Recycling of wood fiber-reinforced HDPE by multiple reprocessing

Dan Åkesson,[1] Torsten Fuchs,[1] Michael Stöss,[1] Andrew Root,[2] Erik Stenvall,[3] Mikael Skrifvars[1]

[1]Swedish Centre for Resource Recovery, University of Borås, Borås, Sweden
[2]MagSol, Tuhkanummenkuja 2, Helsinki 00970, Finland
[3]Department of Materials and Manufacturing Technology, Chalmers University of Technology, Göteborg, Sweden
Correspondence to: D. Åkesson (E-mail: dan.akesson@hb.se)

ABSTRACT: The mechanical recycling of high-density polyethylene (HDPE) reinforced with wood fiber was studied by means of repeated injection moulding. The change in properties during the recycling was monitored by tensile and flexural tests, Charpy impact tests, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), FTIR spectroscopy, and by measuring the fiber lengths. Tests were also done where injection moulding was combined with subsequent accelerated thermo-oxidative ageing and thereafter repeated numerous times. The results showed that the HDPE composites were relatively stable toward both the ageing conditions and the repeated injection moulding. The change of the mechanical properties was mainly observed as an increased elongation at max. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43877.

INTRODUCTION

Environmental concern, legislation, and rising oil prices have increased the efforts to recycle plastics and composites. Mechanical recycling is the preferred method for recycling and is being used where economically feasible. It has been estimated that 6.6 million tonnes of plastics were recycled in Europe during 2012.[1] HDPE is one of the most common plastics with a wide range of applications such as bottles, pipes and containers. Several studies have been done on the mechanical recycling of HDPE.[2–8] As a general conclusion from these studies, HDPE can be reprocessed relatively well. The exact number of processing cycles that HDPE can sustain will however depend on several factors such as processing temperature, type of processing being used, residence time of the polymer at elevated temperature as well as type of stabilizer used.

Wood fiber (flour) is a cheap and renewable resource that can be added as a filler to HDPE in order to decrease the overall cost and to modify some of the properties. Compared to the commonly used mineral fillers, wood flour results in composites with lower density and is non-abrasive to the processing equipment. Furthermore, large amounts of waste wood are being generated in the saw mill industry, and the usage of this waste wood as a filler is a way to use this waste material.[9] Several research groups have studied HDPE reinforced with wood fibers.[10–14] Klason et al. studied the reinforcement of HDPE and other thermoplastics with wood flour. The influence of the wood flour content on the mechanical properties was investigated. The modulus increased with increasing wood flour content, while the increase in stress at yield was practically insignificant.[15]

While the recycling of neat HDPE is relatively well studied, the recycling of wood fiber-reinforced HDPE has not been investigated in detail. The recycling of the composite is complicated since both the fiber and the matrix can degrade during the recycling process. The purpose of this study was to study the mechanical recycling of wood fiber-reinforced HDPE by repeated injection molding. This simulates preconsumer recycling, i.e., recycling of production waste. However, it does not take into account the ageing of the material that occurs during its lifetime. Thus, in order to simulate post-consumer recycling conditions, tests were done where the composite was injection moulded repeatedly in combination with accelerated ageing. The injection molded samples were exposed to thermo-oxidative ageing and then processed again.

EXPERIMENTAL

A Terralene WF 3516 compound containing bio-based HDPE compounded with about 10 wt % soft wood fibers was obtained from FKuR Kunstoff GmbH, Germany. HDPE is a copolymer between ethylene and 1-butene, and it has a narrow molar mass distribution polymer. The HDPE is considered to be bio-based, as the ethylene is of biomass origin. Xylene (mixture of isomers) was obtained from Scharlau.
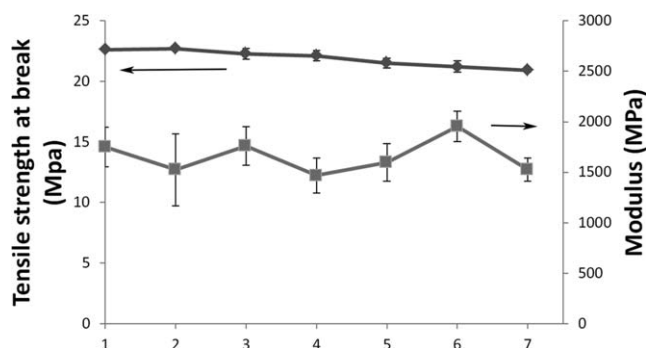
Figure 1. Tensile strength at break and the modulus as a function of injection moulding cycles. The error bars show plus minus one standard deviation.

Figure 3. Fiber length distribution of the virgin material (#0) and after seven cycles (#7).

Dumbbell shaped test bodies, 150-mm long, were injection moulded on an Arburg 221M injection moulding machine. The melt temperature was 180 °C, and the mould temperature was 50 °C. Samples were removed for characterization after each injection moulding, while the rest of the samples were ground with a cutting mill (Retch, SM 100), dried and injection moulded again. The compound was dried at 70 °C for 4 h according to the supplier's specification prior to processing.

Ageing

The injection moulded test bodies were aged by accelerated thermo-oxidative ageing for 120 h at 100 °C in an oven with an atmosphere of air. After ageing, the samples were ground and injection moulded again. The aged samples were denoted with an "A" followed by the cycle number. For example, "A#2" means that the virgin material was first injection moulded, then aged and finally injection moulded again.

Characterization

All test bodies were conditioned in a climate chamber at 23 °C, 50% relative humidity for 72 h before the mechanical tests. Tensile tests were done according to ISO 527 using a tensile tester (H10K, from Tinius Olsen). A minimum of five test specimens was evaluated for each quality. The tensile strength was evaluated at 50 mm min^{-1}, and the modulus was measured at 1 mm min^{-1}. The flexural properties were characterized according to ISO 14125, using a test speed of 10 mm min^{-1} and a span length of 64 mm. The Charpy impact strength was deter-
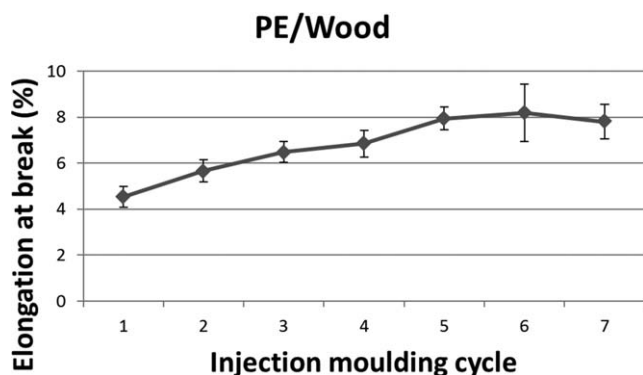
mined according to ISO 179 using a Resil impactor from Ceast. Samples were tested unnotched, edge wise using a 4 J pendulum.

Characterization of the thermal properties was done after each processing step. Dynamic scans were done on a differential scanning calorimeter (DSC, Q2000, TA Instruments, DE) at a heating rate of 10 °C min^{-1} in an atmosphere of nitrogen. The data were recorded from the second heating. The crystallinity was calculated as:

$$\% \text{ Crystallinity} = \Delta H / \Delta H_m \times 100 / W$$

where ΔH is the heat of fusion for the sample, ΔH_m is heat of fusion for 100% crystal polymer and W is the percentage of the polymer in the sample.[16] The ΔH_m was taken from the literature as 293 J g^{-1} for PE.[17] The thermal properties were also characterized by a thermogravimetric analyser (TGA, Q500, TA Instruments, DE). Each sample, about 30 mg, was heated in an atmosphere of nitrogen at a heating rate of 5 °C min^{-1}. Each sample was also characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet iS10, Thermo Fischer Scientific) equipped with an attenuated total reflectance unit (ATR). Spectra were recorded from 525 to 4000 cm^{-1}.

The specific gravity was determined according to the Archimedes method as described by ASTM D792. Samples were first
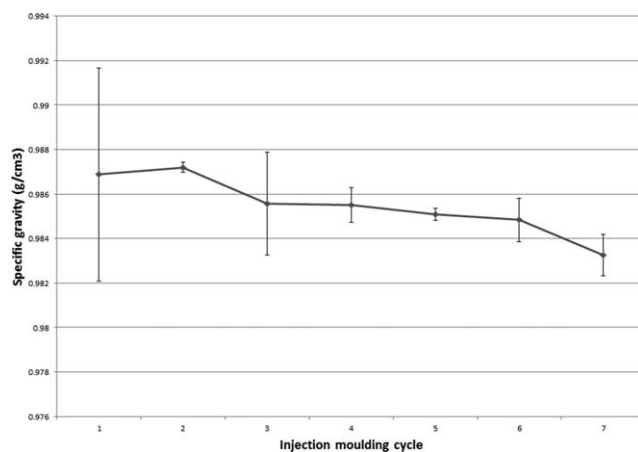

Figure 2. Tensile elongation at break as a function of injection moulding cycles.

Figure 4. Specific gravity as a function of injection moulding cycles.

Table I. Flexural and Impact Properties

Cycle	Flexural strength at max (MPa)	Flexural modulus (GPa)	Flexural elongation (%)	Charpy impact strength (kJ m^{-2})
1	30.3 (0.6)	1.5 (0.02)	5.8 (0.7)	17.6 (2.4)
2	30.9 (0.25)	1.5 (0.02)	5.5 (0.7)	17.8 (2.3)
3	30.1 (0.19)	1.5 (0.04)	6.0 (0.1)	18.7 (2.0)
4	29.7 (0.18)	1.5 (0.02)	6.0 (0.08)	19.5 (2.3)
5	29.8 (0.16)	1.4 (0.03)	6.1 (0.1)	18.8 (2.5)
6	29.8 (0.04)	1.4 (0.03)	5.8 (0.6)	17.1 (2.6)
7	28.5 (0.22)	1.4 (0.04)	6.2 (0.1)	19.5 (2.6)

Standard deviation is given within brackets.

weighed in air and then in ethanol. The specific gravity was calculated according to the standard.

The viscoelastic properties were characterized by dynamic mechanical thermal analysis (DMTA) using a DMA Q800 from TA Instruments. Specimens were measured in single cantilever mode and were heated from $-130\,°C$ to $130\,°C$ using a frequency of 1 Hz and amplitude of 15 μm.

The chemical degradation of the HDPE was analyzed by ^{13}C NMR spectroscopy. About 10–15 wt % solutions of the samples were made in 1,2,4-trichlorobenzene/benzene-d_6 at $120\,°C$. The ^{13}C NMR spectra of the samples were recorded on a Bruker Avance 400MHz spectrometer at $120\,°C$ using a BBO-5 mm-Zgrad probe. The spectra were acquired with NOE using a 45° excitation pulse, 2000 transients and a total recycle time (acquisition time plus delay time) of 3.6 s. Although the NMR spectra were not run under strictly quantitative conditions, the results from each sample should be good enough for comparison purposes. This was the main aim of these experiments.

The fiber lengths were characterized by dissolving the composite material in xylene. About 2 g, cut from the middle part of the dog bone shaped test bodies, were heated at reflux for about 16 h. The remaining fibers were filtered off and dried. The fiber lengths were measured in a stereo microscope (Nikon SMZ800) by spreading the fibers on a glass plate. About 500 fibers of each sample were measured.

RESULTS

The mechanical recycling of HDPE composites was studied by repeated injection moulding. The tensile properties are shown in Figures 1 and 2. There is a very small but continuous
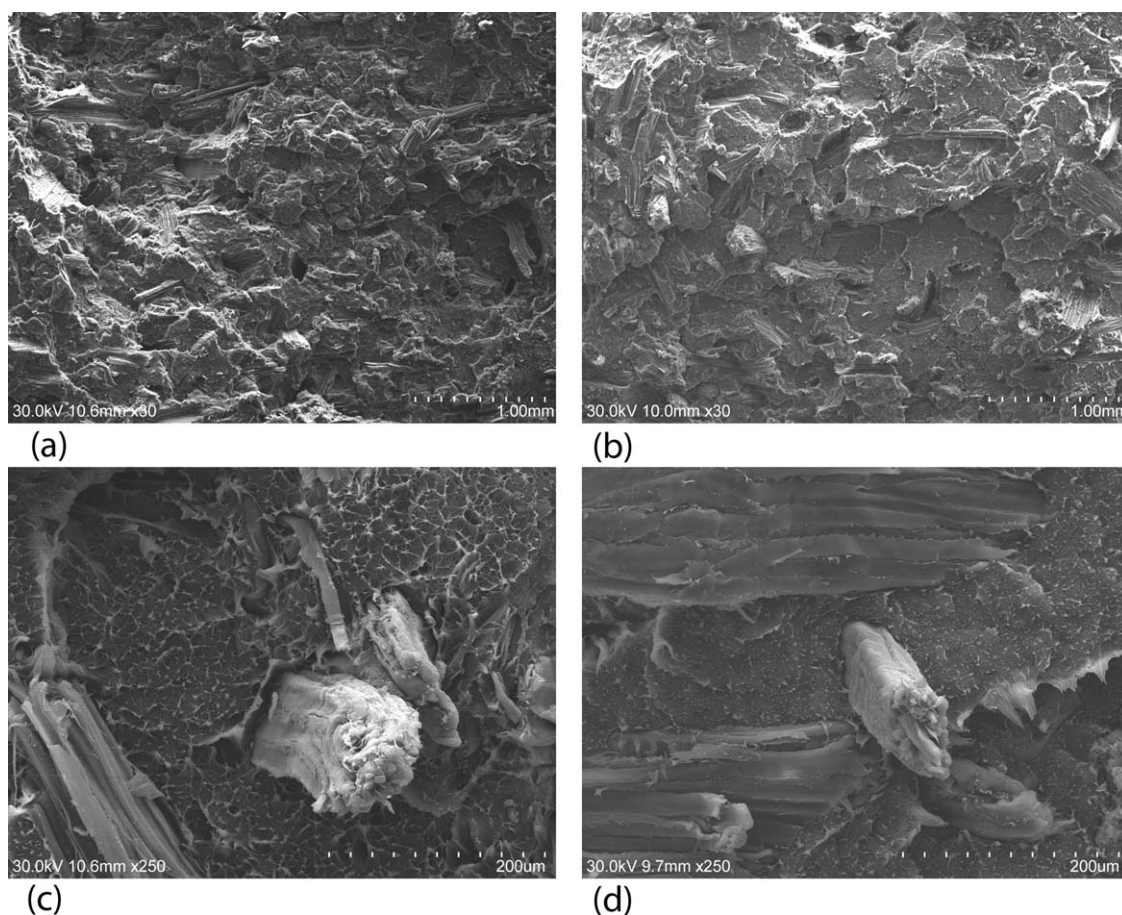

Figure 5. SEM micrographs of: (a) PE #1 at low magnification, (b) PE #7 at low magnification, (c) PE #1 at high magnification and (d) PE #7 at high magnification.

Table II. Thermal Properties of the PE Wood Fiber Composites

	DSC		
Sample	ΔH_m (J g^{-1})	Crystallinity (%)	T_m (°C)
PE #1	171.8 (2.3)	65.1 (0.9)	131.0 (0.4)
PE #4	172.9 (5.6)	65.6 (2.1)	130.8 (0.08)
PE #7	175.5 (3.7)	66.5 (1.4)	130.4 (0.24)
PE A#4	177.6 (0.85)	67.3 (0.32)	130.4 (0.06)

Standard deviation is given within brackets.

reduction of the tensile strength; after seven cycles, the tensile strength dropped from about 23 to 21 MPa. This could possibly indicate that some degradation occurred, but the decrease in tensile strength is relatively small. The modulus is also shown in Figure 1 and there is no significant change. There is however a very clear trend for the elongation at break, as seen in Figure 2. It increased from about 4.5% up to 7.8% after the 7th cycle. Neat HDPE has previously been characterized by Mendes et al.[18] In that study, it was observed that the elongation, on the contrary, decreased with increased number of injection moulding cycles. This was interpreted as an increase of cross-links with increasing number of processing cycles. Thus, the material became more brittle with lower elongation. Bourmaud and Baley studied reprocessing neat polypropylene (PP) as well as PP reinforced with sisal fibers.[19] It was observed that the neat PP showed a decreased elongation with increasing number of processing cycles. However, when the sisal fiber was present, the behavior was the opposite, with increasing elongation. It was suggested that the increase elongation was caused by the decreased fiber lengths. A similar result was obtained by Bakkal et al. who reinforced low density PE with fibers from waste cotton fabrics.[20] PE is a ductile polymer, but when a fiber is present in the matrix, the material behaves differently. Adding the wood fiber will make the resin more brittle with lower elongation.[10,21] As the composites are processed repeatedly, the fiber length is reduced and it gradually loses its reinforcing effect, with increased elongation as a result. The fiber lengths were measured by dissolving the polymer matrix and by measuring the fiber length by optical microscopy. The fiber length distribu-
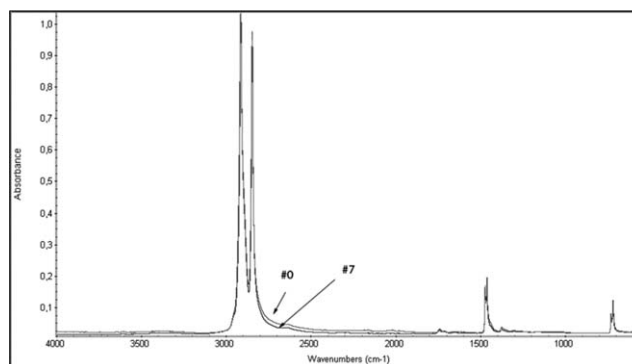

Figure 7. FTIR spectra of the virgin material (#0) and after seven cycles of injection moulding (#7).

tions for the virgin material (#0) and for the 7th cycle are shown in Figure 3. It is clear that the fiber length has been reduced. After seven cycles, the average fiber length was 50 μm, which should be compared to the virgin material with an average fiber length of 140 μm. Thus, it is possible that the increased elongation observed in this study is related to the reduced length of the reinforcement.

The specific gravity was measured after each cycle, and the results are shown in Figure 4. There is a trend toward lower specific gravity as the number of processing steps increase. Mendes et al. studied repeated injection moulding of HDPE and measured the density after each step.[18] A slight reduction of the density was found in that study. It was suggested that the decrease in density was caused by a decrease in crystallinity. The change in specific gravity in this study is rather small, however. Comparing the virgin material with the material after the last injection moulding cycle, the specific gravity changed from 0.987 to 0.983 g cm^{-3}, which can be considered as negligible.

The flexural strength of the PE wood fiber composites follows the same pattern as tensile strength. It dropped from about 30 to 28 MPa, see Table I. Similarly, the flexural modulus and elongation at max are almost unaffected by the reprocessing. The modulus decreased from about 1.5–1.4 GPa. Sarabi et al. examined the flexural strength of wood fiber reinforced HDPE using multiple extrusion. The materials were reprocessed three times with filler
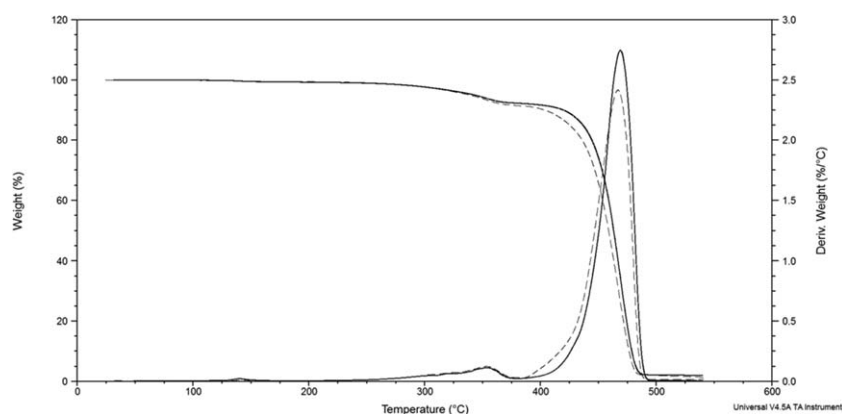

Figure 6. Thermogravimetric analysis of sample #0 (solid line) and sample #7 (dashed line).
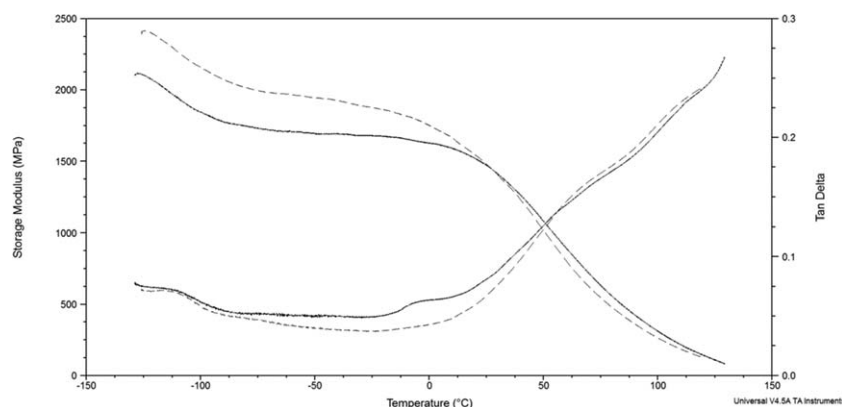
Figure 8. Characterization of sample #1 (solid line) and sample #7 with DMTA.

loading from 50 to 70 wt %. After the last cycle, the flexural strength of the composites showed a relatively modest decrease.[22]

The impact strength is an important material property. It has been shown that adding wood flour to a polymer matrix can decrease the impact properties and that the impact properties can be lowered by an increasing level of wood flour.[21,22] The Charpy impact properties of PE wood fiber composites are also shown in Table I. After processing the material in seven cycles, there was no significant difference between the first and the seventh cycle. Impact strength of low density polyethylene reinforced with an end-of-life cotton fabric has previously been evaluated.[20] After reprocessing the material six times, the polymer reinforced with 12.5 wt % cotton fiber showed a slight decrease in Charpy impact strength. The impact strength of polypropylene reinforced with wood flour was studied by Beg et al., and they found that for the PP composite with 40 wt %

wood flour, the Charpy impact strength was reduced from 10.5 to 6.2 kJ m^{-2}.[16]

SEM micrographs for the PE composites are shown in Figure 5, and fiber bundles covered with polymer can be identified. However, splits between the fiber bundles and the polymer matrix can also be seen, indicating that the adhesion is not perfect. When examining the micrographs at the highest studied magnification, there is not a very large difference in the appearance of the tensile fracture between #1 and #7.

Thermal Properties and FTIR

The result of the DSC characterization is shown in Table II. There was a very small increase in the crystallinity. This can be interpreted as a minor degradation of the polymer matrix. When the length of the polymer chains is reduced, the crystallization of the polymer is enhanced.[16,23] However, the increase in crystallinity is very small (65.1–66.5%) and not significant. The recycling of neat HDPE from containers was previously done by Loultcheva et al.[2] After five times of reprocessing on a twin screw extruder, the melt enthalpy increased from 203 to 216 J g^{-1}.

The peak temperature of the melting was also recorded. A slight decrease in the peak temperature was recorded (from 131.0 to 130.4 °C). This could possibly be a sign of a slight degradation.[16] However, the change in peak temperature is not very significant. The relatively small changes in crystallinity in this study further show that there is either a very small degradation or no degradation of the polymer, which is reflected by both the mechanical and thermal properties.

The samples were also characterized with TGA, and the results are shown in Figure 6. The composite material is roughly stable up to 300 °C, and maximum weight loss rate occurs at about 468 °C. There is a small difference between the curves where #7 degrades at somewhat lower temperatures. The difference is not very significant, however.

FTIR can be used to monitor the reprocessing of thermoplastics as changes in the chemical structure. Oxidation of PE can be observed as changes in the carbonyl peak area at about 1720 cm^{-1}.[24,25] Peaks have also been observed at 1120 cm^{-1} corresponding to stretching of C—O—C.[6] The FTIR spectra after one and seven cycles of processing are shown in Figure 7.

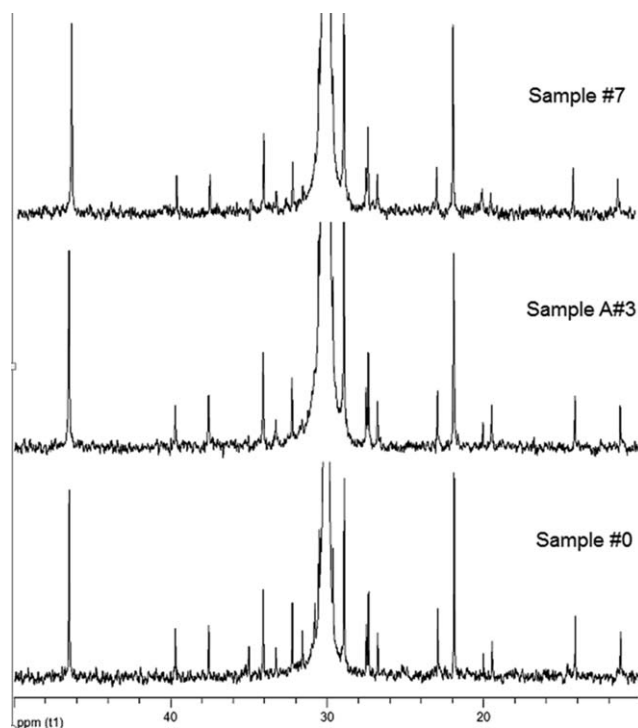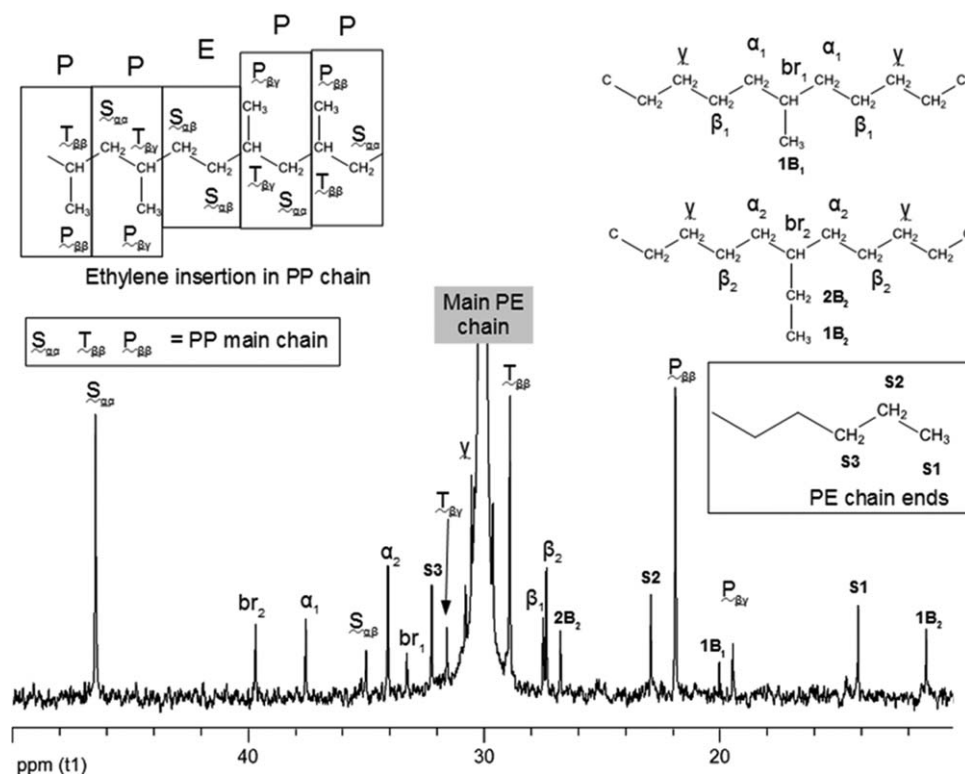**Figure 9.** ^{13}C NMR spectra of samples #7, A#3, and #0.

Figure 10. Assignments of the peaks in the ^{13}C NMR spectra.

The two spectra are very similar. There is no peak at 1720 or at 1120 cm^{-1}. Thus, there is no indication of oxidation.

The influence of multiple processing on the dynamic-mechanical properties of the HDPE composites was investigated using DMTA tests. The storage modulus and the tan delta are shown in Figure 8. Samples were heated from −130 °C to 130 °C. HDPE has a transition (γ-relaxation) in the region −150 °C to −120 °C, and it is related to short range molecular motion in the amorphous region.[26] Under the experiment conditions in this study, the γ-relaxation can barely be seen. The storage modulus drops from over 2 GPa down to 1.3 GPa at room temperature. At room temperature, there is no significant difference between #1 and #7. At lower temperatures, sample #7 had somewhat higher storage modulus than sample #1. The peak of the loss modulus was recorded, and there was a small difference for samples #1 and #7. For sample #1, the peak of the loss modulus occurred at 48.6 °C and for #7 at 52.1 °C.

^{13}C NMR Spectroscopy

After the samples had been dissolved in the solvent for NMR, it was noted that there was some brownish residue present at the bottom of the NMR tube. Although the amount of this residue was not quantified, it appeared that this was present to a lesser degree in the treated samples. This residue was presumably due to residual wood fibers left in the sample after the xylene extraction.

Figure 9 shows a comparison of the ^{13}C NMR spectra of the three samples over the area 10–50 ppm. No other signals (except solvent peaks) were detected outside this area. The assignments of the peaks within this area are shown in Figure 10. The samples mainly contain polyethylene (PE) with some methyl and ethyl side chains. There is also a small amount of
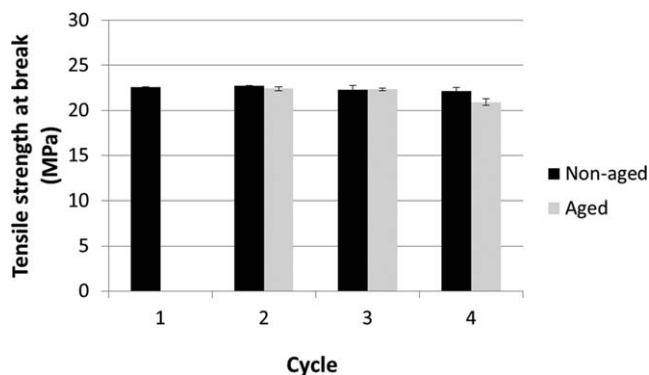
Table III. Summary of the ^{13}C NMR Characterization

	Sample		
	#0	A#3	#7
wt % PE	96.9	97.0	96.7
wt % PP	3.1	3.0	3.3
M_w PE	10,059	13,889	13,284
Methyl/1000C	1.1	1.1	1.0
Ethyl/1000C	1.9	1.9	2.1

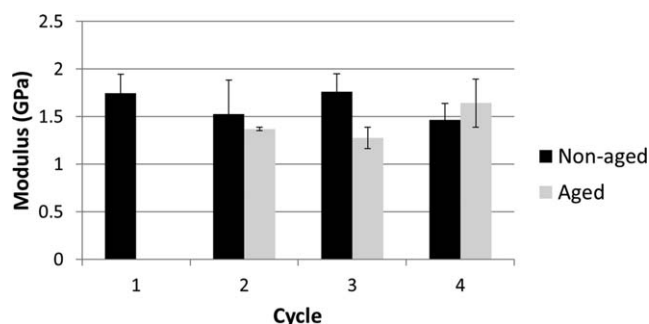**Figure 11.** Tensile strength of nonaged samples and of aged samples.

Figure 12. Tensile modulus of nonaged samples and of aged samples.

polypropylene (PP) present, which appears to have some units of ethylene incorporated into the PP chain. PP may come from a coupling agent that has been used to improve the adhesion between the wood fibers and the polymer matrix. Maleic anhydride grafted polyolefins are commonly used for wood fiber composites. There is, however, no proof of maleic anhydride in the spectrum. It is possible that maleic anhydride groups are not seen under the experimental conditions. The supplier of the HDPE used has not disclosed if there is a PP-based coupling agent in the material.

The amounts of PE and PP were calculated from the peak areas, as well as the density of side branches in the PE chain. From the end groups peaks (S1–S3 in Figure 10), an approximate value of the number average molecular weight can be calculated. These results are shown in Table III.

The levels of the methyl and ethyl side branches on the PE, as well as the level of polypropylene present were the same in all samples, within experimental error. There is some evidence of a higher molecular weight for the treated samples. Because the signal to noise ratio for the end groups is not very high in the NMR spectra, it is uncertain if this is a real effect. If it is real, it might be due to the fact that more of the high molecular weight fraction is being extracted by the xylene from samples that have undergone treatment. Because it also appeared that the amount of wood fibers left in the xylene extracted samples that had been treated was less (less residue in the NMR tube for those samples), this may be evidence that the treatment causes the higher molecular weight polymer material to be released from the wood fibers more easily.

Accelerated Ageing

Repeated processing simulates preconsumer recycling or process waste recycling but does not take the usage of the product into account. When the product is being used, the polymer can be degraded by heat, humidity, UV-light and by oxidation. Polyethylene is generally considered to be sensitive to oxidation, and several authors have therefore studied thermo-oxidative ageing of polyethylene.[27–29] To also simulate post-consumer use under indoor conditions, the composite material was subjected to repeated processing cycles, combined with thermo-oxidative ageing. Combining multiple processing and ageing have previously been used to study the recycling of neat PP[30] and neat PE.[3]

The tensile test results for the aged HDPE composites are compared to the results of the non-aged samples in Figures 11–13. After four cycles, there was very little difference between the samples. There was only a small difference in the tensile strength (22.4–21.3 MPa) after three cycles of ageing. Also, the elongation at break and the tensile modulus were relatively unaffected by the ageing. The aged samples were also characterized by DSC. There was no significant difference between the aged and the nonaged samples. The crystallinity of the aged sample (A#4) after four cycles was 67.3%, which should be compared to the nonaged sample (#4) that had a crystallinity of 65.5%. The aged samples were further characterized by FTIR. The spectra of the aged samples did not differ from the spectra in Figure 7 and are not shown.

Accelerated thermo-oxidative ageing is a common method to evaluate the lifetime of a product. As a general rule of thumb for many reactions, the reaction rate doubles for every 10 °C increase in temperature.[31–33] Thus, with a room temperature of 20 °C, an ageing temperature of 100 °C and an ageing time of 120 h, ageing would correspond to about 3.5 years. This must of course only be seen as a rough estimation. Thus, after the fourth cycle, the materials have been processed four times and have been aged for a total time corresponding to about 10 years use time at room temperature. The ageing test demonstrates that the wood fiber reinforced PE is relatively stable to accelerated thermo-oxidative degradation and can be recycled quite well. It should however be mentioned that there have been no studies regarding the long-term usage of these composites in humid environments.

CONCLUSIONS

The recycling of wood fiber reinforced HDPE was studied. Both preconsumer recycling with multiple injection moulding cycles as well as simulated postconsumer recycling with multiple injection moulding cycles combined with accelerated ageing tests were done. After processing the material seven times, the reduction of the tensile strength was modest (6%). Thermal properties and the change in chemical structure monitored by FTIR were also monitored, and these did not reveal any significant degradation. However, the tensile elongation at break clearly increased with increased number of processing cycles, which was shown to be due to decreasing wood fiber length. Tests show that under the chosen test conditions, the wood fiber reinforced PE can be recycled relatively well. The study of post-
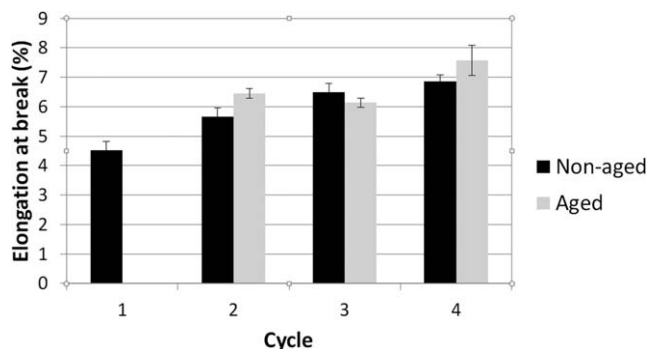

Figure 13. Tensile elongation at break for nonaged samples as well as aged samples.

consumer recycling corresponds roughly to 10 years of usage and four times of mechanical reprocessing. The composites were relatively unaffected by the accelerated ageing. It can, thus, be concluded that recycling of both the aged and the nonaged HDPE wood flour composites can be done without deteriorating the end-use properties too much, except possibly the tensile strength.

ACKNOWLEDGMENTS

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