

Influence of molecular structure and reinforcement on fatigue behavior of tough polypropylene materials

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ABSTRACT: Molecular structure and reinforcement heavily influence the crack growth resistance of polypropylene materials. Aim of this study is to investigate the fatigue behavior of different unreinforced and reinforced tough polypropylene materials used for piping applications. Due to high resistance against crack growth, these materials cannot be tested in the application relevant quasi-brittle failure mode within feasible amounts of time. In this work, the new cyclic cracked round bar test, developed for tough polyethylene materials, has been examined as a possible method to characterize this important type of failure mode in homo-, random-, and reinforced polypropylene. Even though molecular mass distribution, which is often used to explain differences in crack growth resistance of polymers, was similar for unreinforced materials, fatigue lifetimes differed greatly. The mismatch of molecular mass and fatigue lifetime was mainly attributed to the different buildup and morphology of the base polymer. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43948.

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INTRODUCTION

Polypropylene (PP) is a widely spread polymeric material. The PP materials examined in this study are used for piping. Due to performance requirements, these materials are optimized toward high crack resistance. To assure safety and high application times, it is necessary to characterize the crack growth behavior and compare materials with regard to failure behavior in the quasi-brittle failure regime, which is the most important of failure modes for pipes in application. With modern PP grades, especially those optimized for pressurized applications, the quasi-brittle failure cannot be reached within even several thousand hours of testing using established test methods. According to EN ISO 15874-2,¹ which regulates testing of long-term properties of pipes made from PP, polypropylene random-copolymer (PP-R) and polypropylene-homo-polymers (PP-H) are expected to show no quasi-brittle fracture below 50 °C for over 100 years under static loading conditions. Therefore, pipes are usually tested at even higher temperatures (up to 110 °C for PP) or higher stress levels. This either leads to changes in the material due to testing temperatures above the melting onset or large scale plastic failure due to high stress. To characterize the desired mode of failure, which is quasi-brittle failure, within

feasible amounts of time different and faster methods are required.

So far, different PP types and blends have mostly been compared in regard to fracture properties (e.g., toughness) via elastic–plastic (e.g., Refs. 2–4), postyield fracture mechanics like essential work of fracture (e.g., Refs. 5–8) or at high velocities and/or low temperatures (e.g., Refs. 3,9–11), which again does not necessarily coincide with application conditions (around room temperature and up to 80 °C) or mode of failure (quasi-brittle slow crack growth) in actual pipe applications.

Another possibility to accelerate testing is the use of fatigue loads instead of static. This approach has shown promising results as a fast tool for ranking polyethylene (PE) and other materials^{12–16} with regard to crack growth resistance. Even though the loading situation is different in fatigue compared to a static test, authors have thoroughly shown that damage mechanisms of both are comparable for PE.^{17,18} There is also the possibility to use different testing parameters during fatigue testing (ratio of minimum to maximum load—“*R*”) for the same material and extrapolate to the static case, if failure occurs in quasi-brittle failure mode.^{19–21} If this procedure is performed, it offers the possibility to characterize a material under similar

Table I. Description of Used Materials^{27–29}

Material	Application	Young's modulus, 23 °C (MPa)	Yield stress, 23 °C (MPa)	Density, 23 °C (kg/m ³)	MFR 230 °C/ 2.16 kg (g/10 min)
PP-B	Nonpressure pipes	1300	28	900	0.30
PP-H	Nonpressure pipes	1650	36	905	0.30
PP-R	Pressure pipes	900	25	905	0.25
PP-B & Talcum (50 wt %)	Nonpressure pipes	3970	28	1320	<0.20
PP-B & Wollastonite (20 wt %)	Nonpressure pipes	2560	31	1070	<0.20

conditions as in real application (static loading and similar temperature), still within more feasible amounts of time. However, PE pipe materials are usually only tested under $R = 0.1$ for faster results (compare ISO 18489¹²).

First testing results on a pure PP pipe material also demonstrate the potential of fatigue-induced loading using cracked round bar (CRB) specimens for PP.¹⁵ Additionally, mineral reinforced PP materials are usually not used for pressure applications, but sewer, storm-water, and drainages. Due to lack of high internal pressure as a main crack driving force, soil and traffic loads are mainly responsible for stress in these pipes. Two years after installment the soil around the pipe usually carries most of the constant soil load, reducing the acting stress in pipes significantly.²² However, traffic loads are not compensated by the load bearing capacity of the settled soil and still act on the pipe. According to pipe standards (e.g., Ref. 23), the ratio of soil and traffic load to pure soil load are usually in the range of 10:1, corresponding well with the R -ratio of the cyclic CRB test.

Fatigue behavior of PP, similar to most polymers, can be mainly divided into two different stages.^{24–26} At high stress levels and frequencies, specimens fracture due to high loads within very short testing times. This can mainly be attributed to either hysteretic heating or too high applied stress levels close to or even above the yielding point of the material. At reduced stress and frequency, the failure mode changes to the second region, the so called quasi-brittle failure mode. In this mode failure times are significantly longer. The mode changes from either large scale deformation due to yielding, thermally dominated failure or unstable crack growth to a failure mode, where lifetime of the material is associated with the nucleation and growth of flaws.²⁴

Using the methods chosen in this work, it was possible to estimate the resistance against crack growth of different reinforced and unreinforced PP types in different fatigue failure modes. However, especially for PP-R it is necessary to use additional methods, such as compliance or hysteresis analysis, to evaluate transition between failure modes. Especially differences in morphology and constitution of the polymer were found to vastly influence fatigue lifetime.

EXPERIMENTAL

The materials used for experiments including fields of application are listed in Table I. Material data were taken from data sheets^{27–29} or from experiments. For comparison, data from

polypropylene block-co-polymer (PP-B) of a former study was added.

Similar to previous work¹⁵ dynamic-mechanical analysis (DMA) measurements have been performed before fatigue testing, to examine material behavior at elevated testing temperature and frequencies. Measurements (tensile mode, displacement 2 μm , frequencies 1–20 Hz, $\Delta T/\Delta t = 1 \text{ K min}^{-1}$) have been performed on a Mettler DMA/SDTA861 40N (Mettler-Toledo GmbH, Schwerzenbach, CH). Storage- (E') and loss-modulus (E'') and dampening behavior [$\tan(\delta)$] have been evaluated. For comparison of the melting behavior of the unreinforced materials differential scanning calorimetry (DSC) analysis has been used ($\Delta T/\Delta t = 10 \text{ K min}^{-1}$, N_2 50 mL min^{-1} 25–200 °C). Experiments were performed on a DSC 1 (Mettler-Toledo GmbH, Schwerzenbach, CH). The molecular mass distribution of the tested unreinforced PP materials has been measured using size exclusion chromatography. The measurements were performed after a dissolution time of 150 min with a column temperature of 160 °C and an analysis time of 35–40 min. To evaluate the formation of crystal lattices, X-ray scattering techniques (small and wide angle SAXS, WAXS) were used with a 0.154 nm beam in transmission (NanoSTAR, Bruker, Karlsruhe, GER).

Fatigue tests were performed according to ISO 18489¹² with slight variations (testing temperature 23 & 80 °C, frequency 5 Hz, and load levels between 9 and 16 MPa depending on material and applied temperature). Fatigue tests of pure PP-H and PP-R have been performed on an ElectroForce 3450 (Bose Corporation, Eden Prairie, MN) and a 15 kN MTS 858 TableTop system (MTS, Eden Prairie, MN). The diameter of the cylindrical specimens was 15 mm and the initial notch depth 10% of diameter. The tests were performed with a loading ratio (applied minimum to maximum load: $R = F_{\text{min}}/F_{\text{max}}$) of 0.1. Due to the higher compliance at 80 °C, especially for PP-R, it was possible to observe the shape of notch and crack tip of the specimens via travelling microscope. The specimen compliance was evaluated as the ratio of difference between maximum and minimum piston movement and maximum and minimum applied load ($\Delta C = \Delta \text{disp.}/\Delta F$). Afterward data were normalized using the initial value to show the load dependent development more clearly. For more information on the failure behavior of tested materials, fracture surfaces of CRB specimens have been examined via scanning electron microscope (SEM—DSM 962, Carl Zeiss, Oberkochen, GER).

Figure 1. Examination of dynamic-mechanical properties of all tested materials (PP-B, PP-H, PP-R, PP-B + Talcum, and PP-B + Wollastonite) in the range of -25 to 150 °C and a frequency of 5 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Before fatigue testing DMA was performed to determine the behavior at the actual testing temperature (compare Figure 1). Storage modulus E' at the target testing temperature is around 700 MPa for PP-H, 500 MPa for PP-B, and 250 MPa for PP-R. Damping behavior of PP-H and PP-B are rather similar at 80 °C, whereas PP-R has a slightly higher level. It can also be seen, that at 80 °C and above, properties change more significantly for PP-R, compared to the other two materials, which can be explained by the earlier onset of melting, as confirmed via DSC. Glass transition peak-temperature of PP-H and PP-B are around 5–10 °C, and -5 to 0 °C for PP-R. In line with expectations, reinforced materials storage and loss modulus are higher, compared to the unfilled materials. Due to the high content of mineral reinforcement, PP-talcum has a comparable high modulus for PP. Around 23 °C it is around 4000 MPa and drops to roughly 2000 MPa at 80 °C. Wollastonite reinforced PP starts with around 2800 MPa at 23 °C and drops to 1200 MPa at 80 °C. Glass transition peak-temperature is around 10 °C for both materials.

Both PP-H and PP-B show similar melting peak temperatures between 165 and 170 °C. However, PP-B additionally shows the expected second peak of the PE-copolymer material around 120 °C. The melting peak temperature of PP-R is lower compared to the other two materials, around 145 °C. This could be explained by the formation of γ -modification, which is reported to affect the equilibrium melting temperature of PP-R due to changes of the specific enthalpy and/or entropy of melting.³⁰ The shape of the melting peak of PP-R is also not as sharp and pronounced, as shown in Figure 2.

In Figure 3(a) comparison of PP-B, PP-H, and PP-R microtome slices is shown. Slices of 20 μm were taken from the middle of untested fatigue samples. Morphology was investigated using

polarized light microscopy and a magnification of $\times 500$. The picture of PP-B shows dispersed black dots which are presumably the incorporated ethylene blocks. Similar formation of ethylene blocks was found in literature by Doshev *et al.*,³¹ who examined the morphology and phase separation of PP-ethylene co-polymers. Performing optical microscopy under similar conditions [isothermal cooling at 130 °C after melting, Figure 3(d)] yielded a practical identical appearance as in Ref. 31 for ethylene-propylene co-polymer. The second picture [Figure 3(b)] shows the morphology of PP-H. Expectedly it shows formation of spherulites, most likely in α -modification. Even though spherulites are not as pronounced as after isothermal cooling, several structures with sizes up to 40 μm can be found. The third picture [Figure 3(c)] shows the morphology of PP-R. According to literature, PP-R has a tendency to form γ -modification which hinders overall crystallization and decreases spherulitic growth speed.³² In combination with a higher amount of crystallization nuclei, this might explain the formation of a slightly different appearance, compared to PP-H. However, examination via X-ray scattering techniques (wide angle results shown in Figure 4) could not be used to confirm γ -formation. Usually the peaks of indices (111) γ and (117) γ are used to confirm γ -formation. However, close to these peaks there are also the peaks of (110) α and (111) α which can make it difficult to distinguish between both due to overlapping, especially if only small fractions of γ are present. Furthermore, different sizes of crystals can change the peak form and even a shift of peaks is possible due to, for example, residual stresses which induce strain in the lattice.³³ Interestingly, evaluation of SAXS data showed differences in long-period (l_c) of the polymers. Results showed a decrease of l_c by a factor of two when comparing PP-R to PP-H, which was also observed in literature³⁴ and would fit the decreased growth speed reported in Ref. 32. In Figure 5, the molecular mass distribution of the base materials is shown.

Figure 2. Differences in material melting properties of PP-B, PP-H, and PP-R in the first heating run, as shown via DSC measurements.

The materials were measured for a PP-equivalent. It was found, that PP-B has the lowest number average molar mass of the three examined materials, around 89,000, compared to 91,300 of PP-R and 111,000 of PP-H. However, the mass average molar mass was the highest around 605,000, compared to 538,000 of PP-R and 557,000 of PP-H. Therefore, PP-B shows the highest

dispersity of 6.8 (5.9 for PP-R and 5.0 for PP-H). However, the overall shape of the curves is quite comparable for all three materials. This means, even though molecular weight and distribution are somewhat similar, the different chemical structure leads to vastly different morphological appearance in the three materials.

Figure 3. Comparison of the morphology of PP-B (a), PP-H (b), and PP-R (c) at a magnification of 500 under polarized light. Samples taken as 20 μm slices from the middle of CRB specimens and morphology of PP-B under isothermal cooling at 130 $^{\circ}\text{C}$ after melting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Results of wide angle scattering for PP-B, PP-H, and PP-R at 23 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Results of fatigue tests on notched specimens are shown in Figure 6 for unreinforced materials at 80 °C and Figure 7 for the reinforced materials for 23 °C and 80 °C in a fully logarithmic plot of cycles to failure and applied nominal stress. PP-H was tested between 15.5 and 9.5 MPa. Between 15.5 and around 14 MPa the specimens fractured within 24 hours of testing. Fracture surfaces showed signs of unstable crack growth at the

highest load levels. Decreasing the applied load led to large-scale whitening on the surfaces and below 13 MPa, the failure mode changed, coinciding with a change in the slope of the diagram, similar to results found for PE-materials. To gain further information with regard to failure mechanisms in quasi-brittle failure mode, SEM analysis was performed. As shown in Figure 8, fracture surfaces showed signs of quasi-brittle crack

Figure 5. Molar mass distribution of PP-H, PP-R, and PP-B, measured for a PP-equivalent.

Figure 6. Fracture curves of the unreinforced materials PP-H, PP-R, and PP-B¹⁵ for different areas of fracture behavior.

growth in the form of very small ruptured fibrils close to the pre-notch. There was no macroscopically plastic deformation or large scale formation of fibrils. The area close to the razor-blade prenotch showed some warping of the plane of fracture and small areas of ruptured fibrillation (top right). The fibrillation occurred not as single strands but in packages of several branched strands. The warping, as well as the ruptured fibrils might be an indication of a failure due to formation and break-

down of multiple crazes and small scale yielding, as shown in Ref. 35 for impact testing of PP at moderate speed. The area right beside (bottom right) still shows some warping but no fibrillation, correlating well with the testing at higher testing speeds in Ref. 35. The final area of the tested specimen (bottom left) shows a mixture of smooth areas and out of plane fracture as found for unstable crack growth³⁵ at high testing speeds. This similarity of changing failure modes between impact and

Figure 7. Fracture curves of the reinforced materials PP-B & talcum and PP-blend & wollastonite at 23 and 80 °C with pure PP-B from Ref. 15 for comparison.

Figure 8. Fracture surface analysis of PP-H, tested at 80 °C and 12 MPa using SEM at a magnification of 1000×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fatigue tests might be explained by the fact, that specimens in load controlled fatigue tests also experience different strain rates, depending on load level and progression of the test. To further characterize crack initiation and propagation behavior of the material, microtome slices of the centre of stopped specimens have been investigated using an optical microscope. Results, as shown in Figures 9 and 10, yield interesting additional information. In Failure Mode I, PP-H shows formation of masses of small crazes in the area of stress concentration, as found in Ref. 24 for isotactic PP. However, crazes are not strictly limited to the direct vicinity of the crack tip. After several thousand cycles, and close to failure, crazes appear to have coalesced into bigger ones and also the neighboring morphology (e.g., shape of spherulites) has been changed due to large deformations. Failure Mode II shows a somewhat similar behavior in the beginning, but changes to a main craze in front of the crack tip with several small side-crazes, as the test progresses. Interestingly, the crack opening displacement, as seen in the microtome slices, appears to be decreasing during the test, before increasing again toward the end. This was also observed in specimen compliance, which is directly linked to crack opening. Found formation of side-crazes corresponds nicely with warpage and different fracture planes, as found in SEM fractographs (Figure 8).

Data of quasi-brittle failure for PP-B were taken from former work¹⁵ and added for comparison. The block copolymer shows a rather similar behavior to PP-H with regard to the slopes of the different areas in the diagram. However, load levels (7.5–12.5 MPa, change in failure mode around 11 MPa) and cycles

to failure are significantly different. Microtome slices of different test progression are also shown in Figures 9 and 10. Even though slopes of fracture curves are similar to PP-H, the underlying failure mechanism shows a different appearance. Instead of lots of dispersed crazes throughout the sample, here several crazes directly in front of the crack tip coalesce into a damage zone in failure mode I. At lower loads and after the knee in the fracture curve, deformation zones in front of the crack tip changes its appearance to more “classical” wedge-shaped zone, similar to PE materials in literature. However, the size of this wedge-shaped zone is much bigger, as usually found in PE-HD in the quasi-brittle failure mode (e.g., Ref. 36; 0.1–0.4 mm) and also large side-crazes are possible (Figure 10 at 100,000 cycles). Also different to PP-H, clear step-wise crack growth can be found in PP-B, as shown in the last picture of Figure 10, where a crack has already propagated. The fracture surface of PP-B in this failure mode, as shown in previous work,¹⁵ also shows large ruptured craze fibrils, which look quite similar to those of PE materials, but again in a larger size, corresponding to the larger wedge-shaped craze in front of a propagating crack.

PP-R was tested between 11.5 and 9.5 MPa. It can already be seen that the range of applied stresses is significantly smaller compared to PP-H and PP-B. Between 11.5 and 10 MPa PP-R fractured below $4 \cdot 10^4$ cycles, showing signs of unstable crack growth in the middle and stress whitening close to the pre notch. At 9.5 MPa applied maximum stress, the test lasted more than $9 \cdot 10^6$ cycles (≈ 21 days at 5 Hz). Besides the significant increase in cycles to failure, also the appearance of the fracture surface changed drastically at this load level. Whereas at higher

Figure 9. Failure Mode I: Formation of large scale plastic deformation in front of the crack tip of PP-B at 12.6 MPa, PP-H at 14.5 MPa, and PP-R at 9.8 MPa and 80 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10. Failure Mode II: Damage formation in front of the crack tip of PP-B at 6.5 MPa, PP-H at 10 MPa, and PP-R at 9.5 MPa and 80 °C after 10,000, 100,000, and 1,000,000 cycles of the test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11. Fracture surface analysis of PP-R, tested at 80 °C and 9.5 MPa using SEM at a magnification of 1000×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

load levels the fracture surface showed a combination of unstable crack growth and stress whitening, now almost the whole specimen shows a white appearance, except close to the pre-notch (compare Figure 11). Due to extensive testing times of several million cycles no further experiments were carried out below 9.5 MPa. A comparison of fracture surfaces is shown in Figure 12 to show described changes in failure mode. For further investigation microtome slices of a whole CRB specimen stopped after several thousand cycles and close to expected failure at 10 MPa (shown in Figure 9) and at 9.5 MPa (Figure 10) have been examined. At 10 MPa, PP-R showed formation of severe plastic deformation in front of the notch tip without actual crack growth after 1000 cycles. After 10,000 cycles, which is already quite close to final cycle numbers at this load level severe plastic deformation under an angle of 30–45° is additionally visible. Due to specimen failure shortly after this stage, it seems that no further large scale plastic deformation takes place before unstable crack propagation takes place. This coincides also with the fracture surfaces shown in Figure 6, where stress whitening is only visible close to the pre-notch and not in the centre of the specimen. At the lower stress level of 9.5 MPa, both fracture surface in Figure 6 and appearance in the microtome slices changes. Instead of a clear stretching of material in front of the crack tip, as shown in Figure 9, several longer zones of plastic deformation appear and coalesce into a large area of plastic deformation (Figure 10) as the test progresses. Comparing the size of the plastic zone of PP-R in Figure 10 with PP-H and PP-B can also give further insight into the longer cycles to failure in failure mode II. Whereas only small areas in front of

the crack tip are plastically deformed before fracture in PP-B and PP-H, the whole residual area inside the circumferential notch of PP-R is involved. Seeing that plastic deformation dissipates a lot of energy and the larger volume affected during fatigue testing, this could be an explanation of the significant longer testing times in failure mode II.

Figure 11 shows the fractographs of the PP-R specimen at 9.5 MPa, which is suspected to be in the transition area between failure mode I and II, due to the exorbitant long testing times, and different overall appearance. The area of different form can be seen quite clearly in the overview picture as a ring next to the initial pre-notch (dashed lines). In this area several different appearances of the fracture surface can be found. Nevertheless, traces of the formation and breakdown of fibrils due to fatigue damage are present, which cannot be found on all tests performed at stress levels above. The overall stress whitened appearance can be explained by the large scale plastic deformation as seen in Figure 10. Since PP-R could not be thoroughly tested in both failure modes, development of specimen compliance has been investigated as a possible additional method to pinpoint transition between failure mode I and II. In Figure 13, stress dependent development of compliance is shown for this material. For tests which failed in the first failure mode, normalized specimen compliance increased continuously over the whole test. The test performed at 9.5 MPa shows a different development of compliance as a function of cycle number. After a few thousand cycles, when the compliance of the test at 10 MPa and above continued to increase further which ultimately

Figure 12. Comparison of fracture surfaces for PP-H, PP-R, and PP-B at different stress levels.

Figure 13. Development of normalized specimen compliance of PP-R as a function of applied stress level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 14. Development of hysteresis in PP-H (a) and PP-R (b) as a function of applied stress level and cycle number.

lead to unstable crack propagation, it stagnated and even decreased later on. Toward the end of the test first indications of step-wise compliance increase could be detected. Observation of the crack tip using a travelling microscope during the test showed that the step in normalized compliance was accompanied with an increase in crack length. However, before another step could be formed, stress in the ligament area lead to final failure of the specimen. Nevertheless, this change in compliance behavior could be an indication of a change in the damage mechanism, for example, a transition of failure mode I to II.

To further investigate the fatigue behavior of PP-R and PP-H, hysteresis analysis has been performed. In Figure 14(a) the

development of the hysteresis is shown for tests in failure mode I and II. Interestingly, also this analysis shows a clear difference between the two stress levels for PP-R. Above 10 MPa the hysteresis changes in form and slope over the course of testing, indicating a fast damage progression and maybe even hysteretic heating.^{37,38} At 9.5 MPa, the hysteresis' slope and shape stay rather constant until failure. Only the typical shift towards higher strains due to creep were observed. The same trend was found for PP-H [Figure 14(b)], where compliance and hysteresis behavior changed around the transition area of fracture curves although differences were not as pronounced. Using this analysis a clear difference between PP-R and PP-H can be seen with

Figure 15. Fracture surface analysis of PP-B & talcum, tested at 23 °C and 13 MPa using SEM at a magnification of 1000×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

regard to the shape of hysteresis. Whereas PP-H shows rather narrow shapes, hystereses of PP-R are very broad, indicating a higher amount of dissipation.

Fatigue results of the reinforced materials at 23 and 80 °C are shown in Figure 7. Materials were tested at 80 °C as a compari-

son to the unreinforced materials and at 23 °C for an estimation of the fatigue behavior close to actual application temperature. At 23 °C PP & wollastonite and PP & talcum show similar slopes in the fully logarithmic plot. The material with almost 50% talcum reinforcement endures higher loads for similar

Figure 16. Fracture surface analysis of PP-blend & wollastonite, tested at 23 °C and 13 MPa using SEM at a magnification of 1000×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 17. Damage development in a talcum reinforced PP-B at 23 °C, $R = 0.1$ and 15 MPa.^{39,40} [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

failure cycles compared to the material with 20% wollastonite. At 80 °C the slopes of both materials change which can be explained by the influence of T_g , which is still present at 23 °C. Figures 15 and 16 show the fracture surface of the PP-blend with wollastonite and PP-B with talcum in three regions of the specimen. Close to the prenotch, there is formation and breakdown of fine fibrils, with wollastonite needles and talcum plates

in between. Adjacent is a region of transition, where signs of broken down fibrils are visible but they are stretched in packages, rather than single strands. Closer to the center, the wollastonite reinforced material shows a very smooth and brittle surface with signs of broken and pulled out needles. This failure behavior is very similar to unreinforced PP-B at 23 °C.¹⁵ Due to the high crack velocity and strain rates in the center of the

Figure 18. Comparison of all five tested materials at 80 °C in quasi-brittle failure mode.

specimen toward the end of the test, talcum plates and material around them have no time for rearrangement or deformation before fracture. Therefore, the material shows a rock-like fracture surface with a rather brittle failure of PP matrix material and talcum sticking out of the surface. Fracture surfaces of specimens tested at 80 °C showed the same different areas.

Analog to unreinforced materials, damage initiation and propagation has been investigated. Due to high reinforcement contents thin slices and polarized microscopy did not yield satisfactory results. Therefore polished samples have been investigated using reflected light microscopy. Results for a PP-B type with talcum reinforcement^{39,40} are shown in Figure 17 as a function of crack opening displacement. Similar to unreinforced PP-B, areas of crazing in front of the crack tip can be observed early on. During the fatigue test, this area vastly increases in length, until it has propagated almost through the entire specimen. Contrary to unreinforced PP-B, where propagation of an open physical crack can be observed, even at the last picture (around 3.10^6 cycles) directly before fracture of the material, no open crack propagation was found. This was also affirmed by examination of 20 μm thin slices, which showed no physical open crack under light tension. Even after severe fatigue damage in the material and increase in specimen compliance the residual specimen is apparently still too stiff to actually tear both sides apart. This is also indicated by the crack opening displacement values at failure. Where unreinforced materials are usually around 0.3 mm, reinforced materials are in the range of 0.03 mm.

For comparison, all tested PP types are shown in Figure 18 at 80 °C. It can be seen, that reinforcement with minerals tilts fracture curves toward a shallower slope. For low stress applications this can lead to an improvement of long-term performance of the materials. However, at high stress applications, such as pressurized pipes, where applied stress is closer to the transition between failure modes, unreinforced materials show preferable properties.

CONCLUSIONS

Thermal, thermomechanic, and chromatographic methods were used to show differences between examined PP materials. Molecular mass distribution of the unreinforced materials showed a rather similar curve for all three materials. Analysis via WAXS also showed typical peaks of α -formation for all three materials. Nevertheless, appearance in polarized transmission microscopy revealed different morphological appearances, especially with regard to size and shape of spherulites, which can mainly be attributed to the irregularities in the main chain due to copolymerization with PE. Even though molecular weight distribution is very similar for all the materials, these differences in morphology maybe one of the main reasons for vastly different results in fatigue testing.

Similar to PE-HD pipe materials, unreinforced PP materials showed two different areas of failure. These areas are often referred to as ductile and quasi-brittle failure regime for PE-HD pipe materials.^{41,42} However, the definition of the first failure mode is not quite fitting for the tested PP-H and PP-R materi-

als in fatigue, seeing that this region seems to be dominated by unstable crack propagation accompanied with very smooth fracture surfaces. In contrast, PP-B¹⁵ shows behavior more similar to findings in PE-HD, which might be credited to the incorporated PE blocks in the main chain of the polymer. Better performance of PP-H compared to PP-B and PP-R in the first failure regime can mainly be attributed to differences in yield stress and crystallinity. In the second failure region PP-R shows a better performance below 10 MPa, compared to PP-H and PP-B. In this failure mode PP-B showed the lowest fatigue resistance. Incorporated PE blocks seem to weaken the material with regard to fatigue, compared to pure PP-H. Comparing fracture surfaces and microtome slices, PP-R appears to have a higher tendency toward formation of plastically deformed zones (stress whitened fracture surfaces, blunted crack tips, formation of large plastically deformed zones in microtome slices, etc.) than PP-H.

Plastic deformation usually dissipates a lot of energy, which might explain the better performance of PP-R in this failure mode. Observation of the crack tip via travelling microscope during the test also showed blunting of the notch tip which decreases local stress concentrations. Contrary to CRB tests on PE-HD no clear crack growth was observed for PP-H and PP-R until final failure of the specimen. It can be speculated, that the specimen failed due to formation and coalescence of crazes, as discussed in Ref. 24 and indicated by the damage formation in Figure 10. Interestingly, the changes in failure mode and appearance of fracture surfaces seem to correlate to trends found for impact tests on PP at different loading rates.³⁵ Tests at high stress levels and accompanied strain rates in fatigue showed a similar failure mode to tests at high speeds in impact tests, namely unstable crack growth with very smooth fracture surfaces. By decreasing the stress level in fatigue, or velocity in impact tests, warping of fracture surfaces can be found. This was explained in Ref. 35 by the formation and breakdown of multiple crazes, which also corresponds with the damage formation found for fatigue in this work. At the lowest applied stress levels, both PP-H and PP-R showed signs of quasi-brittle crack growth, which is accompanied by the formation of small torn fibrils on the fracture surface. While this failure regime could be tested for PP-H fairly easy, evaluation of PP-R requires additional methods due to otherwise extensive testing times. Hysteresis and compliance analysis was found to deliver additional insights into material behavior during fatigue tests and can be used to assess transition between failure modes. Especially for PP-R, where the second failure mode could not be clearly established, these methods can be used to distinguish between failure modes. Whereas specimen compliance monotonically increases until failure in the first mode of failure, it shows signs of stagnation and even decrease in the second mode of failure. Analysis of hysteresis also showed the difference in dissipation between PP-H and PP-R, which corresponds to the formation and size of plastically deformed material during testing.

Additionally to the unreinforced materials, which already exhibited vastly different fatigue properties, also two reinforced materials were tested in the quasi-brittle failure regime. Due to their actual application temperature, and overall more brittle

behavior, both materials were tested not only at 80 °C but also at 23 °C. At both temperatures, the 50 wt % talcum reinforced material showed superior fatigue properties, compared to the wollastonite 20 wt % reinforced material. Fractographic analysis of failed specimens showed clear formation of fibrils between mineral reinforcement particles. This can be addressed to the matrix material of PP-B. When comparing to the pure PP-B, it can be seen, that the reinforcement changes the failure behavior significantly. Quasi-brittle failure shows a shallower slope, compared to the unreinforced material, which could be useful at low application stress levels.

As a conclusion, testing via cyclic CRB tests at elevated temperature appears to be a suitable method to determine resistance against crack growth for PP-H and reinforced PP materials. Both failure regions of interest can be reached within several hours of testing. Examination of quasi-brittle failure of PP-R is possible, albeit only in the first failure region, or with the downside of rather long testing times. Using other temperatures could provide remedy, although the thermo-mechanical changes have to be considered, due to the rather low melting temperature onset. As a next step, testing the applicability of lifetime estimation concepts, as developed for PE pipe materials,^{19–21,43,44} to the tested PP materials would be of high interest. It was also shown, that differences in morphology, caused by differences in the chemical composition of the main chain can heavily influence the fatigue resistance of PP materials by provoking differences in the plastic deformation behavior and should be considered when designing PP materials for fatigue resistant materials in the future.

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