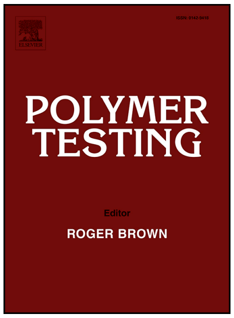

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Author Statement

Farzad Gholami: Investigation, Writing - Original Draft

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Long-term mechanical performance of polyethylene pipe materials in presence of carbon black masterbatch with different carriers

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Abstract

In this paper, two types of carbon black (CB) masterbatch with different carriers, i.e. HDPE and LDPE, are used to produce black compounds using three PE100 resins with various short chain branching distributions. Due to difference in short chain branch (SCB) distribution, the used polyethylene resins behave differently in microstructure development and long-term creep behavior. The microstructural analysis using different DSC techniques and rheological measurements revealed more sensitivity of the polyethylene resin with uniform comonomer distribution to the carbon black aggregates and their polymeric carriers. The Full Notched Creep Test (FNCT) was performed to determine the long-term creep performance of the black compounds; it is shown that the sample having more uniform comonomer distribution is more resistant compared to other samples. On the other hand, by addition of carbon black masterbatch, resistance to slow crack growth in samples decreases since carbon black aggregates can act as stress concentration spots in the structure. However, with addition of the masterbatch with LDPE carrier polymer, the reduction of this value in samples is lower compared to one with HDPE carrier. The reason for this observation is that long branches of LDPE polymer enter the structure of lamellae in the PE100 resins, making them more coherent and increasing the number of tie molecules. The samples that are blended with LDPE polymer have a rougher surface, which means linkage between two sides of crack was stronger due to higher entanglement density in these samples. The impact test confirms the same trend as FNCT test, with the sample containing LDPE carrier having higher impact strength.

Introduction

One of the best replacements for steel and concrete pipes intended for transportation of water and natural gas is polyethylene pipe, thanks to its excellent versatility, chemical resistance and strength. Experiments show that these pipes undergo a specific kind of failure known as slow crack growth (SCG) which occurs at low stress levels (below yield stress) and near room temperatures[1–7]. The mechanism for this failure includes formation of crazes, their growth and final crack propagation[6,8–10]. Craze growth strongly depends on chain entanglements in structure which in turn depends on factors like molecular weight, molecular weight distribution and short chain branches (SCBs) content and their distribution and a slight change in these parameters can influence long-time performance of pipe materials significantly[11,12].

Mechanical properties of polyethylene pipes can be negatively impacted due to sunlight radiation since UV radiation can make a drastic change in the structure of the polymers [13–16] and this is an important problem for these pipes which needs to be addressed. Carbon black (CB) is the most affordable and effective material that is used in pipe production to act as UV-absorbing agent, also giving most plastic transfer pipes their black color. Carbon black aggregates are usually added to polyethylene in the form of masterbatch, containing about 30-40% carbon black with the rest being polymer carrier. The optimum amount of carbon black in the compound is about 2.5 wt. % which means between 4-6 wt.% of polymer carrier exists in the final composition of the compound. This is a considerable amount that can affect mechanical, thermal and rheological properties of pipes as we have addressed it in our pervious works [13,17]. Besides the amount of carbon black, its distribution in the polyethylene can also be of importance. Deveci et al. [18] have extensively studied this phenomenon and its effect on mechanical properties of polyethylene pipes, without pointing out the long term mechanical behavior of the samples.

Due to presence of a considerable amount of carrier in the compound, it can be said that black pipes are a blend of neat polyethylene and carbon black’s carrier polymer. Chain entanglements might be increased or decreased by addition of a second polymer with a different molecular weight distribution to neat PE100 resin [19]. Thus, it is reasonable to conclude that by addition of carbon black masterbatch, while carbon black aggregates can act as nucleation sites for crystallization and stress concentration regions, carrier polymer may also affect the performance of pipe materials.

We have used isothermal crystallization and rheological measurements to predict the resistance to slow crack growth in neat and black PE100 resins in presence of carbon black masterbatches [13,17,20]. It was observed that Avrami equation parameters, which are obtained by fitting the isothermal crystallization data on Avrami equation, can be used as determinative factor for SCG resistance in polyethylene pipe materials. With increasing n (the Avrami index), the resistance to slow crack growth in polyethylene resins is reduced significantly [20], since this parameter is related to the morphology of the crystals in the structure of the polymers. Krishnaswamy et al. [12] investigated the longtime performance of PE pipes, suggesting a schematic model based on their findings in mechanical, thermal, and rheological tests. Also, Sardashti et al. [21,22] suggested that the relaxation time(λ) obtained from fitting the experimental data on Carreau-Yasuda (CY) equation [23,24] is a good determining factor for the amount of chain entanglements in the structure of polymer melts.

In this study we investigate the effect of addition of two different carbon black masterbatches to PE100 resins with different SCB distributions. Samples are examined using thermal, rheological and long-term creep tests with the aim of delineating the role of masterbatch carrier and short chain branch distribution in resistance to slow crack growth.

Materials and methods

Materials and sample preparation

Three different PE100 pipe grade materials were supplied by Iranian petrochemical companies. The used polyethylene resins are HDPE polymers and produced using Ziegler-Natta catalysts under the Hostalen license of LyondellBasell and have a bimodal molecular weight distribution. Table 1 shows some characteristics of the used polyethylene grades. The main difference between three grades is the 1-butene comonomer distribution as we have studied in our previous work [20]. To make black compound in laboratory, two different types of carbon black masterbatches with different polymer carriers, i.e. HDPE and LDPE, were used. The masterbatches are two commercial grades that were provided by Jam petrochemical company.

Table 2 presents some properties of these masterbatches. the code of masterbatch was used for identification of black compounds, i.e. B1-100J1 means the N-100J1 compounded with B1 black masterbatch.

Table 1.Some characteristics of used PE100 pipe grade materials in this study

Samples	Polymer Type	Density (g/cm^3)	MFI (g/10min) 190 ˚C, 5 kg	MFI (g/10min) 190 ˚C, 21.6 kg
N-100J1	Bimodal HDPE	0.952	0.22	6.9
N-100J2	Bimodal HDPE	0.950	0.18	6.2
N-100M	Bimodal HDPE	0.951	0.21	5.8

Table 2. Properties of used masterbatches

Masterbatch	Shape	MFI (g/10min) 190 ˚C, 5 Kg	Carbon black content (wt. %)	T5% (˚C)*	Carrier polymer type
B1	Granule	1.06	39.5	452.4	LDPE
B2	Powder	0.50	39.5	442.5	HDPE

* T5% is the temperature in which 5% of the sample's weight is decomposed in TGA test.

Black samples were produced using a lab scale twin screw extruder with temperature profile of 190-200 -195 -190 ˚C by blending natural polyethylene with carbon black masterbatch. These samples have an overall ~2 wt.% of carbon black and the PE100/masterbatch ratio is 95/5. Dispersion tests were performed according to ISO 18553 standard [25] and the results showed that blending and dispersion of carbon black is acceptable in all samples.

Thermal Analysis

To evaluate carbon black content in masterbatches, TGA test was performed by a METTLER TOLEDO TGA/DSC instrument at nitrogen atmosphere from 25 ℃. to 600 ℃. Isothermal and non-isothermal crystallization as well as SSA-DSC were carried out by TA Q100 differential scanning calorimeter (DSC) to evaluate thermal properties of samples. Approximately 5 mg of samples in Al circular pans were used. For isothermal test, samples were heated to 180 ˚C at 10 ˚C/min and maintained for 3 min and then cooled first to 140 °C at 10 °C/min, held at 140 °C for 2min, and afterwards rapidly cooled (at 40 °C/min) to the 121˚C and maintained at this temperature for 120min. For isothermal DSC, the method suggested by Krishnaswamy et al. [12] was used and crystallization time and the crystallization rate of samples were evaluated. The rational of using 121 ˚C as isothermal crystallization temperature has been discussed in our previous work [17]. In SSA-DSC, test samples were annealed at different temperatures for 15 minutes and in 8℃ steps which leads to fractionation of molecular chains based on their size and their ability to crystallize. Suggested cycles in previous studies [26–30] have been mostly used for LLDPE which has at least 6-7% co-monomer content, while thermal fractionation is more difficult for HDPE resins due to much lower comonomer.

Mechanical tests

Tensile tests were performed at room temperature using Hounsfield H10KS universal frame at the strain rate of 50 mm/min based on ASTM D638 test method after 6 days of aging for samples. Test samples were cut from compression molded sheets according to ASTM-D638 standard. The Charpy impact tests were carried out according to ASTM 6110-04 and impact test samples were cut from 3mm thickness sheets. The reported results are average of at least 5 measurements.

To evaluate the long-term mechanical performance of the samples, a lab scale full notch creep test (FNCT) machine made based on ISO 16770 [31] was used. The samples for the FNCT test were cut from 6mm thick compression molded sheets. The dimension of samples is 6×6×90 mm. The FNCT measurements were carried out at 55˚C and 9MPa load, considering the result of Schilling et al. [32].

The FNCT test is performed using Igepal CO-630 as surfactant. The reported results are average of at least 3 measurements.

Morphological observation

Microstructural evaluation was performed by a TeScan - Mira III field emission scanning electron microscope (FE-SEM). The samples were broken in liquid nitrogen and the amorphous phase was removed by an etchant with composition (H_2SO_4:H_3PO_4: water = 5:2:1 and 1 wt% $KMnO_4$), after which, samples were washed in a solution of diluted sulphuric acid. H_2O_2:H_2SO_4 (diluted) (H_2SO_4:H_2O 2:7). Afterwards, dried samples were sputter coated with a thin gold layer.

Rheological measurements

A rheometric mechanical spectrometer model MCR301 (Anton Paar) instrument was utilized in oscillatory shear measurements. Samples for rheology test were prepared from 2 mm thick compression molded sheets. To study the linear viscoelastic behavior of the samples, in the amplitude of 1%, the following measurements were conducted:

- Isothermal dynamic frequency sweep test at 190℃.
- Isochronal dynamic temperature sweep test at a constant frequency (10 Hz) and 5℃/min temperature ramp.

XRD Test

X-Ray Diffraction tests were performed by X’Pert PRO MPD (PANalytical) to study possible changes induced in the lattice unit cell parameters of black compounds.

Results and Discussion

Characterization of polyethylene resins and masterbatches

Based on supplier’s information, PE100 samples have similar molecular weights, but the comonomer distribution in the samples varies a bit. To confirm this, short chain branches distribution has been investigated by different methods suggested in the literature. Figure 1 (a) shows viscoelastic behavior of natural PE100 samples in different frequencies. Viscosity of samples in whole frequency range are approximately similar, hence, it can be concluded that molecular weight and molecular weight distribution of the samples are almost identical. Figure 1(b) shows heat flow against time for PE100 samples using isothermal DSC, revealing that in spite of the similarities in MW and MWD, PE100 samples show different thermal behaviors. N-100J2 has slower motion in its molecular chains compared to two other samples. It is reasonable to assume that short chain branch distribution is a key difference in three PE100 samples. To further evaluate the distribution of co-monomers in chains, SSA-DSC is performed as a fairly fast and accurate technique.

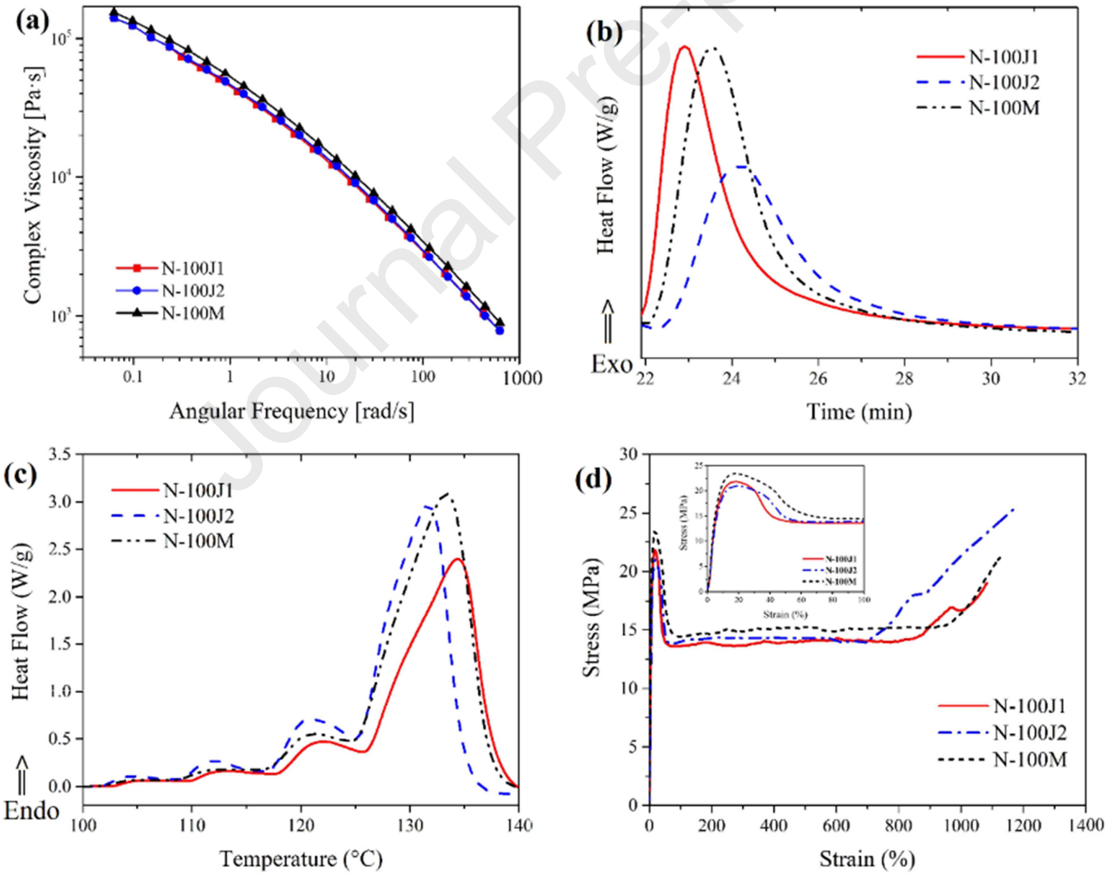

Figure 1. Characterization of neat PE100 samples: (a) complex viscosity vs. frequency, (b) isothermal DSC examination, (c) SSA-DSC analysis, and (d) tensile test.

Figure 1 (c) shows heat flow vs. temperature curves for PE100 samples obtained from SSA-DSC test. It can be observed that in N-100J2, low-temperature peaks, which are a sign of co-monomers being located on longer chains, have a larger area [20,27,28]. Thus, in this sample, long chains are slower because of more SCB located on long chains fraction. There are some studies that use tensile test to investigate the short-chain branches distribution [12,13]. According to these studies, when SCBs are located on chains with higher molecular weight, strain hardening start point occurs at lower strains [12]. Figure 1 (d) compares tensile test curves for these three samples, confirming this observation and the results of isothermal and SSA-DSC.

Effect of masterbatch on crystalline structure of samples

Results of non-isothermal DSC (graphs not shown) for raw polyethylene resins and black compounds are presented in Table 3. There is a similar trend in the thermal behavior of all three samples in presence of different masterbatches. It can be observed that by adding masterbatches to neat PE100 samples, their crystallization behavior is changed. Reduction in crystallinity and increasing their melting temperature indicates that the presence of carbon black aggregates between chains reduces crystallinity because these can disturb the chain folding and mobility. On the other hand, the increase of the melting temperature can be considered from the increase of the lamellas thickness based on Gibbs-Thomson equation [33–35]. It is observed that B1 masterbatch with LDPE carrier has more effect on crystallinity suppression of the samples. Thus, the crystalline structure of the black compounds is affected by two major factors: (i) carbon black aggregates and (ii) type of masterbatch carrier polymer.

To investigate the influence of carbon black masterbatches on molecular motion and chain folding of samples, isothermal crystallization test was performed for black compounds as shown in Figure 2. According to previously reported results [13,17], we expected a significant decrease in crystallization time of sample by adding the carbon black masterbatches, because carbon black aggregates can act as nuclei for crystallization and accelerate the crystallization rate [17]. This trend can be observed in compounds containing HDPE carrier masterbatch, while in LDPE containing compounds, the opposite is true and due to addition of this carbon black masterbatch, crystallization rate has been hindered. The rationale for this observation is that the masterbatch carrier polymers, as well as carbon black aggregates, both can have a significant effect on crystallization rate. In compound containing B2, the carrier of the masterbatch, which is HDPE, is approximately similar with base PE100s, thus carbon black aggregates are a determining component in crystallization rate. On the other hand, in the samples mixed with B1 masterbatch, the carrier is LDPE with long chain branching structure which makes chain folding more difficult [36,37]. In these samples, carbon black also acts as nucleation sites, but the presence of LDPE chain and its entanglement with the other chains, suppress the nucleation effect of carbon aggregates, hindering the PE100 chain folding and reducing the crystallization rate of the samples. Experimental data were fitted on the Avrami equation and obtained crystallization parameters from this equation are presented in Table 3. To calculate these parameters, an Origin software plugin developed by Lorenze et al was employed [38].

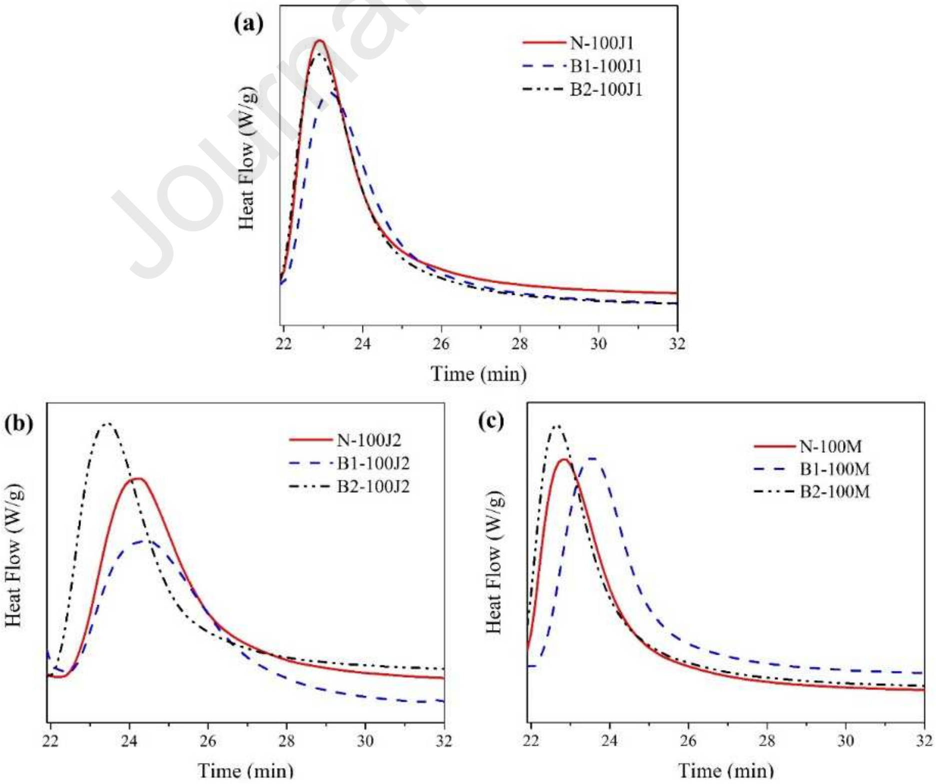

Figure 2- Heat flow vs. time curves for PE100 samples and their compounds obtained from isothermal DSC test.

Table 3. Non-isothermal DSC data and Crystallization parameters obtained from isothermal DSC test

Samples	Tm [℃]	Tc [˚C]	Xc [%]	$t_{1/2}$ (s)	Crystallization rate K (min^{-n})	Avrami index (n)	R^2
N-100J1	131.1	117.3	57.9	48	0.34	2.88	0.9999
B1-100J1	132.1	115.5	52.6	53	0.32	2.90	0.9999
B2-100J1	132.2	116.4	55.0	40	0.35	2.90	0.9999
N-100J2	129.6	115.3	53.0	159	0.11	2.45	0.9999
B1-100J2	130.6	115.5	49.7	191	0.06	2.63	0.9999
B2-100J2	130.7	116.1	52.3	140	0.13	2.71	0.9999
N-100M	131.6	116.7	61.4	60	0.24	2.80	0.9999
B1-100M	131.8	117.1	57.0	71	0.22	2.83	0.9999
B2-100M	131.8	117.2	59.2	52	0.25	2.90	0.9999

In Table 3, it is observed that N-100J2 is significantly more sensitive to the changes in Avrami index than the other two samples with addition of masterbatch. In other words, one can say that the crystallization behavior of the sample having a more uniform SCB distribution on its long chains is more sensitive to addition of masterbatch. For, N-100J1 and N-100M samples, SCBs might have a non-uniform distribution, thus chain segments between two short chain branches are relatively larger and chain folding in these segments will occur more easily, making them less sensitive to foreign chains and particles. This speculation is shown schematically in Figure 3.

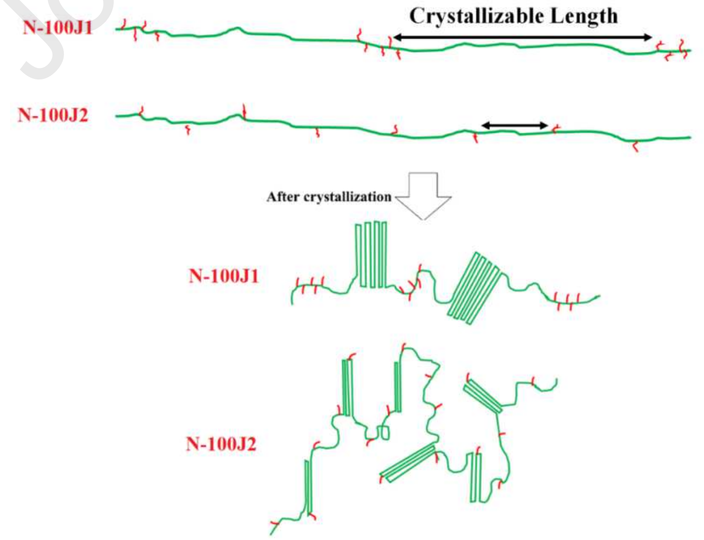

Figure 3. Suggested schematic model for describing the difference among SCB distribution of samples.

To study the effect of carrier resins on crystalline structure of the samples, the XRD test was performed on the PE100-J2 samples and the results were shown in Figure 4. It can be seen that by addition of the masterbatch with HDPE carrier, there is no change in characteristic peaks (2θ=21.58 and 23.97), while in the LDPE case, the corresponding peaks are shifted to the lower angles (2θ=21.45 and 23.81) indicating the increase in the lattice parameters of the polyethylene unit cell. This is in a good agreement with the fact that lattice parameters of LDPE polymer are larger than HDPE [39–41]. In other words, it can be concluded that during crystallization, LDPE chains of masterbatch carrier can enter the crystals of the main PE100 resin and play a role in crystallization of black compounds and increase the coherency and entanglement between lamellas.

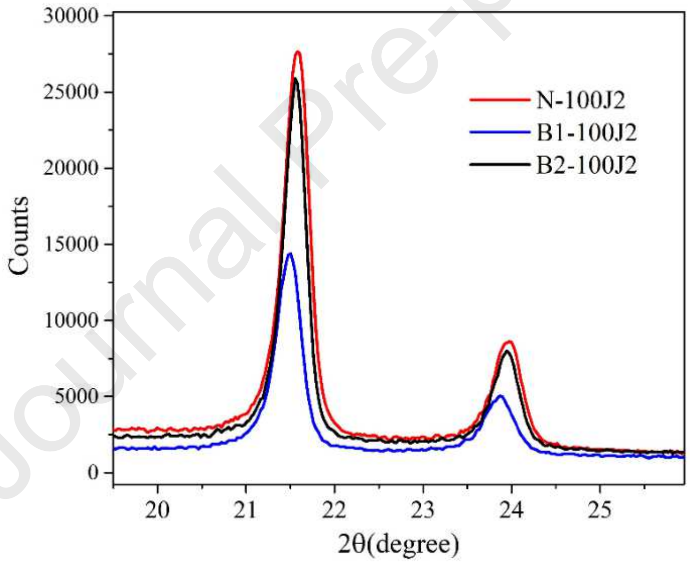

Figure 4. XRD patterns for N-100J2 sample and its compounds.

Rheological behavior and melt miscibility of samples

Rheological measurements, especially in the linear viscoelastic region, have been frequently used in order to assess the microstructure of polymeric samples, including the melt composition and miscibility, which considerably influence the flow behavior of non-Newtonian polymeric melts [42–44]. All samples demonstrate the typical behavior of high molecular weight melts with liquid like rheological behavior at low frequencies region and solid like behavior at higher frequencies, while shear-thinning behavior is observed in the whole frequency range. Figure 5 (a) to (c) show the rheological properties of the neat PE100 and black samples in presence of two different masterbatches. It is obvious that by adding masterbatch to three different PE100 samples they show similar behavior. On the other hand, it can be seen that complex viscosity and storage modulus of all the compounds containing B1 masterbatch (with LDPE carrier polymer) decline in contrast to neat samples, mainly because of lower molecular weight of B1 polymeric carrier as reflected in its higher MFI presented in Table 2. However, the long chain branches of B1 carrier may increase the entanglement chance and increase the overall relaxation time. Contrary to expectation, in the samples using B2 masterbatch, which also has higher MFI than the neat samples as shown in Tables 1 and 2, the complex viscosity and storage modulus was not decreased, which is against of the mixing rule prediction. While the complex viscosity and storage modulus of B2-100M sample is similar to its neat resin, the N-100M, those of the B2-100J1 and B2-100J2 are higher than their base resins, presented in Figure 5 (b) and (c), respectively. According to Figure 5 (b) and (c), it could be observed that the rheological properties changes in B2-100J2 sample is considerable, pointing out the good dispersion of carbon black aggregates which can hinder the movement of long chains molecules with short side chains which can be trapped between carbon black aggregates [13,17]. Based on these results, one can conclude that masterbatch is more effective for 100J2 neat resin, suggestive of the role of short chain branching distribution on interaction with carbon black aggregates. This result is in a good agreement with isothermal DSC that N-100J2 sample is more sensitive than other samples and can be considered as verification for the suggested schematic model shown in Figure 3 for distribution of SCBs on long chains.

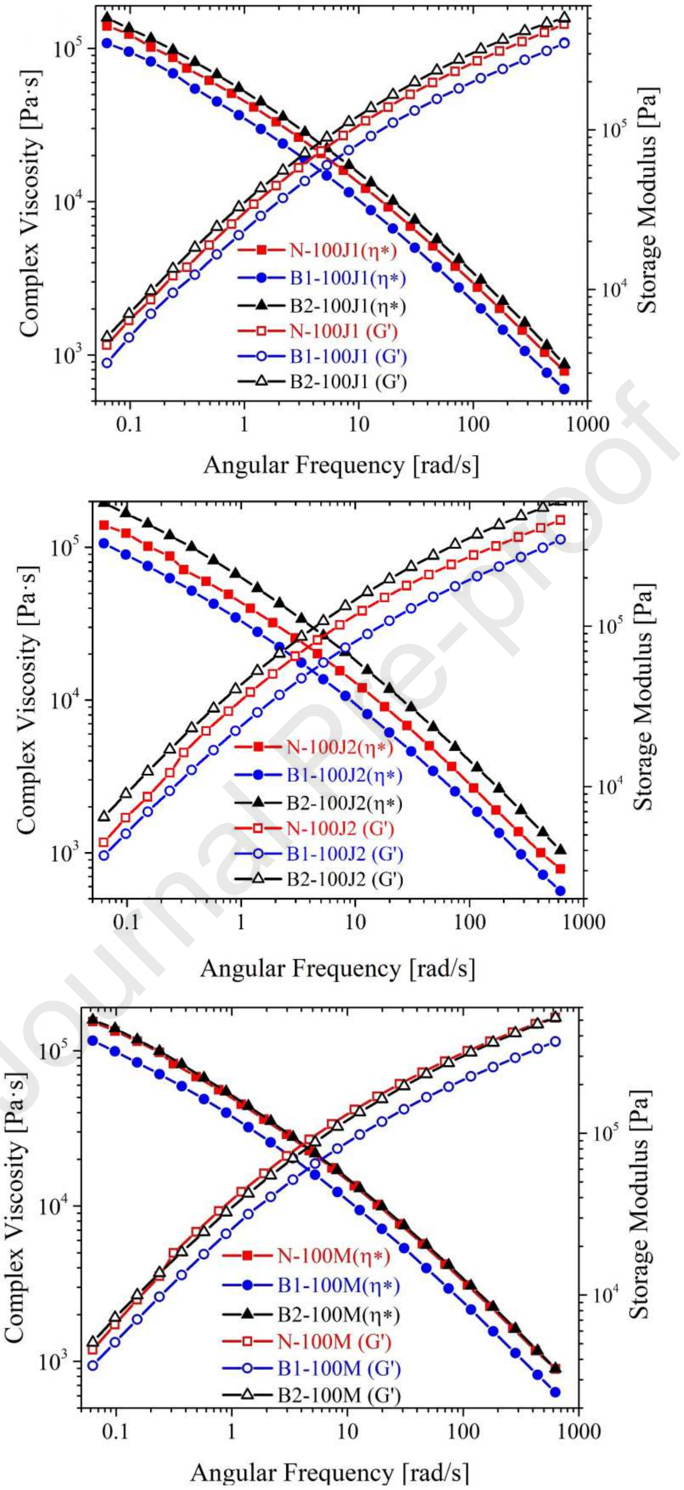

Figure 5. Rheological properties of three (a) N-100J1, (b) N100J2, and (c) N100M samples and their black compounds.

The experimental data of the 100J2 samples were fitted to the Carreau-Yasuda (CY) equation (Eq. 1) and the obtained zero shear viscosity and average relaxation time are presented in Table 4. Relaxation time (λ) can be one of the factors that represent chain motion in molten phase and we can use this factor to have a better judgement on the long-time performance of pipes; the higher the λ value, the higher the amount of chain entanglements and hence more resistance against SCG [21]. Since all three PE100 samples show similar behavior in all tests by addition of carbon black masterbatch, only the data for N-100J2 is reported. It can be seen that in Table 4, λ for N-100J2 increased by addition of two masterbatches and it is a reasonable conclusion that carbon black aggregates make the motion of chains in melt state more difficult. An increase in this parameter by addition of B1 masterbatch is more pronounced than the B2 masterbatch.

$$\eta^* = \eta_0 \, [1 + (\lambda\omega)^a]^{(n-1/a)} \qquad (1)$$

Table 4. Rheological parameters obtained from fitting experimental data on Carreau-Yasuda equation

Samples	η_0 (Pa.s)	λ (s)
N-100J2	504850	1.98
B1-100J2	482430	3.68
B2-100J2	612140	2.74

Phase separation in polymer blends in melt state is an important issue and can have a vital influence on rheological behavior and mechanical properties of blends [45–47]. Temperature-sweep rheology tests were conducted to investigate phase separation in samples. Figure 6 shows the G′, G″ and tanδ against temperature for black 100J2 compounds. In previous studies [48,49], it was observed that change in G′ curve slope is a determinative factor for phase separation. According to these curves, it is clear that in all samples, G' reduces with increasing temperature, due to favored chain motion and reduced elastic behavior of the sample. But in B1-100J2 sample at approximately 195℃, slope of G' curve changes considerably, which is thought to be due to combined effect of the chain mobility and increased elasticity due to interfacial tension, and this is a behavior associated with phase separation. Due to phase separation, the role of interfacial elasticity of LDPE domains in HDPE matrix will affect the chain mobility at higher temperature and hence the storage modulus of B1-100J2 sample is positively deviated from the expected behavior guided with red line in Figure 6 (a). Interestingly, the tanδ curve of B1-100J2 sample shows a clear increasing –decreasing trend, so it can be assumed that the phase separation has been started from ~200 ˚C and continued to ~ 240 ˚C. The increased elasticity at higher temperature may result in flow instability like sharkskin at high production rate.

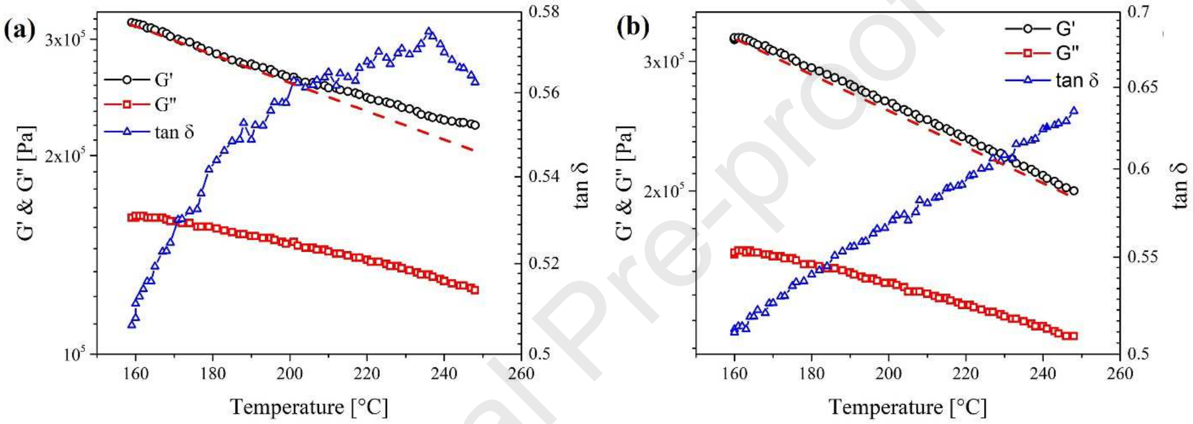

Figure 6. G', G" and tan vs. temperature curves for (a)B1-100J2 and (b) B2-100J2 samples obtained from temperature sweep rheology tests.

Long-term mechanical performance and impact resistance

To investigate the long-term performance of the samples, the SCG tests were performed on 100J1 and 100J2 sample and the data of these tests are presented in Figure 7. The 100M sample is excluded herein because of its similar behavior to 100J1 sample and also its different source of polymerization. As expected, it can be seen that creep failure time of N-100J2 with uniform distribution of short chain branches is considerably higher than other samples. From this figure, it can be inferred that the slow crack growth resistance of the neat PE100 samples is reduced by addition of carbon black masterbatch.

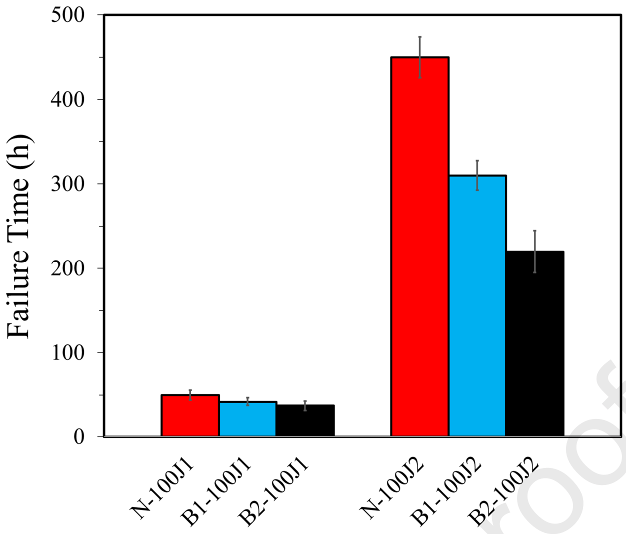

Figure 7. Comparison of failure time of neat and black samples obtained from ESCR test.

Masterbatch presence in structure has a double-faced effect on mechanical properties of PE100 samples, both carbon black aggregates and carrier polymer can influence SCG resistance. It can be observed from SCG test that carbon black aggregates without considering carrier polymer make the neat resins weaker against SCG. Another interesting result that can be seen is that in the samples compounded with B1 masterbatch, the reduction of lifetime of PE100 is lower than B2 compounds due to the fact that presence of LDPE chains in the structure of samples increases the entanglements density because of its long chain branches [50–52]. It is a good confirmation for isothermal DSC and rheological measurements that the presence of LDPE chains makes the resin molecule motion slower. Also, the activation energy (E_a) of linear low-density polyethylene is around 32-34 kJ/mol which is higher than that of the linear and short chain branched polyethylene, 27-29 KJ/mol. In other words, a higher thermal energy or time is needed for fibrillation and growth of the crazes in the sample containing chains with long branches.

Thus, motion of the chains in a resin has a direct relationship with resistance to slow crack growth and long-time performance of pipe material can be predicted with the tests that analyze the behavior of resin’s melt.

To further investigate the effect of carrier polymer on resistance to SCG in PE100 samples, SCG fracture surface of B1-100J2 and B2-100J2 samples were studied by SEM microscope. Figure 8 (a) is an overview image of the sample's fracture surface that has three distinct zones which is due to different stress levels at each area. In Zone I, i.e. the first step of fracture process, the ligament area is larger, hence the stress level is lower than other zones and crazes and fibrillations are smaller and the surface is relatively smoother. Zones II and III in which the stress is higher and fibrillations are larger, can be determining zones for investigation of slow crack growth [53,54] (zone I shows few details and all samples have nearly the same topology). Figure 8 (b) schematically describes the reason for the difference in zones' appearances.

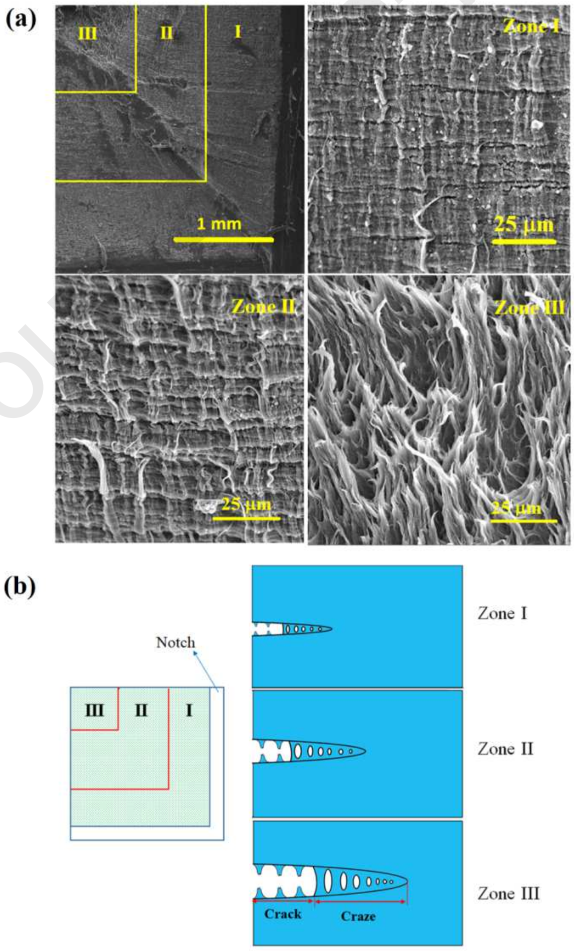

Figure 8. (a) SEM image of different zones in fracture surface in creep test (b) Schematic image for justifying the reason for the difference in fracture surface in different zones

Impact tests were performed on the N-100J2 sample and its black compounds and the results are presented in Table 5. It can be observed that the neat sample has the highest toughness since there is no carbon black aggregates as stress concentration zones in the structure of this material. In the B1-100J2 with LDPE chains the reduction of the impact resistance is lower than B2-100J2 sample as expected from SCG test results.

Table 5. Charpy impact resistance of the N-100J2 sample ant its black compounds

Samples	Toughness (KJ/m^2)
N-100J2	28.12 ± 0.8
B1-100J2	26.17 ± 1.3
B2-100J2	20.07 ± 0.6

SEM images of fracture surface of N-100J2 sample and its black compounds are shown in Figure 9. Three distinct zones can be considered in fracture surface during Charpy test; (i) notch zone, (ii) first step of fracture, and (iii) second step of fracture and the results are in agreement with literature [55]. First zone is a notch that has been made by a razor blade, second zone is first step of fracture, which is the most important and determinative zone in impact test fracture surface and third zone includes the rest of fracture process. It is noticed that the razor blade charpy is not typical test was used for comparative evaluation of the samples. Also it is worthy mention that in the under impact loads, other mechanisms than in SCG are relevant. By studying the second zone, it is possible to obtain some information about the structure and performance of the materials. It can be seen that in B1-100J2, the second zone has largest area and also pulled out fibrillations are more pronounced in higher magnifications which itself can be the reason for higher toughness of this sample compared to B2-100J2. The impact test and SCG test results are in excellent agreement with each other.

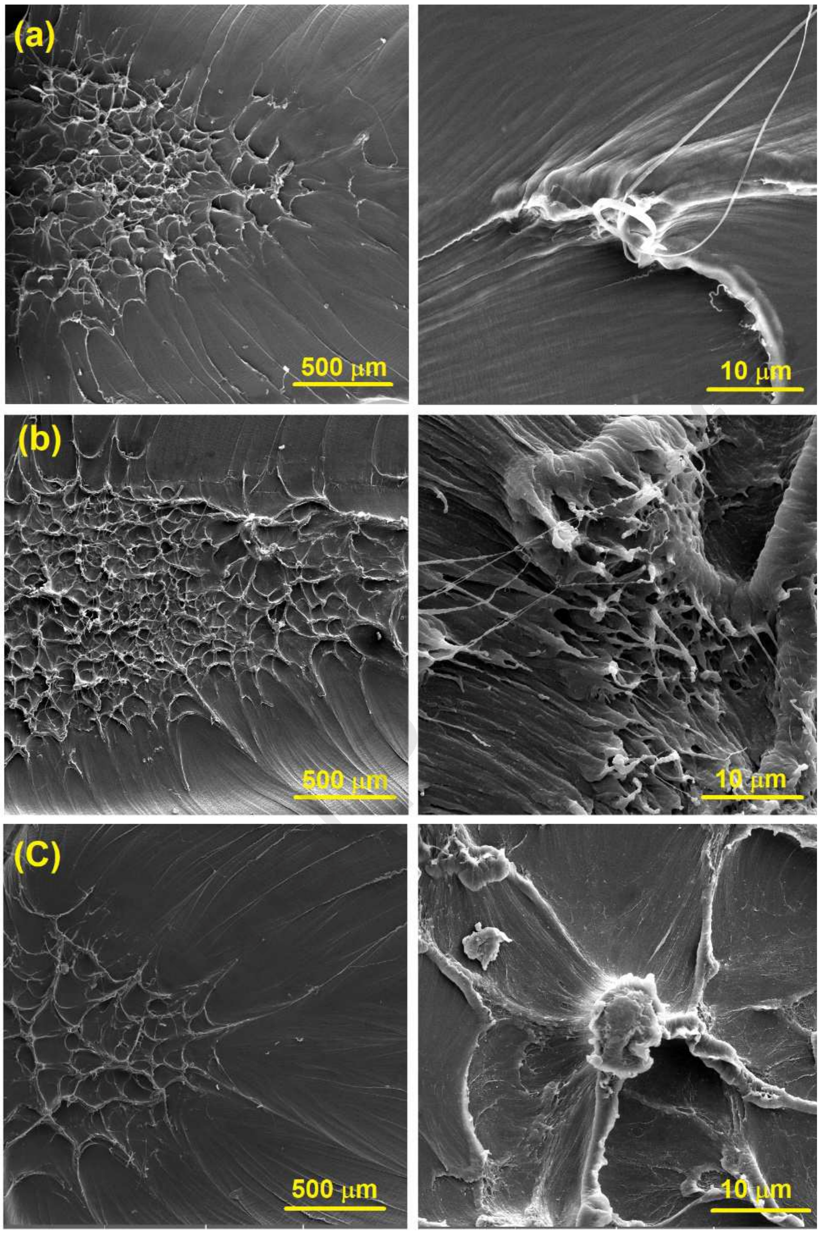

Figure 9. Impact test fracture surface SEM images for (a) N-100J2, (b) B1-100J2, and (c) B2-100J2 in different magnifications.

According to SCG test results, it can be seen that the long-time mechanical performance of N-100J2 sample is significantly higher than N-100J1 sample. Difference in the distribution of short chain branches is most probably the reason for this difference in creep test failure time. As mentioned above, in N-100J1 sample, SCBs are located randomly on molecular chains and thus the crystallize-able length of chains increased compared to N-100J2 in which SCBs located uniformly and with approximately equal length (Figure 3). Suggested schematic model in Figure 10 demonstrates the reason of the difference in resistance to SCG in these two samples. Since long chains usually make tie molecules that are a key factor to resistance to SCG [7,56,57], the difference in SCBs distribution on long chains has a direct effect on long-term performance which in our previous work is investigated completely[20]. Due to less participation of chains in crystals in N-100J2, this sample has more tie molecules naturally and thus its resistance against SCG is higher than N-100J. As mentioned earlier in rheological measurement section, melt relaxation time in the B1-100J2 sample is higher than N-100J2 sample and it was expected that the failure time of black sample in the SCG test be higher than the neat PE100 sample, but it is reverse. To justify this observation, it can be concluded that carbon black aggregates can both act as stress concentration sites and also trap longer chains in amorphous area, making establishment of tie molecules more difficult in solid state. Using this model, we can justify the reduction in failure time in the solid state and the increase of relaxation time of samples in presence of carbon black in melt state. (The same situation may be considered in rubber chains with carbon black, in which the chains can be trapped in between carbon black aggregates [58,59]).

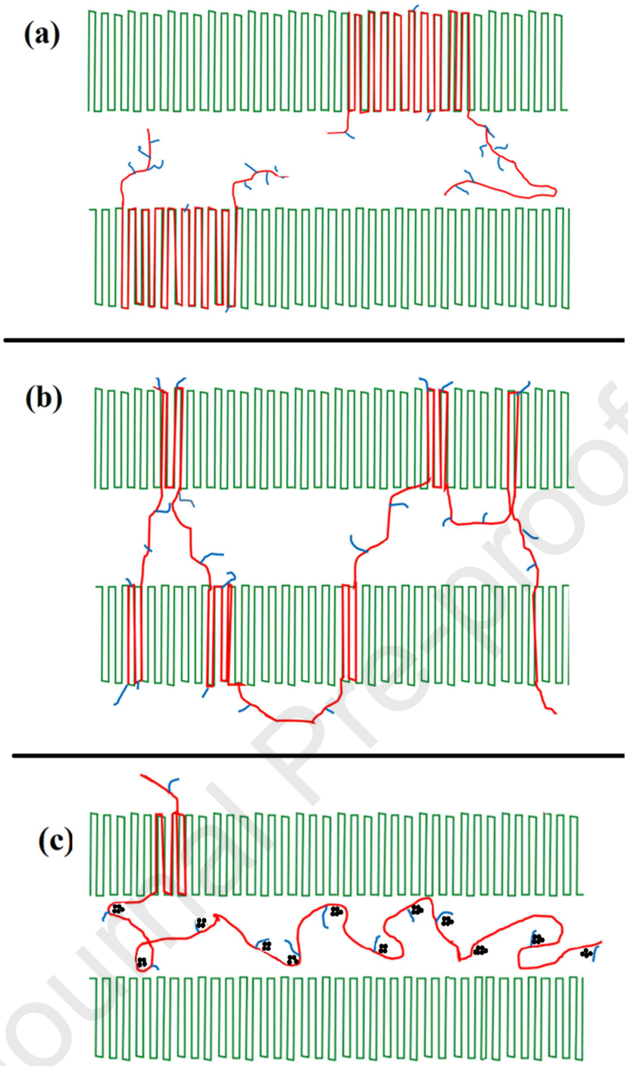

Figure 10. Schematic representation for investigating effect of SCBs distribution of tie molecules; (a) N-100J1 sample with the chaotic distribution of SCBs and (b) N-100J2 sample with uniform SCBs distribution on long chains , (c) Schematic model for studying the effect of carbon black aggregates on preventing long chains to enter the lamellas.

Conclusion

Based on the results obtained from different tests in this study, carrier polymer of black masterbatches and carbon black aggregates make changes in viscosity and chain motion of the PE100 samples. N-100J2 resin with more uniform short chain branch distribution is more affected by carbon black aggregates and the carrier polymer. The changes in both the relaxation time in viscosity test and crystallization time in isothermal crystallization test is noticeably higher for N-100J2 compared to N-100J1 which is the sample with non-uniform SCB distribution. Compared to pure samples, black compounds have lower failure time in slow crack growth due to presence of carbon black aggregates that affect sample properties in two different ways: (i) acting as stress concentration areas and (ii) preventing the branched long chains to enter the crystals and create the tie molecules. In the compounds that used LDPE carrier masterbatch, SCG test failure time is higher than the samples using HDPE carrier. The reason of this phenomenon is that the motion of the chains is more difficult due to long branches of LDPE carrier and a higher value of activation energy for branched polyethylene, meaning more resistance to fibrillation and growth of the crazes which lead to cracks.

Although results of SCG and impact tests indicated the better performance of masterbatch having LDPE carrier, the temperature sweep rheological measurements pointed out the possibility of the melt immiscibility at elevated temperature leading to surface instabilities. Therefore both of these issues should be considered in selection of the right masterbatch.

References

[1] J. Fawaz, S. Deveci, V. Mittal, Molecular and morphological studies to understand slow crack growth (SCG) of polyethylene, Colloid Polym. Sci. 294 (2016) 1269–1280. https://doi.org/10.1007/s00396-016-3888-5.

[2] R.K. Krishnaswamy, Analysis of ductile and brittle failures from creep rupture testing of high-density polyethylene (HDPE) pipes, Polymer (Guildf). 46 (2005) 11664–11672. https://doi.org/10.1016/J.POLYMER.2005.09.084.

[3] A. Peacock, Handbook of Polyethylene, CRC Press, 2000. https://doi.org/10.1201/9781482295467.

[4] J.M. Lagarn, G. Capaccio, L.J. Rose, B.J. Kip, Craze morphology and molecular orientation in the slow crack growth failure of polyethylene, J. Appl. Polym. Sci. 77 (2000) 283–296. https://doi.org/10.1002/(SICI)1097-4628(20000711)77:2<283::AID-APP5>3.0.CO;2-0.

[5] N. Brown, X. Lu, Y.-L. Huang, R. Qian, Slow crack growth in polyethylene - a review, Makromol. Chemie. Macromol. Symp. 41 (1991) 55–67. https://doi.org/10.1002/masy.19910410107.

[6] N. Brown, X. Lu, A fundamental theory for slow crack growth in polyethylene, Polymer (Guildf). 36 (1995) 543–548. https://doi.org/10.1016/0032-3861(95)91563-M.

[7] Z. Zhou, N. Brown, Slow crack growth of blends of high density and linear low density polyethylenes as influenced by morphology, Polymer (Guildf). 35 (1994) 3619–3623. https://doi.org/10.1016/0032-3861(94)90537-1.

[8] M.J. Cawood, A.D. Channell, G. Capaccio, Crack initiation and fibre creep in polyethylene, Polymer (Guildf). 34 (1993) 423–425. https://doi.org/10.1016/0032-3861(93)90100-O.

[9] H.B.. Hamouda, M. Simoes-betbeder, F. Grillon, P. Blouet, N. Billon, R. Piques, Creep damage mechanisms in polyethylene gas pipes, Polymer (Guildf). 42 (2001) 5425–5437. https://doi.org/10.1016/S0032-3861(00)00490-0.

[10] R.A.C. Deblieck, D.J.M. van Beek, K. Remerie, I.M. Ward, Failure mechanisms in polyolefines: The role of crazing, shear yielding and the entanglement network, Polymer (Guildf). 52 (2011) 2979–2990. https://doi.org/10.1016/J.POLYMER.2011.03.055.

[11] C. Li Pi Shan, J.B.. Soares, A. Penlidis, HDPE/LLDPE reactor blends with bimodal microstructures—part I: mechanical properties, Polymer (Guildf). 43 (2002) 7345–7365. https://doi.org/10.1016/S0032-3861(02)00703-6.

[12] R.K. Krishnaswamy, Q. Yang, L.F.-B. And, J.A. Kornfield, Effect of the Distribution of Short-Chain Branches on Crystallization Kinetics and Mechanical Properties of High-Density Polyethylene, (2008). https://doi.org/10.1021/MA070454H.

[13] G. Pircheraghi, A. Sarafpour, R. Rashedi, K. Afzali, M. Adibfar, Correlation between rheological and mechanical properties of black PE100 compounds-Effect of carbon black masterbatch., EXPRESS Polym. Lett. 11 (2017).

[14] ASTM, Standard practice for operating fluorescent light apparatus for UV exposure of nonmetallic materials, (2006).

[15] F. Carrasco, P. Pagès, S. Pascual, X. Colom, Artificial aging of high-density polyethylene by ultraviolet irradiation, Eur. Polym. J. 37 (2001) 1457–1464. https://doi.org/10.1016/S0014-3057(00)00251-2.

[16] L. Guadagno, C. Naddeo, V. Vittoria, G. Camino, C. Cagnani, Chemical and morphologial modifications of irradiated linear low density polyethylene (LLDPE), Polym. Degrad. Stab. 72 (2001) 175–186. https://doi.org/10.1016/S0141-3910(01)00024-6.

[17] A. Sarafpour, G. Pircheraghi, R. Rashedi, K. Afzali, Correlation between isothermal crystallization and morphological/rheological properties of bimodal polyethylene/carbon black systems, Polym. Cryst. 1 (2018) e10014. https://doi.org/10.1002/pcr2.10014.

[18] S. Deveci, N. Antony, B. Eryigit, Effect of carbon black distribution on the properties of polyethylene pipes - Part 1: Degradation of post yield mechanical properties and fracture surface analyses, Polym. Degrad. Stab. 148 (2018) 75–85. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2018.01.011.

[19] T. Kotaka, H. Watanabe, Entanglement in polymer blends: A manifestation of polymer effects, Die Makromol. Chemie. 14 (1985) 179–199. https://doi.org/10.1002/macp.1985.020141985115.

[20] F. Gholami, G. Pircheraghi, R. Rashedi, A. Sepahi, Correlation between isothermal crystallization properties and slow crack growth resistance of polyethylene pipe materials, Polym. Test. 80 (2019) 106128. https://doi.org/10.1016/J.POLYMERTESTING.2019.106128.

[21] P. Sardashti, C. Tzoganakis, M. Zatloukal, M.A. Polak, A. Penlidis, Rheological indicators for environmental stress cracking resistance of polyethylene, Int. Polym. Process. 30 (2015) 70–81. https://doi.org/10.3139/217.2963.

[22] P. Sardashti, A.J. Scott, C. Tzoganakis, M.A. Polak, A. Penlidis, Effect of Temperature on Environmental Stress Cracking Resistance and Crystal Structure of Polyethylene, J. Macromol. Sci. Part A. 51 (2014) 189–202. https://doi.org/10.1080/10601325.2014.871934.

[23] P.J. Carreau, Rheological Equations from Molecular Network Theories, Trans. Soc. Rheol. 16 (1972) 99–127. https://doi.org/10.1122/1.549276.

[24] K. Yasuda, R.C. Armstrong, R.E. Cohen, Shear flow properties of concentrated solutions of linear and star branched polystyrenes, Rheol. Acta. 20 (1981) 163–178. https://doi.org/10.1007/BF01513059.

[25] International Standard Organization, ISO 18553 - Method for the assessment of the degree of pigment or carbon black dispersion in polyolefin pipes, fittings and compounds, 2002. https://bukanpipe.com/images/download/DISPER/EN/ISO 18553.pdf.

[26] M. Razavi-Nouri, Studies of comonomer distributions and molecular segregations in metallocene-prepared polyethylenes by DSC, Polym. Test. 25 (2006) 1052–1058. https://doi.org/10.1016/J.POLYMERTESTING.2006.07.004.

[27] R.A. Shanks, G. Amarasinghe, Comonomer Distribution in Polyethylenes Analysed by DSC After Thermal Fractionation, J. Therm. Anal. Calorim. 59 (2000) 471–482. https://doi.org/10.1023/A:1010141508932.

[28] K. Pielichowski, K. Flejtuch, J. Pielichowski, Step-scan alternating DSC study of melting and crystallisation in poly(ethylene oxide), Polymer (Guildf). 45 (2004) 1235–1242. https://doi.org/10.1016/J.POLYMER.2003.12.045.

[29] G. Balbontin, I. Camurati, T. Dall’Occo, A. Finotti, R. Franzese, G. Vecellio, Determination of 1□butene distribution in LLDPE by DSC analysis after thermal fractionated crystallization, Angew. Makromol. Chemie. 219 (1994) 139–160. https://doi.org/10.1002/apmc.1994.052190112.

[30] M.Y. Keating, E.F. McCord, Evaluation of the comonomer distribution in ethylene copolymers using DSC fractionation, Thermochim. Acta. 243 (1994) 129–145. https://doi.org/10.1016/0040-6031(94)85048-8.

[31] International Standard Organization, ISO 16770 - Plastics - Determination of environmental stress cracking (ESC) of polyethylene - Full-notch creep test (FNCT), 2004. https://webstore.ansi.org/Standards/ISO/ISO167702004?gclid=CjwKCAjwkcblBRB_EiwAFmfyyzH3ll-2tNObZODeuUDN1baJ727iS2Ro2WftnEXSpOrlRlRM_qKCJRoCkJ4QAvD_BwE.

[32] M. Schilling, U. Niebergall, M. Böhning, Full notch creep test (FNCT) of PE-HD – Characterization and differentiation of brittle and ductile fracture behavior during environmental stress cracking (ESC), Polym. Test. 64 (2017) 156–166. https://doi.org/10.1016/J.POLYMERTESTING.2017.09.043.

[33] Y. Furushima, M. Nakada, M. Murakami, T. Yamane, A. Toda, C. Schick, Method for Calculation of the Lamellar Thickness Distribution of Not-Reorganized Linear Polyethylene Using Fast Scanning Calorimetry in Heating, Macromolecules. 48 (2015) 8831–8837. https://doi.org/10.1021/acs.macromol.5b02278.

[34] L. Lu, R.G. Alamo, L. Mandelkern, Lamellar Thickness Distribution in Linear Polyethylene and Ethylene Copolymers, Macromolecules. 27 (1994) 6571–6576. https://doi.org/10.1021/ma00100a048.

[35] C.G. Vonk, The determination of the lamellar thickness in semi-crystalline polymers by small-angle scattering, Makromol. Chemie. Macromol. Symp. 15 (1988) 215–222. https://doi.org/10.1002/masy.19880150116.

[36] Z. Li, Chain-Packing and Chain-Folding Structures of Isotactic Polypropylene Characterized by Solid-State NMR, University of Akron, 2015.

[37] S.K. Rana, Crystallization of high□density polyethylene–linear low□density polyethylene blend, J. Appl. Polym. Sci. 69 (1998) 2599–2607. https://doi.org/10.1002/(SICI)1097-4628(19980926)69:13<2599::AID-APP10>3.0.CO;2-Q.

[38] A.T. Lorenzo, M.L. Arnal, J. Albuerne, A.J. Müller, DSC isothermal polymer crystallization kinetics measurements and the use of the Avrami equation to fit the data: Guidelines to avoid common problems, Polym. Test. 26 (2007) 222–231. https://doi.org/10.1016/J.POLYMERTESTING.2006.10.005.

[39] S. Kavesh, J.M. Schultz, Lamellar and interlamellar structure in melt-crystallized polyethylene. I. Degree of crystallinity, atomic positions, particle size, and lattice disorder of the first and second kinds, J. Polym. Sci. Part A-2 Polym. Phys. 8 (1970) 243–276. https://doi.org/10.1002/pol.1970.160080205.

[40] M. Heink, K.-D. Häberle, W. Wilke, Wide-and small-angle x-ray scattering studies on the real structure of fractions of (ethylene-α-olefine)-copolymers, Colloid Polym. Sci. 269 (1991) 675–681. https://doi.org/10.1007/BF00657404.

[41] T. Ito, H. Marui, Pressure–Strain and Pressure–Volume Relationships in the Crystal Lattice of Polyethylene at 293°K, Polym. J. 2 (1971) 768–782. https://doi.org/10.1295/polymj.2.768.

[42] N. Mieda, M. Yamaguchi, Flow instability for binary blends of linear polyethylene and long-chain branched polyethylene, J. Nonnewton. Fluid Mech. 166 (2011) 231–240. https://doi.org/10.1016/J.JNNFM.2010.11.011.

[43] L.A. Utracki, M.R. Kanial, Melt rheology of polymer blends, Polym. Eng. Sci. 22 (1982) 96–114. https://doi.org/10.1002/pen.760220211.

[44] M. Gahleitner, Melt rheology of polyolefins, Prog. Polym. Sci. 26 (2001) 895–944. https://doi.org/10.1016/S0079-6700(01)00011-9.

[45] E. Manias, L.A. Utracki, Thermodynamics of Polymer Blends, in: Polym. Blends Handb., Springer Netherlands, Dordrecht, 2014: pp. 171–289. https://doi.org/10.1007/978-94-007-6064-6_4.

[46] S. Reich, Y. Cohen, Phase separation of polymer blends in thin films, J. Polym. Sci. Polym. Phys. Ed. 19 (1981) 1255–1267. https://doi.org/10.1002/pol.1981.180190809.

[47] H.L. Snyder, P. Meakin, S. Reich, Dynamical aspects of phase separation in polymer blends, Macromolecules. 16 (1983) 757–762. https://doi.org/10.1021/ma00239a011.

[48] R. Li, W. Yu, C. Zhou, Investigation of Phase Separation in a Partially Miscible Polymer Blend by Rheology, J. Macromol. Sci. Part B. 46 (2007) 1051–1062. https://doi.org/10.1080/00222340701457519.

[49] M. Mohammadi, A.A. Yousefi, M. Ehsani, Thermorheological analysis of blend of high- and low-density polyethylenes, J. Polym. Res. 19 (2012) 9798. https://doi.org/10.1007/s10965-011-9798-9.

[50] A.D. Gotsis, B.L.F. Zeevenhoven, C. Tsenoglou, Effect of long branches on the rheology of polypropylene, J. Rheol. (N. Y. N. Y). 48 (2004) 895–914. https://doi.org/10.1122/1.1764823.

[51] P.C. Dartora, R.M.C. Santana, A.C.F. Moreira, The influence of long chain branches of LLDPE on processability and physical properties, Polimeros. 25 (2015) 531–539. https://doi.org/10.1590/0104-1428.1732.

[52] C. Gabriel, H. Münstedt, Influence of long-chain branches in polyethylenes on linear viscoelastic flow properties in shear, Rheol. Acta. 41 (2002) 232–244. https://doi.org/10.1007/s00397-001-0219-6.

[53] P.W.R. Beaumont, R.J. Young, Failure of brittle polymers by slow crack growth - Part 1 Crack propagation in polymethylmethacrylate and time-to-failure predictions, J. Mater. Sci. 10 (1975) 1334–1342. https://doi.org/10.1007/BF00540823.

[54] C.J.G. Plummer, A. Goldberg, A. Ghanem, Micromechanisms of slow crack growth in polyethylene under constant tensile loading, Polymer (Guildf). 42 (2001) 9551–9564. https://doi.org/10.1016/S0032-3861(01)00476-1.

[55] R.D. Goolsby, A.M. Chatterjee, Notch sensitivity and fractography of polyolefins, Polym. Eng. Sci. 23 (1983) 117–124. https://doi.org/10.1002/pen.760230303.

[56] N. Brown, X. Lu, Y.-L. Huang, R. Qian, Slow crack growth in polyethylene - a review, Makromol. Chemie. Macromol. Symp. 41 (1991) 55–67. https://doi.org/10.1002/masy.19910410107.

[57] X. Lu, Z. Zhou, N. Brown, A sensitive mechanical test for slow crack growth in polyethylene, Polym. Eng. Sci. 37 (1997) 1896–1900. https://doi.org/10.1002/pen.11839.

[58] S.J. Park, K.S. Cho, S.K. Ryu, Filler-elastomer interactions: Influence of oxygen plasma treatment on surface and mechanical properties of carbon black/rubber composites, in: Carbon N. Y., Pergamon, 2003: pp. 1437–1442. https://doi.org/10.1016/S0008-6223(03)00088-5.

[59] W. Balasooriya, B. Schrittesser, G. Pinter, T. Schwarz, L. Conzatti, The Effect of the Surface Area of Carbon Black Grades on HNBR in Harsh Environments, Polymers (Basel). 11 (2019) 61. https://doi.org/10.3390/polym11010061.

Highlights

- Resin with more uniform SCB distribution is more affected by carbon black aggregates and the carrier polymer.
- Carbon black aggregates act as stress concentration areas and prevent the branched long chains to enter the crystals and create the tie molecules and consequently decrease the creep lifetime of the pipe grade PE material.
- Because of more contacts between the chains, the changes in both the relaxation time in viscosity test and crystallization time in isothermal crystallization test in sample with uniform SCBs distribution is noticeably higher than non-uniform sample.
- For resistance to slow crack growth, LDPE carrier is better than HDPE carrier, since branched structure of the LDPE causes formation of more tie molecules and enhances the mechanical properties relatively.
- In processing temperature range, no immiscibility is observed between PE100 resin and both HDPE and LDPE carriers.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: