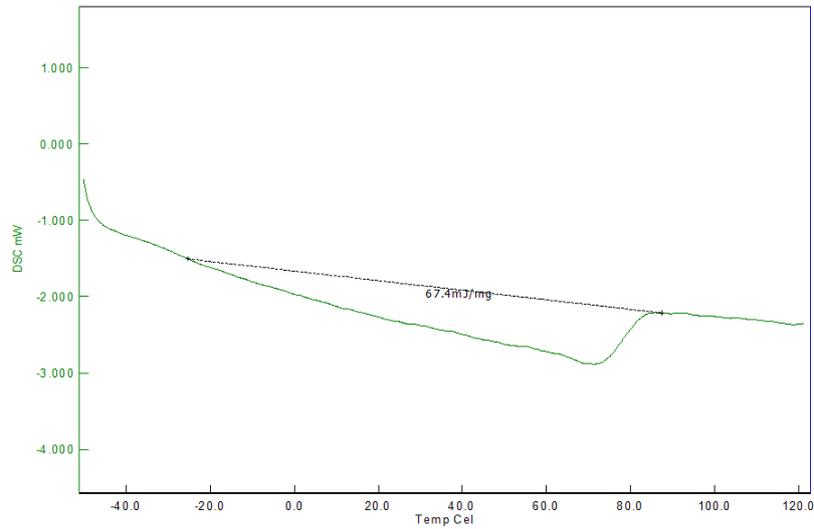


Figure 11. Thermogram of the second melting stage for the EVA28 copolymer supplied by Supplier 1.

In Figure 12 the thermogram for the recrystallization of the EVA28 polymer is shown. The thermogram shows that the polymer starts to recrystallize at approximately 65°C. The heat of recrystallization is 61.8 mJ/mg.

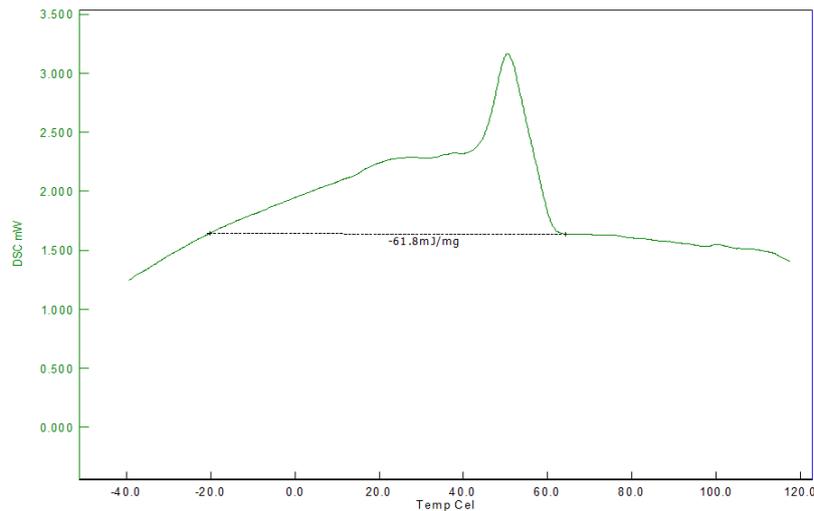


Figure 12. Thermogram of the crystallization stage for the EVA28 polymer supplied by Supplier 1.

By using Grubbs test, see equation B1 and B2 from the appendix, the data set were concluded to not include any outliers and therefore all the data will be used to calculate an interval for the degree of crystallinity from the different values of the heat of fusion. This includes the replicate DSC thermograms found in part A in the appendix.

Table 3. The table show a summary of the physical and thermal properties for EVA28 for the results from the DSC.

Supplier of EVA28	Supplier 1
T _m	87°C
T _c	65°C
Heat of fusion	67.4-71.9 mJ/mg
Degree of crystallinity	23.0-24.5%

The obtained results for the EVA28 polymer do agree with earlier studies of the polymer [2]. Degree of crystallinity is close to values seen in other studies [4]. The T_m and T_c are close to values obtained in earlier experiments [1, 2]. To summarize, the DSC experiments for the EVA28 polymer provided good characteristic information about the polymer which matches with earlier studies in the area.

5.1.3 EVA9

In Figure 13 the thermogram of the first melting stage for the EVA9 polymer is presented. The thermogram shows a T_m of 108°C and a heat of fusion of 112 mJ/mg. These are much higher than the EVA40 and EVA28 which it is expected to due to larger crystalline regions which will require more energy to melt.

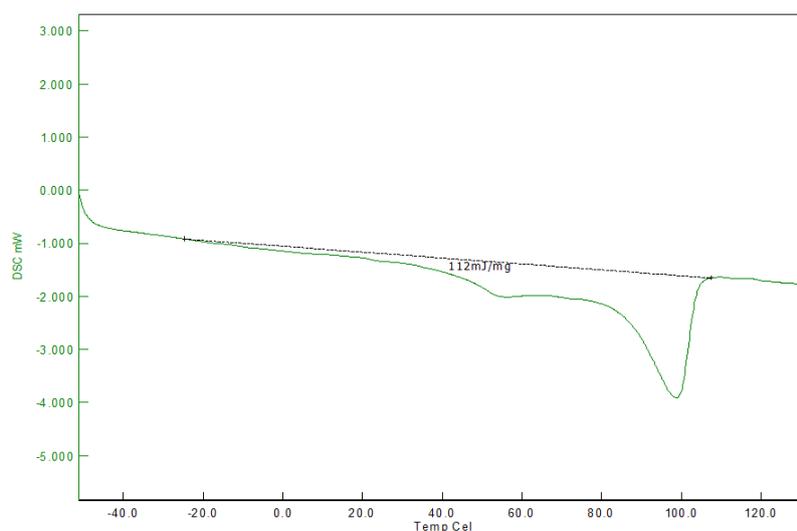


Figure 13. Thermogram of the first melting stage for the EVA9 copolymer supplied by Supplier 3.

In Figure 14 the thermogram for the second melting of the EVA9 polymer is presented. It looks similar to the thermogram in Figure 13 except that the small endothermic peak at 55°C is flattened. The T_m is the same, 108°C, and the heat of fusion is a bit higher at 116 mJ/mg.

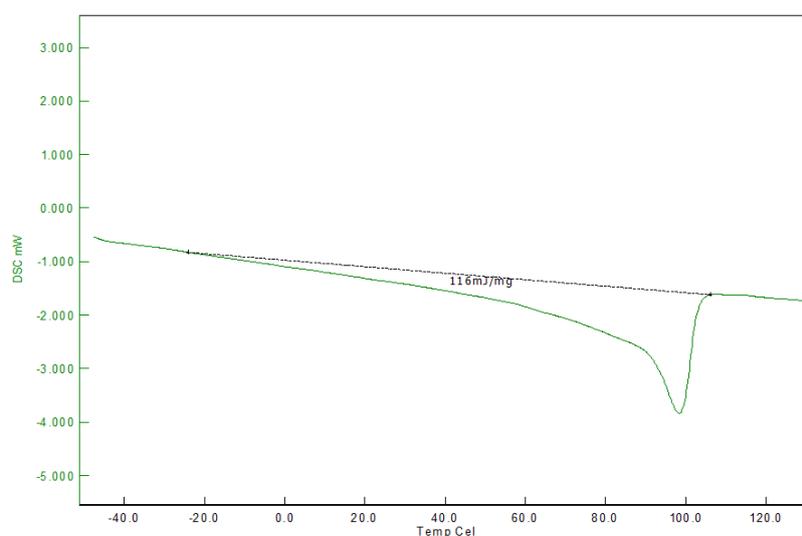


Figure 14. Thermogram of the second melting stage for the EVA9 copolymer supplied by Supplier 3.

The thermogram of the recrystallization stage is presented in Figure 15. The thermogram shows that the recrystallization starts at approximately 87°C and that the exothermic heat of recrystallization is 103 mJ/mg.

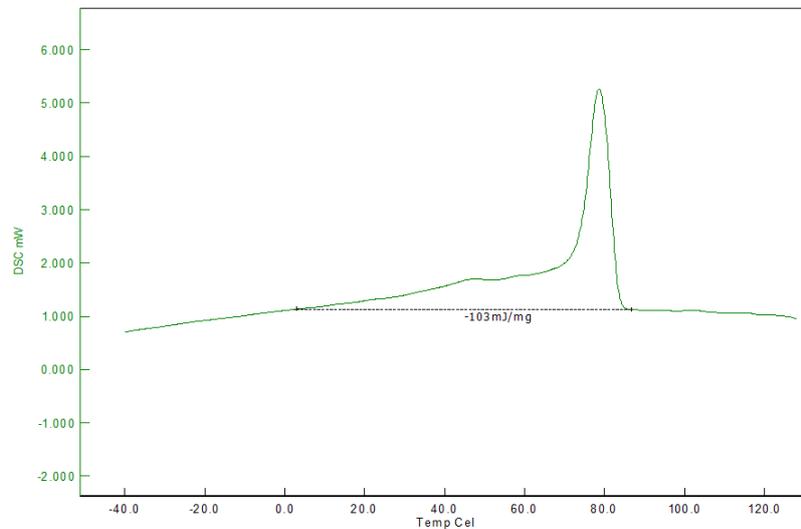


Figure 15. Thermogram of the crystallization stage for the EVA9 polymer supplied by Supplier 3.

By using Grubbs test, see equation B1 and B2 from the appendix, the data set were concluded to not include any outliers and therefore all the data will be used to calculate an interval for the degree of crystallinity from the different values of the heat of fusion. This includes the replicate DSC thermograms found in part A in the appendix.

Table 4. Thermal properties for the EVA9 polymer for the results from the DSC.

Supplier of EVA9	Supplier 3
T_m	108°C
T_c	87°C
Heat of fusion	106-116 mJ/mg
Degree of crystallinity	36.1-39.5%

The obtained results for the characteristics investigation of the EVA9 polymer should be considered as good because they match results from earlier studies. The degree of crystallinity is close to earlier obtained values [4]. The T_m can also be considered to match values in earlier studies [2, 7].

5.2 Modelling of the welding process

5.2.1 4 mm fibers 90 °C

In Figure 16 the result of the modelling for a 4 mm thick fiber for the time 10, 20 and 30 seconds and the temperature 90°C is shown. Seen for the time 10 seconds, furthest to the left, the core fiber (circle) has not reached the desired temperature after this time. It is known from the DSC results above that the melting temperatures are 74°C, 87°C and 108°C for EVA40, EVA28 and EVA9, respectively. With the results of the modelling in Figure 16 this should for EVA40 result in a weld that is only fully welded in the outer area of the core where $T > 74^{\circ}\text{C}$. For EVA28 the weld should be weaker since only a thin outer area of the core reaches the melting point of 87°C when welded 10 seconds. EVA9 is predicted to not weld at all regardless of the time since the weld temperature is not reaching the melting temperature of the polymer.

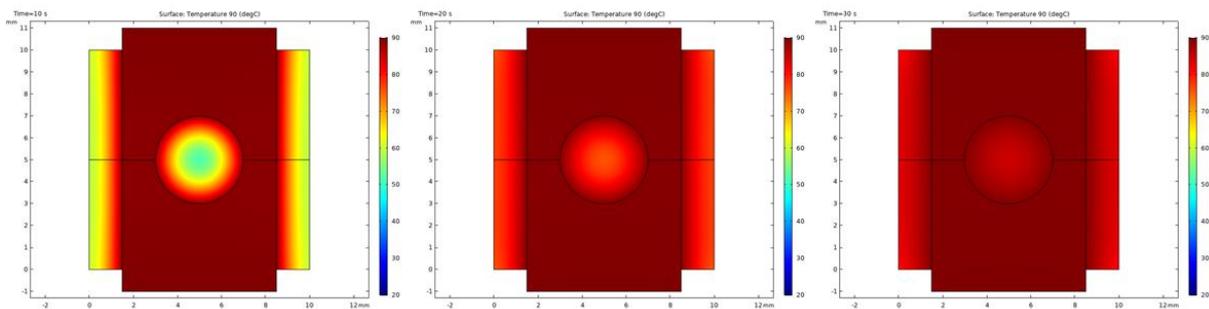


Figure 16. Image for the temperature profile for the weld at the temperature 90°C and the welding times 10, 20 and 30 seconds.

When increasing the welding time to 20 seconds, middle picture, the model shows that the core of the fiber reaches approximately 75°C which in theory should result in that the EVA40 polymer with a melting temperature of 74°C could be fully welded over the entire cross-section area if the polymeric chain segments have enough time to entangle over the interface. This is of the case for the welding time 30 seconds as well. For the EVA28 polymer the model suggest that 20 seconds is not enough time for the core to reach the polymers melting temperature of 87°C which should result in poor welds. At 30 seconds the core of the fiber can be seen to have a temperature close to 85°C which is very close to the melting temperature for the EVA28 which should make it possible for the fiber to weld together completely over the cross-section. For EVA9 the temperature is still too low to produce any good welds.

5.2.2 4 mm fibers 100°C

In Figure 17 the result of the modelling for a 4 mm fiber at 100°C for the welding times 10, 20 and 30 seconds is presented. Seen in the picture furthest to the left in Figure 17 the core is reaching the temperature of approximately 60°C while the outer part is reaching the heating temperature of 100°C after welding 10 seconds. This means that the three polymers will only be partly welded since the core is not reaching high enough temperature to melt these polymers. EVA9 should create an extremely weak weld since only a very small part of the polymer will be able to weld due to the low welding temperature.

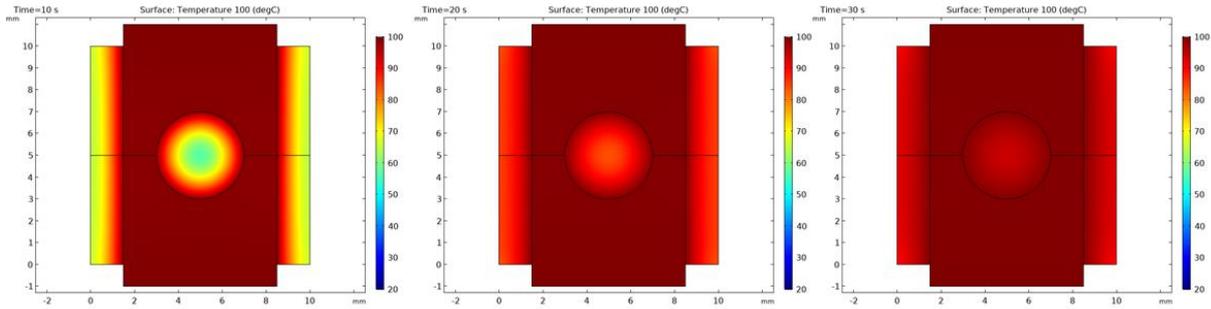


Figure 17. Image for the temperature profile for the weld at the temperature 100°C and the welding times 10, 20 and 30 seconds.

After heating at 100°C for 20 seconds the fiber core is approximately 90°C according to the model. This is well above the melting temperature for EVA40 and EVA28 why these polymers can be expected to be fully welded. Obviously, this is the case for 30 seconds as well since the core then is above 95°C. For EVA9 the time 20 seconds should create a stronger weld than the 10 second welding, but the weld should not be fully complete due to the low core temperature. At 30 seconds the core is 95°C which still is below the T_m for EVA9 and therefore the set temperature should not be enough to create a fully welded ring.

5.2.3 4 mm fibers 110 °C

In Figure 18 the result of the modelling for a 4 mm fiber at 110°C and the welding times 10, 20 and 30 seconds is presented. For 10 seconds, furthest to the left in the figure, the model shows that the fiber core has reached about 65°C which is not close to any melting point of the three EVA polymers. For EVA40 it is fair to expect a weld which is fully welded from the yellow area (~75°C) and out since it is above the polymers melting temperature of 74°C. EVA28 has a melting point of 87°C which for the welding time 10 seconds is reached from the orange color and out to the end which should result in a partly welded ring. For the EVA9 the model shows that the outer part of the core is reaching 110°C which is above the polymers melting temperature at 108°C but since the welding time is only 10 seconds this should not be enough time for the polymeric chains to entangle over the entire interface.

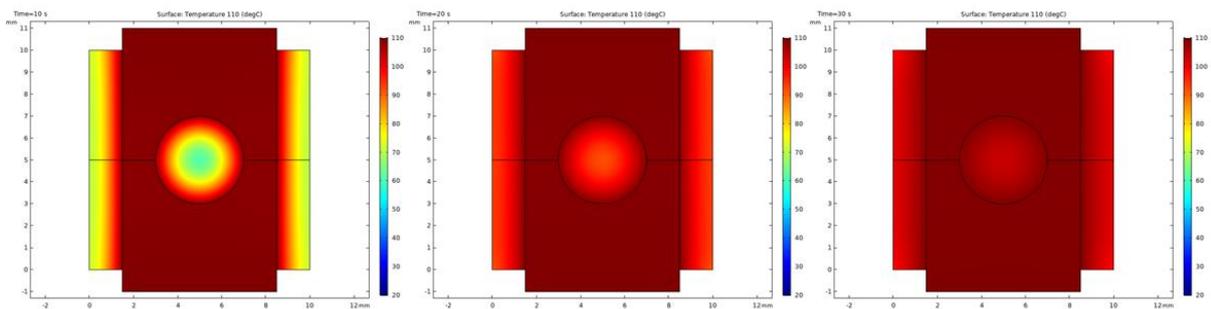


Figure 18. Image for the temperature profile for the weld at the temperature 110°C and the welding times 10, 20 and 30 seconds.

If the welding time is increased to 20 seconds the core reaches approximately 100°C which should be enough to provide a fully welded ring for the both EVA40 and EVA28 polymers which have melting temperatures below the core temperature. The same is expected for the time 30 seconds shown furthest to the right in Figure 18. For EVA9 20 seconds is not enough since the light red color in the core suggest a temperature of 100°C which should result in a partly welded ring. In the picture furthest to the right in Figure 18 the core is almost 110°C which is close to the melting temperature of EVA9

which possibly could provide completely welded rings.

5.2.4 5 mm fibers 90°C

In Figure 19 the modelling result for the welding of a 5 mm fiber with the welding temperature 90°C and the welding times 10, 20 and 30 seconds is presented. Seen in the picture furthest to the left, where the welding time is 10 seconds, the temperature is not reaching 40°C in the core of the fiber. This is far below all the melting points of the three polymers why it is safe to say that this welding time and welding temperature should not result in a good weld for any of the three polymers. The outer layer of the fiber reaches approximately 90°C which is above the melting point of EVA40 and EVA28 which could make some welding possible in the outer area of the fiber. EVA9 has a melting point of 108°C and a peak melting temperature of 97°C which should make it very hard for any welding to occur under these welding settings.

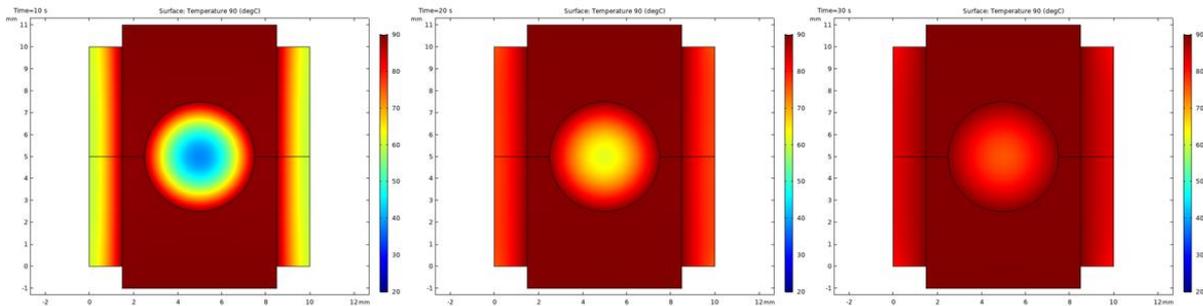


Figure 19. Image for the temperature profile for the weld at the temperature 90°C and the welding times 10, 20 and 30 seconds.

In the middle picture of Figure 19 the fiber has been welded for 20 seconds. The core of the fiber is reaching approximately 65°C which again is below melting temperature for all three polymers. This should result in a not fully welded ring for all polymers, though since the temperature at the outer area of the fiber is increasing this should for EVA40 and EVA28 create a stronger, but still very weak, weld compared to the welding time of 10 seconds. EVA9 should again not be welded at all.

For the picture furthest to the right where the fiber is welded 30 seconds, the core reaches approximately 75°C. This temperature is high enough to create a complete weld for the EVA40 polymer since it is above the polymers melting temperature. For the EVA28 polymer this weld should be stronger than the rings welded 10 and 20 seconds since more of the fiber reaches the melting temperature of the polymer. Regarding the EVA9 this condition should not provide a weld since it will not even reach the peak melting point of 97°C at the fibers surface.

5.2.5 5 mm fibers 100°C

In Figure 20 the modelling result for the welding of a 5 mm fiber with the welding temperature 100°C and the welding times 10, 20 and 30 seconds is presented. The 10 second heating. Furthest to the left in the figure, is not enough to heat the core to the desired temperature. This will result in weak welds for all three polymers.

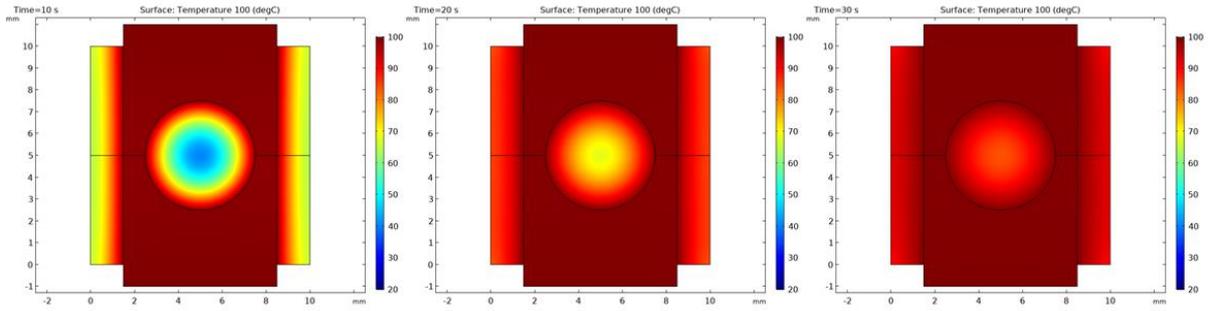


Figure 20. Image for the temperature profile for the weld at the temperature 100°C and the welding times 10, 20 and 30 seconds.

In the middle picture in Figure 20 the fiber is heated 20 seconds resulting in a core temperature of 70°C. This core temperature is not high enough for any of the three polymers to weld completely since it is below the three polymers melting points. In the picture furthest to the right in Figure 20 the core reaches approximately 90°C which is still below the melting temperature for EVA9 but high enough to weld EVA40 and EVA28 completely.

5.2.6 5 mm fibers 110°C

In Figure 21 the modelling result for the welding of a 5 mm fiber with the welding time 110°C and the welding times 10, 20 and 30 seconds is presented. The picture furthest to the left in Figure 21 is showing the fiber welded 10 seconds and it shows a cold blue area in the core which is approximately 45°C. This is far below the temperature of all three polymers. From the yellow area, 75°C, and out to the surface of the fiber, the EVA40 should be welded since it is above the polymers T_m . For EVA28, with a melting temperature at 87°C, this should be partly welded from the orange colored area and out to the surface of the fiber. In these conditions EVA9 should also be partly welded since the outer area of the fiber reaches above the polymers melting temperature of 108°C.

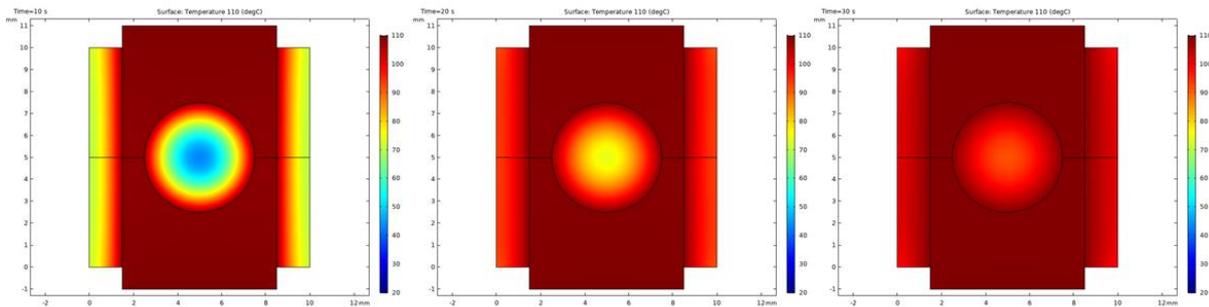


Figure 21. Image for the temperature profile for the weld at the temperature 110°C and the welding times 10, 20 and 30 seconds

For 20 seconds welding of the EVA40, the ring should be fully welded since the core temperature is above the polymers melting point. EVA28 should not be fully welded because the core temperature is below the melting point of the polymer, though a bigger area of the fiber is above the melting point which should result in a stronger weld than the fiber welded 10 seconds. The same is expected with the EVA9 which has a bigger part of the fiber reaching 108°C which should provide a stronger weld than the fiber welded 10 seconds.

In the picture furthest to the right in Figure 21 the core reaches 100°C. This should provide a fully welded ring for both EVA40 and EVA28. For EVA9 the core temperature is a few degrees below the melting point, but the weld should be stronger than the fibers welded 10 and 20 seconds.

5.3 Tensile strength of the weld

The results of the tensile testing will be presented in the sections below. Since the result of the modelling was not the same as the result for the trials, not all temperatures presented in the modelling will be presented here. For EVA40 the IVRs were not possible to weld higher than 90°C because of the low melting point of 74°C which made the polymer get stuck in the equipment at higher temperatures. EVA28 only provided full welded rings at 100°C and EVA9 only provided welded rings at 110°C.

5.3.1 Stress at break results for EVA9 IVRs

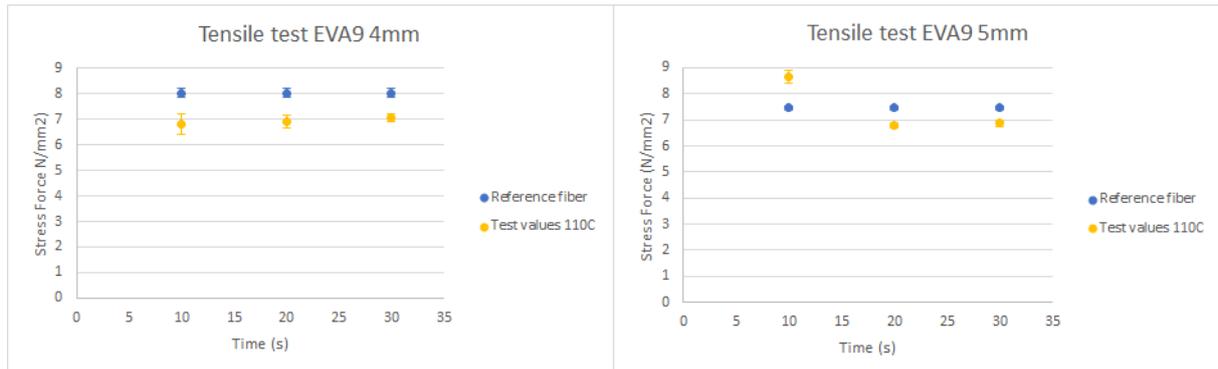


Figure 22. Stress at break results for EVA9 IVRs welded at 110°C and different times.

Figure 22 presents the results for the stress at break of the EVA9 IVRs. To the left are the 4 mm rings and seen in the figure the stress at break, measured in N/mm², results (yellow dots) lies a bit below the reference fiber values (blue dots). If one compare the time the rings are welded it is possible to see that there is an increasing trend with the time for the stress force at break and the standard deviation becomes lower the longer the rings are welded suggesting the welds gets more even when welded for a longer time.

In the picture to the right in Figure 22 the stress at break values of the EVA9 IVRs with the 5 mm diameter are shown. Immediately it is clear that the first value welded at 10 seconds is very high while the other values looks more reasonable just below the reference values. There is a possible explanation for this increase in stress at break for the IVRs welded at this time and temperature. The welding equipment is affected by thermal expansion between the aluminum and the plastic material since they expand differently when heated. This makes it possible for the polymers, especially EVA40 and EVA28 which are melting earlier than EVA9, to escape into spaces in the equipment and in that way it blocks and pushes out the temperature sensors. In return this will increase the cycle time of the welding a lot and more likely these IVRs are welded far more than 10 seconds and probably even further than 30 seconds which would be a reasonable explanation for this high stress at break value. In the batch manufacturing record for this trial it is commented that EVA9 with 5 mm welded at 10 seconds was the last try before the equipment had to be changed and cleaned due to the temperature sensors not working correctly.

Finally, if looking at the IVRs welded at 20 and 30 seconds in the right picture in Figure 22 it is seen that the time do affect the stress at break since a rising trend is seen.

5.3.2 Stress at break results for EVA28 IVRs

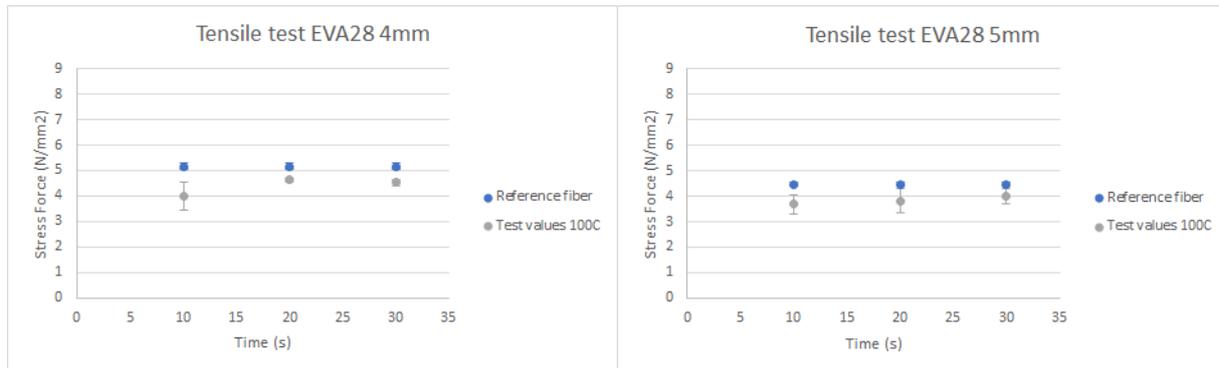


Figure 23. Showing the stress force results for EVA28 IVRs welded at 100°C and different times.

In Figure 23 the results for the tensile testing for EVA28 IVRs are presented. To the left in the figure the stress at break for IVRs with the 4 mm diameter are presented. The biggest difference occurs between the rings welded 10 and 20 seconds where an increase is shown in stress at break when raising the welding time to 20 seconds. For the 30 seconds there is almost no difference in stress at break compared to the rings welded 20 seconds, suggesting that it is indifferent for the weld strength if the ring is welded 20 or 30 seconds.

For the picture to the right in Figure 23, where the EVA28 IVRs have the diameter of 5 mm, there is a difference for the stress at break results. There is a minor increase in stress at break between the rings welded at 10 and 30 seconds, though the value for 30 seconds is in the range of the standard deviation for the IVRs welded 10 seconds. This indicates that the welding time parameter has some impact on the stress at break of the weld.

5.3.3 Stress at break results for EVA40 IVRs

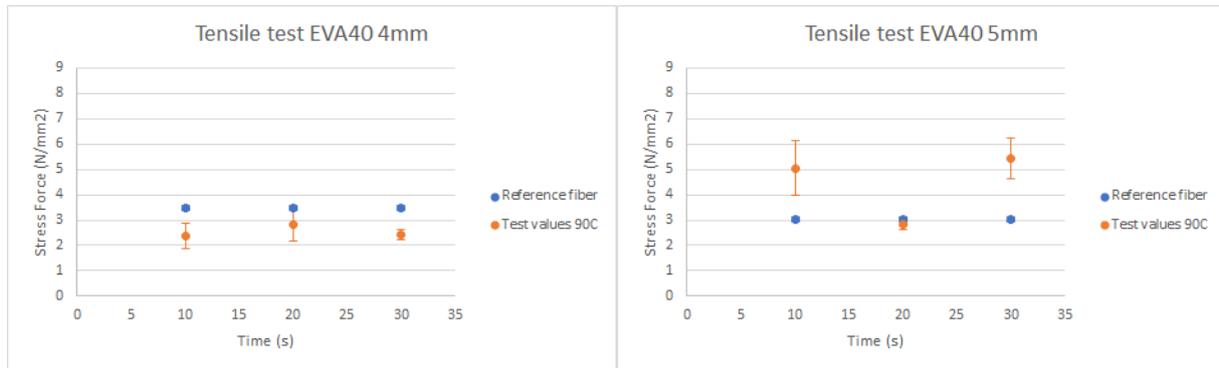


Figure 24. Stress at break results for EVA40 IVRs welded at 90°C and different times.

Seen in Figure 24 are the results for the measurements of stress at break for the EVA40 IVRs. In the left picture with the 4 mm EVA40 IVRs the stress at break (yellow dots) is below the value from the reference fiber (blue dots). It is noticeable to observe that the IVRs welded at 10 seconds and 30 seconds almost get the same result in stress at break which indicates that in this case the time the rings are welded does not affect the stress at break.

To the right in Figure 24 is the EVA40 IVRs with a 5 mm diameter. Here the result is not as clear since the values of the rings welded 10 and 30 seconds are very high compared to the reference fiber values. It is seen that these welds also have a very high standard deviation suggesting that the rings welded for 10 and 30 seconds are not welded evenly but instead has a very high variation of the quality of the weld which likely is due to the errors with the welding equipment. Though all EVA40 IVRs with the diameter of 5 mm are almost equal or above the reference value.

Table 5. Differences between the test values and the reference values in % for the stress force for the IVRs.

Welding temperature (°C)	VAc (%)	Time (s)	Diameter (mm)	Difference
110	9	10	4	-15,1%
110	9	20	4	-13,6%
110	9	30	4	-11,8%
110	9	10	5	16,2%
110	9	20	5	-9,00%
110	9	30	5	-7,78%
100	28	10	4	-22,4%
100	28	20	4	-10,6%
100	28	30	4	-12,6%
100	28	10	5	-17,4%
100	28	20	5	-15,0%
100	28	30	5	-10,3%
90	40	10	4	-32,0%
90	40	20	4	-17,9%
90	40	30	4	-30,0%
90	40	10	5	67,4%
90	40	20	5	-6,65%
90	40	30	5	80,1%

In Table 5 the differences between the test values of the EVA9 IVRs and the EVA9 reference fibers are presented. The negative values are if the test value is below the reference value and the positive

differences are if the test value is above the reference value. For the rings with the diameter 4 mm the difference decreases with time. This is what is expected both from the modelling but also in theory where the polymers get a longer time above its melting point to entangle and diffuse over the interface. For the rings with 5 mm in diameter the first value is known to be incorrect due to error in the welding equipment. For the values welded 20 and 30 seconds the same trend as for the 4 mm IVRs is shown. Therefore, it is safe to say that the strength regarding stress at break of the weld increases with time when welded at 110°C for the EVA9 IVRs.

In Table 5 the differences between the test values for the EVA28 IVRs and the EVA28 reference fibers are presented. For the rings with the diameter 4 mm a large decrease in the difference can be seen between the IVRs welded 10 and 20 seconds. There is a small rise of 2% in difference between the time 20 and 30 seconds. For the rings with 5 mm diameter a clear trend is shown where the difference decreases with the time suggesting that the time parameter is of high importance for the weld strength and that the 30 second is the best of the three different welding times.

In Table 5 the differences between the test values for the EVA40 IVRs and the EVA40 reference fibers are presented. Though, it is hard to see any clear trends or result due to strange test values which most likely is due to the high temperature and the problem with the welding equipment.

A possible explanation for the strange results for the EVA40 IVRs are the properties of the polymers and the welding equipment as described before. Since the EVA40 polymer has much more sticky properties and is melted fully at 74°C it will be very hard to weld at 90°C. It was discovered during the welding process that a lot of the EVA40 polymer got stuck in the welding equipment and at the surface of the equipment. This behavior was not observed for the welding of EVA28 and EVA9 IVRs and can be a possible explanation for the difference in the results between the materials.

5.3.4 Elongation at break results for EVA9 IVRs

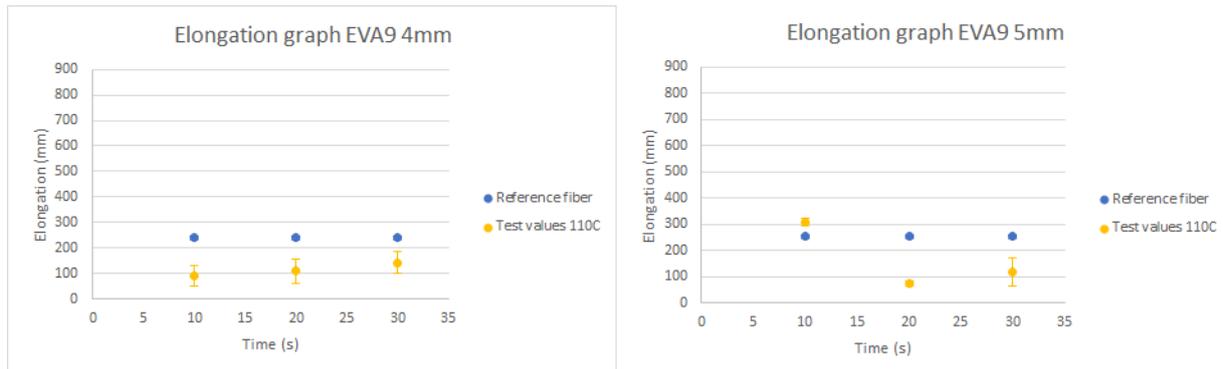


Figure 25. Showing the elongation results for EVA9 IVRs welded at 110°C and different times.

Shown in Figure 25 are the elongation results for the EVA9 IVRs. In the picture to the left the results for the 4 mm IVRs are shown where a clear trend is seen where the elongation distance increases with the time. This is in theory not surprising since the T_m for EVA9 is 108°C so the temperature 110°C is just above T_m . This will in return make the time a crucial parameter for the welding since the core needs to reach above 108°C to fully melt and create a strong weld. The standard deviations are not differing significantly between the IVRs welded at different times. Observe that the IVRs welded at 30 seconds still are far below the elongation results of the reference fibers.

The picture to the right in Figure 25 above shows the elongation results of the EVA9 IVRs with the 5 mm diameter. As in the stress at break results for EVA9 shown in Figure 22, the IVRs welded 10 seconds have very high values. This has the same explanation as for the stress at break results above where the error in the equipment causes the cycle time to increase a lot and therefore welding the IVRs far more than 10 seconds. For the IVRs welded 20 and 30 seconds the results look like the 4 mm rings where they have an increasing trend with the time but still not high enough values to reach the reference fibers. The reason for this has the same explanation as in the paragraph before, the T_m for the polymer lies just below the welding temperature making it hard for the core to reach above the polymers T_m .

5.3.5 Elongation at break results for EVA28 IVRs

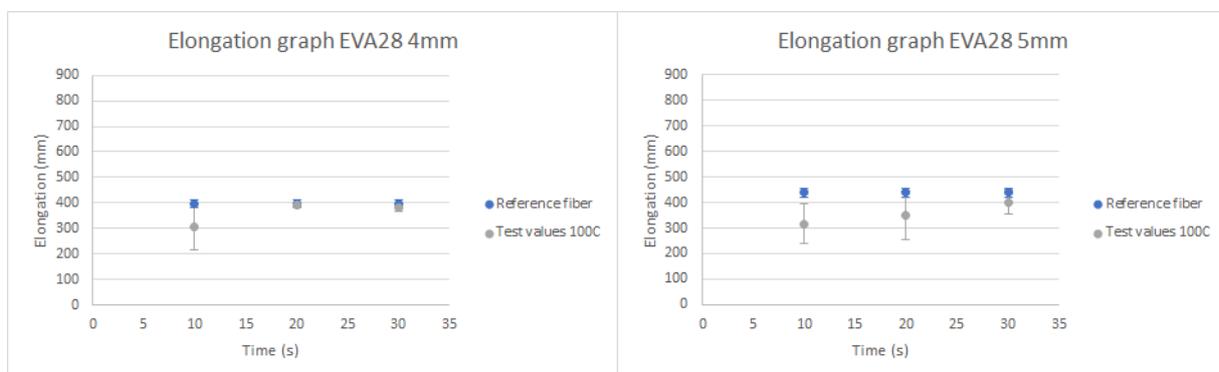


Figure 26. Showing the elongation results for EVA28 IVRs welded at 100°C and different times.

Figure 26 presents the elongation results for the EVA28 IVRs. To the left are the rings with the diameter of 4 mm. It shows a big difference regarding the time parameter between 10 seconds and 20 seconds where an increase in elongation distance is seen. The standard deviation for the rings welded 10 seconds is also much higher than the IVRs welded 20 and 30 seconds. This is probably since the polymer rings welded 10 seconds do not reach high enough temperature inside the entire fiber core to result in a fully completed weld. For 20 seconds the result is almost the same as the reference fiber values which suggest that this time and temperature is enough to provide a strong weld. When comparing the times 20 and 30 seconds there are a very small difference in elongation but no significant difference at all.

In the picture to the right in Figure 26 the elongation result for the EVA28 IVRs with 5 mm are presented. It is a clear trend that the elongation here increases with time where the rings welded 30 seconds almost reach the elongation result of the reference fibers. The IVRs welded 10 and 20 seconds have a high standard deviation and are below the reference fiber values suggesting that the core temperature of the fiber does not reach high enough temperature to provide a fully completed weld.

5.3.6 Elongation at break results for EVA40 IVRs

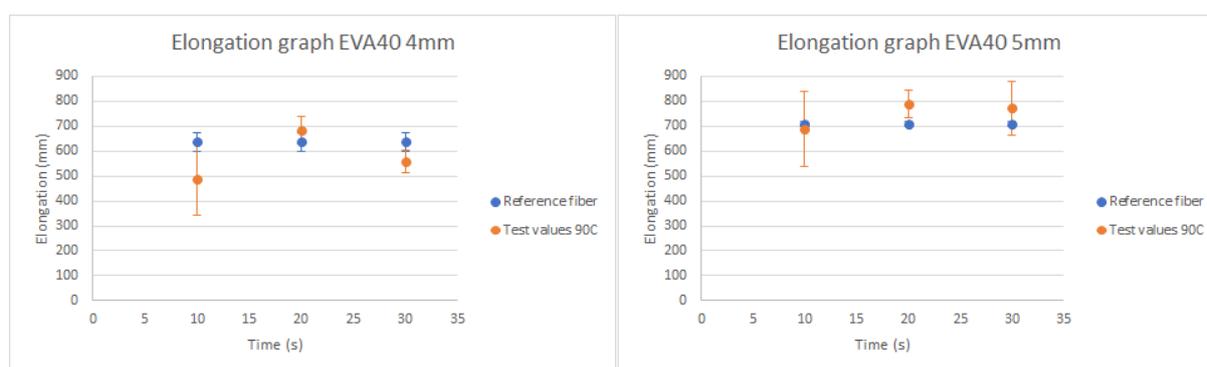


Figure 27. Showing the elongation results for EVA9 IVRs welded at 110°C and different times.

In Figure 27 the elongation result of the EVA40 IVRs is presented. To the left are the 4 mm rings where it is hard to interpret the result. For the rings welded 10 seconds a very high standard deviation is obtained which put some uncertainty to the result. A possible explanation for this is that the short time is sometimes enough for some polymer chains to entangle and sometimes it is not. In the figure the result also show that the elongation decreases when increasing the time from 20 seconds to 30 seconds. In theory the extra time should provide the polymers with more time to entangle into each other and therefore create a better weld i.e. higher elongation result, but this is not the case here. The explanation for this is again the welding equipment. Since the T_m where all crystals in the polymer structure is at 74°C for EVA40, 90°C should have made the polymer less viscous and due to the thermal expansion in the equipment more polymer material can move into the small spaces in the equipment when the time is increased from 20 seconds to 30 seconds. This results in that the weld loses more material at 30 seconds which logically would make the weld thinner and weaker. It was also observed when welding the IVRs that the longer the EVA40 rings where welded, the more material got stuck in the equipment, theoretically resulting in a thinner diameter for the weld.

To the picture to the right in Figure 27 are the results for the EVA40 IVRs with the 5 mm diameter. A clear rise between 10 seconds and 20 seconds in elongation distance is seen as well as a decrease in standard deviation. This suggests that the IVRs welded 20 seconds results in a stronger weld with more entanglements over the interface. Between the times 20 and 30 seconds there are no significant

difference, though it is observed that the standard deviation is increasing for the IVRs welded 30 seconds. This can be due to the thermal expansion of the polymer in equipment and the same phenomena as for the EVA40 4 mm IVRs, described earlier, can occur when the polymer is heated too long.

Table 6. Differences between the test values and the reference values in % for the elongation for the IVRs.

Welding temperature (°C)	VAc (%)	Time (s)	Diameter (mm)	Difference
110	9	10	4	-61,4%
110	9	20	4	-54,1%
110	9	30	4	-40,1%
110	9	10	5	21,5%
110	9	20	5	-70,3%
110	9	30	5	-53,2%
100	28	10	4	-22,8%
100	28	20	4	-2,3%
100	28	30	4	-4,3%
100	28	10	5	-27,6%
100	28	20	5	-20,4%
100	28	30	5	-9,5%
90	40	10	4	-23,2%
90	40	20	4	7,5%
90	40	30	4	-12,5%
90	40	10	5	-2,5%
90	40	20	5	11,7%
90	40	30	5	9,3%

In Table 6 **Fel! Hittar inte referensskälla.** is the elongation result for the differences between the test values for the EVA9 IVRs and the EVA9 reference fibers. For the rings with a 4 mm diameter the difference decreases with time, observe the big difference here. The 5 mm rings have the first value above the reference value, and the reason for this was discussed before. If the IVRs welded 20 and 30 seconds is investigated instead it shows the same trend with decreasing difference with the welding time suggesting that the time parameter strongly affect the elongation result.

The difference in the elongation between the test values of the EVA28 IVRs and the EVA28 fibers is presented in Table 6. For the 4 mm rings a clear decrease in difference is shown between rings welded 10 and 20 seconds. Both 20 and 30 second welds show a very small difference compared to the reference fibers which indicates a very good weld. For the 5 mm rings a trend where the difference decreases with time is shown, again suggesting that the welding time parameter strongly affect the elongation result of the IVRs.

In Table 6 **Fel! Hittar inte referensskälla.** the elongation differences between the test values for the EVA40 IVRs and the EVA40 reference fibers are presented. As in the stress at break section before, the EVA40 results are not as expected where three test values are above the reference fiber values. The result of this is that it is not possible to find any trends or draw any conclusions about how the time affects the elongation for the EVA40 IVRs.

If one compare the diameters in Table 6 for EVA28 and EVA9 IVRs it is seen that the 4 mm diameter have the lowest difference, i.e. the test values are closer to the reference values. This is a result that were already seen in the modelling section which is due to the thickness of the fiber. Since 4 mm will reach a higher core temperature than a 5 mm fiber will at the same welding time, the welding should

therefore be better for the 4 mm IVRs. This is seen for both EVA28 and EVA9 in Table 6 and probably is because as seen in the modelling the 5 mm fibers can not get fully heated through the entire fiber as fast as the thinner 4 mm fiber can.

5.3.7 The VAc content parameter

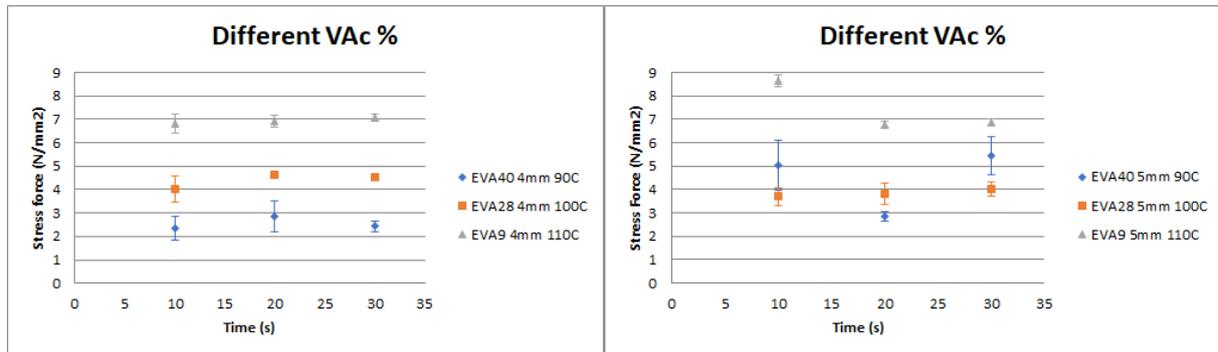


Figure 28. The stress force results for each EVA polymer to compare the VAc content parameter.

Figure 28 shows the stress at break results for the parameter VAc content. The three different EVA's are shown at different temperatures. The temperatures were selected to be above the melting point of each polymer, though for EVA9 110°C is not as far above as the temperature is for EVA40 and EVA28. This is since 110°C was the highest welding temperature in this trial. In the left picture are the IVRs with 4 mm diameter and the lowest weld strength, measured in stress at break, is the EVA40 polymer and highest weld strength has the EVA9. This is most likely due to the crystallinity of the polymers, since EVA40 has large amorphous regions and less crystals, the mobility in the polymer is much higher than it is in EVA9. The mobility of the chains causes the polymer to be more flexible and will therefore make it possible to pull the polymer almost like a rubber band. Though, since its lack of large crystal regions the force will not be high since it is the crystalline regions that cause the robustness of the polymer. With the high result for EVA9 it is concluded that the stress at break in the welded intersection of the polymer can reach high levels due to the polymers crystallinity. The reason for this is the opposite to EVA40, since EVA9 contain large crystal regions which are ordered and structured very well and a higher molecular weight, these regions will require a larger force to break them. Think of a diamond which have a very ordered crystal structure. EVA28 has more crystal regions than EVA40 but less than EVA9 so unsurprisingly the result in stress at break lies in between EVA40 and EVA9.

In the picture to the right in Figure 28 are the results of the IVRs with the 5 mm diameter presented and there are some strange results. The 10 seconds and 30 seconds welds for EVA40 are much higher in stress at break than expected since they are above EVA28. This should not be the case since EVA40 contains less crystal regions than EVA28 and should therefore require less force to break the weld. Though as discussed in an earlier paragraph these results may be affected by errors with the welding equipment. The results for EVA28 seem normal with a low raise in stress at break with the time but still below the values for EVA9. For the stress at break results for EVA9, the first point at 10 seconds has a very high value. This is due to an error in the welding equipment as described before. To sum up the stress at break and the results regarding the parameter VAc content it is safe to say that the less VAc content the polymer contains the higher the stress at the breaking point of the IVR will be.

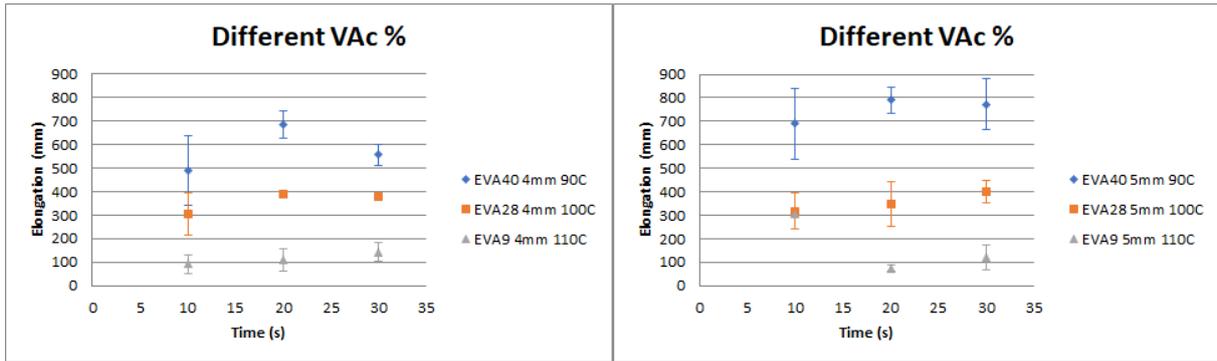


Figure 29. Elongation at break results for each EVA polymer to compare the VAc content parameter.

In Figure 29 is the elongation result for the different polymers to compare with the parameter VAc content. In the picture to the left are the results of the IVRs with the 4 mm diameter. It shows that the elongation decreases with the decreasing amount of VAc in the polymer. The EVA40 has the highest elongation with has the same explanation as in the paragraph above with the stress at break results. Since EVA40 contain more amorphous regions that easily can move, the polymer will be much easier to elongate because these chains can stretch out and move when they are being pulled out. For EVA9 where there are large crystal regions instead, which make the material very brittle, they can't move and stretch as easily as the amorphous regions and the elongation will not be very large since instead of chains stretching out, crystal regions will break and cause the weld interface to break.

In the picture to the right in Figure 29, the IVRs with the 5 mm diameter are presented and the same results as for the 4 mm IVRs can be observed. The elongation decreases with a decreasing amount of VAc content. Though again the EVA9 rings welded at 10 seconds is very high which is due to the error in the welding equipment. For the elongation results it is safe to say that the VAc content parameter is heavily affecting the weld by decreasing the elongation when decreasing the VAc content in the polymer.

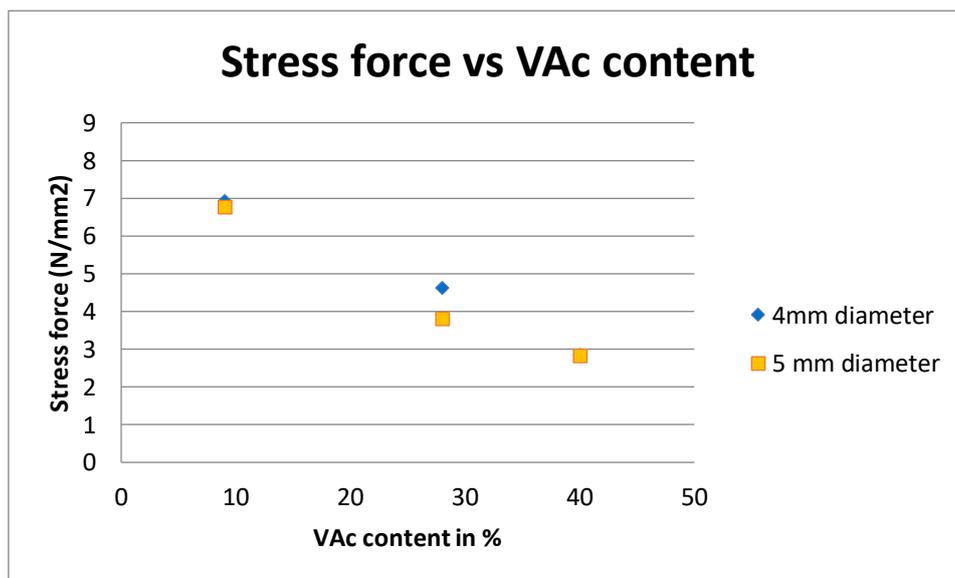


Figure 30. The stress force vs the VAc content for the different diameters where time is set to 20 seconds.

In Figure 30 the result for the IVRs welded 20 seconds is presented for the different diameters. It is a clear trend where the stress at break decreases with an increasing amount of VAc for both diameters,

strengthening the conclusion above that the increasing content of VAc will decrease the stress at break for the weld.

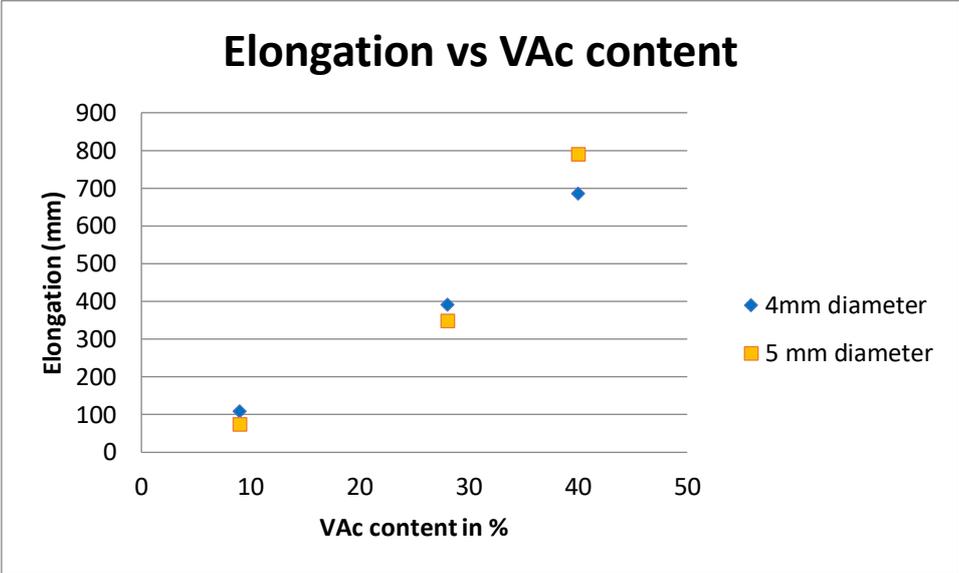


Figure 31. The elongation at break vs the VAc content for the different diameters where time is set to 20 seconds.

In Figure 31 above the result for the IVRs welded 20 seconds is presented for the different diameters. As stated before, it is here presented again that the elongation increases when increasing the VAc content for both diameters. With all previous results in mind it is safe to conclude that the VAc parameter heavily affects both stress force and elongation at break for the weld.

6 Conclusions

Based on the information presented in the results and discussion it can be concluded that the EVA40 produced in two different ways do not result in the same properties of the polymer. Big differences in the recrystallization onset temperature and the melting temperature are found which is clear evidence that the structure in the polymer differs. It can also be concluded that the EVA40 supplied by Supplier 2 contains larger crystals which means it has areas with a very high content of ethylene and low content of VAc.

From the EVA28 and EVA9 DSC measurements it can be concluded that the results match well with the pre known values from different studies. It is also confirmed that the thermal characteristics of the EVA polymer, T_m and T_c , decreases with increasing VAc content and that the degree of crystallinity decreases when increasing the amount of VAc content.

It is concluded that the VAc content parameter influences the weld strength since the elongation will decrease with decreasing amount of VAc and the stress at break will increase with a decreasing amount of VAc.

For the EVA28 and EVA9 IVRs it is concluded that the time parameter does have an effect in meaning of that the longer the IVRs are welded at the given temperatures the better the weld will be. Nothing can be concluded about the EVA40 IVRs when looking into the time parameter more than if it is welded too long more material will get stuck in the welding equipment.

7 Future work

Further investigation is needed on several parts of this project. To investigate the temperature parameter further, on its effect on the weld strength, 130°C for EVA9 also needs to be tested. A suggestion would be to try two temperatures for each polymer that lies 15°C and 25°C above each polymer melting point to investigate if this rise in temperature affects the weld strength at set times. Also to measure the length of the polymer chains and the polydispersity would give further knowledge about the polymer.

The VAc content parameter and the time parameter are concluded to affect the weld strength in different ways and no further testing needs to be done on these parameters. Though EVA40 has strange results and should be re-investigated in other welding equipment to avoid errors like the polymer getting stuck inside the equipment.

The pressure parameter will also need to be investigated in further work. This is to be sure that all influential parameters have been tested and evaluated on their effect on the weld strength.

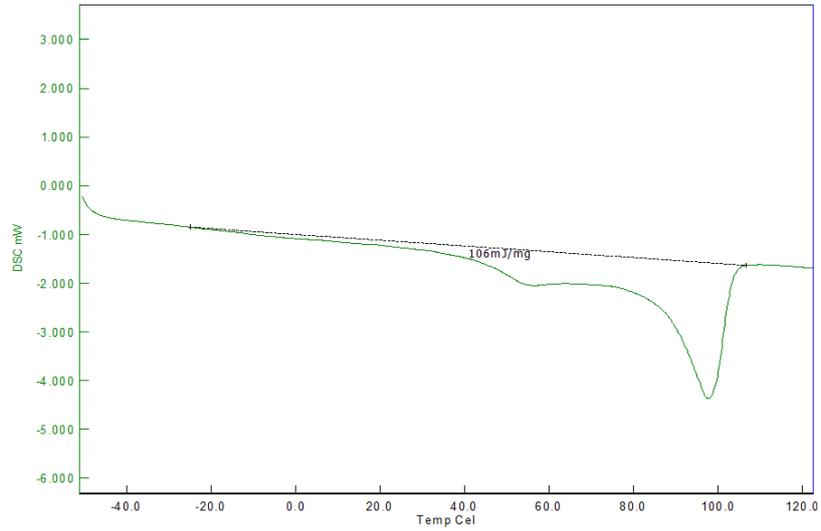
When all mentioned parameters are evaluated the IVRs should be tested in other conditions than the surrounding air to get more knowledge how the weld strength holds in more body like conditions.

8 References

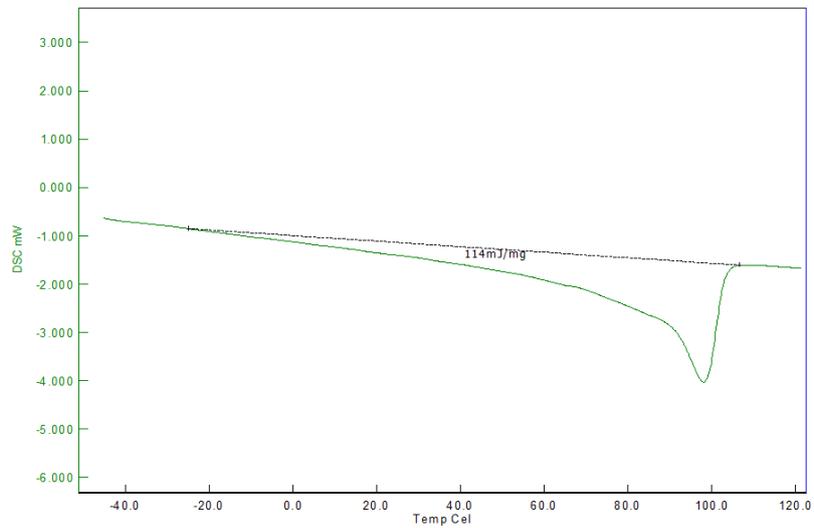
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9 Appendix

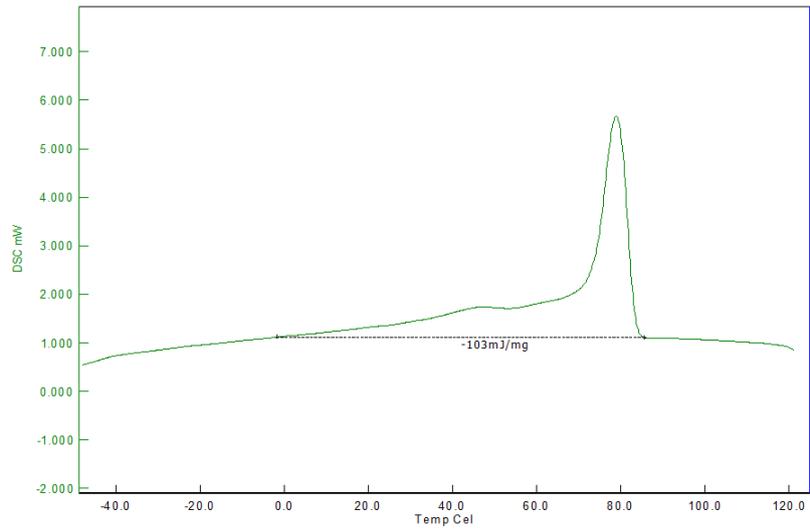
A. DSC thermograms



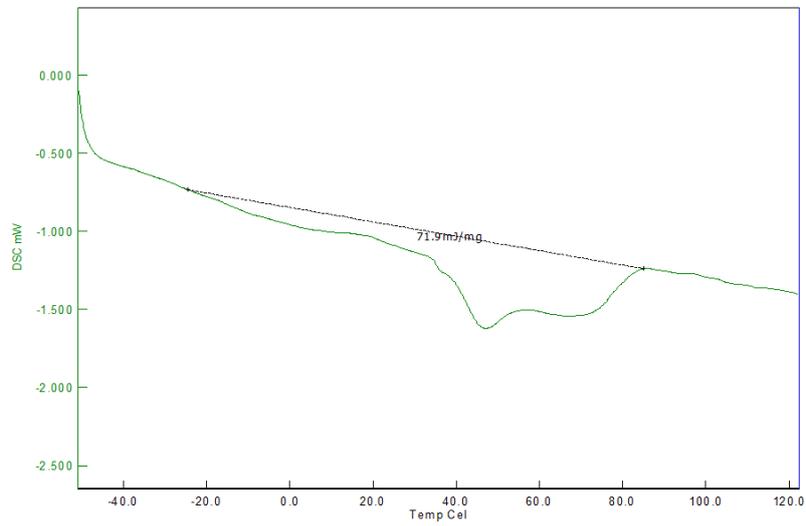
Figur A1. Thermogram of the first melting stage for the EVA9 polymer supplied by Versalis.



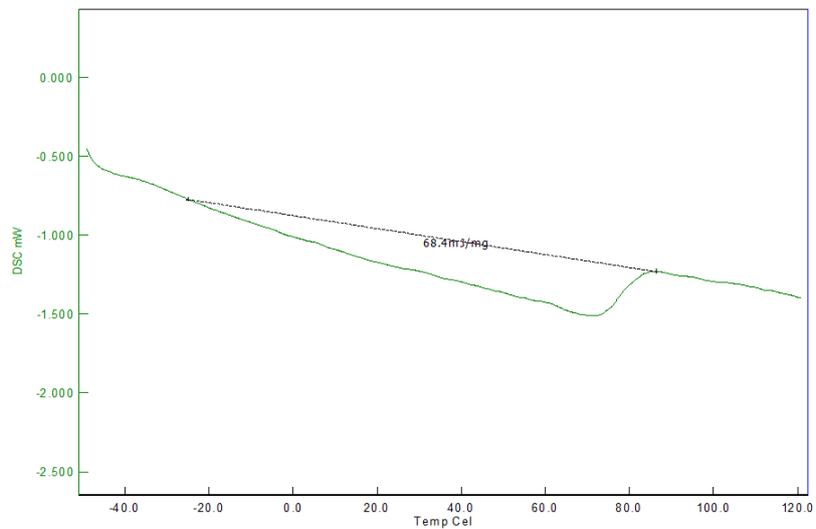
Figur A2. Thermogram of the second melting stage for the EVA9 polymer supplied by Versalis.



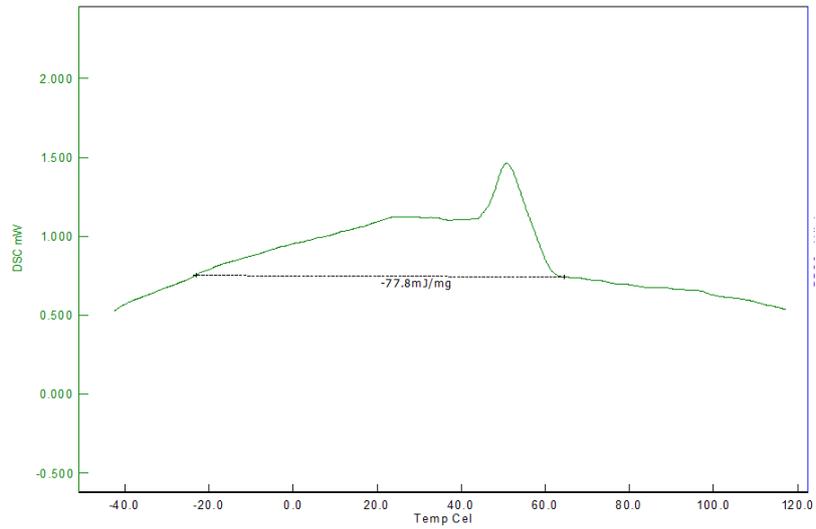
Figur A3. Thermogram of the re-crystallization for the EVA9 polymer supplied by Versalis.



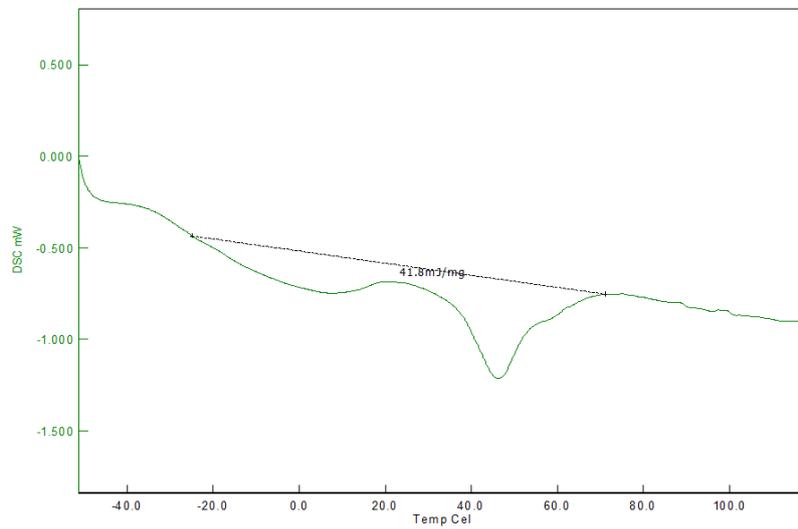
Figur A4. Thermogram of the first melting stage for the EVA28 polymer supplied by Celanese.



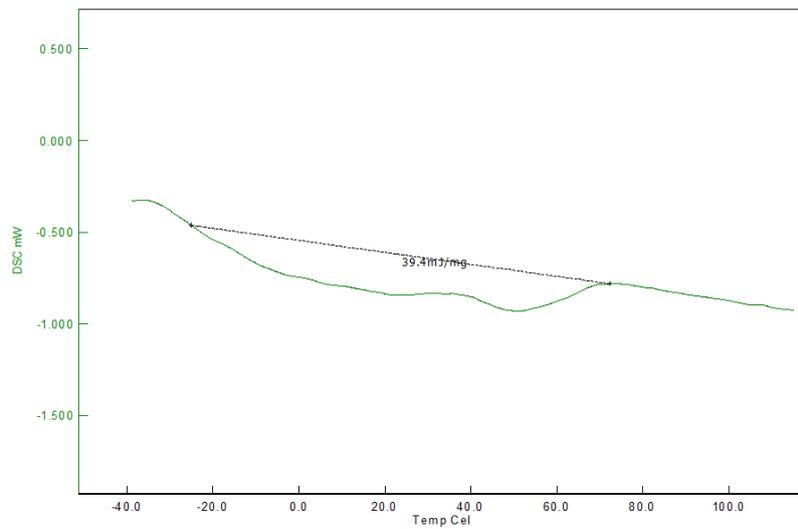
Figur A5. Thermogram of the second melting stage for the EVA28 polymer supplied by Celanese.



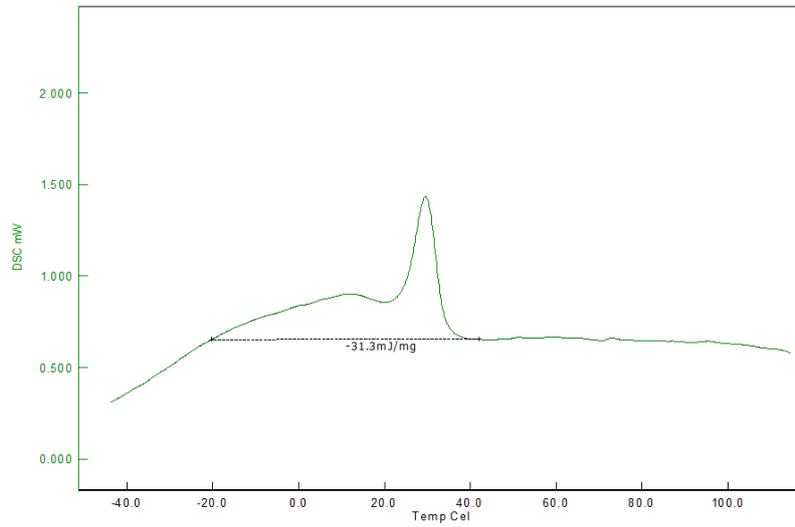
Figur A6. Thermogram of the re-crystallization stage for the EVA28 polymer supplied by Celanese.



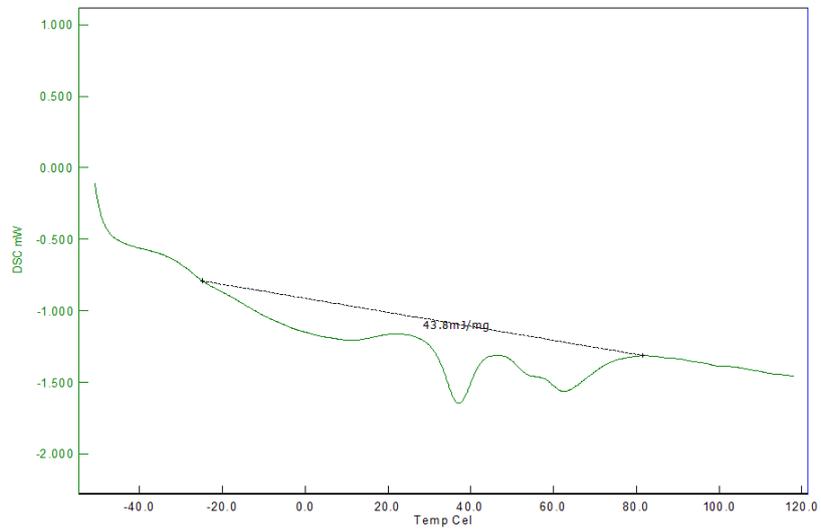
Figur A7. Thermogram of the first melting stage for the EVA40 polymer supplied by Celanese.



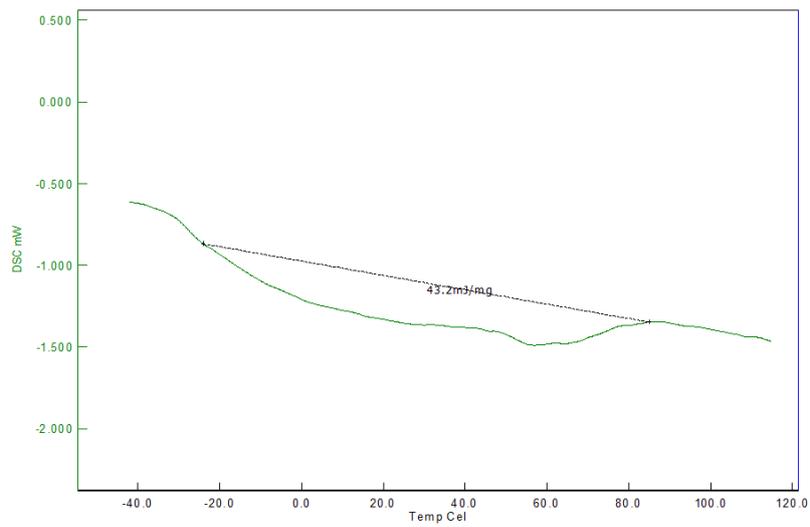
Figur A8. Thermogram of the second melting stage for the EVA40 polymer supplied by Celanese.



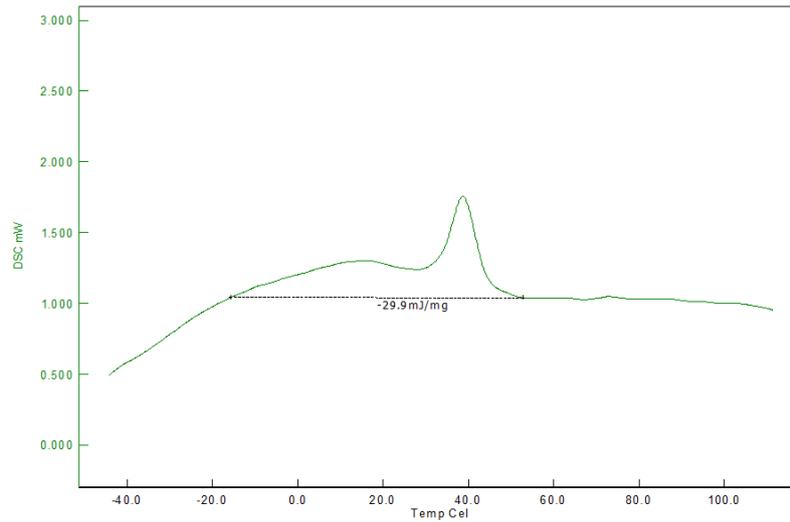
Figur A9. Thermogram of the re-crystallization stage for the EVA40 polymer supplied by Celanese.



Figur A10. Thermogram of the first melting stage for the EVA40 polymer supplied by PolyScience.



Figur A11. Thermogram of the second melting stage for the EVA40 polymer supplied by PolyScience.



Figur A122. Thermogram of the re-crystallization stage for the EVA40 polymer supplied by PolyScience.

B. Statistics

Formulas used to calculate statistics of the data [8]

$$G = \frac{Y_{max} - \bar{Y}}{s} \quad (B1)$$

Where:

G = Grubbs test

Y_{max} = Possible outlier with max value of the data set Y

\bar{Y} = Mean value of the data set Y

s = Standard deviation of the data set Y

$$G = \frac{\bar{Y} - Y_{min}}{s} \quad (B2)$$

Where:

G = Grubbs test

Y_{min} = Possible outlier with min value of the data set Y

\bar{Y} = Mean value of the data set Y

s = Standard deviation of the data set Y