

## SLOW CRACK GROWTH RESISTANCE OF REPROCESSED PVC

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### **KEYWORDS** (*Mandatory, please give ~3-5 keywords*)

*PVC, slow crack growth, lifetime, recycles, sustainability, circular economy*

### **ABSTRACT**

*The Cyclic Cracked Round Bar (CRB) Test has been applied to study the slow crack growth (SCG) resistance of virgin, recycled, and reprocessed PVC-U. This fracture mechanical test allows a quick ranking of the SCG resistance of PVC-U. A clear correlation between the K-value and the SCG resistance has been elaborated. The investigated recycled PVC-U materials show a similar SCG resistance as virgin grades. However, further research is needed to investigate the effects of impurities and plasticizer residues on the SCG resistance. The results also demonstrate that repeated reprocessing of up to 10 runs creates no significant negative influence on the SCG resistance of PVC-U.*

## INTRODUCTION

Recycling of polymers has become a major economic, environmental, and social challenge for our current and future society [1,2]. In September 2019, the Circular Plastics Alliance, which represents the European plastics industry in the European Commission, announced to deliver on the circular economy for plastics and to substantially increase the use of recycled plastics into new products. A key target of this “*Declaration of the Circular Plastics Alliance*” is to include at least 10 million tons of recycled plastic per year into new plastic products in Europe by 2025 [3]. In 2018, the global production of polymeric materials counted 359 million tons, with a share of 17 % from Europe [4]. Within the EU28 countries, from 51.2 million tons of plastic products the three main segments have been identified with packaging (39.9 %), building & construction (19.8 %) and automotive (9.9 %) [4]. A share of 49 % was related to polyethylene (PE) and polypropylene (PP), followed by another 10 % for polyvinylchloride (PVC) [4]. These numbers emphasize that special attention must be addressed to the materials PE, PP and PVC in order to create a significant improvement in the Circular Economy of polymers.

In Europe, recycling of post-consumer plastics has doubled since 2006 and exceeded a ratio of 32.5 % in 2018 [4]. The European plastic pipe industry contributes to this development with activities focusing on a reduction of the carbon footprint and improvements in the Circular Economy of plastic pipes. In agreement with existing standards, by 2017 already more than 240'000 tons of recycled polyolefins and more than 110'000 tons of recycled PVC were manufactured into non-pressure pipes and underground water management systems such as sewage and stormwater applications.

In contrast to virgin pipe grades with defined and very narrow material property profiles specifically designed for injection molding or extrusion, recycled materials are typically characterized by a relatively huge variation in their material property profiles which is a result of the high diversity of material sources. Hence, products made out of recyclates often show very different material properties when compared to products made out of virgin grades. To reach the designed minimum service time of several decades, the structural reliability of pipes and other underground applications is of essential importance. Polymers used in this field have to pass several standards which focus on the different potential failure mechanisms of stage I, ductile damage, stage II, crack initiation and slow crack growth (SCG), and stage III, chemical degradation. Not only for pressure pipes but also for any other stress loaded structure such as non-pressure pipes, especially the resistance against SCG is the prime property for the long-term failure behavior of stress loaded components [5,6]. For polyethylene pipe grades, recently the Strain Hardening Test [7,8] as well as the Cyclic Cracked Round Bar (CRB) Test [9,10] have been developed and standardized which allow a modern and quick evaluation of the SCG resistance.

Apart from the aspired positive ecological and environmental effects, it must be considered that the use of recycled polymers can also have a negative effect on the above mentioned failure mechanisms. For polyolefin post-consumer recyclates a significant reduction of the SCG resistance has been reported [11–13]. As for unplasticized PVC (PVC-U) almost no similar representative studies are available, the current paper is dedicated to investigate the applicability of the CRB test for the SCG characterization of PVC-U, especially in the context of recycled and reprocessed material. Therefore, a fracture mechanical screening of different virgin and recycled PVC-U was conducted, followed by a systematically study of the effects of K-value and repeated reprocessing on the SCG resistance of PVC-U.

## BACKGROUND

Only limited published data is available which investigated the influence of reprocessing or recycling on long-term relevant material properties of PVC-U. For PVC in cable applications it has been demonstrated that after two repeated remolding and reprocessing steps neither the material composition nor the mechanical properties or the thermal stability changed significantly [14]. A different paper investigated a rigid PVC after up to five re-extrusion steps observed a slight increase in mechanical properties like elongation at break and tensile strength which was attributed to an increase in the degree of gelation. Moreover, after oven aging also a decrease in the activation energy was observed, indicating shorter aging resistance with increasing number of reprocessing runs [15]. With specific focus on PVC-U for pipe applications one work demonstrated that even after eight regrinding steps, mechanical properties and thermal resistance have not changed significantly [16]. The same study also concluded that with the quality criteria of K67, recycled PVC may be used in core layers of multi-layer pipes up to 100 % [16]. While these studies show promising results for the use of recycled PVC, it has also been reported that PVC-U sewer pipes failed by SCG after 34 years in service. While for this pipe no material aging was detected, inherent defects based on foreign inclusions were identified as crack initiating impurities [17].

The long-term resistance of polymers in pipe applications is typically characterized by internal pipe pressure tests according ISO 9080 (MRS-method) or ASTM D2837 (HDB-method) [18,19]. Similar to polyolefins, also for PVC-U the typical failure modes stage I and stage II are observed in dependency of the applied hoop stress [6,20]. The SCG resistance (stage II) is directly linked to the K-value of the material, which is a representative value of the viscosity and the average molecular mass in PVC, respectively [6,21,22]. For pipe applications, typical values lie within a range between K57 and K68 [23]. Scientific studies have already proven that the crack growth behavior of PVC-U under creep correlates directly to the crack growth behavior under fatigue, and that laboratory fatigue tests can be used for a significant time reduction in the qualitative characterization of the SCG resistance [24,25]. For a quick material ranking based on SCG resistance, for polyethylene pipe grades the Cyclic CRB Test has been standardized in ISO 18489 [10]. First studies confirmed that this ranking test can also be applied to PVC-U grades by using similar test conditions [13].

## EXPERIMENTAL

To proof the general applicability of the CRB test, and to generate a basic overview about the SCG resistance of PVC, 11 different PVC-U pipe grades were involved in the current study. While five of the materials were virgin PVC-U compounds (PVC-b, -c, -d, -i, -k), further six materials were based on recyclates, from which PVC-a, -e, -f, -j were based on post-consumer recyclates, PVC-g was an internal re-processed non-virgin material, and PVC-h was a post-industrial recycle mainly based on window profiles and pipes. Except material PVC-a, all materials were manufactured into pipes with a wall thickness of at least 12 mm. Material PVC-a was compression moulded into a sheet with a thickness of about 12 mm. The CRB specimens were manufactured directly out of the pipe walls and from the sheet, resulting in specimen diameter between 11 and 14 mm.

To investigate the effects of the K-value and the repeated reprocessing on the SCG resistance, a representative compound was prepared as it is typically used for the manufacturing of PVC-U pipes. The formulation was based on a calcium/zinc stearate for heat stabilization and several other additives as usually used for such compounds. Two different grades with K57 and K66 were produced. By blending these two materials, a third grade with K62 was provided. The material was processed with a twin-screw extruder of the type Gottfert DS-35 using a 5-string die and medium screw compression. After manufacturing of the PVC-U formulations, for each K-value the processing

was repeated up to 10 times. The average residence time of the polymer in the extruder during each processing run was approx. 105 s. From the material of the first run, as well as after run 2, 4, 6, 8 and 10, sheets with a thickness of 10 mm were prepared with a kneader of the type Brabender Plastograph.

After each processing run the thermostability of the materials was evaluated by the resistance against dehydrochlorination according to ISO 182-3 [26] using a device of the type Metrohm 763 PVC Thermomat. From each sheet, the color coordinates of the  $L^*a^*b^*$  color space were measured with a X-rite Spectrophotometer. All CRB tests were executed on a servo-hydraulic closed-loop testing system of the type MTS Table Top (MTS Systems GmbH; Berlin, GER) according to ISO 18489 [10]. The force-controlled cyclic load was applied between  $\Delta\sigma_0=6$  and 20 MPa with a frequency of  $f=10$  Hz. All tests were conducted at ambient temperature of  $T=23$  °C. In addition, a system of three extensometers of the Type 632.13-20 (MTS Systems GmbH; Berlin, GER) was positioned at equal distance around the specimen notch to measure the difference in crack opening displacement  $\Delta COD$  during each test [27]. The CRB specimens were manufactured from the kneaded sheets to a diameter of 9 mm and a length of 80 mm. On a conventional lathe, the initial notches were inserted into the rotating specimen with a razor-blade to a depth of 1 mm. For some CRB specimens the fracture surface after failure was analyzed with a scanning electron microscope (SEM) of the type EOScan VEGA XL H (Tescan, CZE).

## DISCUSSION

The results of the CRB test for the 11 different virgin and recycled PVC-U pipe grades are summarized in Fig. 1, left. The chart shows the measured failure cycle number  $N_f$  as a function of the applied stress levels  $\Delta\sigma_0$ , as well as the corresponding failure regression lines. For almost all conducted CRB tests, the failure was achieved within one day, which emphasizes the high potential of this test method for a quick characterization of the SCG resistance. It can be observed that in log-log scale, for each material a clear linear correlation between  $N_f$  and  $\Delta\sigma_0$  has been determined. All specimens failed in stage II failure mode of SCG and all materials, except material PVC-f, show a more or less parallel failure curve. A typical observation in stage II failure is the fragmentation of the total failure into crack initiation and SCG. As an example, for one test on PVC-d the  $\Delta COD$  signals are shown in Fig. 2 left. A constant value during the first phase of the test confirms a constant specimen geometry, and a constant crack length, respectively. After about 6'000 loading cycles the signals start to increase as a result of crack propagation by SCG. In case of stage I failure the curves would have shown a continuous increase already from the start of the test. A further indication of failure by SCG can be derived from the fracture surface appearance. In Fig. 2, right a SEM image of the corresponding fracture surface of the PVC-d sample shows a relatively rough structure with many fibrillar structures which is a result of crazes. The formation of crazes is a combination of local shearing in the amorphous phase and a transformation of the crystalline phase, leading to highly drawn fibrils which continuously enlarge the craze. As the result of the applied stress, the craze zone increases and continues the formation of fibrils until molecular disentanglement leads to a breakdown of the craze. This procedure of permanent craze formation and breakdown is a characteristic physical process of SCG in thermoplastic polymers and has been well observed in many materials including PVC-U [28–31].

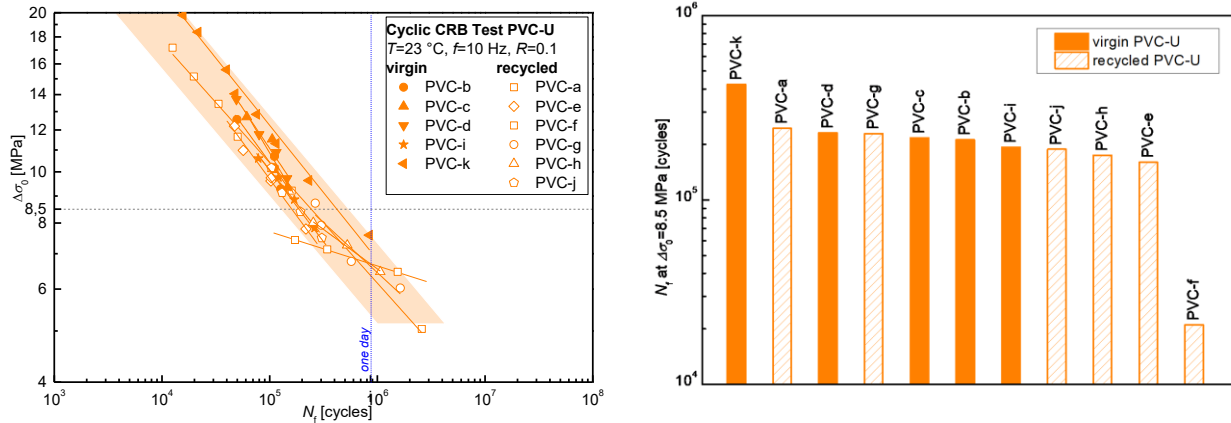


Fig. 1: Left: CRB ranking curves for different virgin (full symbols) and recycled (light symbols) PVC-U for pipe applications. Right: Corresponding single point values  $N_f$  at  $\Delta\sigma_0=8.5\text{ MPa}$ .

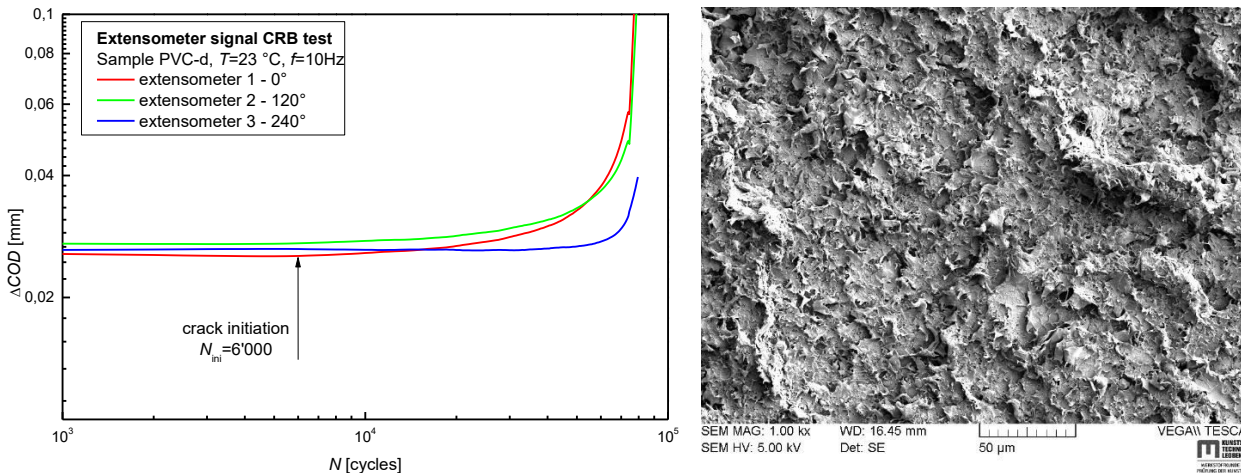


Fig. 2: Left: Crack opening displacement signals  $\Delta\text{COD}$  of a CRB test with PVC-d; Right: Corresponding SEM image of the CRB fracture surface of PVC-d.

The ranking of the different materials in Fig. 1, left demonstrates that - except for material PVC-f - the SCG resistance of all investigated PVC-U lie within a certain range with more or less similar slope of the failure curves. In order to correlate the materials in a quantitative way, the single point values of each regression line at a reference stress level of  $\Delta\sigma_0=8.5\text{ MPa}$  have been determined and summarized in Fig. 1, right. The virgin grade PVC-k shows the highest SCG performance with about 424'000cycles (~12 h). For the other materials the failure cycle numbers are at somewhat lower values between 245'000 cycles (~7 h) and 160'000 cycles (~4,5 h). No significant difference in the SCG resistance can be observed between virgin and recycled materials. However, a significant difference in the failure characteristics can be noticed for the recycled material PVC-f, as the slope as well as the SCG resistance at the reference stress level with only 21'000 cycles deviates clearly. Additional analyses with this material revealed a content of approx. 0.8 % of plasticizer and epoxidized soybean oil (ESO) inside the compound.

Following two conclusions can be drawn from these results:

- Recycled PVC-U grades show a quite comparable SCG resistance to virgin grades.

- Residues of plasticizer, even with low content, may have a significant impact on the SCG resistance of PVC-U grades.

In order to simulate several recycling loops, a PVC-U compound with three different K values was reprocessed up to ten times and manufactured into solid sheets. In Fig. 3, cut cross sections of the sheets for K57, K62 and K66 are shown after the first run as well as after 2, 4, 6, 8 and 10 reprocessing runs. While the colour appearance of all samples after the first processing is quite similar, with increasing numbers of processing a darkening can be observed which gets more pronounced with higher K-value. For a quantitative evaluation of the colour change, the colour coordinates  $L^*$ ,  $a^*$  and  $b^*$  are shown in Fig. 4, left. The lines clearly show the effect of changing colour with increasing processing runs. Especially for K66, after 6 reprocessing runs  $L^*$  and  $a^*$  deviates stronger and the darkening is higher as for K57 and K62. The resistance against dehydrochlorination is summarized in Fig. 4, right. While the PVC-U with K57 and K62 have a similar value of about 20 min, which is also not significantly changing with the number of reprocessing, the material with K66 lies somewhat higher at 25 min and shows a slight decrease starting with reprocessing run 6. However, in general the dehydrochlorination resistance is not changing dramatically after 10 times reprocessing.

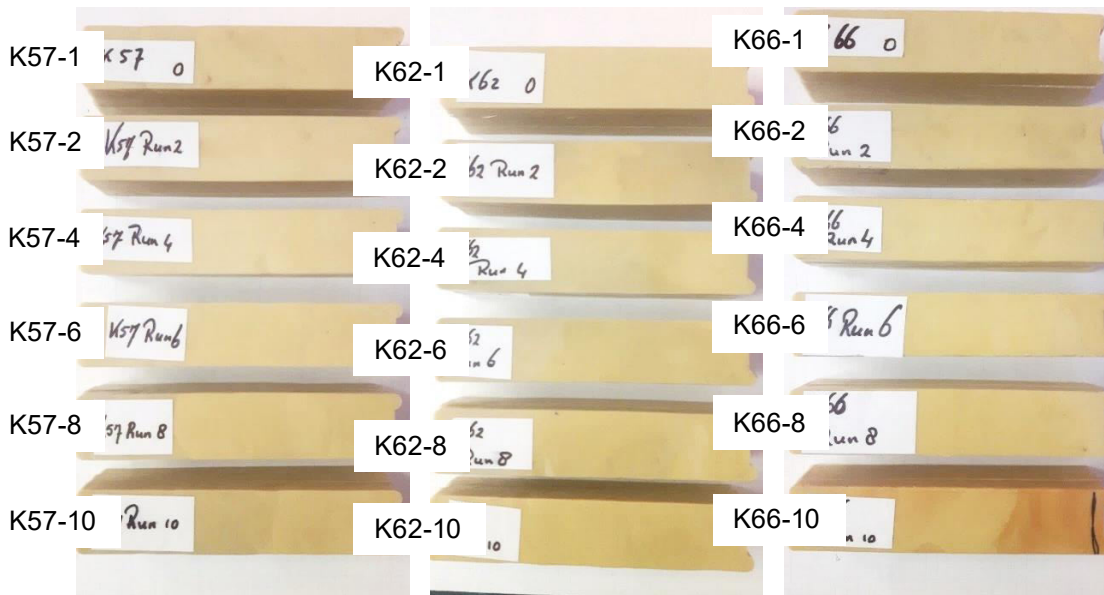


Fig. 3: Photographs of PVC-U sheets with different K-values as a function of reprocessing runs. The numbers after the hyphen indicate the numbers of processing.

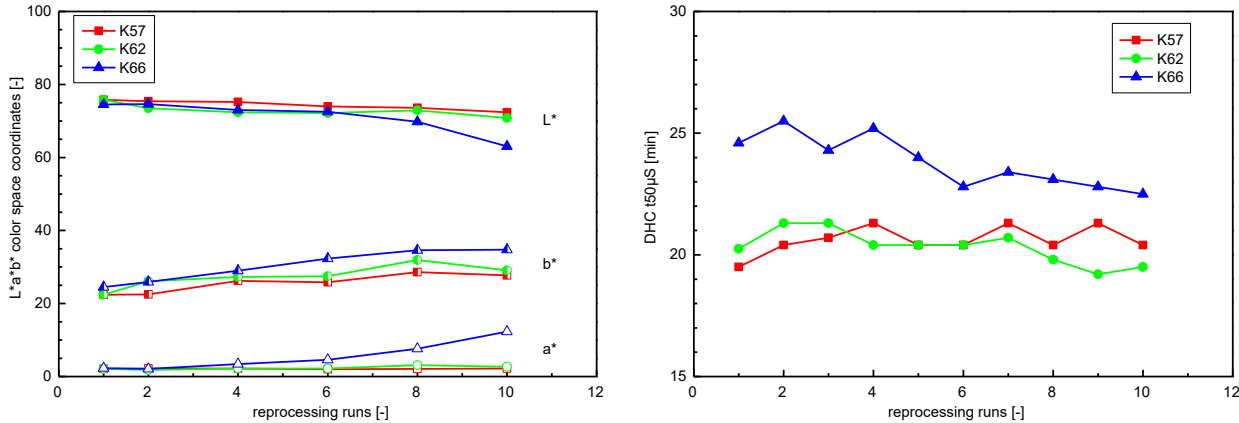


Fig. 4: Left: Color space coordinate L\*, a\*, b\* of PVC-U with different K-values as a function of reprocessing runs. Right: Dehydrochlorination of PVC-U with different K-values as a function of reprocessing runs.

The results of the Cyclic CRB Tests are summarized in Fig. 5. From top to bottom, on the left side the failure curves for the materials are shown with increasing K-value and up to 10 reprocessing runs. The area of the PVC-U failure curve range (Fig. 1, left) has been inserted for orientation. On the right side, the corresponding single point values  $N_f$  at  $\Delta\sigma_0=8.5$  MPa are shown. It can be noticed that the SCG resistance clearly increases with higher K-value, from 162'000 cycles for K57, to 200'000 cycles for K62, and to 445'000 cycles for K66. This is in agreement with the expectations and with previous studies, in which internal pipe pressure tests confirmed that with increasing K-value the resistance against stage II failure also increases significantly [8]. With respect to repeated reprocessing, the results in Fig. 5 demonstrate that, apart from statistical deviations, the SCG resistance is not changing significantly. The statistical deviations are most possibly a result of the small CRB specimen diameter of 9 mm (below the recommendations of ISO 18489), which were limited by the sheet manufacturing, and the higher relative effects of measurement errors, respectively. However, for this study these effects have been consciously accepted as the missing negative influence of repeated reprocessing on the SCG resistance is quite obvious for all K-values.

As described before, the physical processes during SCG (craze development and breakdown) are dominated by the formation of fibrils and the ability of the macromolecules for molecular disentanglement [28–31]. In PVC, mechanical and fracture mechanical material properties are mainly defined by the crystalline microdomain structure of the primary particles. The polymer chains within a primary particle are held together and cannot interact with other primary particles. At high temperatures during processing, some of the crystallites at the primary particle surface melt and interact with macromolecules of other primary particles. While inside the primary particles the crystalline structure is not significantly changing, during the cooling process the interface molecules connect the primary particles together into a three dimensional network by newly formed crystallites [30–34]. This fusion like thermodynamic behaviour is characteristic for PVC and also describes the observations from the CRB tests. On the one hand, longer macromolecules (higher K) not only statistically connect more crystallites within the primary particles, but also create a higher number and density of tie molecules. Hence, with increasing K-value a stronger tie molecule network between the primary particles finally results in a higher resistance against molecular disentanglement during SCG. On the other hand, the same mechanisms of only partial melting into primary particles is also responsible for the low influence of repeated reprocessing on the SCG resistance. While during



melting and cooling especially the primary particle interface region is active, the intrinsic material properties within the primary particles remain almost unaffected in their crystalline microstructure, so that typical molecular degradation mechanisms as known from other polymers, such as chemical degradation or chain scission, do not happen.

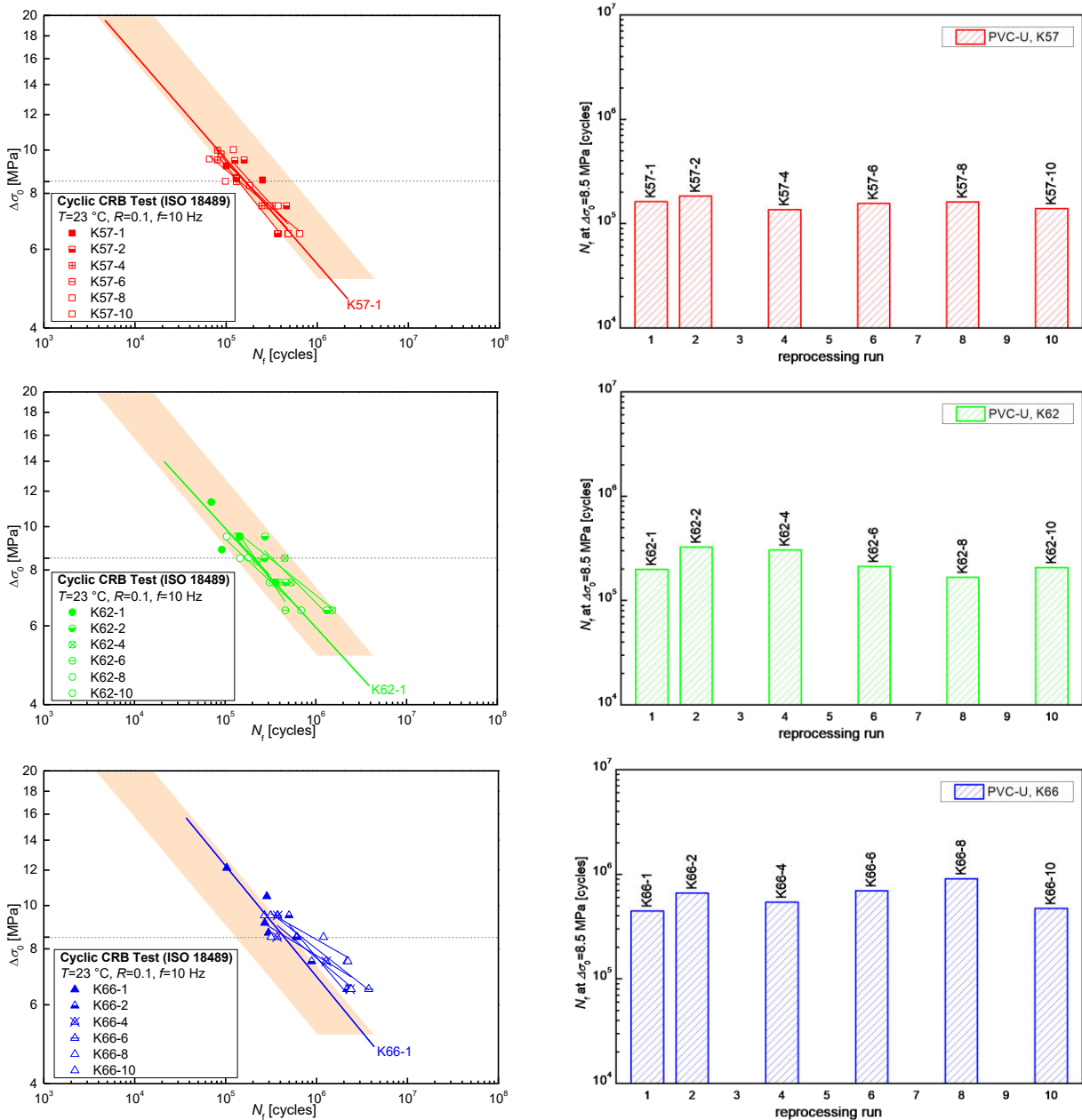


Fig. 5: Left: CRB failure curves for PVC-U with K57 (top), K62 (middle), and K66 (bottom) after up to 10 reprocessing runs. Right: Corresponding single point values  $N_f$  at  $\Delta\sigma_0=8.5$  MPa.

## CONCLUSIONS

The Cyclic CRB Test according ISO 18489 is a suitable method to characterize the SCG resistance of PVC-U. With testing times of only several days for a full ranking curve, this method is an interesting alternative compared to time consuming tests such as internal pipe pressure tests. The



test results presented within this paper show that the SCG resistance of post-consumer or post-industrial recycled PVC-U does not differ significantly from virgin PVC-U grades. For one material a significant deviation in the SCG resistance has been observed which might be a result of the presence of plasticizer residues. As no systematically studies are available in this context, further research about the effects of impurities and plasticizer residues on the SCG resistance are recommended. In any case, this result emphasizes the importance of clean and precise material sorting during mechanical recycling of PVC-U. As long as a sufficiently high purity in mechanical recycling is provided, for recycled PVC-U a comparable SCG resistance in long-term pipe applications can be expected as for virgin grades.

With respect to repeated reprocessing, the generated data of this study show a negligible influence on the SCG resistance. While for PVC-U with increasing K-value a higher SCG resistance has been confirmed, a repeated reprocessing of up to 10 runs demonstrate that the long-term relevant fracture mechanical failure resistance was not negatively affected. Providing the above considerations regarding material purity, this knowledge is not only of interest for the repeated reprocessing of internal PVC-U waste in production lines, but also for the recycling and reprocessing of post-consumer recyclates in terms of Circular Economy.

## ACKNOWLEDGMENTS

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Transport, Innovation and Technology and Federal Ministry for Economy, Family and Youth with contributions by Borealis AG (AUT), Fränkische Rohrwerke Gebr. Kirchner GmbH & Co. KG (GER), Pipelife International GmbH (AUT), Poloplast GmbH & Co KG (AUT), Polypipe Ltd. (UK), Rehau, AG & Co. KG (GER), DYKA (NL), Vynova Group (BE) and Wavin T&I (NL) as well as the Technical University Wien (AUT) and the Montanuniversitaet Leoben (AUT). The PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

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