Autohesion in Press Fitted Polypropylene-Polypropylene Interfaces

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Abstract

This study examines press fitted injection moulded components of a PP homopolymer (PCGH19) and PP random copolymer (PCGR25) that requires a force above the specified range for disassembly after sterilization in an autoclave. Examining the disassembled components under an optical microscope show that the components bond due to interference pressure and post assembly autoclaving at $121^{\circ}C$. From literature study, DSC and DMTA analysis, it is proposed that the interface exhibits autohesion, from chain inter-diffusion, in the outer most skin-layer, contributed by a highly mobile amorphous region. DMTA shows a 80% decrease in storage modulus of both polymers, with PCGR25 to exhibit the lowest value of stiffness at $121^{\circ}C$. Observing a large deformation of the PCGR25 components post autoclaving supports the theory of a viscous flow, hence inter-diffusion occurring at elevated temperatures. Autohesion is assumed to be greatly dependant on this deformation and viscous flow. Without changing material, it is suggested and discussed to inhibit autohesion by cold-crystallization, as well as self-induced surface migration of low molecular additives. Further studies are needed to establish which solutions that can be utilized.

Keywords: Polypropylene, autohesion, press fit, heat treatment, crystallinity, autoclave, rheology

1. Introduction

Press or interference fits is widely used in mechanical applications. The nature of polymers in interference fits, do however require special attention. Especially when considering creep, chemical adhesion, adhesion in general, processing and post processing of the polymer parts, etc.

Two different grades of commercial polypropylene (PP), PCGH19 (homopolymer) and PCGR25 (random copolymer), both produced by SABIC, are used in a simple, thin shelled, non-permanent press fit application. The assembly consists of 6 contact points, with ribs running the entire length of the components. A cross sectional view of the contact point can be seen in Fig. 1.



Fig. 1 Schematic view of the assembly cross sectional interface.

The parts are injection moulded before being assembled and sterilized, in an autoclave at $121^{\circ}C$. Optimal disassembly would require a pull force in the range 1-14 N. From initial testing, 10 specimens where pulled apart and reassembled three times. An average pull force of 12.8±2.7, 10.5±2.4 and 14.0±4.6 N is seen prior to autoclaving. Repeating the test, on 50 specimens, after autoclaving the pull force is on average 18.2±3.1 N and drops to an average of 3.4 ± 0.6 N for second and third pull. Based on the high drop in pull force, for the autoclaved components, from the first to the second pull it seems that the normal force from the press fit and friction only accounts for a small fraction of the pull force. This is also seen by initial testing where the mould, used to manufacture the components, were polished and revealed no decrease in the pull force. The first pull the pull force spans from 12.3 N to 24.6 N suggesting that some non constant parameter influences the pull force.

Full disclosure: The pull test is performed externally according to the manufactures standard.

Damage at the interface becomes noticeable after pulling apart the autoclaved samples. This damage is seen in the form of cracks, scratches, deformation and a high degree of what appears to be abrasive damage. Consequently, due to the drop of the pull force and the damage observed at the interface, it is suggested that creep and relaxation play a significant role as well as the adhesion or miscibility between the two PP's.

Analyzing the crystallinity from differential scanning calorimetry (DSC) melting curves, the onset melting temperature prior to autoclaving is seen approaching the autoclave temperature of $121^{\circ}C$. The miscibility of the two PP blends in the amorphous phase may therefore see to approach something that would allow adhesion to occur in the interface. For a semi-crystalline polymer however, viscous flow will generally only occur above the crystalline melting point (T_m) . From DSC analysis, T_m is seen at approximately $48^{\circ}C$ and $28^{\circ}C$ above the autoclave temperature for the PCGH19 and PCGR25 respectively. [1]

Fourier-transform infrared spectroscopy (FTIR) analysis shows only a slight difference in chemical composition of the materials. From data sheets, these differences may be seen to be additives in the polymer. Interstitial diffusion of additives to the surface, may also present the possibility of chemical adhesion between the PP blends. Chemical adhesion is usually only occurring on the surface of the polymer. [1, 2, 3]

For semi-crystalline polymers, properties are influenced by its amorphous and crystalline phase. The degree of crystallinity will be defined by temperature. As long as the polymer is above the glass transition temperature (T_a) , molecular motion in the amorphous region will take place. This molecular movement can lead to autohesion. Autohesion of polymers is a process where two polymer surfaces is bonded together upon contact. For semi-crystalline, non reactive, polymers like PP autohesion can occur by two processes; molecular chains entanglement and secondary bonding such as co-crystallization of the polymers across the interface. The latter process results in the weakest bonding. For both processes to occur preceding interdiffusion must take place. The contribution of the two processes to the bonding strength depends on the crystallinity, molecular weight and the conditions (time, temperature and pressure) at which the bonds is created. [4, 5, 6, 7]

This work investigates if the high pull force, observed upon disassembly of press fitted polypropylene components, can be caused by autohesion. It examines if the pull force can be directly correlated to the crystallinity of the components. To study the materials softening during autoclaving, a Dynamic Mechanical Thermal Analysis (DMTA) is preformed to obtain the storage modulus. Furthermore, the dimensional change, caused by autoclaving, of the interface is measured. The molecular weight of the polymers is established by small strain oscillatory rheometry and the melt flow index (MFI). This is assumed to play a significant role in an autohesion process. [4] Last, possible methods to overcome the high pull force are discussed.

2. Experimental

Visual study of the interface

Light optical microscopy is used to study the deformation of the interface caused by autoclaving compared to non autoclaved components. The specimens is moulded into epoxy before being cut and polished. The polishing could lead to some visco elastic deformation of the interface, but this is considered negligible, compared to the large deformation seen on autoclaved components. The dimensional change of the ribs is determined by

$$\Delta L = \frac{L_0 - L_c}{L_0} \cdot 100\% \tag{1}$$

where L_c is the rib height after deformation, L_0 is the original(nominal) height of the rib. [8, 9, 10]. From measuring specifications, inner diameter of the outer specimen is $11.42mm \pm 0.09$ and diameter from rib to opposite rip is $10.65mm \pm 0.08$. This can be seen in Fig. 2. Nominal height of rib is therefore assumed to be

$$L_0 = \frac{11.42mm - 10.65mm}{2} = 0.385mm$$



Fig. 2 Nominal dimensions of the outer component.

Crystallinity

The crystallinity of the polymers is studied through DSC using a 'TA Q2000' with a Heat procedure. The samples is heated from $20^{\circ}C$ to $250^{\circ}C$ with a rate of $10^{\circ}C/\text{min}$ in a nitrogen atmosphere with a flow of 50 mL/min.

The crystallinity is calculated using the enthalpy of fusion (ΔH_m^0) for a 100% crystalline PP of 207 J/g [11, 12].

From the first law method, the crystallinity is found by

Degree of crystallinity
$$= \frac{\Delta H_m}{\Delta H_m^0} \cdot 100\%$$
 (2)

where ΔH_m is enthalpy of fusion, presented by the endothermic reaction on DSC melting curves. [13] ΔH_m is found using the 'Integrate Peak Linear' function in *TA Univerisal Analysis* from below the onset temperature and above the melting point illustrated on Fig. 3.



Fig. 3 DSC 1st heating curve showing onset melting temperature $[T_{onset}]$, enthalpy of fusion $[\Delta H_m]$ and crystalline melting temperature $[T_m]$

Tensile test of press fit assembly

Ultimate tensile pull force of assembled and autoclaved parts are analyzed in regards of polymer crystallinity. A 'Mecmesin VersaTest' tensile test machine is used. Parts are pulled once, at a rate of 20mm/min and ultimate tensile pull force is logged at full disassembly.

Full disclosure: Since equipment is currently not available on location, tensile test is done externally according to standards of previously performed tests. Data processing is done by authors of this text.

DMTA

The DMTA is preformed using a 'PHYSICA MCR 500' programmed to; **Step:** room temperature to 90°C, **Isothermal:** 20 min at 90°C, **Ramp:** 90°C to 121°C with $1.6^{\circ}C/min$, **Isothermal:** 20 min at $121^{\circ}C$, **Step:** $121^{\circ}C$ to $90^{\circ}C$, **Isothermal:** 18 min at $90^{\circ}C$, **Step:** $90^{\circ}C$ to room temperature. All temperatures is with a error margin of $\pm 1.5^{\circ}C$. The program resembles the autoclave process of the components during manufacturing. During manufacturing, steam is used to transfer heat to the components. This is not possible to duplicate on the equipment where dry heat is used.

The specimens used is ASTM tensile bars moulded with a 'Babyplast 610P'. The crystallinity of the tensile bars

is within 10% of the components analyzed in this study. This is presented in table II.

Molecular weight

The small strain oscillatory rheometry is preformed with a 'TA Discovery HR-3' in a plate-plate configuration. The test temperature is $230^{\circ}C$ and the frequency range is 0.06-600 rad/s. Before the test is started the sample is heated in 5 minutes, to ensure isothermal conditions.

From the test the zero shear rate viscosity (η_0) can be established as the viscosity of the plateau in the lowest frequency range. This can then be related to the weight average molecular weight (\overline{M}_w) through the empirical Mark-Houwink power law. [14, 15]

$$\eta_0^* = K \bar{M_w}^{3.4} \tag{3}$$

K is a material constant related to the polymer type.

3. Results

Deformation

The largest amount of deformation is seen when the assembly has been autoclaved. Post cooling, the deformation is seen twice the magnitude of non autoclaved assemblies. The data is based on 12 measurements on four components for both the autoclaved and non autoclaved components.

	Nominal	Average	Average
	$L_0[\mu m]$	$L_c[\mu m]$	$\Delta L[70]$
Autoclaved	385	251.31 ± 12.62	34.73 ± 3.28
Non autoclaved	385	334.77 ± 8.68	13.05 ± 2.25

Tab. I Average deformation prior and post autoclaving. Reference measurement of L_0 is the nominal height of the rib.

On Fig. 4a and 4b the height measurement for a rib is illustrated for an autoclaved and a non autoclaved specimen. It is clearly seen that post autoclaving deformation of the rib have occurred.



(a) Autoclaved (b) Non autoclaved Fig. 4 Measurement of rib height. The black dot in (b) is an air bubble trapped in the epoxy during curing and filled with residue from the polishing.

Crystallinity

In Tab. II, the crystallinity evolution due to the thermal processing. From the DSC analysis, PCGH19 is assumed to exhibit a higher stiffness at elevated temperatures compared to that of PCGR25. This is also seen when considering torque curve in Fig. 7 during the final cooling cycle.

	PCGH19	PCGR25
Feedstock	42.01%	38.37%
Moulded component	39.38%	36.91%
Autoclaved component	47.12%	40.53%
Moulded DMTA test bars	43.03%	37.34%

Tab. II Calculated crystallinity of the materials based on DSC measurements.

On Fig. 5 the crystallinity of autoclaved components for PCGH19 and PCGR25 versus the pull force needed to disassemble the components is plotted. Analysing the linear correlation between the crystallinity and pull force gives $\rho_{\text{pull force, PCGH19}}$ =0.11 and $\rho_{\text{pull force, PCGR25}}$ =-0.3.



Fig. 5 Crystallinity of autoclaved components for PCGH19 and PCGR25 versus the pull force needed to disassemble the components.

DMTA

On Fig. 6 the storage modulus as a function of temperature for PCGH19 and PCGR25 is shown. Both materials have a significant decrease in storage modulus as the temperature rises. At ambient temperature the storage modulus for PCGR25 is higher than for PCGH19 but due to a higher decreasing rate the storage modulus for PCGR25 is lower than for PCGH19 at $121^{\circ}C$. During cooling the storage modulus have the approximately same increasing rate for both materials.



Fig. 6 Storage modulus as a function of temperature for PCGH19 and PCGR25.

Considering the normalized torque curve in Fig. 7, the change in stiffness from the two polymers are only seen evident at temperatures around $121^{\circ}C$. For PCGR25 there is a loss in stiffness, compared to PCGH19, upon cooling.



Fig. 7 Torque comparison of PCGH19 and PCGR25

Molecular weight

On Fig. 8 the average complex viscosity \pm the standard deviation, for three test, is plotted as a function of frequency for the feedstock material. The zero shear rate viscosity, measured at 0.06 rad/s, is 232.2 $Pa \cdot s$ for PCGH19 and 182.2 $Pa \cdot s$ for PCGR25.

Since the constant K from Eq. 3 is unknown it is not possible to directly calculate the molecular weight with this method. However since K is related to the polymer type, it can be assumed that this is the same for both materials. On that premise, the ratio between the molecular weight of the two materials can be established, giving as a result $\bar{M}_{w,PCGH19}/\bar{M}_{w,PCGR25} = 1.07$.



Fig. 8 Complex viscosity as a function of frequency of PCGH19 and PCGR25.

To establish the molecular weight, the MFI stated in the data sheets [2, 3] is used along with the result from [16]. They showed that a linear relation between the inverse MFI and the weight average molecular weight to the power of 3.4 for polypropylene can be expressed as

$$\bar{M_w}^{3.4} \cdot 10^{-21} = 0.0334 \frac{1}{MFI} + 0.0004$$
 (4)

The result is a linear curve fit ($R^2 = 0.97$) based on five PP grades with a MFI in the range 0.6-12 dg/min. [16]

The MFI for PCGH19 is 19 dg/min and for PCGR25 25 dg/min. The MFI for PCGH19 and PCGR25 and the MFI from [16] is measured at 230°C and 2.16 kg. Inserting this data on Eq.4, the resultant molecular weight is PCGH19: $\bar{M}_w = 215 \cdot 10^3 \ g/mol$ and PCGR25: $\bar{M}_w = 193 \cdot 10^3 \ g/mol$.

The calculated molecular weight gives a relation of $\bar{M}_{w,PCGH19}/\bar{M}_{w,PCGR25} = 1.11$ similar to the one established by rheology, with a 3% difference within them.

The MFI is measured on feedstock material. Due to chain scissoring caused by degradation while the manufacturing process is carried out, a decrease on the molecular weight is expected. [17] However the difference between the molecular weight is assumed the same due to the similarity of the process.

4. Discussion

Examining the crystallinity of the autoclaved components versus the pull force revealed a random correlation with $\rho_{\text{pull force, PCGH19}}$ =0.11 and $\rho_{\text{pull force, PCGR25}}$ =-0.3. The correlation was tested on 10 specimens with an average pull force of 15.94 ± 1.62 N and a maximum and minimum pull force of 19.25 N and 14.10 N. Given that the test was only preformed on 10 specimens and the pull force have a narrower distribution compared to data mentioned in the introduction, the test is considered inconclusive. To obtain a more reliable result the test should be repeated with a larger sample size and a wider distribution of pull force.

It has been proposed that polymer chain movement and entanglement across the interface may reinforce adhesion. [4, 6] This process is due to: (1) Intimate surface interaction and (2) Diffusion. When the two surfaces are in contact due to an applied pressure, the process of the autohesion strengthening within the interface is affected by the temperature, the time and the available layer in which diffusion can occur. [18, 6] This available layer is in amorphous phase and it can be seen on the surface of post cooling after the components are injection moulded. [19, 20] On that premise and based on the fact that in amorphous interfaces of identical polymers autohesion, or selfhesion, is often seen, [4, 5, 6] it is expected that at the interface of the sample (Fig. 1) autohesion will occur.

To back up this assumption, the surface analysis is done using an optical microscope. The failure observed of the components after disassembly show an adhesive characteristics. [21] Immediate depth and failure mode of surface damage, may give an indication of autohesion only occurring in the amorphous layer and phase, i.e. the semi-crystalline bulk material do not contribute significantly to immediate adhesion strength. The reason for this may be seen in molecular mobility, which is known to be much higher in the amorphous phase at elevated temperatures. [4, 7]

It is important to clarify the two phenomena that can happen when diffusion takes place. Depending on the manufacturing conditions, either the inter-diffusion of chains and crystal growth dominate or chain entanglement happens. The key variables that define this is the T_g and the molecular weight. [4, 6] Due to the high mobility of the chains along the interface, when the polymer is above T_g , the vanishing of the interface will be promoted. As a result, healing process and mechanical strength development will happen. [5, 4, 6] The increase on the pull force after autoclaving supports this hypothesis.

Deformation in the PP interface seems quite apparent when considering mechanical interference fits. In general creep is seen to be greatly dependant on the

temperature and stress level applied. At high temperatures, creep is seen more significant and with permanent deformation after cooling. [8] Considering the temperature at $121^{\circ}C$ the results from the DMTA shows the polymer is significantly softened, resulting in a highly mobile amorphous phase, being close to T_{onset} . The approximately 80% drop in storage modulus, is naturally assumed to contribute greatly to the deformation of the polymer. [22] This deformation is seen when the dimension of the ribs is measured after autoclaving. The rib length decreases and the width (contact surface) increases (Fig. 4), creating a larger area for the polymer to diffuse and create secondary bonds. From DMTA it is suggested that deformation happens in the ribs, because of a approximately 2 times lower storage modulus in the PCGR25. The cooling history of the polymers in Fig. 7, may give an indication of crystallization being inhibited in PCGR25. This is proposed to be caused by the material being clarified in the additive polymeric process. PCGH19 is without additives. [2, 3]

Seen that polymer chain entanglement correlates with the molecular weight of two polymers, the assumption of entanglement across the interface is also reasonable. This phenomena occur after the full relaxation of interdiffused molecular chains. [4, 23] Rheological studies of PP has found, that at elevated temperatures around $180^{\circ}C$, entanglement occurs after 30 minutes. [24] With chain entanglement occurring after self-diffusion, and considering temperatures and duration of the autoclaving process, entanglement across the interface could show to contribute greatly in autohesion strength.

A thought-experiment on whether adhesion strength is obtained by secondary bonds in the amorphous region (surface skin-layer) due to permanent deformation is proposed. Supposed that at room temperature, the pull force is only governed by friction and normal forces in the press fit. This will induce a constant stress in the interface, further resulting in a small deformation of the PP, but no adhesion. This is assumed reasonable when considering assembled parts, which has not yet been autoclaved. During autoclaving of the parts at $121^{\circ}C$, the amorphous region is in a melted state. Assuming the stress is still present and constant, will result in an increase in secondary forces in the interface by smoothing of the surfaces. [4, 5] The high mobility of the polymer at this temperature will potentially further result in interdiffusion with a vanishing interface. This experiment is proposed due to the fact that the accuracy of the results given by looking at the interface are not significant. With the used methods to prepare the sample, due to the

behaviour of the material, the interface bonding cannot be directly observed.

In view of this, it is important to consider that after the manufacturing process the samples will be stocked. The nature of PP and the interaction between the interfaces allow the changes in crystallinity and diffusion within the materials happen continuously in a lower rate. Then the pull force will be different depending on the stocking time. Further discussion will be given.

It is possible to inhibit chain entanglement and movement over the interface. By ensuring the material crystallization at the interface, the inhibition of the movement of the amorphous phase will occur. [4] The molecular chains can also be shortened to at state where entanglement is not possible. [25]

It is proposed that Ultra Violet radiation of the surface could potentially contribute in inhibiting the self diffusion and entanglement of the polymer chains. UV radiation is a photo degradation process often referred to as Chemi-crystallization, why one should be aware of surface embrittlement due to spontaneous formation of surface cracks. However, due to the self-healing properties of the material [5], this crack formation could potentially show to not impact the bulk material performance. [26] Chemi-crystallization is process in which molecular chains are split through chemical degradation, and consequently enable un-entanglement of the amorphous regions letting them recrystallize. [26, 27] This usually followed by photo-oxidation, forming the functional group carbonyl (-C=O) or aldehyde (-CHO), why it is possible to also track any surface change in Infrared spectroscopy. [27, 28] Considering the FTIR spectrum on both PCGH19 and PCGR25 from 1720-1740 cm^{-1} [29], there is no indication in Fig. 9 and 10 of the moulded or autoclaved components being degraded. Considering only the outermost amorphous



Fig. 9 FTIR spectra of PCGH19 in the $1720-1740 cm^{-1} {\rm range}$

skin layer of the polypropylene, any UV radiation could



Fig. 10 FTIR spectra of PCGR25 in the $1720 - 1740cm^{-1}$ range

see to only occupy a single or a couple of atom layers beneath the surface. Assuming the surface to be in an oxidized state, work depth can be considered to be very small, and the effect on the bulk material minimal. Only convex surfaces could see to be treated, meaning only one part of the assembly is considered.

Another way of ensuring a higher degree of crystallinity before autoclaving would be to anneal the components pre-assembly. [30]

Before producing the components in PCGH19 and PCGR25 both were produced in Moplen HP548R. For the Moplen components the same phenomenon with a high pull force and then a large decrease is observed. However testing components that have been on storage for several months, the pull force decreases to an average of 1.3 ± 0.9 , 4.0 ± 2.3 and 3.9 ± 2.3 N. This could be caused by the migration of additives to the surface based on a similar observation by [31]. They showed that a decrease in the weld-ability of polymers after storage was caused by surface migration of low molecular components in the polymer and lubricating agents. It was observed on polyethylene which like PP is a semi-crystalline polymer with T_q below $0^{\circ}C$. The migration of additives can break secondary bonds between the two components by inhibit direct surface contact. [31]

Due to the constant stress in the interface, creep is occurring. Therefore, a higher creep rate in Moplen HP548R compared to PCGH19 and PCGR25 could cause a difference in the pull force after storage. It has been shown that the mechanical properties including the creep rate can be effected by nucleation agents. [32, 33] From the data sheets it is known that nucleation agent is added in Moplen HP548R and not added in PCGH19. For PCGR25 it is not mentioned in the data sheet. The type and amount of nucleation agent in Moplen HP548R is unknown. [2, 3, 34] It needs to be mentioned that since the material change is quite recent, components produced in PCGH19 and PCGR25, that have been on storage, does not yet exist.

The change in material can also promote chain movement over the interface. Having materials with a difference in molecular weight, as our result show for PCGH19 and PCGR25, inter molecular diffusion is enhanced. [4]

Besides the plausible use of Ultra Violet radiation other methods for decreasing the pull force is discussed. The most obvious would be to change PP grades to some where the problems is not present, but this is a complicated and expensive process. Additives could also be utilizied. Adding a lubrication agent that will migrate to the surface before autoclaving can prevent direct contact between the polymers and inhibit polymer bonding. [31] Adding nucleation agents in the right amount can increase the creep rate of the polymers, this could cause the outer polymer to slightly expand, due to the constant stress at the interface, during storage after autoclaving and thereby decrease the pull force. [32, 33] For the company that produces the components the content of the polymer is be very critical, therefore it would be necessary to examine which additives that can be used while upholding product requirements.

A review of other commercially available sterilization techniques shows that it will be impractical and for some cases impossible to change sterilization technique. The other commercially available techniques is: dry heat, ethylene oxide (EtO), gamma irradiation and electron beam. [35] Using dry heat sterilization requires a temperature minimum as high as for the autoclave process which will lead to the same movement and possible bonding in the amorphous phase. Using gamma irradiation and electron beam requires a polymer that is radiation stable to prevent material degradation. [35, 36] The use of EtO is prevented because the inner part is sealed from the surroundings and polypropylene have a very low gas permeability. [37] EtO also rises some health and safety concerns being a highly flammable gas causing nausea, vomiting, neurological disorders upon acute exposure and is known to cause cancer with long term exposure. [38]

5. Conclusion

Due to the large drop in pull force from the first to the second pull for autoclaved components, and the examination of the components by optical microscopy, it is highly plausible that autohesion between the components is occurring during autoclaving. The autohesion can occur by entanglement and secondary bonding of the materials. The acute rise in pull force after autoclaving can be caused by molecular chain entanglement and secondary bonding across the interface. This is supported by DMTA and DSC that shows the material, during autoclaving, is in a state that will promote chain movement and hence diffusion. The difference in molecular weight also promotes diffusion supporting this theory. Last, the deformation of the ribs smoothens and widens the interface, optimizing the possibility of forming secondary bonds. To establish which processes that contributes the most further studies is needed.

By comparing the pull force and crystallinity for 10 autoclaved components showed a random correlation with $\rho_{\text{pull force, PCGH19}}=0.11$ and $\rho_{\text{pull force, PCGR25}}=-0.3$. Due to the narrow distribution of pull force (15.94±1.62 N) the test is considered inconclusive.

Possible solutions to overcome the high pull force have been presented in the discussion but further studies will be needed to establish of any of those can be utilized.

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