Characterization of Properties of Virgin and Recycled High-Density Polyethylene under Cyclic Loading

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Abstract

The focus of this project is to quantify differences between virgin HDPE (vHDPE) and post-consumer recycled HDPE (rHDPE) under cyclic loading, to achieve a higher confidence in material properties than found in tensile tests. This study uses sinusoidal cyclic loading to compare the fatigue properties of vHDPE and rHDPE along with blends of 20% and 29% rHDPE with vHDPE. Cyclic loading has proven to be a more sensitive mechanical testing method than testing the short term static loading properties in tensile testing. Using power law fitting parameters, a critical stress has been calculated for a theoretical service lifetime of 50 years, in which vHDPE obtained a 36% higher critical stress compared to rHDPE. Examination of the melting and crystallinity properties of rHDPE and vHDPE using Differential Scanning Calorimetry (DSC) showed no significant indications of degradation of rHDPE with regard to the vHDPE. Rheometry testing of rHDPE and vHDPE showed a lower average molecular weight for rHDPE than vHDPE.

Keywords: Polymer recycling, Cyclic loading, High-density polyethylene

1. Introduction

Increasing concern for the environment presents why recycling of plastics is an important subject in science and industry, due to the vast volumes being produced. This leads to a heightened focus on the value of recycled polymers in production. Utilizing recycled polymers in place of virgin material presents the problem of the degradation of properties in products made from recycled material [1].

This project focuses on the comparison between virgin and recycled High-Density Polyethylene, HDPE, in order to uncover the advantages and drawbacks of utilizing recycled HDPE (rHDPE), in any degree, in place of virgin HDPE (vHDPE). To accomplish this, the mechanical and rheological characteristics of the two materials must be researched. Numerous research papers and projects on this topic already exist, with different aspects of the properties and characteristics of HDPE being the focus.

In [2], tensile, relaxation and creep testing results are evaluated in order to create a constitutive creep model that describes the long-term behavior of vHDPE and rHDPE. The expectation in the study was an observation of increased sensitivity in creep and relaxation tests compared to tensile tests. Similar experimental tensile data were seen for vHDPE and rHDPE. For ductile failure of HDPE under tensile creep conditions, similar lifetimes were shown in the model for vHDPE and rHDPE, with stress-time to failure diagrams of these practically coinciding.

In [3], DSC, tensile, relaxation, creep and cyclic loading results of vHDPE and rHDPE are evaluated, with regard to the effect of strain rate on the performance in these tests. It is stated that the difference in fatigue properties is more evident at low strain rates, while varying the maximum stress. This should be further studied. This study also showed no significant difference in degree of crystallinity from DSC testing of virgin and recycled. This study also included the injection molding process which allowed the procurement of dogbone specimens for further testing. The same study also carried out relaxation and creep tests in order to examine the possible difference in viscoelastic properties. No significant difference was found from the relaxation tests. In creep, the recycled was able to deform as much as virgin, but the resistance to creep was much lower, resulting in a decreased creep strength.

Although some recycled HDPE show similar tensile properties as their virgin counterpart, significant differences can be seen in fatigue lifetimes. This is expanded in [4], where it is concluded that similar trends are seen in tensile tests of vHDPE and rHDPE, while significant differences are seen in fatigue properties. Tensile properties are not enough to give a full understanding of the mechanical properties. Therefore, fatigue testing has been proposed as additional testing method to characterize the materials' long-term mechanical properties.

The addition of vHDPE to rHDPE in increasing fractions has been evaluated in [5] through differential scanning calorimetry, tensile testing and cyclic loading. The higher the percentage of vHDPE, the better mechanical properties are seen in cyclic loading, suggesting that the quality of rHDPE can be greatly improved with the addition of vHDPE. A higher vHDPE content improves the fatigue lifetime of the tested samples, as well as the Young's modulus and tensile strength. Fatigue properties also clearly decline with an rHDPE content above 30%, whereas only a small change is seen for recyclate contents less than 30%.

A model to describe the viscoelastic response of vHDPE has been described in [6]. This was done using short-term tensile tests, as well as short- and medium-term tests under relaxation and creep conditions. The developed model is then compared with stress-time to failure diagrams. This paper outlines the behavior of vHDPE under creep conditions and forms part of the base for parameters chosen for further testing in this project.

In this paper, the behavior of vHDPE and rHDPE as well as two mixes of 20% and 29% rHDPE in vHDPE will be investigated. Given the current state of the art, the focus will be on identifying a more sensitive testing method to display the lifetime differences between the four HDPE batches. The tensile properties are determined in order to validate the injection molding production by the degree of coinciding results, as well as validate the statements from the state of the art by comparing results with previous research carried out under similar conditions [2]. Tensile and creep data show low difference in properties between vHDPE and rHDPE. Therefore, the long-term mechanical properties are determined under similar conditions as in [2, 3, 6], in order to gain more sensitive data, thus revealing the difference in characteristics between the batches of HDPE. Finally, differential scanning calorimetry (DSC) and rheometry experiments are carried out in order to research the thermal and rheological characteristics of the HDPE batches.

2. Materials and Methods

The virgin HDPE used is HDPE Borsafe HE3490-LS from Borealis with a density of 959 $[\frac{kg}{m^3}]$ and melting temperature of 130 $[°C]$. This material could be used for pressure pipe systems, and shows terrific resistance to rapid crack propagation and indicates slow crack growth [7]. For comparison with a recycled HDPE, PE-HD-R-E-GREY from Aage Vestergaard Larsen A/S (Denmark) was used. This HDPE, based on post-consumer household plastic waste, had a density of 960 $[\frac{kg}{m^3}]$ and melting temperature of 130 $[°C]$. HDPE polymer character has minimal hygroscopic properties so this can be assumed to be negligible [8].

Dogbone test specimens were injection molded according to ISO 527-2-1B with an injection temperature of 230 $[°C]$ using a Ferromatik Milacron K110. Molded dogbones are of total length 145 $[mm]$, gauge length 65 $[mm]$, and cross sectional area 9,81 $[mm] \times$ 3,95 $[mm]$. The composition of each batch with corresponding nomenclature is listed in table I. Dogbone specimens used for further testing were molded with a film gate, which minimizes the effects of orientation caused by preferential flow in the mold [9].

Batch	Recycled %	Virgin %
vHDPE	0	100
20HDPE	20	80
29HDPE	29	71
rHDPE	100	0

Tab. I Contents of recycled and virgin HDPE in each injection molded batch

2.1 Tensile

Uniaxial tensile testing was performed on the specimens using an Instron 5568 machine. This was done by aligning the specimen in the top grip first, parallel to the tensile direction. Then, the extensometer was fastened to the middle of the specimen and all values on the software were balanced to ensure an identical starting position for each test. After this, the specimen was fastened to the lower grip using the specimen protect mode, enabling the machine to regulate the stress put upon the specimen, namely keeping this value zero, by incrementally pulling or compressing the specimen as it was fastened. Immediately after, the tensile test was initiated.

During the tensile testing a cross-head speed of 50 $\left[\frac{mm}{min}\right]$ was imposed on the specimens until failure for the vHDPE and mixed samples. Because the rHDPE elongated more than expected, these tests were stopped when above 100% strain. The test was repeated five times for all four series of tests and room temperature was maintained throughout tensile testing to ensure consistency of results.

For some materials, such as polyethylene it can be hard to distinguish between the linear and non-linear elastic regions, thus presenting difficulty in determining the Young's modulus and yield point. Therefore, the secant modulus, E_s, is determined in place of Young's modulus by the slope of a line between ϵ_0 and a strain value of 2%. The yield strength at the end of elastic deformation will be defined as the maximum obtained stress [10]. For some polymers, necking on the gauge part of the sample occurs at the yield point followed by a near horizontal stress-strain curve in the plastic region. Within the neck the polymeric chains become oriented, such that they are aligned parallel to the elongation direction, strengthening the sample locally [11, 12].

2.2 Cyclic Loading

Applications, such as pipes, where a material undergoes cyclic loading requires insight into the degradation in properties, called fatigue. Repetitive loading and unloading of component can lead to fatigue failure which happens well below the yield strength of the material [11]. Since tensile tests only show small changes in mechanical properties, a more sensitive testing method for detecting differences between the polymer batches is sought in fatigue testing [2].

Cyclic loading tests were performed using the Instron E10000 in order to characterize the long term fatigue properties of vHDPE, 20HDPE, 29HDPE and rHDPE. The test parameters programmed in the software were set to subject the specimen to a repetitive loading between a minimum stress, σ_{min}, common for all tests, and a maximum stress, σ_{max}, ranging from 17,5-26 $[MPa]$. These tests were repeated 5 times for each σ_{max}, with the exception of one low stress where only two tests were completed due to time constraints. The minimum stress, σ_{min}, was 0,5 $[MPa]$ to prevent the specimen from buckling during the unloading part of the cycle. The tests ran with a strain rate of 20 $\left[\frac{mm}{min}\right]$ until fracture occurred. Since the loading mechanism is sinusoidal, a frequency of $0,115$ $[Hz]$ was used, corresponding to the chosen strain rate parameter. A single cycle with this frequency takes approximately 8,7 $[s]$. The tests were carried out for both vHDPE, rHDPE along with the 20HDPE and 29HDPE at room temperature.

When fatigue testing, a cyclical loading is exerted upon the specimen, in which it undergoes a maximum and minimum stress a number of times until fracture. The stress amplitude alternates about the mean stress, σ_m, which is given by the average of the maximum and minimum stresses. The stress amplitude, σ_a, is one half of the stress-range, as illustrated in figure 1.

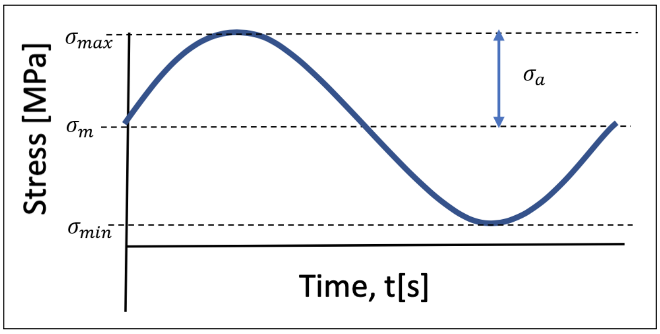


Fig. 1 Stress cycle of asymmetric constant amplitude

The fatigue behavior of polymers is more sensitive to the frequency of cycling compared to other engineering materials. This is due to localized heating arising at high frequencies causing softening of the material which can lead to thermal failure rather than typical mechanical fatigue failure. Fatigue damage is governed by fluctuations in stress rather than just the maximum stress level, therefor the stress range is of more importance when assessing fatigue damage [11, 12].

2.3 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed in order to gain insight into the thermal properties of vHDPE and rHDPE. The melting temperature and degree of crystallinity allow for direct comparison between the two batches. To ensure that no degradation occurs during injection molding, samples cut from the molded dogbones were also tested. Based on the similar densities of the vHDPE and rHDPE, the crystallinities should be similar, as a higher density results in a more crystalline structure [9, 13].

As the properties of the 20HDPE and 29HDPE batches fall between vHDPE and rHDPE, these are not tested.

Samples were prepared from granulate of vHDPE and rHDPE, along with dogbones of each. Each sample was cut to approximately 10 $[mg]$ and placed in an aluminium crucible. Samples were cut by hand, and thus vary in shape and size. The TRIOS software used for DSC analysis accounts for this discrepancy by normalizing the heat flow. Two samples were prepared for the granulate of rHDPE and vHDPE, in addition to one sample from an injection molded dogbone of vHDPE and rHDPE.

A Heat/Cool/Heat/Cool/Heat process was conducted using a TA Q2000 DSC, with a nitrogen flow of 50 $\left[\frac{mL}{min}\right]$. The test ramps from 20 $[°C]$ to 300 $[°C]$ at a heating rate of 10 $\left[\frac{°C}{min}\right]$ and a cooling rate of 5 $\left[\frac{°C}{min}\right]$. The first heating cycle represents the deletion of the samples thermal history. The first cooling cycle immediately following the heating exposes the sample to a slow controlled cooling. The second and third heating cycles, having experienced the same cooling processes, should thus have identical heat flow curves. Deviation in the second and third heating cycles can indicate a degradation of the sample during the test. These cycles will therefore give the most accurate comparison between samples of vHDPE and rHDPE.

The degree of crystallinity, X_c, can be calculated using the enthalpy of melting of the tested sample, ΔH_m, divided by the enthalpy of melting of a 100% crystalline sample, $\Delta H_{m,100\%}$ as in equation 1 [9]. The enthalpy of melting for a theoretically 100% crystalline HDPE sample is found in literature as 293 $\left[\frac{J}{g}\right]$ [14].

$$X_c = \frac{\Delta H_m}{\Delta H_{m,100\%}} \cdot 100\% \tag{1}$$

As the glass transition temperature for HDPE is low, approximately -120 $[°C]$, it is not present on the thermogram [15]. Thus, only melting temperatures, T_m, and the corresponding enthalpy, ΔH_m, will be analysed.

2.4 Rheometry

Rheometry testing was conducted on rHDPE and vHDPE granulates and dogbone cut pieces. All specimens were tested under the same experimental conditions and parameters. The apparatus used was the AR-G2 magnetic bearing rheometer, with a 25 $[mm]$ stainless steel parallel plate sample fixture, by TA Instruments.

For rheological testing of polyethylene, molecular weight (MW) determination can be achieved by finding the zero shear viscosity, η_0, via small amplitude oscillatory tests, such as frequency sweeps. These were carried out at constant amplitudes with variability in frequencies. A sample's zero shear viscosity can be determined at low angular frequencies and low shear rates, and is directly proportional to the average MW. MW affects the mechanical properties of the polymer. High MW polymers indicate stronger mechanical properties; on the other hand, lower MW polymers indicate poorer mechanical properties [16].

During low shear rates, the angular frequency of a polymer melt indicates Newtonian behavior with constant viscosity, and that viscosity is called zero shear viscosity, located at the Newtonian plateau. The Newtonian plateau viscosity is directly proportional to the average MW, according to the equation:

$$\eta_0 = K \cdot (MW)^a \tag{2}$$

Where a is the relaxation time exponent, which is approximately 3,4 for most standard polymers. K is a constant that depends on the size and shape of the polymer molecule [17].

Amplitude and frequency sweep testing took place at a temperature of 250 $[°C]$. Amplitude sweep was done at 1 $[Hz]$ to accurately determine the linear viscoelastic region, and determine rheological stability within, prior to reaching macrostructure deterioration [18]. The frequency sweep cycle was run at 2,5% strain to investigate the material's storage and loss modulus at different frequencies. Rheometry testing parameters are summarized in table II.

Amplitude sweep		Frequency sweep	
Strain %	Frequency $[Hz]$	Strain %	Frequency $[Hz]$
0,1 - 100	1	2,5	0,01 - 100

Tab. II Rheometry testing parameters

The amplitude sweep was conducted to determine the crossover point of G' and G'', which defines the limit of rheological stability of the linear viscoelastic region. Frequency sweeps were conducted to investigate the virgin and recycled HDPE material properties within a range of deformation rates. In this test, the strain and frequency fluctuations were monitored, with the purpose to investigate the storage and loss moduli. The constant strain for the frequency sweep testing was chosen conservatively from the amplitude sweep, resulting in an oscillation strain equal to 2,5%. During frequency sweep, sinusoidal strain is applied between two parallel plates, with the purpose of applying torque

Material	$\overline{\sigma}_y$ [MPa]	$\delta_{\overline{\sigma}_y}$ [MPa]	$\overline{E}_s$ [MPa]	$\delta_{\overline{E}_s}$ [MPa]	$\overline{\epsilon}_b$ [%]	$\delta_{\overline{\epsilon}_b}$ [%]
vHDPE	28,5	0,235	800,3	13,2	27,4	1,37
20HDPE	27,7	0,142	800,9	7,56	34,9	2,53
29HDPE	28,2	0,16	830,3	7,89	39,2	3,48
rHDPE	24,4	0,091	805,6	13,4	>100	

Tab. III Average results from tensile tests of vHDPE, 20HDPE, 29HDPE and rHDPE

and determining the delay in response. Via this technique, the storage(elastic behavior), G' and loss(viscous behavior) modulus, G" can be determined. The complex viscosity of a sample tested can be determined by the storage and loss modulus in conjunction with angular frequency graphically, which consequently can be used to calculate the viscosity of the sample and MW [19].

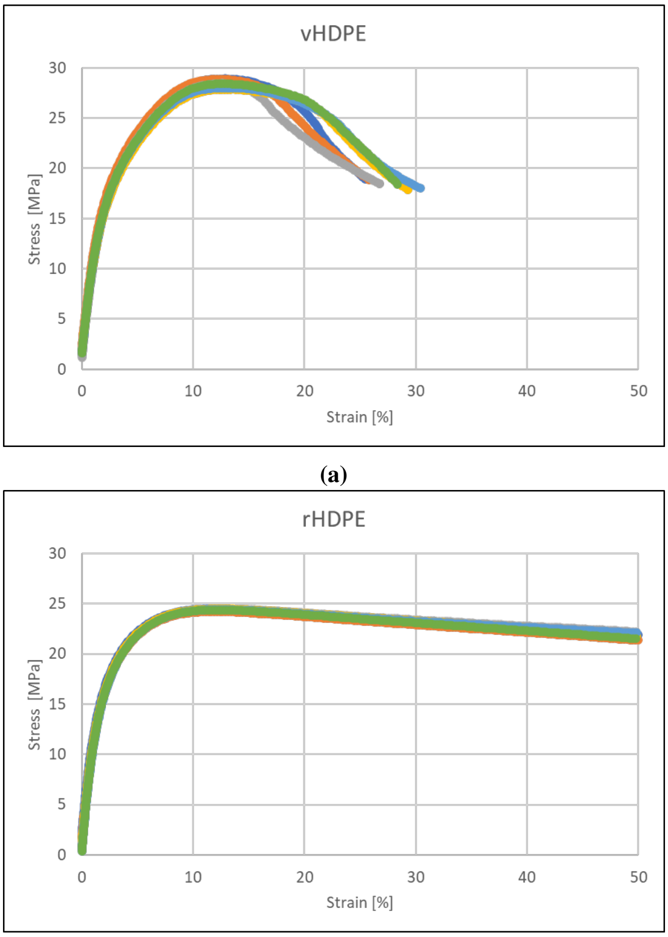
3. Results and Discussion

3.1 Tensile

As evident from the results in table III and figure 2, the vHDPE displays higher strength than rHDPE. For vHDPE the stress reaches up to 28,5 $[MPa]$ ± 0,235 $[MPa]$ in tensile strength, where the rHDPE yields at 24,4 $[MPa]$ ± 0,091 $[MPa]$. The 20HDPE and 29HDPE showed only minor decrease in strength compared to the vHDPE, and virtually no difference in strength is evident between 20HDPE and 29HDPE. The high degree of strainabilty of rHDPE have slightly carried over into the mixed samples, which display some higher levels of strain before break than vHDPE.

The toughness related to the rHDPE is also evident in table III where rHDPE strained above 100% and the two mixed inherited this trait. The 29HDPE and 20HDPE samples obtained strains at break, $\overline{\epsilon}_b$, of 39,2 ± 3,48 % and 34,9 ± 2,53 % respectively. The calculated secant moduli are very similar apart from 29HDPE, which displayed the highest E_s of all batches. The standard deviations of yield strengths, $\delta_{\overline{\sigma}_y}$, are below 1% of the average within each batch, which speaks to the repeatability of the test setup and the fabrication of the specimens. The deviation in secant moduli, $\delta_{\overline{E}_s}$, and the deviation in strain at break, $\delta_{\overline{\epsilon}_b}$, reaches relatively higher values.

The suspected slight decrease in short-term strength between vHDPE and rHDPE is evident and even less difference is seen between vHDPE when comparing with the 20HDPE and 29HDPE. Based on this test method only a minor difference is evident.



(a)

(b)

Fig. 2 Tensile test results for (a) vHDPE and (b) rDHPE

3.2 Cyclic Loading

The results of fatigue testing are gathered in an S-N master curve with error bars seen in figure 3. This shows the data from the fatigue testing along with the master curves connecting the data points for the four batches; vHDPE, 20HDPE, 29HDPE and rHDPE. The difference in fatigue life between vHDPE and rHDPE is approximately a decade on the logarithmic scale for all stresses. The 20HDPE and 29HDPE are both closer to the behavior of vHDPE than rHDPE. The difference in lifetime is much more remarkable for this test compared to tensile and creep tests [2, 3, 6].

$$\sigma_f = A \cdot N_f^b \tag{3}$$

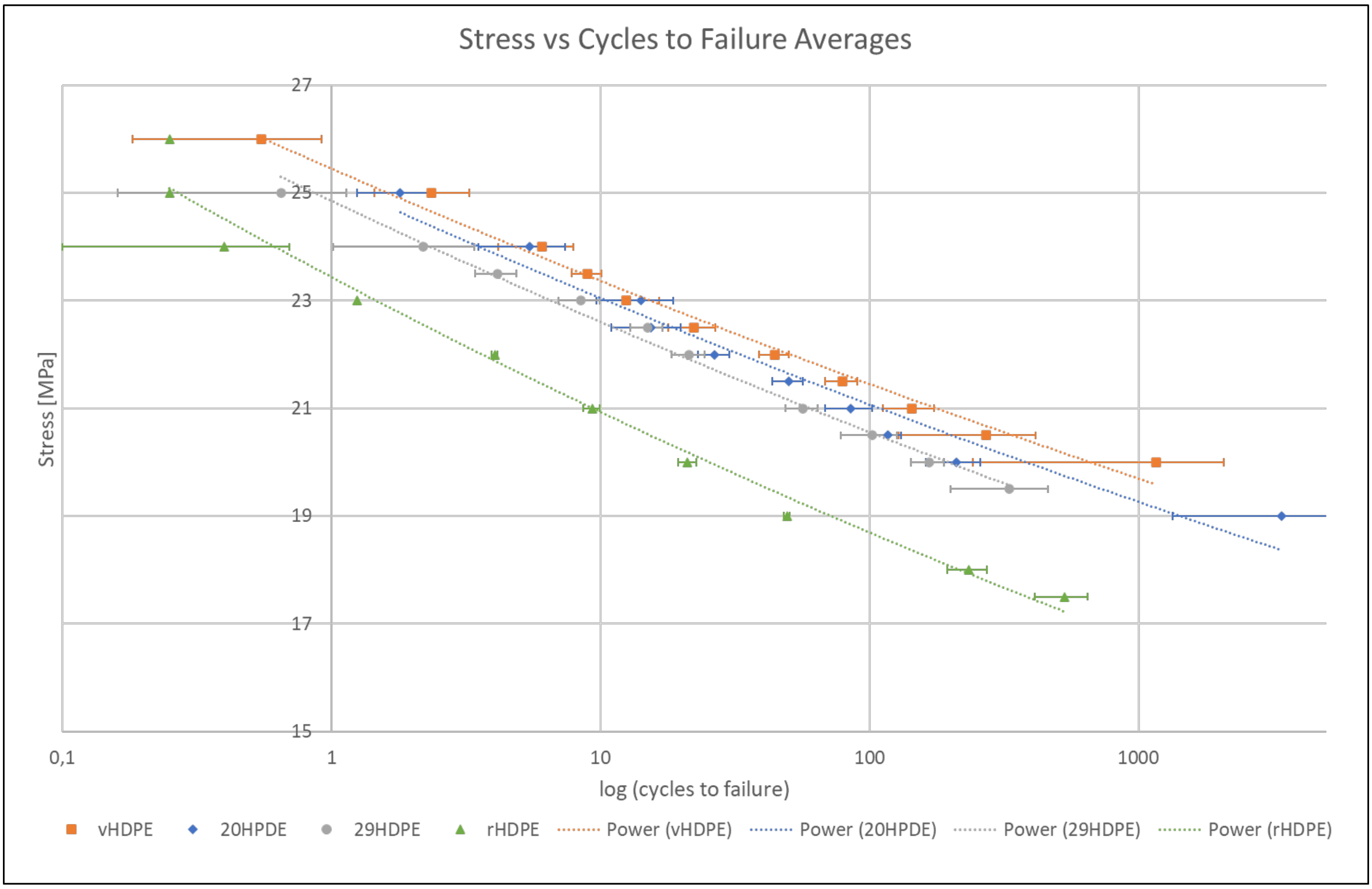


Fig. 3 Fatigue test results for vHDPE, 20HPDE, 29HDPE and rHDPE

Using the power law equation describing the line fitted to the data points in figure 3 the stress corresponding to a specific number of cycles can be estimated. The relation can be described by equation 3, where σ_f is the fatigue stress and N_f is the fatigue lifetime [12].

	A	b
vHDPE	25,453	-0,037
20HDPE	25,211	-0,039
29HDPE	24,854	-0,041
rHDPE	23,438	-0,049

Tab. IV Power law fittings for Stress-Cycles to failure

The constants in the relations for the four different batches are seen in table IV.

The stress prediction for experimental data points at 1000 cycles as well as a 50 year model estimation can be calculated using the power law fittings for each batch. From this, the percent difference in stress after 1000 cycles is approximately 18% between vHDPE and rHDPE. After a number of cycles corresponding to a 50 year lifetime, the difference in stress increases to 36,4% between vHDPE and rHDPE. When compared to the results of another research paper [5], investigating the percent difference in stress in creep testing, a much smaller difference of 5,5% was found between vHDPE and rHDPE. The difference between vHDPE and the two mixes was found to be below 6% for 1000 cycles and below 11% for 50 years, which is significantly smaller than the difference between vHDPE and rHDPE.

The rHDPE is distinguished by higher strain in fewer cycles than the vHDPE, 20HDPE and 29HDPE.

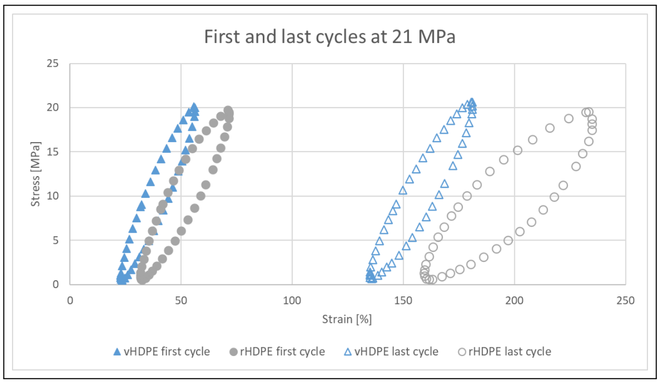


Fig. 4 Stress-strain hysteresis loops for vHDPE and rHDPE at 21 MPa

This is shown in figure 4, with the areas of hysteresis loops created by stress-strain curves from cyclic loading shown for the first and last cycles of vHDPE and rHDPE. For rHDPE the larger area and increase in area of the hysteresis loop indicates more straining of the material. The vHDPE, 20HDPE and 29HDPE show similar strain behavior, whereas the rHDPE strains at a rate much higher than the other batches. The first cycle for rHDPE is 1,37 times larger than the first cycle of vHDPE. The last cycle of rHDPE more than doubles in size, increasing to 2,24 times the size of the first cycle of rHDPE. A much smaller increase is noted for the vHDPE growing only to 1,58 times the size of the initial hysteresis loop. Another form of degradation is seen in the stress-strain curve in figure 4 as the slope decreases in the late cycles, meaning a decrease in the stiffness modulus.

3.3 DSC

In comparison of the second and third heating of each sample of vHDPE and rHDPE, as seen in figure 5, it is clear that there is no change in thermal properties between the two cycles. Thus, the samples remain stable during the test, as expected.

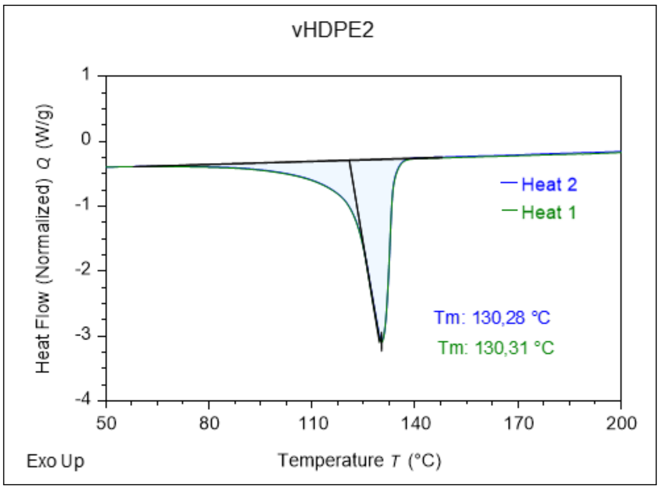


Fig. 5 First and second heating of vHDPE

The melting temperature, T_m, enthalpy of melting, ΔH_m and degree of crystallinity, X_c, of each sample in the second heating are presented in table V.

Sample	$T_m[^\circ C]$	$\Delta H_m\left[\frac{J}{g}\right]$	$X_c[\%]$
vHDPE 1	131,38	209,21	71,40
vHDPE 2	130,28	195,30	66,66
vHDPE dogbone	130,97	200,30	68,36
rHDPE 1	132,05	216,93	74,04
rHDPE 2	132,10	210,81	71,95
rHDPE dogbone	132,25	208,70	71,23

Tab. V DSC results for the second heating

Minimal differences occur in the melting onset and melting temperatures of the samples, with peak temperatures at $130,83 \pm 0,55[^\circ C]$ for vHDPE and $132,08 \pm 0,34[^\circ C]$ for rHDPE. There appears to be no change in the placement of the melting peaks when comparing vHDPE and rHDPE, as well as injection molded vHDPE and rHDPE.

The degree of crystallinity of vHDPE varies between 66,66% and 71,40%, with the majority of rHDPE samples having a crystallinity within this range as well. There is little difference between the placement of peaks in the curves. The melting peaks shown in figure 6 have little deviation, and similar enthalpies are seen.

The DSC thermogram of the first cooling cycle and the second heating cycle for vHDPE and rHDPE is shown in figure 6.

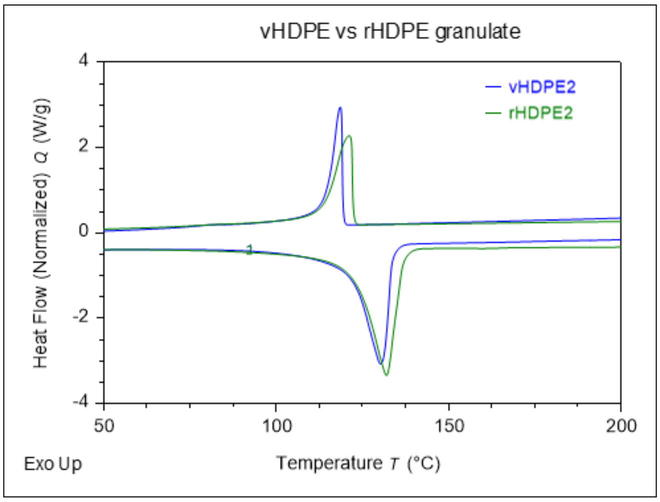


Fig. 6 rHDPE vs vHDPE granulate DSC thermogram

An insignificant difference in parameters is in seen when comparing the DSC data and corresponding thermograms. This trend is clear for both the melting temperature and the calculated degree of crystallinity. Larger deviations in crystallinities occur within the same batch than between batches, as such these values are comparable in vHDPE and rHDPE. Based on DSC analysis, there are no indications of thermal degradation due to recycling and/or injection molding.

3.4 Rheometry

The amplitude sweep conducted, determined the crossover point of G' and G'', which defines the limit of rheological stability of the linear viscoelastic region. This point was determined to be at 71,41% oscillation strain and 0,04 $[MPa]$, from which a conservative oscillation strain of 2,5% can be chosen for the frequency sweep.

	$\overline{G}$ $[MPa]$	$\delta_{\overline{G}}$	$\overline{\omega}$ $\left[\frac{rad}{s}\right]$	$\delta_{\overline{\omega}}$
vHDPE	0,03327	0,00077	2,6164	0,0805
rHDPE	0,03038	0,00050	19,3608	1,0984
vHDPEdogbone	0,03272*	-	2,7270*	-
rHDPEdogbone	0,03170*	-	18,8567*	-

*indicates single experimental value

Tab. VI Shear modulus and Angular frequency at crossover point

Similar trends were observed for the rHDPE granulate and rHDPE dogbone. Therefore, the injection molded dogbones and the raw material granulates exhibited equivalent properties. The same was seen for vHDPE dogbone versus granulate. In the frequency sweep in figure 7, where the granulates of rHDPE and vHDPE are compared, it can be observed that the vHDPE has more stable properties than recycled, since its G' and G" curves are higher than rHDPE.

The modulus and angular frequency at the cross over point for vHDPE and rHDPE can be seen in table VI. The deformation rate of the rHDPE was larger than that of vHDPE, and the same trend can be observed in both granulates and dogbone pieces.

The cross over point of storage and loss modulus, in figure 7, presented vHDPE to have higher MW compared to rHDPE. The vHDPE average zero shear viscosity, $\overline{\eta_o}$, for granulates was 71184 $[Pa{\cdot}s]$, while for the dogbone pieces, 69491 $[Pa \cdot s]$, with a difference of 2,4%. In addition, rHDPE average zero shear viscosity for granulates was 20346 $[Pa{\cdot}s]$, while for the dogbone pieces, 21447 $[Pa{\cdot}s]$, with a difference of 5,3%. To sum up, minimal deviation was observed due to the injection molding process in rheological behavior between the same material of dogbone pieces and granulate tested.

	$\overline{\eta_o}$	$\overline{MW \times K}$ $\left[\frac{g}{mol}\right]$	$\delta_{\overline{MW \times K}}$
vHDPE	71184	26,74	0,03
rHDPE	20346	18,50	0,30
vHDPEdogbone	69491*	26,55	-
rHDPEdogbone	21447*	18,79	-

*indicates single experimental value

Tab. VII MW of granulate vHDPE and rHDPE and dogbone vHDPE and rHDPE

The expectation that the MW of the rHDPE would be lower than that of vHDPE, was validated and verified by the higher MW, as seen in table VII based on equation 2.

4. Conclusion

The scope of this project was to investigate cyclic loading testing as a method with higher sensitivity, i. e., demonstrating the greatest difference in performance between the specimen batches. Additionally, for the connection to a material's mechanical properties, the degree of crystallinity was investigated through DSC testing, as well as the rheological properties through rheological testing.

The injection molding process was successful in producing uniform film-gate dogbones of vHDPE, 20HDPE, 29HDPE and rHDPE. The quality of specimens produced was validated through tensile testing which confirmed that no significant deviation was present within each batch individually. A cross-head speed of 50 $\left[\frac{mm}{min}\right]$ was used under the tensile testing to ensure comparability with previous works [2]. The difference in short-term strength of vHDPE and rHDPE is only slightly evident and even less difference is seen between vHDPE, 20HDPE and 29HDPE. Based on this test method only a minor difference is evident.

Next the fatigue characteristics were investigated through cyclic loading testing. This was done with a cross-head speed of 20 $\left[\frac{mm}{min}\right]$, again, in order to compare with previous works [2, 3, 6]. Because of the poor ability of tensile and creep testing to display differences in properties for the specimens from this project and other projects, a more sensitive testing method for detecting differences of the materials is sought in cyclic loading testing.

From the S-N curve a large difference of around a decade in the number of cycles for a given maximum stress, σ_{max}, is seen between vHDPE and rHDPE. It is also noted that 20HDPE and 29HDPE data are closer to that of vHDPE than rHDPE. Generally the rHDPE strains faster and more than the three other batches,

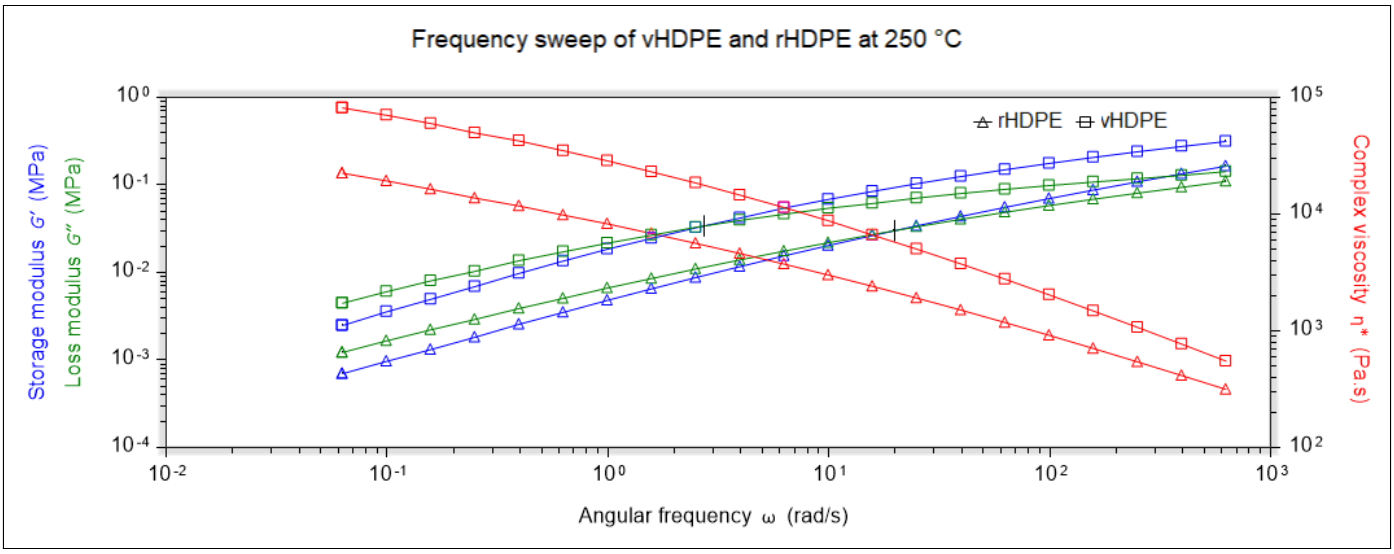


Fig. 7 Frequency sweep of vHDPE and rHDPE at 250 $^\circ C$

with the area of hysteresis loops reaching 2,24 times larger from the first to the last cycle. Compared to the hysteresis loop of vHDPE which only increased in area with a factor of 1,58. As the slope decreases in the late cycles, a decrease in the stiffness modulus is apparent for rHDPE.

The difference between vHDPE and rHDPE is much more remarkable for cyclic loading tests compared to state-of-the-art tensile and creep tests. At a low number of cycles to failure of $N_f = 1000$ the difference in fatigue stress, σ_f, between vHDPE and rHDPE proved to be 18%. For a desired service lifetime of 50 years with a corresponding number of cycles to failure of N_f, the difference in σ_f elevated to 36,4%, by far exceeding the 5,5% difference found in [5] for creep testing at the same lifetime. These percent differences confirms this as a more sensitive test for characterizing the long-term mechanical properties of HDPE.

For the DSC testing, an insignificant difference is seen when comparing the thermograms of vHDPE and rHDPE. This is clear for both the melting peaks and degree of crystallinity. Larger deviations in crystallinities occur within the same batch than between batches, thus these are comparable in vHDPE and rHDPE. Based on DSC analysis, there are no indications of degradation due to recycling and/or injection molding.

The expectation, that the molecular weight of the rHDPE was lower than that of vHDPE, was confirmed. The cross over point of the storage and loss modulus presented vHDPE to have higher molecular weight, but similar molecular weight distribution, compared to rHDPE. Based on rheometry analysis, there are no indications of degradation due to injection molding. However, a clear difference is seen between vHDPE and rHDPE as a result of the recycling process, which was not evident in the DSC testing.

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References

[1] H. B. Stiftung, *Plastic Atlas*. Heinrich Böll Foundation, first ed., 2019.
[2] A. D. Drozdov, R. Høj Jermiin, and J. de Claville Christiansen, “Lifetime predictions for virgin and recycled high-density polyethylene under creep conditions,” 2023.
[3] M. Dahl and R. H. Jermiin, “Comparative study on mechanical properties of virgin and recycled high density polyethylene,” Master’s thesis, Aalborg University, 2019.
[4] J. Zhang, V. Hirschberg, and D. Rodrigue, “Mechanical fatigue of recycled and virgin high-/low-density polyethylene,” *Journal of Applied Polymer Science*, vol. 140, no. 2, p. e53312, 2022.
[5] J. Zhang, V. Hirschberg, and D. Rodrigue, “Blending recycled high-density polyethylene HDPE (rHDPE) with virgin (vHDPE) as an effective approach to improve the mechanical properties,” *Recycling*, vol. 8, no. 1, 2023.
[6] A. D. Drozdov, R. Høj Jermiin, and

J. de Claville Christiansen, “Lifetime predictions for high-density polyethylene under creep: Experiments and modeling,” *Polymers.*, vol. 15, no. 2, 2023-1-09.

[7] Borouge, *PRODUCT DATA SHEET - POLYETHYLENE BorSafeTM HE3490-LS*, 2018.

[8] Y. Xu, Z. Luo, Y. Tao, M. Xu, and J. Liao, “Transforming hydrophobicity of high-density polyethylene surface to hydrophilicity and superoleophobicity by surface grafted with polyvinyl alcohols for oil contaminants cleanup,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 655, p. 130313, 2022.

[9] T. A. Osswald and G. Menges, *Materials Science of Polymers for Engineers*. London: Hanser Gardner publications, second ed., 2003.

[10] A. J. Peacock, *Handbook of Polyethylene: Structures, Properties and Applications*. Marcel Dekker, 2000.

[11] W. D. Callister and D. G. Rethwisch, *Materials Science and Engineering*. Wiley & Sons, ninth ed., 2015.

[12] R. L. Norton, *Machine Design An Integrated Approach*. Pearson, fifth ed., 2014.

[13] D. Li, L. Zhou, X. Wang, L. He, and X. Yang, “Effect of crystallinity of polyethylene with different densities on breakdown strength and conductance property,” *Materials*, vol. 12, p. 1746, May 2019.

[14] R. L. Blaine, “Thermal applications note: Polymer heats of fusion,” *TA Instruments: Application Notes*.

[15] M. Wagner, *Thermal analysis in practice: fundamental aspects*. Munich: Hanser, 2018.

[16] Anton Paar, “Rheological investigation of polymers.”

[17] Anton Paar, “Calculation of the weight average molar mass mw based on the zero-shear viscosity measurement using a frequency sweep.”

[18] Rheology Testing Services, “Amplitude sweep - probing sample structure and properties to produce a rheological profile,” 2017.

[19] J. Aho, *Rheological Characterization of Polymer Melts in Shear and Extension: Measurement Reliability and Data for Practical Processing*. PhD thesis, Tampere University of Technology, 2011.