Utilization of recycled household waste HDPE and the effect of introducing Nexamite R301

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Abstract

In this paper it was examined how adding post-consumer recycled High Density Polyethylene (rHDPE) to virgin High Density Polyethylene (vHDPE) influences the properties of the mix. In order to enhance the properties of rHDPE and make it more compatible with vHDPE, Nexamite R301 was used. According to the producer, Nexamite R301 is a PE based additive used to decrease the melt flow rate (MFR) and increase the mechanical properties as well as the environmental stress cracking resistance (ESCR) of rHDPE. Blends containing 0%, 30%, 50% of rHDPE mixed with vHDPE and different amounts of Nexamite R301 were extruded into pellets. Dogbone shaped specimens for testing were injection moulded. Utility of different mixes was determined by various characterization methods, which were rheology, impact test, tensile test, differential scanning calorimetry (DSC), oxygen induction time (OIT), melt mass-flow rate test (MFR) and Fourier Transform Infrared Spectroscopy (FTIR). The results of performed tests pointed in the direction of R301 being a crosslinking agent.

Keywords: rHDPE, vHDPE, Effects of Nexamite R301, Material properties characterization, Crosslinking, Chain-scission, Molecular weight

1. Introduction

High density polyethylene (HDPE) is a versatile semi-crystalline polymer widely used in e.g the pipe industry and household products such as bottles and food wrapping. It is produced by polymerization of ethylene and propylene using natural gas and oil. Its thermoplastic properties make it possible to recycle it, as it becomes less viscous and formable when heated above its melting temperature and solidifies after cooling down [1]. Recycling of polymers is a very researched area, due to the increasing demand for polymer products, leading to production of 359 million tons of plastic products in 2019. Most of them are single use, and are either sorted by the consumer or found in the environment, the latter being approximately 9 billion tons annually [2][3][1].

The sorted material can be mechanically recycled into pellets, which are used for manufacturing new products [4]. One disadvantage of recycling occurs when a material is reprocessed multiple times, leading to a higher chance of a decrease in the mechanical strength, increase in MFR and appearance of degradation due to chain-scission. In addition, the use of rHDPE obtained from household waste can be problematic due to inconsistent quality. The thermal and chemical history of the household waste is unknown, which can lead to slightly different properties from one rHDPE batch to another. In some processing methods 100% rHDPE has sufficient properties to be used successfully for production, whereas other methods require addition of vHDPE or additives.

As vHDPE and rHDPE can have different properties, such as higher melt mass-flow rate (MFR) in rHDPE, a masterbatch can be introduced in rHDPE in order to make it more compatible with vHDPE. Nexamite R301 (R301), used in this study, is a polyethylene (PE) based additive, which has the purpose of decreasing the MFR, increasing the environmental stress cracking resistance (ESCR) and mechanical properties. Crosslinking could be responsible for those changes [5].

Crosslinking and chain-scission are two competing degradation mechanisms. Molecular degradation of PE can be induced by processes such as thermal, mechanical or photo-oxidative. It leads to changes in e.g. thermal and mechanical properties of degraded materials. The principle of crosslinking is tying carbon atoms from separate polymer chains together, lowering the chances of crystal structure creation and slipping of molecules in amorphous regions. This leads to a decrease in stiffness and improvement in properties such as ESCR, ultimate tensile strength and impact resistance. Crosslinking can indicate a free-radical degradation process happening in a polymer. However, when performed in a controlled environment, it can enhance the material properties. The mechanism of free-radical degradation can be seen in figure 1. Due to the thermal decomposition of peroxides (reaction 1), free-radicals appear and can attack free chains in PE.

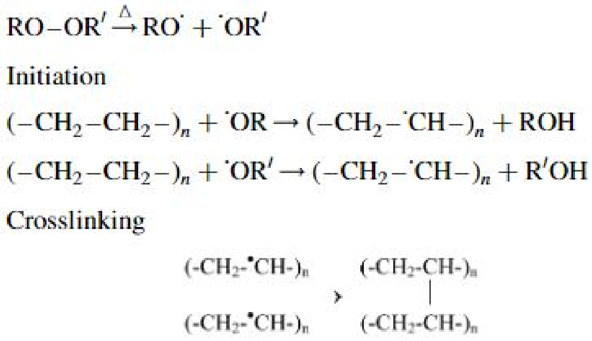


Fig. 1 The mechanism of free-radical degradation: R stands for $C(CH_3)_3$, R' stands for $C(CH_3)_2C_6H_5$ [5].

Crosslinking has its drawbacks too. Firstly, the recyclability decreases with crosslinking due to problems with melting at high temperatures. Secondly, an increase in degree of crosslinking results in a decrease in the crystalline regions and therefore brittleness [6]. The lack of crystallinity is due to the crosslinking disrupting and restricting the molecular chains to align and rearrange into crystalline lamellae, when cooling down [7][8]. For that reason e.g. pipes have a limit for their degree of crosslinking between 65% and 89% [6].

Currently, there are 3 ways of crosslinking PE: by high energy radiation, with the use of peroxide and silane-water crosslinking [9]. Radiation and use of peroxide agents cause free radical processes, whereas silane agents use a multi-step mechanism [6]. The first step of the reaction is silane being grafted onto backbones of PE through a free radical reaction initiated by peroxide, new PE radicals also form in that phase. Next step is the hydrolysis resulting in formation of Si-O-Si bridges that crosslink PE chains [10]. In contrast, the first two methods will only have C-C bonds present [11].

A mechanism responsible for degradation competing with crosslinking is chain-scission. The molecular weight (MW) increases due to crosslinking, but decreases if chain-scission is present. Parameters such as temperature, stabilizers and chemical environment have influence on the balance between crosslinking and chain-scission [3].

Other researchers have studied degradation mechanisms in HDPE. Cruz et.al. studied degradation in post-consumer rHDPE with the use of FTIR, OIT, MFR, and cone-plate rheometry. They discovered that MW increases and MWD widens after reprocessing HDPE recovered from post-consumer waste. That is an indication of degradation processes occurring in the material. Increased MW might be due to crosslinking while broad MWD indicates that the system was more heterogeneous after reprocessing [12]. Dvorak et. al. tested different types of rHDPE and compared them with vHDPE. They reported that MFR for all rHDPE samples was lower than for vHDPE [13]. Erbetta et.al. studied rheological behaviour of HDPE in 3 different temperatures: 150°C, 190°C and 230°C. Oscillatory tests at low frequencies showed a significant difference between samples tested at 150°C and 190°C compared to those tested at 230°C. The authors suggest that it might be due to thermo-oxidative degradation with crosslinking being the initially predominant mechanism and that the processing temperature should not exceed 230°C unless specific additives were used [14].

In this paper the utility of rHDPE has been investigated, when extruded with different amounts of vHDPE and R301. Tests on material properties have been run, from which the effect was analysed. The material is intended to be used in the pipe industry, why it has to fulfill requirements such as a OIT of more than 20 min, as it indicates a lifetime longer than 50 years, which is also a requirement [15]. The mechanical properties have been tested by tensile test and impact test. The thermal properties have been investigated by differential scanning calorimetry (DSC), from which the difference in the melting temperature (T_m) and degree of crystallinity (X_C) were analysed. Oxidation induction time (OIT) was performed to measure how long it takes for the material to oxidate in oxygen environment. To investigate the change in MFR, standardized tests were conducted, and compared with rheometry results, as MFR and MW are inversely proportional [16]. Fourier transform infrared spectroscopy (FTIR) was performed in order to investigate which functional groups the R301 contains and get more understanding of its possible influence on molecular structure of HDPE. ESCR experiment was prepared but has not been performed in this paper. This has been elaborated on in the discussion.

2. Experimental

2.1 Materials

Materials used in this study supplied by Aage Vestergaard Larsen A/S (AVL) were vHDPE and rHDPE, while the additive R301 was supplied by Nexam Chemical. The following properties of the granulates have been included in the data sheets supplied by the producer. The given density (ISO 1183-1) of rHDPE was 944-962 kg/m^3, for vHDPE it was 959 kg/m^3 and 922 kg/m^3 for R301. The MFR (ISO 1133-1, 190°C, 5.0 kg) was 0.2-0.5 g/10 min for rHDPE and 0.23 g/10 min for vHDPE, while for R301 (190°C, 2.16 kg) it was 2 g/10 min. The minimum OIT (ISO 11357-6, 210°C) for rHDPE was 20 min, while for vHDPE it was 30 min.

2.1.1 Material processing

Extrusion of ten mixes with different amounts of rHDPE, vHDPE and R301 was performed, presented in table I. Granulates were weighed, mixed by hand and extrusion moulded into pellets at 250°C for the 100% rHDPE batch and 260°C for the other batches using COLLIN Teach-LineZK 25T with a double-screw extruder. Extrusion pressure for 100% rHDPE batch was lower than for the other batches, due to the higher MFR of rHDPE. Granulates of the 100% vHDPE were extruded in order to keep the same thermal history for all tested batches. The extruded pellets were injection moulded into dogbones using Ferromatic Milacron K110. The used parameters were temperature of 220°C, injection pressure of 90 bar, back pressure of 65 bar, back pressure time of 30 s, cooling time of 25 s and form temperature 40°C. Obtained dogbones were approximately 100 mm long, 9.7 mm wide and 3.5 mm thick. They were used for further testing either whole or cut into smaller pieces.

2.2 Mechanical properties characterization

2.2.1 Tensile test

An uni-axial tensile test was performed to investigate the ultimate tensile strength of rHDPE, and the effect of adding R301 and vHDPE. The test was performed on INSTRON 5568 with Bluehill universal software, according to ISO 527-1 at approx. 21°C. Strain rate was set to 100 mm/min until fracture. An extensometer was used to measure the elongation. Ten samples from each batch were tested in order to ensure the repeatability of results. The average ultimate tensile strength and its standard deviation were calculated.

Tab. I Mixes prepared for testing.

Batch	rHDPE[%]	R301 in rHDPE[%]	vHDPE[%]
1	30	0	70
2	30	1	70
3	30	3	70
4	50	0	50
5	50	1	50
6	50	3	50
7	100	0	0
8	100	1	0
9	100	3	0
10	0	0	100

As a result of this test a stress-strain curve was achieved, with the engineering stress (σ [MPa]), given as equation 1, and engineering strain (ϵ [%]), as equation 2.

$$\sigma = \frac{F}{A} \tag{1}$$

F - applied force [N]; A - cross-sectional area [mm]

$$\epsilon = \frac{\Delta L}{L_0} \tag{2}$$

ΔL - change in length; L_0 - initial length [mm]

The ultimate tensile strength is found as the highest stress the material can withstand before fracture [1].

2.2.2 Impact test

The Izod impact (ISO 180:2019) was performed to compare the differences between mechanical properties of the mixes. The machine used was Instron CEAST 9050 with CeastVIEW 5.94 4D software. Ten specimens from each batch were tested. The injection moulded dogbones were shortened to 70 mm of length, notched and conditioned in approximately 21°C for more than 24 hours before performing the test.

The impact strength can be calculated using the formula:

$$a_{iN} = \frac{W_c}{h \cdot b_N} \cdot 10^3 \tag{3}$$

where:
W_c - the corrected energy absorbed by breaking the test specimen [J]; h - thickness of the test specimen [mm]; b_N - width of the test specimen [mm] [17].

2.3 Thermal properties characterization

2.3.1 Differential Scanning Calorimetry

By performing the DSC test, thermal properties such as X_C and T_m were obtained. A heat-cool-heat program in a TA Q2000 calorimeter in a nitrogen atmosphere was used. The test sample was a 10±0.5 mg cut out from the dogbone which was placed in a tzero aluminium crucible.

The temperature used for the first heating was from 20°C to 160°C at a rate of 10°C/min, a cool down to -70°C with a rate of 5°C/min and the second heating to 160°C with a rate of 10°C/min again. Given is a thermogram with two endothermic peaks and a exothermic peak. The first heating informs about the T$_m$ and X$_C$ of the injection moulded dogbone. As the sample is heated above its melting temperature, the thermal history is erased. The first heating curve is disregarded, as the thermal history from the extrusion and injection moulding is not important for this study. The cooling ensures slow recrystallization of the melt, and the second heating informs about the properties of the reset melt [1].

The X$_C$, calculated by equation 4, is given as the ratio between the heat of fusion from the tested sample (ΔH_{SC}), and the enthalpy of fusion for a theoretically 100% crystalline HDPE sample (ΔH_C) [7]. The value for (ΔH_C) was found to be 293 J/g in literature [18].

$$X_c = \frac{\Delta H_{SC}}{\Delta H_C} \tag{4}$$

The program used to calculate this was TA universal analysis.

2.3.2 *Oxidation Induction Time*

By performing OIT the thermal stability of the material in oxygen atmosphere was determined, using a TA Q1000 machine and analysed with TA Universal analysis. A 5±0.5 mg sample cut out from the dogbone was placed in a tzero aluminium crucible with no lid, when the test was run.

The test was run in a nitrogen atmosphere (50 $\frac{mL}{min}$) with a heating from 50°C to 220°C, at a 20°C/min rate. When the temperature reached 220°C, it was held isothermal for 5 min and the gas was switched to oxygen (50 $\frac{mL}{min}$) and held for 100 min.

The results were given in a heat flow [$\frac{W}{g}$] vs. time [min] curve. The OIT is given as the time between the first exposure to oxygen and the onset point of degradation. This is read from the point where the heat flow changes from constant to increasing, and thereby when oxidation starts. From this test it is possible to see, if antioxidants were used [7].

2.3.3 *Melt mass-flow rate*

MFR (ISO 1133) was measured for the extruded pellets. The pellets were dried using Mettler Toledo dryer, until the moisture content had been stable for 1 minute. Then, about 2 g of dry pellets were tested in 190°C and 5 kg load (load suitable for pipe grade HDPE) for 5 minutes using a Tinius Olsen apparatus. MFR was calculated using formula 5:

$$MFR(T, m_{nom}) = \frac{600 \cdot m}{t} \tag{5}$$

where:
T - test temperature [°C]; m_{nom} - mass exerting the nominal load [kg]; 600 - factor used to convert grams per second into grams per 10 min; m - average mass of the cut-offs [g]; t - cut-off time -interval [s] [19].

2.3.4 *Rheometry*

The test was performed in order to explore the degradation mechanism by comparing the MW and molecular weight distribution (MWD). The machine used was TA discovery HR-3 hybrid rheometer accompanied by TRIOS software with parallel plate geometry: plate diameter 25 mm, gap 1000 μm, made of stainless steel. Materials tested were R301 granulate and extruded pellets of batches number 7 and 10. Frequency sweep was additionally performed for batches 8 and 9. Two amplitude sweeps at 200°C and 250°C, frequency of 1 Hz and strain within range of 1-100% were ran in order to find the linear elastic region of each material. Then, frequency sweep in two repetitions per material was done in order to compare the molecular changes between materials (MW and MWD). Parameters for the frequency sweep were: 200°C, 3% strain, frequency 79.5775 Hz - 0.0159155 Hz. Next, a temperature ramp using the parameters: start temperature 200°C, end temperature 320°C, rate of 5°C/min, frequency of 1 Hz and 3% strain was performed to find out if the material would degrade. A 10 min long time sweep at 260°C, 1 Hz and 3% strain was ran in order to characterize the degradation mechanism occurring in the material.

An example of curves obtained from a frequency sweep can be seen in figure fig. 2. The cross-over point of storage modulus (G'), and loss modulus (G"), can be an indicator of differences in MW and MWD for compared materials [20].

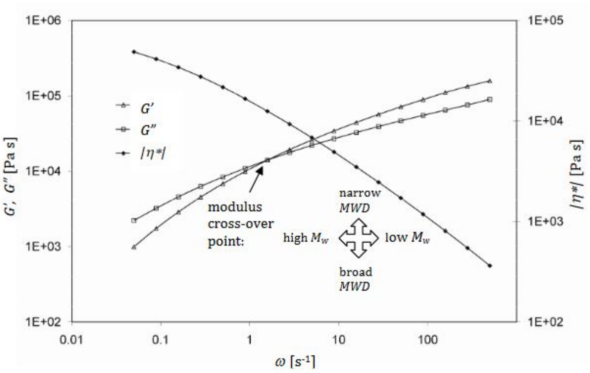


Fig. 2 Exemplary curves obtained from a frequency sweep and their meaning [20].

2.4 Fourier Transform Infrared Spectroscopy

In order to identify which chemical group Nexamite R301 belongs to and investigate its influence on HDPE, FTIR was used. The test was performed on injection moulded dogbones using Nicolet iS20 from Thermo Fisher Scientific and OMNIC software. The spectra were collected in 4000 to 650 cm^{-1} range with 32 scans, using a diamond indenter. In total, one sample from each batch was tested and additionally, a measurement on R301 granulate was performed.

3. Results

3.1 Mechanical properties

Tensile test

The results for the tensile tests are shown in table II. It can be seen that the ultimate tensile strength is increasing when more R301 is added. The ultimate tensile strength for 100% vHDPE and 100% rHDPE are very similar, with the difference being 0.32 MPa. It is seen that when adding R301, the ultimate tensile strength increases more for rHDPE, than when R301 is added to vHDPE. This means that the highest increase is seen for batches 7-9 and the highest value for batch 9.

Impact test

The results from this test were not useful, as the test machine and analysing program showed an impact strength below 2 kJ/m^2 for most of the batches, whereas some specimens showed a value of above 10 kJ/m^2. It is given in literature, that the value is to be around 16 kJ/m^2 [21]. As the results obtained were very low compared to this, the results were disregarded. As 10 repetitions for each batch were performed, this was not due to deviation.

Tab. II Results from tensile testing of the 10 batches.

Batch	Tensile avg. [MPa]	Std Dev
1	26.85	0.48
2	26.86	0.55
3	27.57	0.47
4	27.21	0.34
5	27.29	0.33
6	28.20	0.31
7	26.87	0.19
8	27.61	0.54
9	29.02	0.38
10	26.55	0.53

3.2 Thermal properties

Differential Scanning Calorimetry

The heat-cool-heat program from the DSC test resulted in a thermogram, with two endothermic peaks and one exothermic. The thermogram for batch 9 containing the T_m and X_C for the 2nd heating is shown in figure 3.

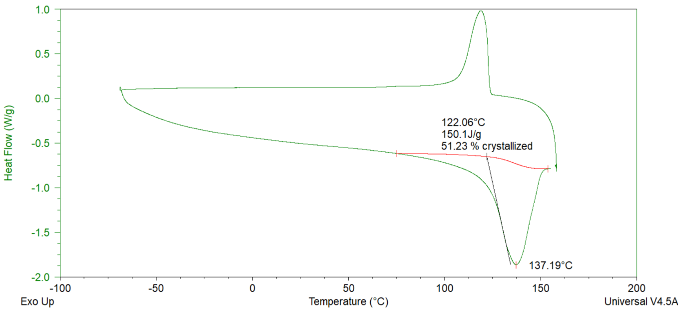


Fig. 3 DSC thermogram of batch 9.

The results for all batches and R301 are shown in table III. It is seen that T_m is increasing with higher amount of R301, whereas the X_C decreases. Batches 4-6 showed stable results, as the T_m is at approx. 131°C for all, while the X_C is at approx. 62%. A more pronounced difference can be seen in batches 7-9, with the highest decrease in X_C from 59.34% in batch 7 to 51.23% in batch 9. When comparing batches 1, 4, 7 and 10 it is seen, that the mixes have a higher X_C than the pure materials which proves the influence of the high X_C of rHDPE on vHDPE.

Oxidation Induction Time

The OIT informs about how long it takes in oxygen atmosphere for the material to oxidate. The results are shown in table IV, where it can be seen that the OIT was 78.33 min for the vHDPE. This was much higher than the OIT seen for rHDPE at 1.30 min and 1.25 min for R301. This is reflected on the other batches, as the more rHDPE and R301 the batch contains, the lower the OIT. Batches 7, 8 and 9 have the lowest OIT, which

Tab. III DSC results.

Batch	2.T_m [$^\circ C$]	2. X_c [%]
1	131.94	60.57
2	130.82	57.37
3	137.83	53.95
4	131.63	62.35
5	131.42	62.57
6	131.91	62.65
7	134.82	59.34
8	132.52	58.41
9	137.19	51.23
10	134.68	57.37
R301	112.42	28.30

is plausible as they are mixes of two materials with low OIT.

Melt mass-flow rate

The results of MFR measurements are presented in table V. When comparing the two pure materials the difference in MFR is quite large, as batch 10 has a MFR at 0.240 g/10 min, where batch 7 is at 1.300 g/10 min. When comparing batches 1-6 to batch 10 and 7 it is seen, that rHDPE's influence on the mixes was low, as the values are closer to the MFR of batch 10. Batches 4-8 showed a decrease of MFR when R301 was added. The opposite was seen for batch 1-3. By comparing batch 7 to batch 8 a decrease by 0.160 g/10 min was found. It was not possible to measure the MFR for batch 9 on the same machine and with the same time interval between extrusion and MFR measurement. Performing the test on a different machine and with a larger time interval would introduce a lack of consistency and thus lack of reliability for the obtained results.

Rheometry

The amplitude sweeps showed the linear elastic region being at 3% strain for all tested materials and that is the strain used for frequency sweeps. Comparison of the frequency sweeps for batches 7, 8 and 9 is shown in figure 4 and for batches 7, 10 and R301 in figure 5. The more R301 was added to the rHDPE, the higher the MW was. Batch 9 with the highest content of R301 also had the broadest MWD. Based on the frequency sweeps, it can be seen that pure rHDPE has a lower MW and a broader MWD than pure R301 or pure vHDPE.

Tab. IV Results from OIT.

Batch	OIT [min]
1	28.27
2	25.15
3	23.07
4	16.15
5	14.10
6	13.21
7	1.3
8	3.77
9	1.73
10	78.33
R301	1.25

Tab. V Results of MFR measurements for extruded pellets.

Batch	MFR [g/10 min]
1	0.284
2	0.350
3	0.314
4	0.464
5	0.492
6	0.229
7	1.300
8	1.140
9	-
10	0.240

FTIR

Spectra acquired for mixes 1-10 all showed characteristic HDPE peaks at: approximately 2915 and 2848 cm^{-1} which is stretching vibration of CH group of the main chain, 1460 cm^{-1} showed CH deformation vibration and a doublet near 725 cm^{-1} showed rocking vibration of CH [22]. No carbonyl groups were observed at 1700 cm^{-1} which indicates that the chemical structure of the samples was not affected [14].

Spectrum of R301, shown in figure 6 had all aforementioned peaks, due to it being a PE based additive. Additionally 1198.86 cm^{-1} and 1186.54 cm^{-1} peaks could indicate Si—alkoxy compound $(-Si-O-CH_2-)$ presence, as they appear at 1190-1140 cm^{-1} [22] .

4. Discussion

When looking at the results of the mechanical properties in table II, it is seen that the ultimate tensile strength is increasing with added R301, which corresponds with the decrease in X_C, seen in the DSC result in table III. Ultimate tensile strength values for vHDPE and rHDPE were both approx. 27 MPa. The results also show, that the R301 had a higher effect on rHDPE, as the strength increases more for the 100% rHDPE mixes, compared to batches 1-6.

A decrease in X_C was seen from DSC when R301 was added, which can indicate a predominance of the crosslinking mechanism. This is due to the broken chains connecting with the closeby bonds, decreasing the polymer's mobility. This hinders the production of crystalline structures and thereby an increase in the

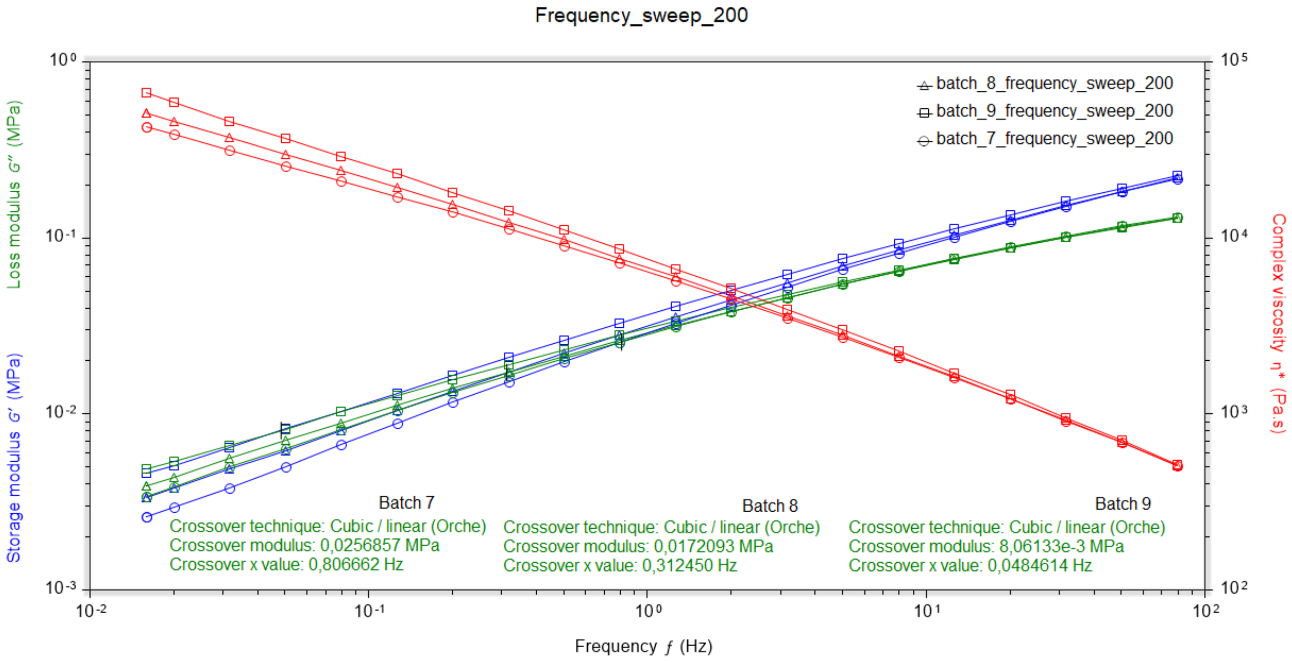


Fig. 4 Frequency sweep for batches 7, 8 and 9.

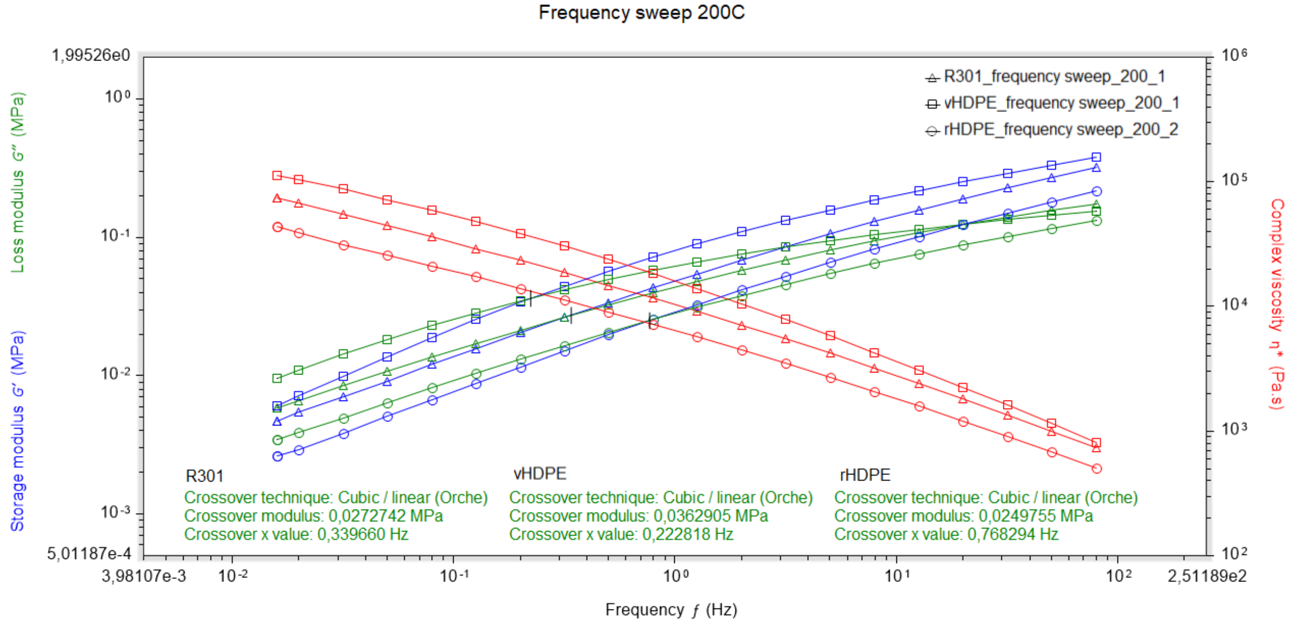
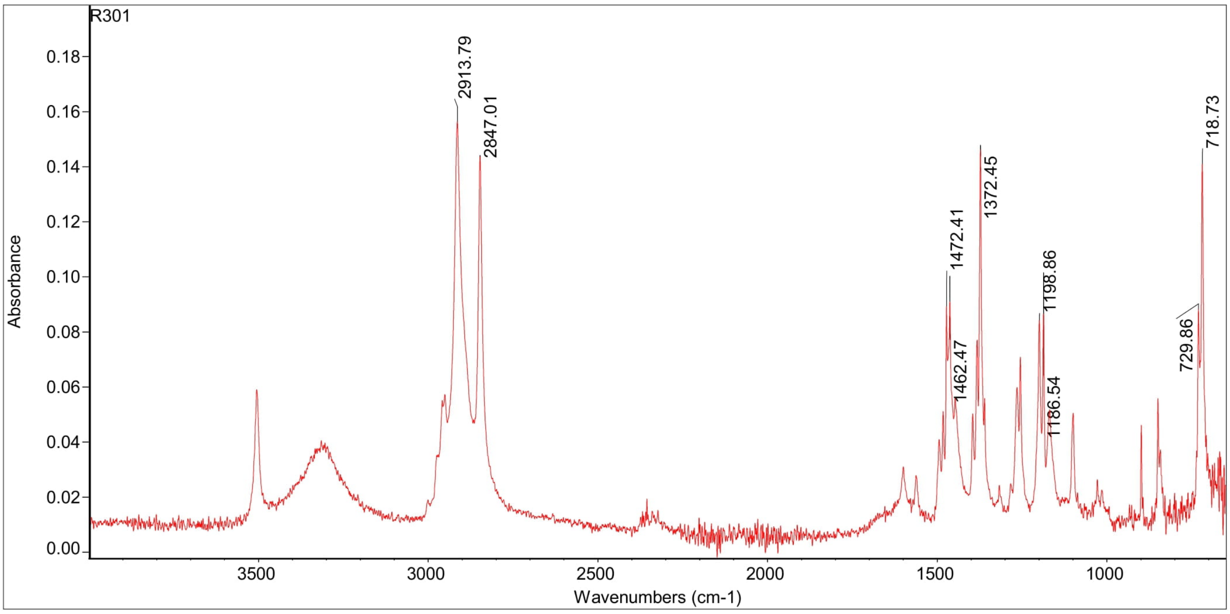


Fig. 5 Frequency sweep for R301, batch 7 and batch 10.

tensile strength is seen [5][7]. Seeing as the X_C is 24.76% for R301, which was significantly lower than for the 10 batches, a decrease was expected in all batches containing R301. The highest decrease was found in the pure rHDPE mixes, which decreased from 61.91% for batch 7 to 51.20% for batch 9. Batches 4-6 showed a stable result for both T_m and X_C, despite different amounts of R301 added. For batches 1-3 and 7-9 a tendency is seen, for T_m to decrease when 1% R301 is added and increase significantly when 3% is added. When comparing all batches, the highest T_m was seen for batches 7-9. What is important to notice is that the T_m is increasing with added R301. This is an opposite reaction to what is expected from a crosslinking agent in HDPE. Research has shown, that the T_m decreases when a crosslinking agent is introduced [5] [23].

Knowing the correlation of high MW meaning low MFR, the results from rheometry and MFR can be compared [16]. The highest MFR was seen for batch



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Fri Apr 29 11:39:55 2022 (GMT+02:00)
FIND PEAKS:
      Spectrum:           R301
      Region:             3999.88      649.89
      Absolute threshold: 0.077
      Sensitivity:        100
      Peak list:
                          Position:    718.73    Intensity:    0.141
                          Position:    729.86    Intensity:    0.0881
                          Position:   1186.54    Intensity:    0.0866
                          Position:   1198.86    Intensity:    0.0842
                          Position:   1372.45    Intensity:    0.146
                          Position:   1462.47    Intensity:    0.0910
                          Position:   1472.41    Intensity:    0.0893
                          Position:   2847.01    Intensity:    0.144
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Fig. 6 FTIR spectrum of Nexamite R301.

7 and the lowest for batch 10 in the MFR test, as the value for rHDPE was 1.300 g/10 min and a significantly lower value was seen for vHDPE at 0.240 g/10 min. Seeing as rHDPE is most probably a heterogeneous mix of granulates with different thermal histories, the chain-scission degradation is high likely. This leads to the high MFR.

A significantly higher MFR was seen in vHDPE, due to the material having no previous thermal history and thereby no degradation by chain-scission. When looking at the mixes, batch 7 did not have a high influence on batches 1-6, as they all had values more similar to batch 10. From batches 4-8 a decrease in MFR was seen with increased R301, whereas an increase was seen in batches 1-3. Rheometry results confirmed the MFR measurements, as pure rHDPE had a lower MW than pure vHDPE. The MWD was broader for batches 7-9 than for batch 10, pointing to that system being more heterogeneous, which corresponds with the unknown thermal histories of rHDPE obtained from post-consumer waste. The increase in MW observed for batches 7-9 with increasing content of R301 can be due to crosslinking induced by the R301. What is more, the time sweep showed that rHDPE is more crosslinked than vHDPE or R301. Additionally, temperature ramp showed that none of the tested batches degraded below 320°C, which is way above the processing temperature.

OIT was performed to investigate the thermal stability of the materials, and the residual thermal stability in rHDPE. This was investigated, as a requirement for the district heat pipe industry is a lifetime of approximately 50 years [15]. As the pipes are used in very oxidative environments, this is an important factor. It was seen from the results, that batch 10 had a very high OIT, which indicates that antioxidants have been used to ensure a longer lifetime. Batch 7 had a much lower OIT, which can be explained by low residual thermal stability, due to multiple thermal histories and reaction between the free radicals from degradation by chain-scission and oxygen atoms. Seeing as the rHDPE is recycled post consumer plastic, the low OIT can also be due to antioxidants not being added, as it is not needed in single use products. Furthermore, the addition of antioxidants inhibits the free-radical crosslinking reaction, what was studied by Li et.al. They compared the extrusion with antioxidant and crosslinker added at the same time to a two step extrusion. They found out that adding the crosslinker and the antioxidant separately resulted in higher crosslinking density [15]. R301 is not known to be an antioxidant, as it was not mentioned in its datasheet, and will thereby have a low OIT as well. When looking at the batches, the OIT decreased with increased content of both rHDPE and R301 in vHDPE, due to the influence of their low OIT. The highest values were found in batches 1-3, which had the lowest amount of rHDPE.

A $-Si-O-CH_2-$ peak was found in R301 spectrum. As siloxanes are used to crosslink HDPE, their presence in R301 indicates that the R301 could be a crosslinking agent that makes use of the silane-water crosslinking mechanism [9]. Comparing FTIR spectra of the ten batches did not show much difference. Characteristic bands for HDPE were identified on all of the spectra, with different intensities. A peak for carbonyl group (C=O, around 1700 cm^-1) was not identified on any of the spectra, so it can be concluded that the chemical structure after mixing, extruding and injection moulding was not changed [14].

Due to the increase in ESCR being one of the effects of using R301, the full notch creep test (FNCT) was planned to be performed. Due to the set-up being too complicated to make, and the needed weights being too large, this test was disregarded. It was replaced with the Bell-Telephone test, which is another method for ESCR testing. The test set-up was ready for testing, but due to the delay in delivery of Igepal CA-630, this test was also disregarded. Lastly, a strain hardening test was performed, but without usable results, as a pronounced necking was not possible to get with the used dogbones. It was aimed to decrease the cross-sectional area, which was not achieved due to the machines melting the polymer surface, and thereby changing the thermal properties.

5. Conclusion

The purpose of this paper was to investigate the influence of vHDPE and R301 on rHDPE. R301 was used as a masterbatch supposed to increase the mechanical properties and ESCR and decrease MFR. Those properties could be improved by introducing a crosslinking agent. To confirm which functional group the R301 contained, FTIR was performed. It was found that it was PE based, where siloxane groups were present. Seeing as the use of silane-water is one of the crosslinking methods, the focus when testing mechanical and thermal properties was on proving that R301 was indeed a crosslinking agent.By performing DSC, a decrease in crystallinity was seen the more R301 was used, meaning an increase in crosslinking. This corresponded with the increase in tensile strength, when the R301 content was increased. When comparing the strength for pure vHDPE and rHDPE, approximately the same strength was observed. It was seen that the highest increase in the tensile strength was for the 100% rHDPE batches with R301. This confirms that R301 is increasing the tensile strength. From MFR and rheometry it was seen that the MW increased when more R301 was added. This points to R301 being a crosslinking agent, as well as confirming that R301 is decreasing the MFR. The OIT showed a high amount of antioxidants in vHDPE due to the high OIT. Meanwhile rHDPE had a significantly lower value due to residual stability, seeing as it has previously been exposed to oxygen, before it was recycled. Another reason could be the lack of added antioxidants, as single use plastic does not require a long lifetime. R301 also had a low OIT, confirming antioxidants were not present.

It was seen that the OIT was decreasing with higher percentage of rHDPE and R301 used. In batches 1-3 the OIT was between 27.71 min and 23.14 min, which fulfills the criteria from the pipe industry, requiring a miniumum OIT of 20 min [15]. For batches 4-6 the value was lower than 20 min, meaning an antioxidant has to be used, if the content of rHDPE is more than 30%.

It was not possible to confirm the effect of R301 on ESCR in this paper. This is recommended to test in order to verify if R301 had an influence on ESCR.

Seeing as the tensile strength values were very similar for all the batches, the use of rHDPE did not cause a decrease in mechanical properties, as even the 100% rHDPE value was very similar to 100% vHDPE. DSC also showed that the high content of rHDPE did not affect the X_C significantly.

By performing the tests it was confirmed that R301 is increasing the tensile strength and decreasing the MFR of rHDPE. As FTIR showed siloxane characteristic groups in R301 it is likely that it is a crosslinking agent with a positive influence on rHDPE.

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