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크리프와 반복 피로하중에 의한 폴리에틸렌의 실시간 구조 변화

전혜진 · 유석근 · 표수호 · 최선웅 · 송현훈†
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In-situ Determination of Structural Changes in Polyethylene upon Creep and Cyclic Fatigue Loading

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초록: 일정 하중에 지속적으로 노출되는 고분자의 장기간 사용을 위해서는 재료의 수명을 평가할 수 있는 가속화된 시험 방법이 필요하다. 반복 피로하중 시험법은 이러한 방법들 중 하나로 많은 관심을 받고 있다. 본 연구에서는 X-선 회절법을 이용하여 고밀도 폴리에틸렌의 반복 피로하중에 의한 구조적 변화와 크리프 변형을 비교하고자 하였다. 이를 위하여 별도의 인장시험기를 제조, X-선 회절기에 부착하여 장시간 변형 과정을 성공적으로 관찰하였다. 그 결과 크리프와 반복 피로하중 사이의 거시적이고 뚜렷한 차이에도 불구하고 결정화도, 결정크기 및 면간거리와 같은 결정의 미세구조는 두 방법에서 거의 동일하게 관찰되었다. 그러나 항복점 전(BYP), 항복점(YP) 그리고 항복점 후(AYP)로 각각 변형시킨 후 시험한 시료의 경우 AYP와 다른 두 시료간 뚜렷한 구조적 차이를 확인할 수 있었다.

Abstract: Long-term performance of polymer under constant sustained load has been the main research focus, which created a need for the accelerated test method providing proper lifetime assessment. Cycling fatigue loading is one of the accelerated test method and has been of great interest. Microstructure change of high density polyethylene under cyclic fatigue loading and creep was examined utilizing a tensile device specially designed for creep and fatigue test and also can be attachable to the X-ray diffractometer. In this way, the crystal morphology change of polyethylene under creep and cyclic fatigue load was successfully monitored and compared. Despite the marked differences in macroscopic deformation between the creep and cyclic fatigue tests, crystal morphology such as crystallinity, crystal size, and *d*-spacing was as nearly identical between the two test cases. Specimens pre-deformed to different strains, i.e., before yield point (BYP), at yield point (YP) and after yield point (AYP), however, showed markedly different changes in crystal morphology, especially between AYP and the other two specimens.

Keywords: crystal morphology, cyclic fatigue test, creep test, X-ray diffraction.

Introduction

Polyethylene (PE) has been utilized in many applications, including pipes for conveying fuel and water as well as the waste water.[1-4] These applications are structural in nature that nowdays requires lifetime performance of 50 years or more. Because of its wide use and demand that continues to show increase, studies on enhancing properties through structure-properties investigations have also been extensive.[5,6] In particular, studies on mechanical behavior of PE have been of much interest, as their structure is simple and is known to provide engineered properties pertinent to long-term applications. With regard to long-term performance of PE under sustained constant loads, slow crack initiation and crack growth have been on the focus.[7] Mechanisms leading to slow cracking behavior is now well understood and hence resulted in the development of much enhanced, higher performing PE resins in term of crack initiation and crack growth. This improvement in long-term behavior, however, has created a need for less time consuming accelerated test methods from which the results obtained are utilized with certain degree of confidence in making proper judgement for the lifetime design assessment. Among the accelerated

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tests under consideration, cyclic fatigue method has been of interest as it has demonstrated the value in terms of mimicking the actual field performance behavior in much shorter time duration than the case of using creep loadings.[8-14] Although experience with cyclic fatigue testing is growing, how cyclic fatigue accelerates crack initiation and growth in terms of microstructural change has not been well understood.

As with other many materials such long term performance or the lifetime of PE is much dependent on the micro-structure of the material. For example, the tie molecule in the amorphous region linking crystalline lamella was identified as the key element in the enhancement of the slow crack resistance. On the other hand, how tie molecules are held together in crystalline lamella is not well understood. And how this is affected by the crystallinity, lamella size, orientation as well as possible strain induced transformation of the crystal lattice needs to be investigated. This in turn would help providing better understanding of the macroscopic cracking behavior in relation to microstructure evolution. Accordingly, by *in-situ* monitoring the microstructure change during the macroscopic deformation would be of great value in the identification of the details of failure mechanism involved.

In this article, *in-situ* measurement of micro-structures under creep and cyclic fatigue loadings is examined. The micro-structure change under loading is examined by X-ray diffraction on a specially designed creep and cyclic fatigue fixture.

Experimental

For this study a commercial grade of high density polyethylene (HDPE) (Korea Petrochemical. Ind. Co.) was used. The weight average molecular weight and the density were approximately 210 kg/mol and 0.957 g/cm^3, respectively. The HDPE resin was compression molded to 2 mm thick plaques by first melting the resin at 190 °C between polyethylene terephthalate (PET) sheets in a press then applying the pressure for 15 min and pressure cycled 5 times between 1 and 5 ton to remove any air bubbles. Plaques were then air cooled to room temperature. The tensile specimen of 5.3 mm× 2.5 mm×54 mm was prepared by a template cutter and tensile properties were determined by using a tensile tester (Shimadzu AG-5000G) equipped with a 50 kgf load cell at a speed of 1 mm/min, at room temperature.

A tensile device was designed for performing creep or fatigue test which also had the feature for accommodating simultaneous wide angle X-ray diffraction measurement. The device is shown in Figure 1 and the loading is achieved by using a pneumatic cylinder and the deformation was monitored

Figure 1. Creep device attached to X-ray diffractometer.

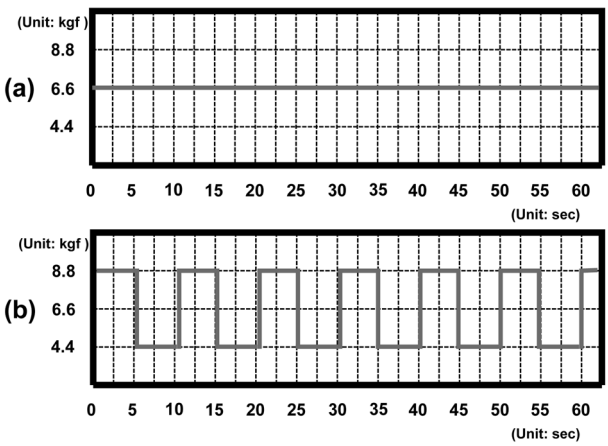

Figure 2. Load applied for static creep (a); dynamic fatigue test (b).

by an electronic micrometer positioned over the piston rod. The load and crosshead displacement were recorded by the data acquisition system throughout the test.

The creep test was performed using a load of 30% of the yield load and for the cyclic fatigue test 20% and 40% of yield loads were selected for the minimum and maximum loads in square wave load profile with the frequency of 0.1 Hz. The loading modes for creep and cyclic fatigue are illustrated in Figure 2.

Three different pre-deformed specimens (strains of 0.05, 0.14 and 1.00) were tested for both creep and fatigue experiments. Here, 0.05 strain is a strain below the yield

point (BYP), strain 0.14 is at the yield point (YP), and 1.0 is a strain after the yield point (AYP). The positions of the selected strains are depicted in the tensile stress-strain curve shown in Figure 3.

The X-ray diffraction was carried out using a rotating anode generator (d/max-2500, Rigaku; CuKα) operated at 40 kV and 70 mA. The point focused beam was used in a transmission mode. The data collection was made for 20-30 sec for each data frame. Crystallinity was calculated as $X_{cr}= A_{cr}/(A_{am}+A_{cr})$ where A_{am} and A_{cr} being the reflection areas of amorphous and crystalline phase, respectively. The contributions of each phase to XRD intensities were then resolved from the curve-fits of reflections using Gaussian functions. And crystallite size, t, was obtained from Scherrer equation $t = 0.9\lambda/(B\cos\theta_B)$ where, λ, B and θ_B are X-ray wavelength, full width at half maximum or integral breadth and Bragg angle, respectively.

Results and Discussion

The deformations of specimen under creep and fatigue load as measured by a digimatic indicator are plotted in Figure 4(a) and (b), respectively. The plots are representing that the deformation of the specimen AYP (1.0 strain) shows far larger deformation than the specimens BYP (0.05 strain) and YP (0.14 strain) in both cyclic fatigue and creep test. It is also noted that the fatigue test (Figure 4(b)) induced somewhat larger deformation than that of the creep test (Figure 4(a), implying that cyclic load accelerates the changes of the internal structures). It is also noted that the specimen

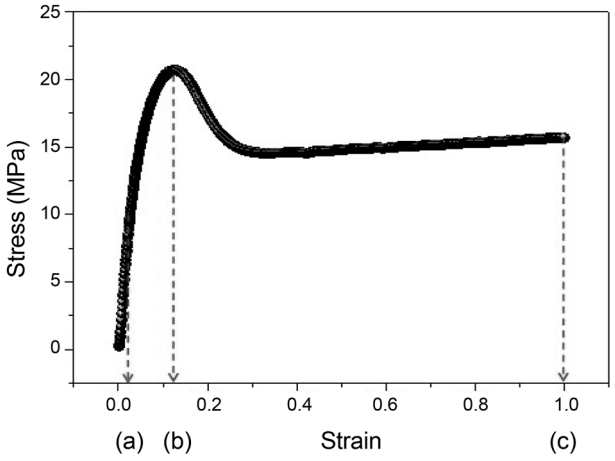

Figure 3. Stress-strain curve of HDPE. The strains indicated by arrows denote strains selected for creep and dynamic tests; (a) strain 0.05, before yield point (BYP); (b) strain 0.14, at yield point (YP); (c) strain 1.0, after yield point (AYP).

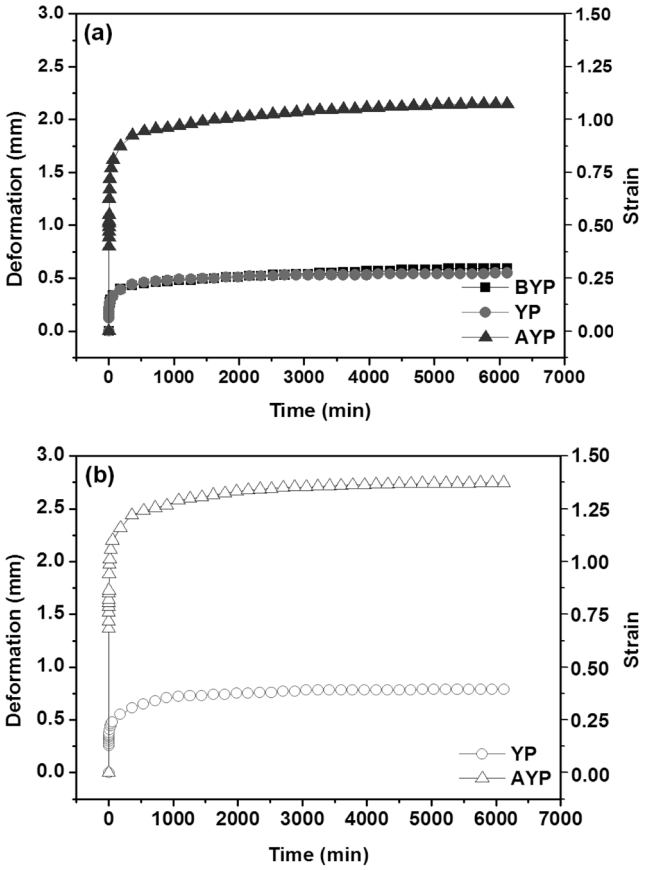

Figure 4. Deformation measured during creep (a); fatigue tests (b).

AYP shows more pronounced deformation difference between the two tests.

This may be attributed to the fact that the specimens BYP and YP are partially or fully recovered to their original state when the stress is removed prior to conducting the X-ray diffraction measurement, while the recovery may not be allowed to occur in the specimen AYP, which was pre-deformed beyond the yield point. Therefore, the specimen of AYP should have larger deformation with higher structural defects than the other two specimens when loaded.

The fatigue test was carried out only with the pre-deformed specimens, YP and AYP. But it is to be noted that the most of the difference in deformation took place before 500 min of the fatigue or creep test. After the initial rapid increase of deformation during the first 500 min the increase of deformation in both creep and fatigue test is only minimal. This can probably be attributed to the orientation of amorphous chains parallel to the tensile direction and the strain-induced crystallites, if any.

The changes in crystallinities of the specimen during creep

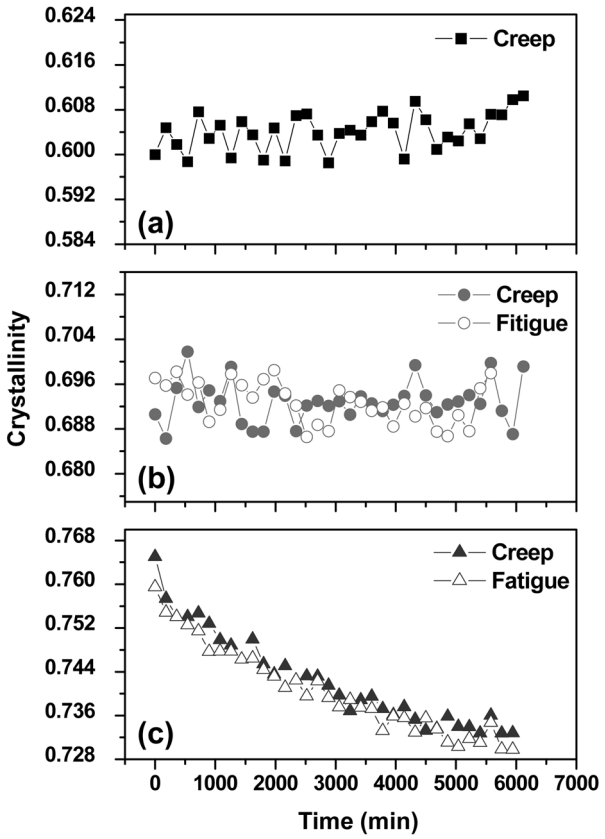

Figure 5. Change of crystallinity during creep and fatigue tests for BYP (a); YP (b); AYP specimen (c).

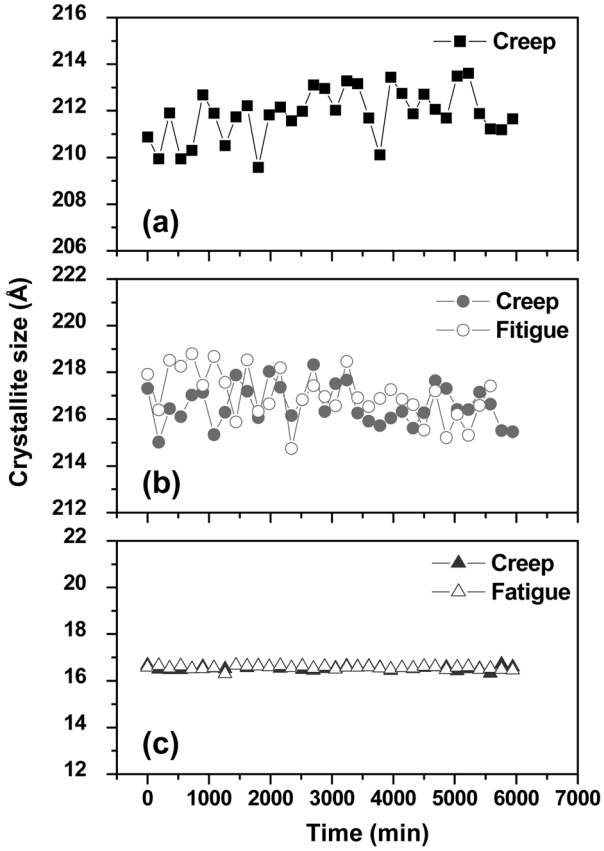

Figure 6. Change of crystal size of (110) plane during creep and fatigue tests for BYP (a); YP (b); AYP specimen (c).

and fatigue tests are depicted in Figure 5. Here, the crystallinity was obtained from the X-ray diffraction patterns simultaneously measured during the creep and fatigue test. Despite the difference in deformation is marked between the two tests, the difference in crystallinity is not observed. The difference in crystallinity change, however, was observed between the samples, BYP, YP and AYP (Figures 5(a), (b) and (c)). This can be attributed to the different initial structures of the specimens. The crystallinity of pre-strained specimen BYP (Figure 5(a)) showed a slight increase with the creep test, while that of YP (Figure 5-(b)) remained unchanged for both creep and fatigue tests. The crystallinity of specimen AYP (Figure 5(c)), however, showed a drastic decrease with time. The result therefore suggests that the initial structure of the specimen determines the structural response to external forces, either increase, remain or reduction in crystallinities. Despite the rapid decrease of crystallinity in AYP specimen, macroscopic destruction of the specimen was not observed.

In Figure 6 changes of crystallite size ((110) plane) during the creep and fatigue were also compared. We note that the initial crystal size ((110) crystal plane) of AYP is much smaller than the other two specimens, BYP and YP. We recall, however, the cystallinity of AYP is rather higher than the other two specimens. The initial morphology of AYP compared with other two specimens implies that the crystallites in AYP are highly fragmented without losing its crystallity. We note that crystallite size steadily increases in BYP, but in YP and AYP it remained nearly constant under both creep and fatigue loads.

Figure 7 shows *d*-spacing of (110) plane and its change with time during the creep and fatigue test. We first note that the initial *d*-spacing differs between the specimens (the lowest value with the AYP). It is interesting to note that a quite marked decrease in *d*-spacing is observed in (110) of AYP, while little change is observed in that of BYP and AYP. The change in d-spacing with respect to the tensile deformation can be associated with the chain slip, where (110) plane is the fold plane as has been suggested.[15,16] Chain-slip is one of the key mechanisms in the transformation process of polymer crystal structure under defor-

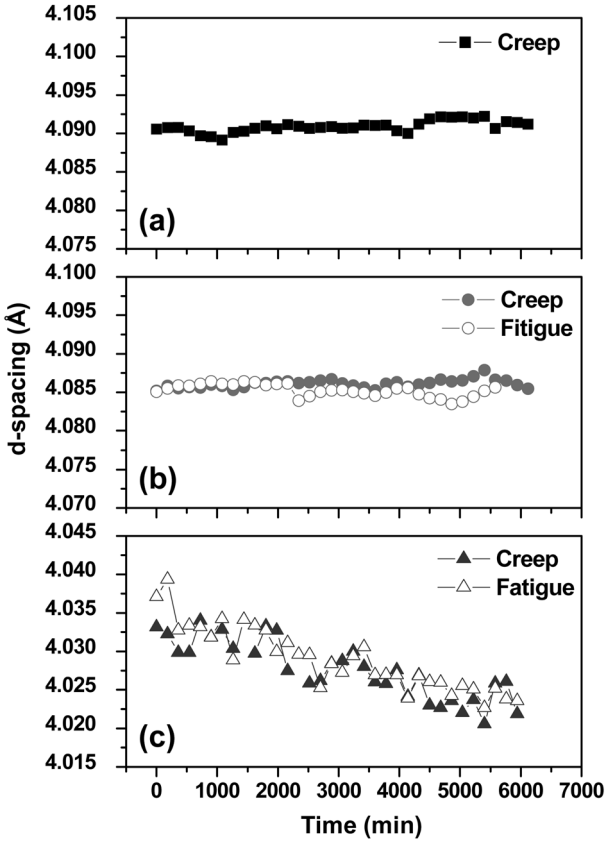

Figure 7. Change of *d*-spacing of (110) plane during creep and fatigue tests for BYP (a); YP (b); AYP specimen (c).

mation. Heavy chain slip and crystal destruction (Figure 5) conspicuously take place in the AYP specimen.

Conclusions

The crystal morphology and its changes in response to creep and cyclic fatigue tests were investigated. In order to simultaneously monitor the fine structural changes accompanying the creep and fatigue loads, a specially designed creep and fatigue device attachable to an X-ray diffractometer was designed and utilized. Cyclic fatigue test showed greater macroscopic deformation than that of static test, while the most of deformation occurred in the first 500 min of the test. Despite the marked differences in macroscopic deformation, morphological changes such as crystallinity, crystallite size and d-spacing were found to be nearly identical between the two tests. Three specimens pre-deformed to different strains (BYP, YP, and AYP), however, exhibited quite different changes in crystal morphology. In particular, the differences were noted between AYP and the other two, where the initial morphologies were different between the two specimens. AYP specimen showed much greater changes in crystal morphology during both creep and cyclic fatigue tests.

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