

The Effect of Carbon Black on Degradation of Pipe Grade Black Polyethylene in High Concentration Chlorine Dioxide Solutions

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Abstract

In this research, the impact of carbon black on the accelerated degradation of pipe grade polyethylene (PE100) exposed to high levels of chlorine dioxide (150 ppm) is examined. Tensile testing reveals a faster degradation rate in black samples compared to natural samples, indicating a detrimental effect of carbon black aggregates on the polymer's aging process. Rheological analysis shows changes in molecular weight and structure due to chemical degradation and chain scission and can be a reliable method for detecting slight changes in molecular structure. Isothermal crystallization shows a slowdown in crystallization kinetics at first, explained by gel-formation due to crosslinking which hinder the crystallization, and then an increase in the kinetics as apparently the chain scission gets dominant again. Neat samples exhibit a higher density of tie molecules, indirectly revealed by much more fibrils in crack wall observed in FESEM images, suggesting better resistance to chemical degradation while the black sample shows a much less fibrillar crack wake and becomes almost completely devoid of any fibrils at later stages of aging. The fibrils, which essentially offer a load-bearing role against the widening and growth of the crack play a key role in resistance to slow crack growth (SCG). Therefore, the higher SCG resistance is expected for neat grade compared to black samples. The study proposes a dual-layer pipe design with a UV-resistant black outer layer and an oxidation-resistant neat inner layer to prolong the lifespan of PE100 pipes by protecting against UV radiation and chemical reactions. This solution offers increased durability, lower maintenance costs, and environmental sustainability benefits.

Keywords: Chlorine dioxide, PE100, oxidation, chemical degradation, aging, tie molecules

1. Introduction

Over the past decades, plastic pipes have become a popular option for water transportation purposes, either for delivering pot water from treatment plants to urban households or for wastewater transportation and sewage systems. Polyethylene (PE) pipes, especially the pipe grade bimodal PE100 material, has become one of the most popular materials of choice due to ease of handling and manufacturing, excellent mechanical performance, and resistance to chemical elements, resulting in an expected theoretical lifetime of multiple decades [1]. However, it has been reported in widely accepted that addition of oxidating disinfectant agents like free chlorine or chlorine dioxide to water can lead to significant degradation and reduction of lifetime and properties of the PE pipes [2–7]. This degradation occurs due to consumption of antioxidant by the aggressive environment and eventually leads to the failure of the pipe material [8–11].

It has been shown that depending on the condition of the applied stress, the polymer pipes can undergo three different types of failure [12]. At higher stress levels, the main mechanism for failure is ductile deformation, while at lower stress levels, brittle failure due to slow crack growth (SCG) is dominant. The brittle failure itself consists of three stages: crack initiation, slow crack growth and fracture. When environmental elements also affect the lifetime, stress corrosion cracking at lower stress levels will become the governing failure factor. These failure modes are distinct from each other in the hoop stress-lifetime graph of the pipe where a mechanical and a chemical ‘knee’ can be observed [13].

The degradation steps of the polyolefins exposed to a chlorinated environment include the antioxidant depletion, degradation of the surface layer, reduction in molecular weight due to chain scission, micro-crack and crack formation and eventually crack propagation until the final failure

stage [9,14]. This poses a serious performance risk for the pipes as detecting an upcoming failure in the pipe is not possible, thus it is very important to study the mechanisms involved in this degradation process and come up with new ways to overcome this issue.

Black PE pipes are produced by compounding carbon black (CB) with the base PE, in which the carbon black acts as one of the most effective and robust stabilizers against UV radiation and weathering of PE pipes. Several studies, including authors' previous works, have investigated various properties of black PE compounds, including morphological and thermal properties [15], rheological and mechanical properties [16], long term creep performance [17–19] and degradation in presence of chlorine dioxide [9]. However, a comprehensive and direct study comparing the chemical degradation of pipe grade PE samples with and without carbon black in an accelerated chlorine dioxide media has not been conducted to the best knowledge of authors. The precise function of carbon black in the degradation process and the potential mechanisms by which carbon black particles might participate have largely eluded researchers in the field of studying chemical oxidation mechanisms in polyolefins, including polyethylene.

The studies by Gholami et al. [17,18] demonstrated that carbon black does indeed decrease the resistance to SCG in PE100 pipes, where it was suggested that the carbon black particles in amorphous areas can act as physical inhibitors for long chains that prevent their entrance from one crystalline region to another. This reduces the tie molecule density, role of which as a key element in polymer resistance to slow crack growth has been verified by various studies [20–23]. The challenge being posed by adding carbon black as a UV-absorbent additive is striking a balance between UV-stability of the sample and the long-term mechanical performance of the material. While both parameters are equally important, a further understanding of the precise role that

carbon black plays in chemical oxidation can help in development of polyethylene materials suitable for use in chlorinated water transportation and distribution.

There have been different studies on changes in the molecular weight distribution in bimodal polyethylene material and how it affects the morphology and properties of the polyethylene [24–26]. Research indicates that when polyethylene is exposed to chlorine oxidizers, it undergoes a complex process involving both crosslinking and chain scission events. As the material ages and degrades under continued exposure, the balance shifts towards chain scission, which becomes the predominant phenomenon over crosslinking. [27–30], since polyethylene has been shown to have a higher tendency for chain scission than crosslinking [31]. On the other hand, less studies have focused on how an unwanted, oxidation-induced change in the molecular weight by chain scission/crosslinking affects the rheological properties and morphology simultaneously.

It is reported that beyond a certain chlorine concentration, the presence (or lack thereof) of stabilizers does not make a difference anymore since the chlorine concentration as the oxidative species completely dominates the oxidation resistance role of the stabilizers [28]. Therefore, in presence of a very high concentration of chlorine species, it is expected that stabilizers are completely overwhelmed by the highly oxidative media and therefore their role as an initial inhibitor can be neglected.

Given that the concentration of chlorine dioxide used in drinking water supply is typically very low (less than 1 mg/L [32]), conducting tests in real-life situations to evaluate pipe grade materials may require months or even years. Therefore, it is crucial to develop accelerated aging tests to study chemical degradation mechanisms within realistic time frames. In this study, black and neat PE100 samples (with exact same properties and molecular characteristics except for the presence of the carbon black particles in black sample) are compared to each other with respect to their

aging process and mechanism in a very oxidative environment containing a high percentage of chlorine dioxide. This approach enables us to delve into the impact of carbon black aggregates on the degradation mechanism, paving the way for a deeper exploration of chlorine dioxide-induced effects and the role played by additives like carbon black in the chemical oxidation process.

2. Experimental Section

Neat (N) and Black (B) stabilized bimodal pipe grade PE100 (HM-CRP100N and HM-CRP100 Black respectively) produced by Jam Petrochemical Company (Iran) using Ziegler-Natta catalysts under the Hostalen license of Lyondell-Basell and 1-Butene as comonomer were used in this study. The black grade uses the same neat PE100 resin in addition to 2.25 wt% p-type carbon black. Both grades use an identical package of antioxidants and processing agents, and this makes it possible to solely focus on the role of carbon black in oxidation and degradation mechanism of the PE100 in presence of chlorine dioxide.

Sheets of 1 mm were produced using a hot press machine and tensile specimen of ASTM D638 type V were punched from the sheets. The samples were then put in a 3-liter glass container on a heater-stirrer device in a solution of approximately 150 ppm ClO_2 at the constant temperature of 50°C. The whole setup was covered under a suitable cover to prevent light from interacting with chlorine dioxide. A Schematic representing the aging process is shown in Figure 1. The concentration of ClO_2 was measured and calibrated using single factor test strips to keep the ClO_2 concentration constant during the test period. Batches from the samples were removed from the solution after the times of 48, 96, 144, 192, 240, 312 and 360 hours, however due to complete degradation of both black and neat samples in 96-144h afterwards, most experimental results

except some meaningful mechanical characteristics are presented for times of up to 144h for convenience.

Tensile tests were conducted on the samples at room temperature with a gauge speed of 50 mm/min. After a certain amount of aging time and due to degradation, samples began to fail at small strains with no necking just after the yielding. Small cracks appeared all over the gauge length and their morphology was characterized using field emission scanning electron microscope (FE-SEM).

A TA Instruments Q100 differential scanning calorimetry (DSC) device was used for isothermal DSC analysis to evaluate thermal properties and crystallization kinetics of the samples based on the rate of degradation and changes in molecular weight in the samples. A temperature of 122°C was chosen for isothermal crystallization based on our previous studies on this grade [15,17].

Rheological characteristics of the samples were evaluated using an Anton Paar MCR 301 at frequency sweep mode and temperature of 190°C in the linear viscoelastic region using the parallel plate geometry. In order to evaluate the formation of oxidation-induced chemical groups quantitatively, ATR-FTIR analysis was utilized and the values of carbonyl index were measured using SAUB method, details of which are explained in [33]. The morphology of the cracks created in the gauge length of the prematurely failed tensile samples were studied using a TESCAN field emission scanning electron microscope. Samples were coated with a thin conductive gold to be observable in electron microscope.

3. Results and Discussion

3.1. Tensile properties

Figure 1 shows representative specimens following tensile tests, highlighting both non-aged and 144-hour aged neat and black samples. This visual comparison illustrates the maximum strain and the occurrence of fully brittle failure under extreme aging conditions. The complete stress-strain graphs of the neat and black samples are presented in Figure 2(a) and Figure 2(b), respectively, for aging times of up to 144h, after which all samples show almost the same mechanical properties. As it appears in the graphs, the black sample already shows degradation after 48 hours of aging as it is obvious in its premature failure in strain hardening section of the tensile test. The same trend for neat samples appears only after 96 hours of aging as this sample does not show any influence on mechanical properties after 48 hours of aging. The lack of strain hardening in the aged sample can be a solid indicator that the sample has basically lost its long term mechanical performance as strain hardening has been shown to be a good and relatively reliable and fast method for assessment of polymers' long term properties [34].

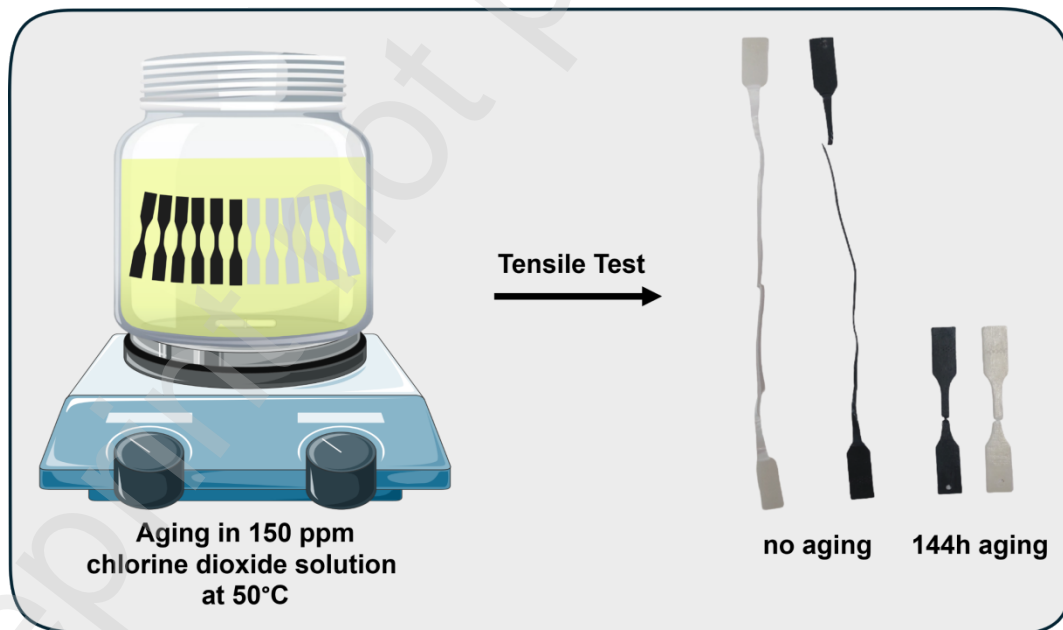


Figure 1- Schematic representing the aging method of the samples and a visual comparison of specimens after tensile test

Figure 2(c) and (d) display the results of yield strength and elongation at break for samples aged up to 360 hours. The trend of decreasing yield strength is observed in both black and neat samples in Figure 2(c). Initially, neat samples exhibit lower yield strength, possibly due to the lack of reinforcement from carbon black particles [35]. However, at intermediate aging times (144 and 192 hours), neat samples show a delayed decline compared to black samples. Beyond 192 hours, it appears that the high degradation rates of the base polymer led to a resurgence in the yield strength of black samples, highlighting the role of carbon black particles in enhancing strength. Overall, very few studies have focused on the changes in yield strength of polyolefins in general and PE100 in particular when exposed to chlorine oxidizers, with them reporting either a slight increase in yield strength due to re-crystallization effects when exposed to warm chlorine solution [36] (for polypropylene), or no noticeable changes at all [2,37]. It appears that yield strength variations may not be a substantive basis for judgement on degradation extent when it comes to polyolefins. However, the trends shown in this study may be of interest as a distinct variation pattern is observed for black and neat samples as they show there is indeed a difference when carbon black particles is added to the base polymer.

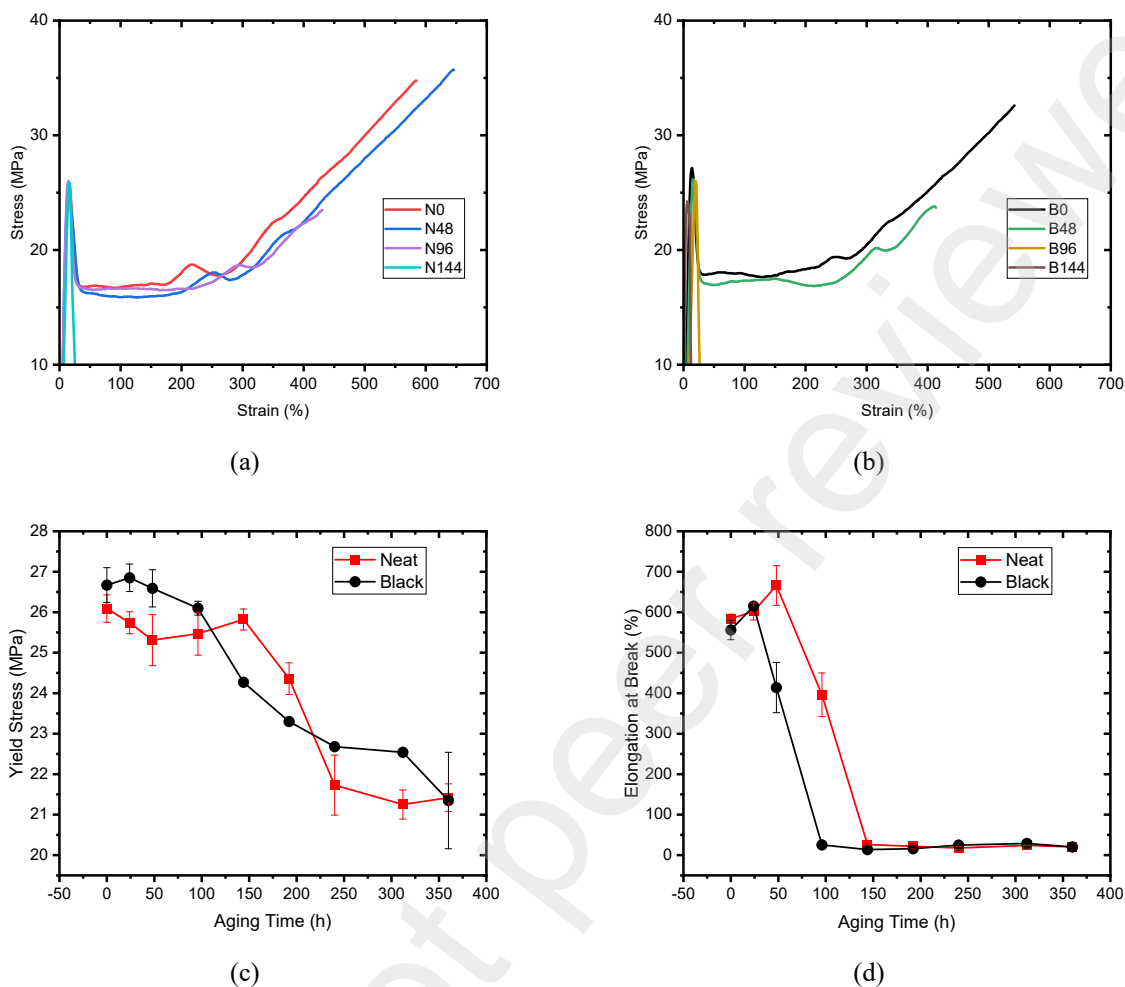


Figure 2- Results for a) Yield strength and b) Elongation at Break vs. aging time for neat and black samples

Elongation at break is a critical indicator of degradation induced by chlorine-based disinfectants, as demonstrated in previous research [2,6,38–40]. The results in this figure reveal that both black and neat samples eventually lose their elongation properties entirely and fail rapidly after reaching the yield point. Notably, the black sample shows a faster degradation rate starting at 48 hours of immersion, while the neat sample follows a similar trend after 96 hours. This observation suggests that the presence of carbon black particles the oxidation and degradation process is accelerated, leading to a reduced lifespan when exposed to oxidizing environments compared to pure PE.

3.2. Isothermal Crystallization

To evaluate the dimensionality and kinetics of crystal growth in samples with different extents of aging, isothermal crystallization behavior of the samples was evaluated. The resulting isothermal data were fitted into Avrami equation (1):

$$1-V_c(t) = \exp(-Kt^n) \quad (1)$$

where $V_c(t)$ is relative fraction of transformed volume, n is the Avrami index and K is a constant related to crystallization rate. Figure 3(a) and (b) show the isothermal curves of neat and black samples respectively. It appears that for black samples, the crystallization rate decreases as aging time increases, while the same observation also exists for neat sample, except for 144h aging time, where it appears that the rate of crystallization exceeds even that of non-aged sample. This may be explained for the fact that chain scission at extreme oxidation times becomes the dominant situation in this sample, resulting in larger number of small chains with higher mobility and enhanced crystallization. In black samples however, it seems that the carbon black particles are enhancing the crosslinking compared to chain scission as aging time increases which leads to a decreased crystallization rate [41]. The Avrami index values in Figure 3(c) show an initial rise followed by a decline in the Avrami index for both samples. While previous research by Gholami et. al. [18] suggests a correlation between the Avrami index and failure time during slow crack growth events, where an increase in n , or the likelihood of spherulitic crystal growth, is linked to a shorter failure time. It may be due to the difference in nature of degradation where an extreme oxidizing environment leads to a significant amount of chain scission and crosslinking.

The graph in Figure 3(d) illustrates how the values of crystallization rate, K , change over time for black and neat samples. Initially, there is a noticeable deceleration in the crystallization rate, particularly prominent in the black samples, suggesting a potential crosslinking process at the onset of oxidation [41]. However, for neat sample with prolonged aging in highly oxidizing conditions,

the frequency of chain scission events surpasses the impact of the crosslinking of free radicals. This results in a considerable acceleration in the crystallization rate due to the facilitated crystallization of shorter polymer chains. While, for the black samples the crystallization rate is decreased even at prolonged aging times, indicating the different route in degradation of polymer chains in the presence of the CB aggregates. Accordingly, it is expected to have different molecular structure affected by chemical degradation in neat and black samples which is explored in the next section using rheological measurements.

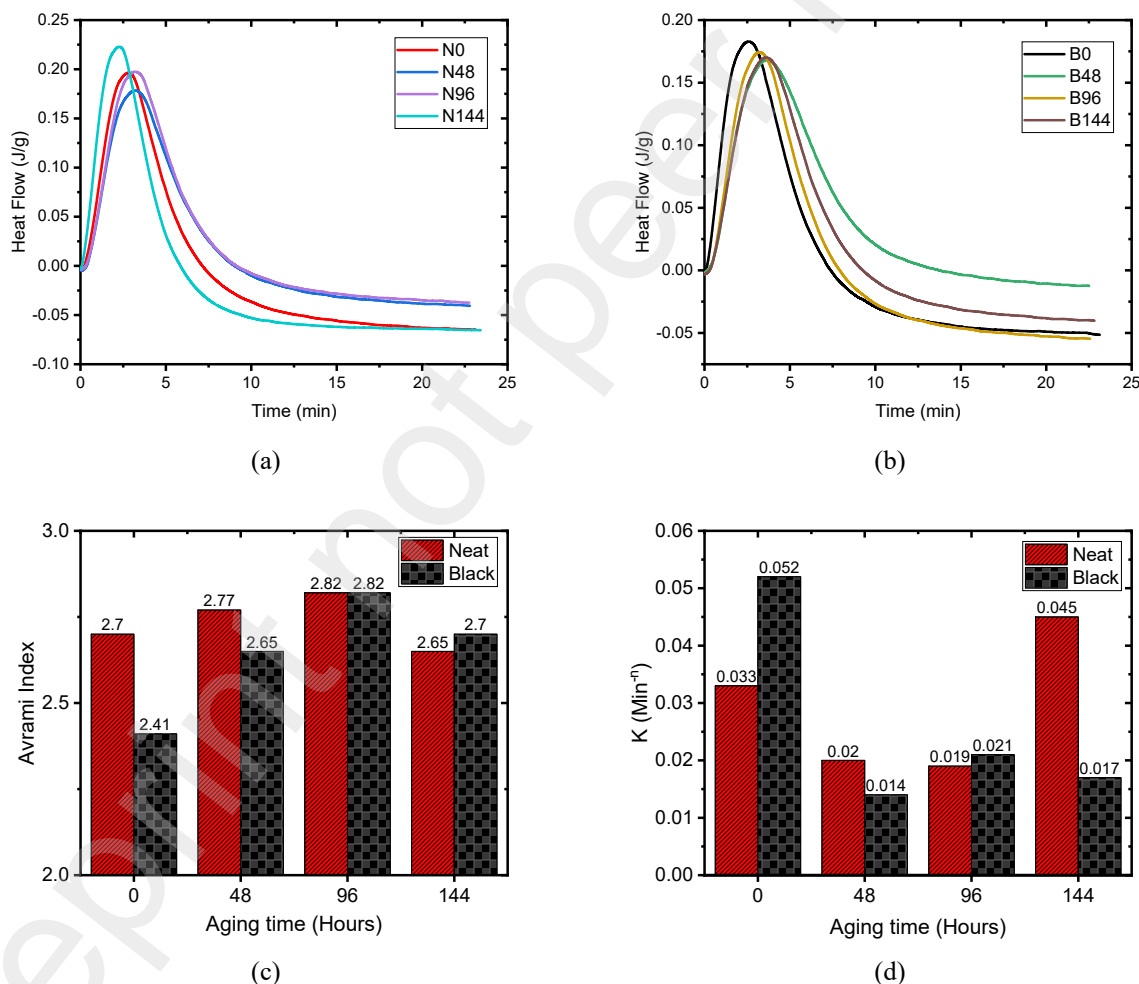


Figure 3- Isothermal crystallization curves of a) neat and b) black samples. Charts of c) Avrami Index and d) crystallization rate constant (K) of Avrami equation versus aging time.

3.3. Rheological properties

It is well known that rheological measurements are quite sensitive to changes in molecular structure of polymers including molecular weight and its distribution [20,42–45]. The complex viscosity graphs in Figure 4 illustrate the variations in complex viscosity over a wide frequency range at different aging durations. A consistent downward trend in viscosity with aging time is observed. Notably, the neat sample exhibits nearly identical viscosity levels for both the non-aged and 48-hour aged samples. Although, the viscosity upturn at low frequency observed for neat sample is diminished for 48-hour aged sample, indicating the selective scission of long chains. For 96-hour aged sample the complex viscosity is considerably decreased in whole frequency range, because of severe chain scission and molecular weight decrement, showing the onset of chemical degradation. In 144-hour aged sample, the complex viscosity is decreased in low frequencies and increased in high frequencies compared to N96 sample, probably due to recombination of some macroradicals, small chains, and formation of larger chains or local crosslinks.

In contrast, the 48-hour aged black sample shows significant deviations from the non-aged sample, particularly at lower frequencies, suggesting the onset of chemical degradation after 48 hours. The observed decrease in complex viscosity across various aging times substantiates the reduction in molecular weight, a consequence of chain scission. The 144-hour aged black sample demonstrates higher viscosity at lower frequencies compared to the 96-hour mark, attributed to the prevalence of crosslinking over chain scission at extended aging periods, leading to the formation of gel-like structures. At higher frequencies, the black samples display a converging viscosity, possibly indicating the significant influence of carbon black particles at higher oscillation ranges. Based on the findings depicted in Figure 4, it is apparent that chain scission and crosslinking in the aged neat and black sample followed different pathways, primarily due to varying rates of chemical

degradation in specific chains and regions within the neat and black samples. Consequently, it can be inferred that the molecular structure of the black and neat samples would differ at the same aging time.

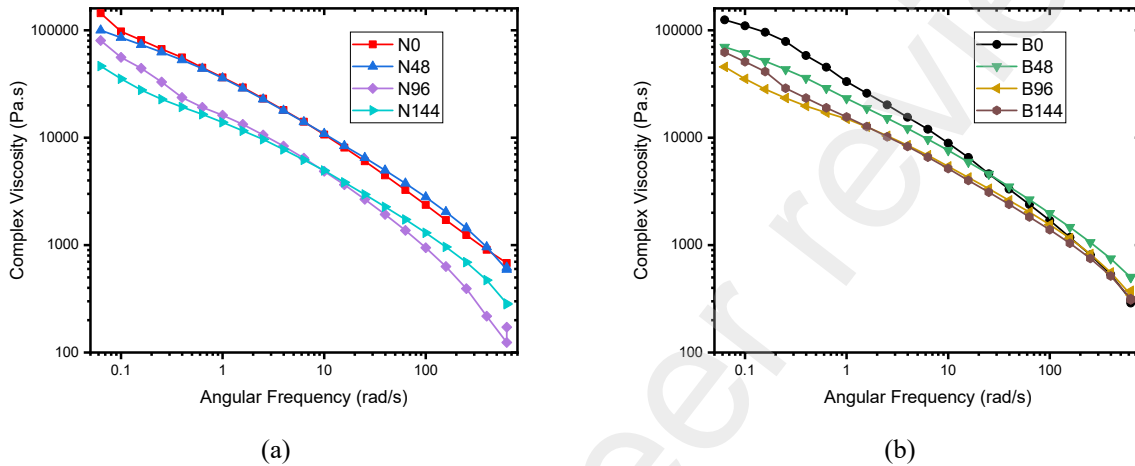


Figure 4- Complex viscosity of the a) neat and b) black samples for different aging times

The results for dynamic frequency sweep rheological tests can be presented and interpreted through multiple rheological graphs. **Error! Reference source not found.**(a) and (b) show the results for storage modulus (G') of neat and black samples respectively while **Error! Reference source not found.**(c) and (d) show the same for loss modulus (G''). As it appears for both storage and loss modulus, for the neat sample, no significant changes happen after 48h of aging, which is consistent with mechanical test results, while the black samples already show a clear decline in both parameters after 48 hours. The significant decrease in storage modulus at low frequencies in N144 sample indicates the absence of high molecular weight chains, because of the chemical degradation which lead to tremendous decline in elongation at break in tensile test, as shown in Figure 2(d). On the other hand, this behavior is observed at B96 sample, indicating a premature chemical degradation or more selective scission of long chains which can act as tie-molecules. Therefore, the elongation at break is suddenly reduced for this sample. The enhancement of storage

modulus at low frequencies region in B144 sample may be attributed to the recombination and crosslinking of macroradicals and formation of local gels.

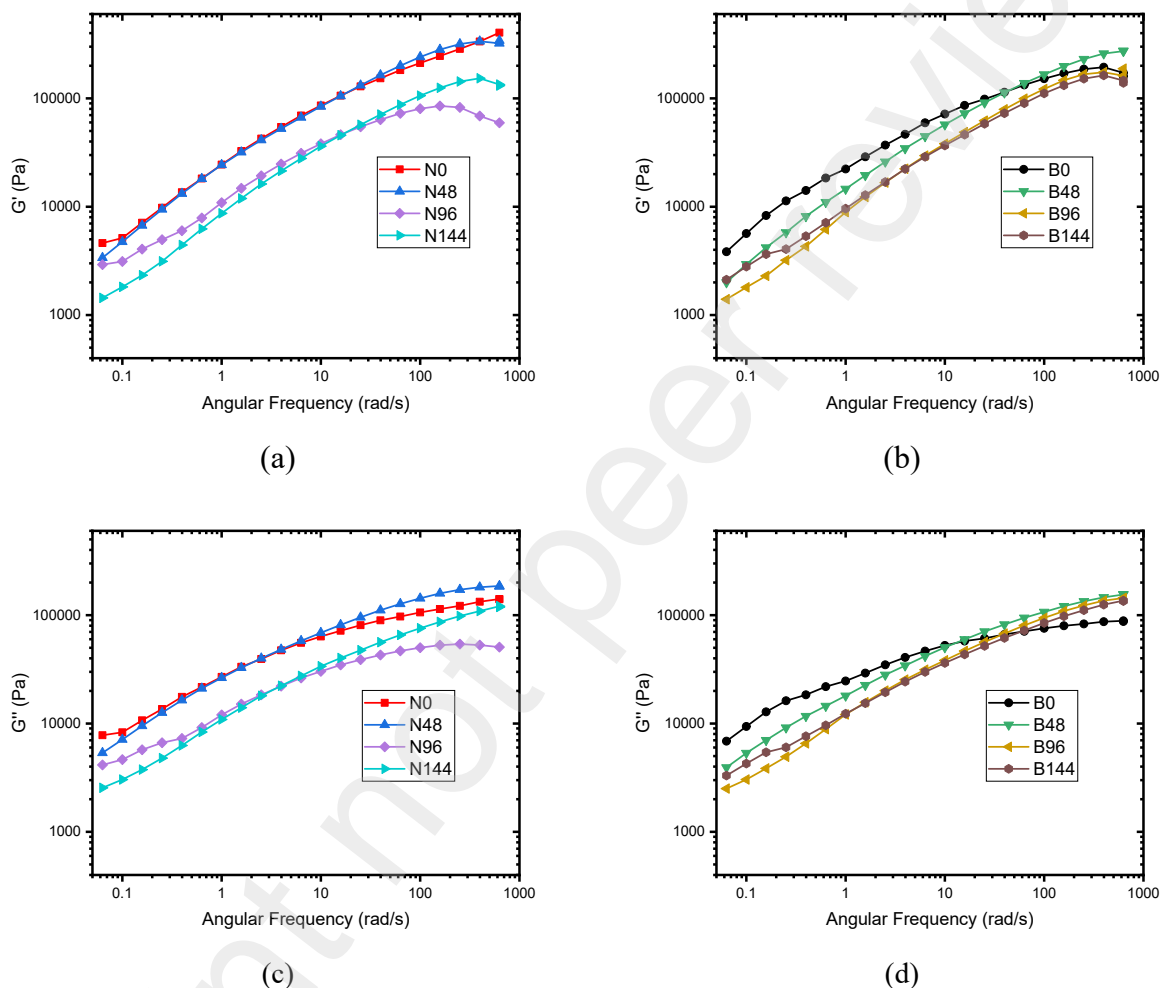


Figure 5- Plots of storage modulus (G') for a) neat and b) black samples and loss modulus (G'') for c) neat and d) black samples

The Cole-Cole and Van Gurp-Palmen plots of the black and neat samples are given in Figure 6 for better insight on molecular structure of samples after chemical degradation. In the Cole-Cole plot, which measures the imaginary part of complex viscosity against the real one, a smooth semi-circular shape of the plot indicates good miscibility for the polymer melt. In both neat and black samples, it is observed that they exhibit a broader and higher value of η'' across various η' values.

This suggests a more elastic response, likely due to the bimodal molecular weight distribution of these samples. A downward trend is noticeable after only 48 hours for black sample. On the other hand, the neat sample aged for 48 hours shows a striking similarity to the non-aged one, almost overlapping it entirely and only losing the highest imaginary viscosity point. This further corroborates its higher resistance to oxidative media.

The 96h neat sample and 144h black sample show a positive deviation from the semi-circular shape and appearance of upturn at higher viscosities, and this might indicate some gel-formation due to crosslinking. Moreover, comparing the N96 and N144 samples, the high viscosity tail disappears, because of progressing chain scission which overcomes the crosslinking. Based on the rheological results, it can be concluded that in the aged neat samples, degradation is initiated with chain scission of long chains and then crosslinking at middle times and finally severe chain scission at prolonged aging time. On the other hand, for the aged black samples, degradation is initiated with chain scission of almost all chains, followed by severe chain scission at middle aging time and finally recombination and crosslinking of small chains.

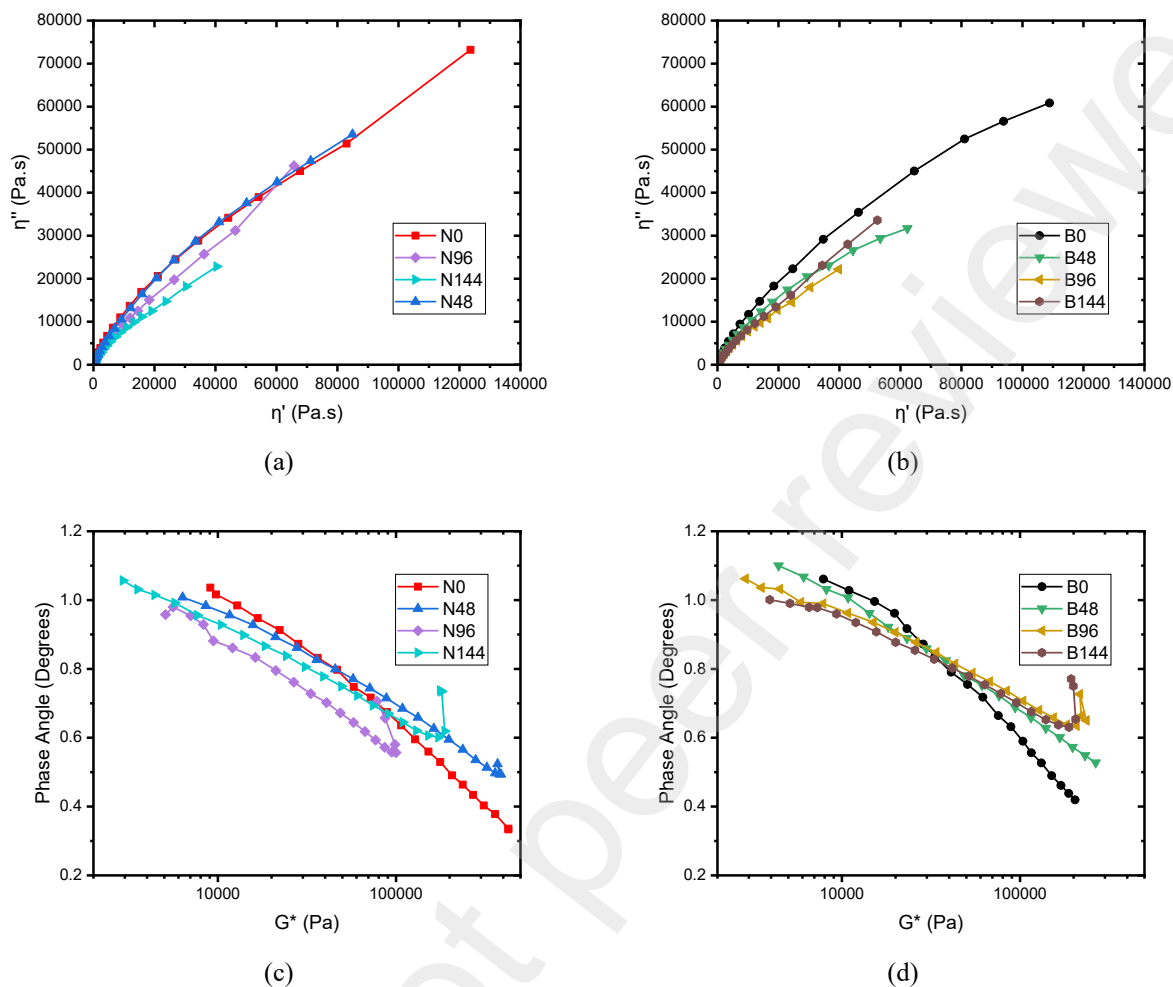


Figure 6- Cole-Cole plots of a) neat and b) black samples. Van Gorp-Palmen plots of c) neat and d) black samples.

The plots for Van Gorp-Palmen can be useful for interpretation of branching and molecular weight distribution of the samples. At higher values of G^* , as the aging time increases, so does the value of phase angle, which indicates a more viscous behavior. In other words, the higher molecular weight fraction increases the melt elasticity as the complex modulus value approaches the plateau modulus ($G^0_N = G'(\omega_{\text{at min tan}\delta})$). In this regard, the N0 and B0 samples show the lowest phase angle at plateau modulus because of their high molecular weight. For the aged samples, the phase angle is increased in this region, indicating a more viscous behavior of degraded chains.

The situation appears to be reversed in lower G^* values as the more degraded samples seem to have a lower phase angle or higher elasticity. This, however, can be misleading as the graph does not explicitly consider the terminal relaxation time, as explained in depth by Trinkle et. al.[46]. When an equivalent relaxation status for all samples is considered and since higher molecular weight fraction has a much longer relaxation time, it is revealed that the sample with higher percentage of high molecular fraction do indeed demonstrate a more elastic melt behavior.

3.4. FTIR Results

Figure 7(a) and (b) show the IR spectra of the neat and black samples respectively. It is clear as shown in highlighted regions that there is a shift in the range of carbonyl peak as the aging time increases. To quantify the results, value of carbonyl index (CI) for each sample was calculated by dividing the peak area in the range of $1850-1650\text{ cm}^{-1}$ to the corresponding reference peak in the range of $1500-1420\text{ cm}^{-1}$. It is evident in Figure 7(c) that the formation of carbonyl groups, a testament to chemical degradation, is accelerated for both samples with increasing aging time. While the two samples mostly overlap each other until 96 hours of aging times, the black sample appears to show an accelerated degradation rate after up to 144 hours.

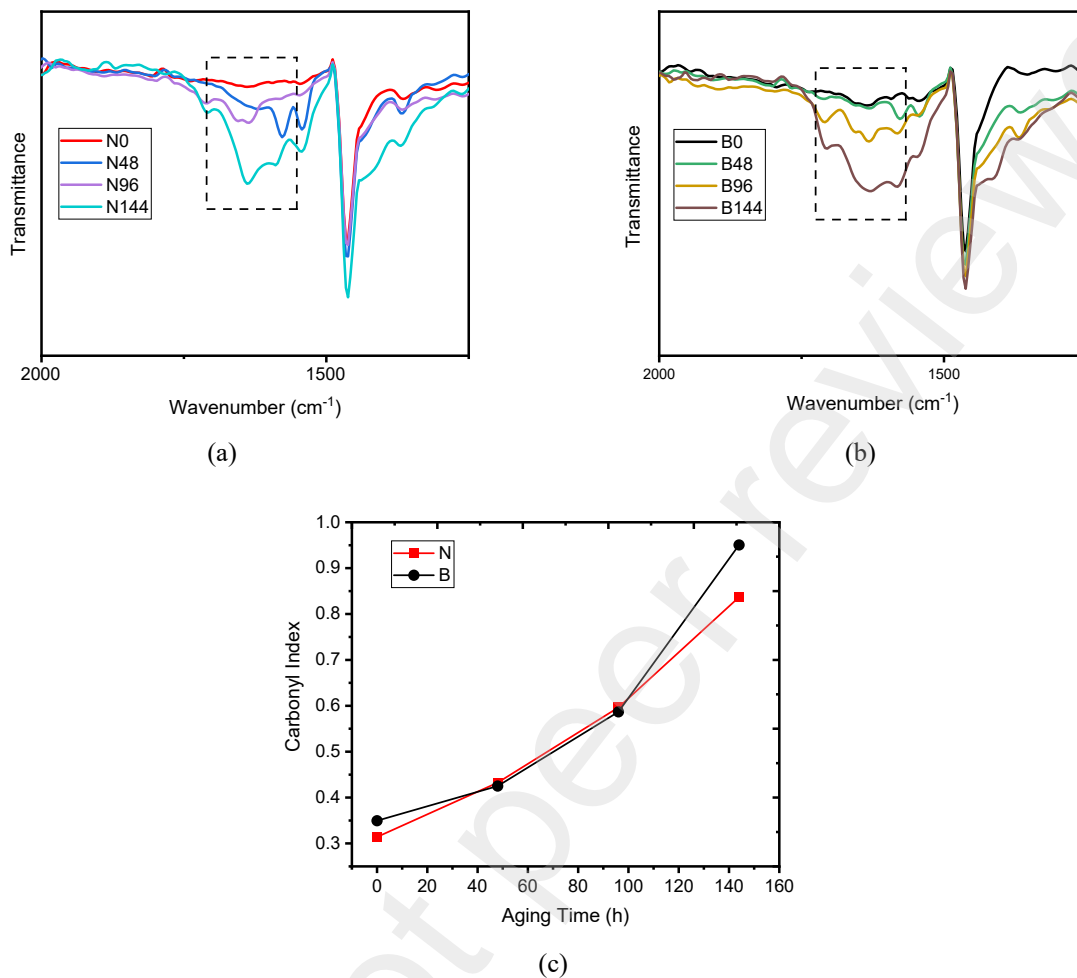
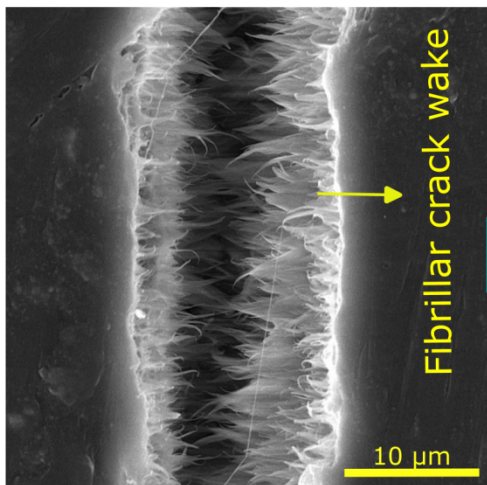


Figure 7- FTIR spectra of a) neat samples, b) black samples. c) values of carbonyl index (CI) versus aging time for all samples.

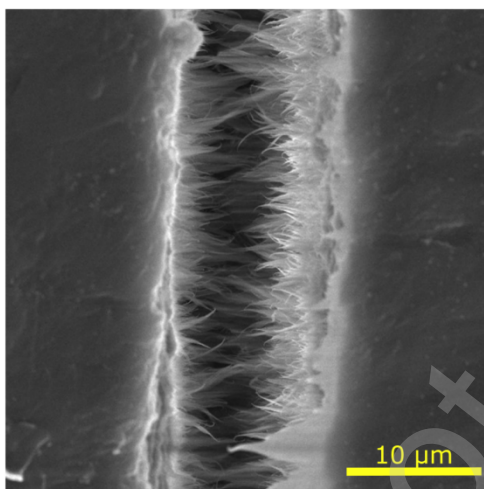
3.5. Morphology and Crack formation

In order to gain a deeper insight into how aging impacts the formation and appearance of cracks, FE-SEM images of crack formations on tensile test specimen that exhibited brittle failure after 144 hours of aging were obtained. The results for black and neat samples are shown in Figure 8.

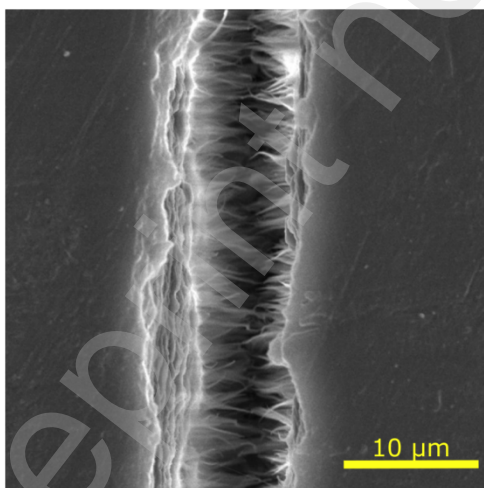
White samples



144h



240h



360h

Black samples

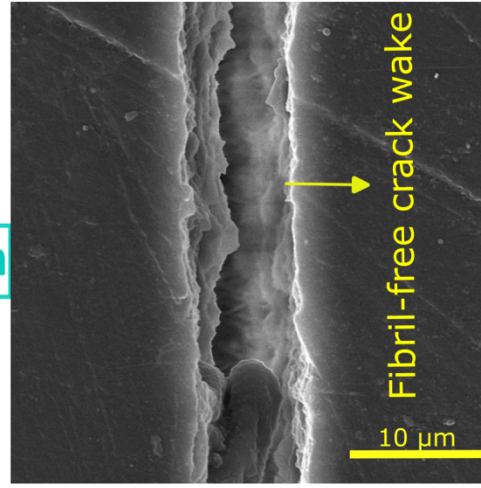
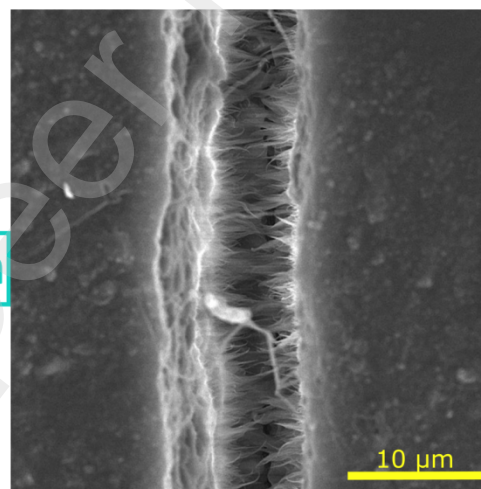
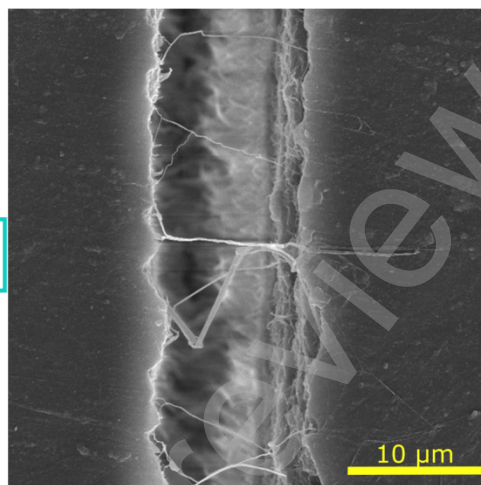


Figure 8- FE-SEM images of the black and neat samples at extreme aging times of 144, 240 and 360 hours.

A notable observation emerges when comparing the crack pattern morphologies in black and neat PE100 samples. In the neat sample, a significant number of fibrillations is evident at 144 hours, diminishing as aging progresses to 240 and 360 hours. Conversely, the black samples show minimal fibrillations at 144 and 240 hours, with complete absence of fibrillations at 360 hours. This discrepancy can be explained by the presence of more fibrillations, indicating a more ductile failure mode in the neat sample. The longer 'tie' molecules in the amorphous region can better hold the crack walls together, forming bridges that eventually fail as the crack widens, leaving behind fibrils. A higher density of fibrils at crack walls signifies greater resistance to crack propagation. The lower number of fibrils in black samples and eventual "de-fibrillation" at 360 hours suggests a reduced load-bearing capacity of the amorphous region in the crack wake due to a fewer number of bridging tie molecules. These findings align well with mechanical and dynamic rheological test results, indicating that carbon black particles disrupt morphology and mechanical properties, resulting in decreased tie molecule density and reduced crack resistance. The fact that carbon black itself can accelerate the oxidation process is also of particular importance, since non-aged neat and black samples usually show similar mechanical properties and strain hardening, although slow crack growth test has revealed a lower resistance in black samples compared to neat PE100 [17]. Based on the rheological results, it can be concluded that the chain scission is facilitated in the aged black samples compared to the neat ones.

Schematics showing how the carbon black particles may effectively inhibit the tie molecule formation and subsequent crack morphologies are presented in Figure 9.

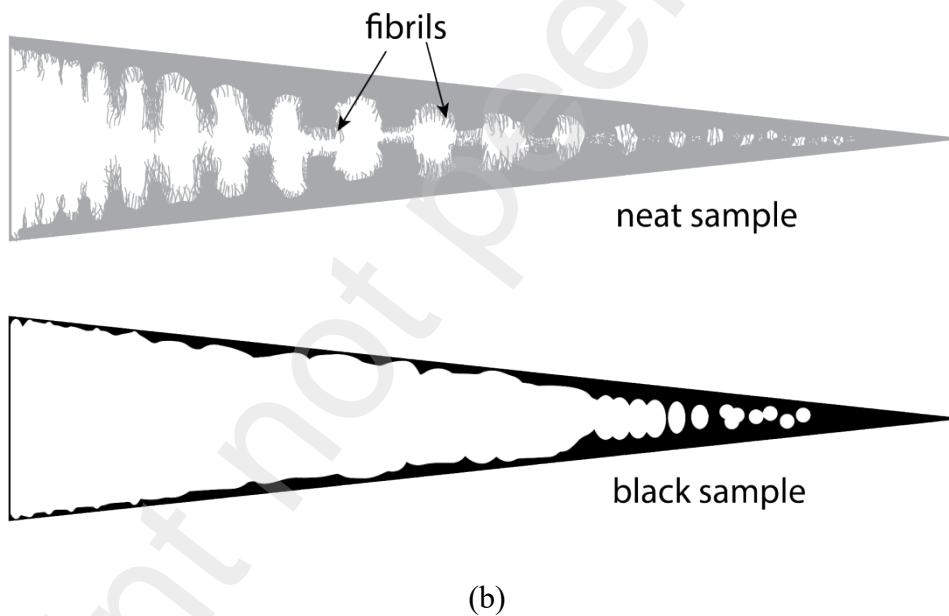
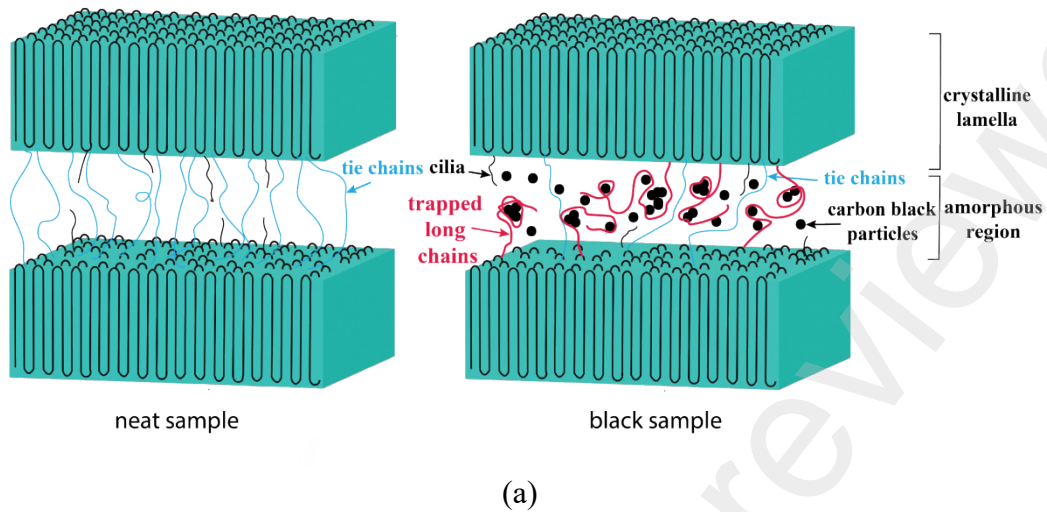


Figure 9- a) Schematic showing the inter-lamellar region of neat and black samples, demonstrating one possible scenario that inhibits tie molecules formation b) Schematics showing crack morphology in neat and black samples.

Figure 9(a) and (b) show how the presence of carbon blacks in the interlamellar region can physically prevent a tie molecule formation. As stated in the previous work [17], it is expected that the long chains, which form tie-molecules, are physically trapped in carbon black aggregates and

remain in the amorphous phase, which is susceptible to chemical degradation [47]. The long chain scission and formation of shorter chain will suppress the fibrillation potential of the samples, as observed in the morphology images shown in Figure 8.

While this is one factor affecting the tie molecule density, there might also be another catalytic effect for carbon black which accelerates the chemical oxidation of polymer chains, especially the longer tie molecules, effectively advancing the chemical degradation even further. The latter concept should be further studied in future research and if confirmed, it means that carbon black can synergistically accelerate the deterioration of long-term performance of the PE100 both physically (special inhibitor for tie molecule formation) and chemically (acting as a catalyst that accelerates chain oxidation).

Figure 9(c) demonstrates the crack morphology of black and neat samples schematically. As confirmed by electron microscope images, the black sample has a lower ability to establish stretching fibrils in the crack wake, while the neat sample shows an opposite behavior, which in turn reflects its better ability to resist crack growth. The neat sample's extensive fibril formation is expected to create a larger plastic zone ahead of the crack tip, dissipating more energy and thereby increasing resistance to crack growth, while the black sample clearly shows a more brittle failure pattern.

The findings of this study can indicate that implementing dual-layer pipes could significantly extend the lifespan of PE100 pipes as explained below:

Outer UV-Resistant Black Layer: By incorporating an outer layer with UV resistance (typically black), we shield the pipe from the harmful effects of ultraviolet radiation. This layer acts as a

protective barrier, preventing UV-induced degradation and maintaining the pipe's structural integrity.

Inner Oxidation-Resistant neat layer: The inner layer, with proven oxidation resistance in chlorinated media, provides excellent protection against chemical reactions. When exposed to aging factors like chlorine-containing pot water, this layer remains robust and resilient.

4. Conclusion

In this study, black and neat PE100 with same base polymer were exposed to a high concentration chlorine dioxide media to achieve an accelerated aging and assess the effect of carbon black aggregates on the oxidation process and properties of the black compounds. The various characterization tests revealed the following key findings:

Pipe grade PE100 containing carbon black demonstrates a more accelerated degradation compared to neat sample as shown in tensile tests, which indicates a deteriorating effect of carbon black particles in the aging mechanism. This worsening effect of carbon black and its role in increased chain scission/oxidation events shall be studied further in future works. The oxidation and following reduction in molecular weight can be characterized using rheological analysis of the samples which gives an insight in melt morphology, slight changes in molecular weight and its distribution and the extent of degradation. Based on rheological insights, it is proposed that in neat samples, selective chain scission occurs in long chains during the initial stages. This is followed by chain branching and crosslinking during the middle aging stages, and finally, severe overall chain scission during prolonged aging. Conversely, in black samples, overall chain scission happens early, followed by severe chain scission and branching in the middle stages, and some branching and crosslinking during prolonged aging.

As revealed by isothermal crystallization parameters coupled with rheological properties, it can be concluded that there is a competition between chain scission and crosslinking of free radicals at chains' end at very high concentrations of chlorine dioxide. For black samples, a gel-like structure may be formed due to crosslinking which hinders the crystallization kinetics and spatial movement and arrangement of the chains. For neat samples, while there is a reduction in crystallization kinetics at first, indicating some branching and crosslinking in middle stages, with further aging, crystallization rate increases again, which demonstrates the dominance of chain scission in later aging stages.

Morphological features seen in FE-SEM images of the cracks formed in the prematurely failed tensile samples at higher aging times revealed that neat samples have much more fibrils in their crack walls compared to the black samples, indicating a more ductile failure at micro-scale. These fibrils are indicative of presence of more bridging tie molecules in the neat sample, while the black one is almost completely free of fibrils at higher aging times. It can be concluded that the presence of carbon black does indeed facilitate the degradation of long chains and reduce the tie molecule density, which is a key element for bimodal resins in their lifetime and resistance to creep failure and slow crack growth. By adopting dual-layer pipes, an extended lifespan, lower maintenance costs due to fewer replacements and failures and more sustainability due to lesser material waste can be achieved. A dual-layer PE100 pipe where UV resistance meets oxidation resistance may present a cost-effective solution for infrastructure longevity.

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