

ESCA and Other Morphological Investigations of the Brittle Failure Caused by an Environmental Stress Cracking (ESC) of a HDPE Milk Crate*

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Synopsis

The causes of a drastic reduction in the service life of a HDPE milk crate have been investigated. The mechanism and the type of crate failure have been deduced from a detailed morphological examination of its fracture surface as well as the interior. Various factors responsible for a rapid failure of the milk crate have been identified. An ESCA study of ESC of weathered milk crate surfaces revealed the presence of heavy oxidative degradation on the surface and a diffusion-controlled oxidation mechanism being operative in successive inner layers. The brittleness of this surface layer and formation of sharp cracks therein have been exhibited in SEM micrographs. Optical micrographs clearly show the presence of a surface layer, formed due to degradation, which is nonspherulitic and thus identifiable from the bulk, which is imperfectly spherulitic. Evidence for a migration of polymer additives from bulk to the surface is provided by the ESCA data and the SEM micrographs. DSC thermogram of the microtomed surface layer reveals bimodal endothermic peaks attributed to two phases present in the surface layer—one original phase and the second being degradation-induced. The formation of this brittle surface layer and its effect on the long-term fracture performance of milk crates are discussed, and suggestions for improving their durability are given.

INTRODUCTION

Aging resistance becomes a limiting parameter to plastic materials, when a long-life application is required. This is true for milk crates used in India, which are molded from pigmented HDPE material. The expected service life of milk crates is 18–20 months, but they fail prematurely in 6–8 months of useful service. During their service period, milk crates are subjected to harsh and aggressive environments, such as: exposure to sunlight (UV radiation); exposure to high temperatures; exposure to chemical stress-cracking agents (e.g., milk from leaky pouches, detergent used for washing, etc.); exposure to low temperatures as well, since milk pouches are usually kept refrigerated or ice-chilled; multiaxial mechanical stresses produced during materials handling and transport; sudden impacts under load. At any given time during the service period of milk crates, several of the above-stated factors may act in unison, although the nature of their interaction is likely to be complex and cannot be easily ascertained. However, there would be consensus that most forms of environmental attack begin at polymer surface and penetrate from there in the sequence: diffusion → plastification/crosslinking → degradation. The worst effects of the degradation of the milk crate, caused by a hostile

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environment, are likely to be confined to its surface. Still, this degradation is sufficient to reduce the resistance towards fracture initiation and cause an environmental stress cracking (ESC) failure¹⁻⁹ of the milk crate.

The present paper uses a diagnostic approach to understand the reasons underlying the brittle failure^{7,10-14} and poor service life of milk crates. The structure, morphology, and mechanical characteristics of the degraded surface layer^{12,14} and the bulk material have been characterized and compared using a combination of microscopic, spectroscopic, and polymer characterization techniques. ESCA has been used to investigate weathering and ESC failure of the milk crate. Microscopic methods have been employed to reveal the structure of the surface layer, generation of microcracks and to elucidate the structure of the subsurface. DSC scans have been useful in exhibiting the biphasic structure of the surface layer. Suggestions to improve the durability of milk crates are presented.

EXPERIMENTAL

ESCA

The XPS spectra were obtained on a V.G. Scientific ESCALAB MK II Spectrometer with Al K α X-ray source. Polymer samples were stable in the X-ray beam and showed no evidence of X-ray damage during the experiment. Pressure in the analyzer chamber during measurements was 5×10^{-9} torr. Data were collected by means of an Apple IIe microcomputer interfaced with the spectrometer and stored on a disc. All spectra were referenced to the C (1S) peak for neutral carbon, which was assigned a value of 285 eV.

DSC

DSC thermograms of surface and inner layers of the HDPE crate were obtained in inert N₂ atmosphere on a DuPont thermal analysis system (Model 990) at a heating rate of 10°C/min.

Microtoming

Microtoming was carried out to obtain the surface and bulk layers from the milk crate and perform ESCA, DSC, and optical microscopic characterizations on them.

Polarized Light Microscopy

Microtomed layers were mounted in paraffin on microscope slides and examined under crossed polars on a Carl Zeiss Model NU-2 microscope, equipped with photomicrographic attachment.

SEM

The morphology of the milk crate was studied on a JEOL scanning electron microscope (Model JSM 35C) at 7 kV. Before this, the polymer surface was sputter-coated with gold using a JEOL fine coat unit (Model JFC-1100).

Tensile Behavior

A portion of the crate was cut by hand saw and tested on an Instron tensile tester (Model 1195) at a strain rate of 5 cm/min.

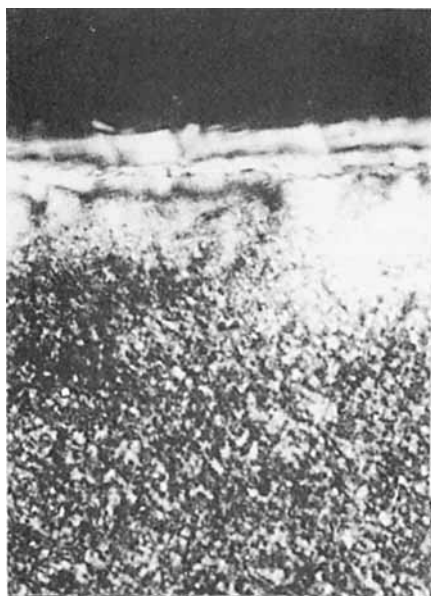
RESULTS

The visual appearance of the fracture of the milk crate is *brittle* as also revealed by the lack of fibrillation, absence of stress whitening, and sharpness of the edges of the fracture surface. The fracture surface is highly glossy. This indicates that the fracture surface is brittle in nature and has probably been caused by oxidation of the surface layer. Oxidation of HDPE would therefore be a major contributing factor towards a reduction in the long-term strength of the milk crate.

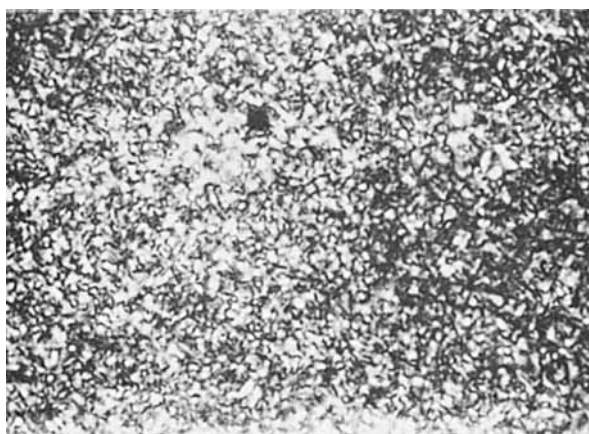
Figure 1 shows two polarized light photomicrographs of cross sections of the wall of the milk crate. The existence of a surface layer (termed the "oxidation skin") can be clearly distinguished from the bulk structure of HDPE crate [Fig. 1(a)]. This layer is nonspherulitic and is bestowed with a structure which is different from the structure of the bulk HDPE material. Formation of this layer very probably occurs as a result of the oxidative degradation of the milk crate surface.¹⁴ A photomicrograph of the bulk material of the milk crate [Fig. 1(b)] reveals an imperfect spherulitic structure consisting of very small spherulites which were formed during quenching of the melt. This figure also shows a pigment particle having dimensions much larger than those of spherulites.

In order to better understand the nature of surface chemical changes occurring due to aging and weathering of the milk crate during service, ESCA spectra were obtained from microtomed sections of the surface and of the interior of the crate wall (Fig. 2). A comparison of the spectrum of the interior or bulk material [Fig. 2(a)] with the spectrum of weathered, degraded surface [Fig. 2(b)] brings out the following facts:

(a) A sufficient amount of oxygen has been incorporated on the surface of HDPE crate after weathering. An atomic concentration calculation of data reveals that incorporation of oxygen has increased from 1.9 atomic percentage in the bulk to approximately 13% on the surface. This finding supports the diffusion-controlled mechanism^{15,16} of autooxidation of HDPE, in which oxidative degradation begins at the surface and penetrates below in proportion to the concentration gradient of oxygen present at successive depths. It is observed that when oxygen is incorporated by different treatments of polymer surface modification, a broadening of the carbon region of the spectrum occurs^{17,18} due to the formation of carbon-oxygen bonds. In the present work, a deconvolution of data was not attempted because the line positions¹⁹ of HDPE carbon-oxygen bonds are crowded together²⁰ at 286.6, 287.9, and 289.1 eV (attributed to bonds of one carbon atom with one, two, and three oxygen atoms, respectively). ESCA spectra of the carbon region of the bulk and surface layers of milk crate are illustrated in Figure 3, where the line positions have been indicated. The oxygen (1S) spectrum was less informative, giving a single broad band at 532.8 eV which could not be subjected to further analysis.



(a)



(b)

Fig. 1. Photomicrographs (magnification: $200\times$) of cross sections of the wall of the milk crate, taken with crossed polars.

(b) Lines at 102.4 and 152.3 eV signal the presence of silicon on the weathered milk crate surface. The origin of this silicon may be in air-borne silica particles¹⁹ which contaminate the milk crate during its service life.

(c) Traces of calcium and chlorine have been detected on the weathered polymer surface by ESCA. These may originate from polymer additives which migrate to the surface: calcium stearate (lubricant) and Tinuvin 327 (UV stabilizer).

DSC scans of the microtomed surface layer and the bulk material have been compared in Figure 4. Whereas the bulk material gives rise to a single peak,

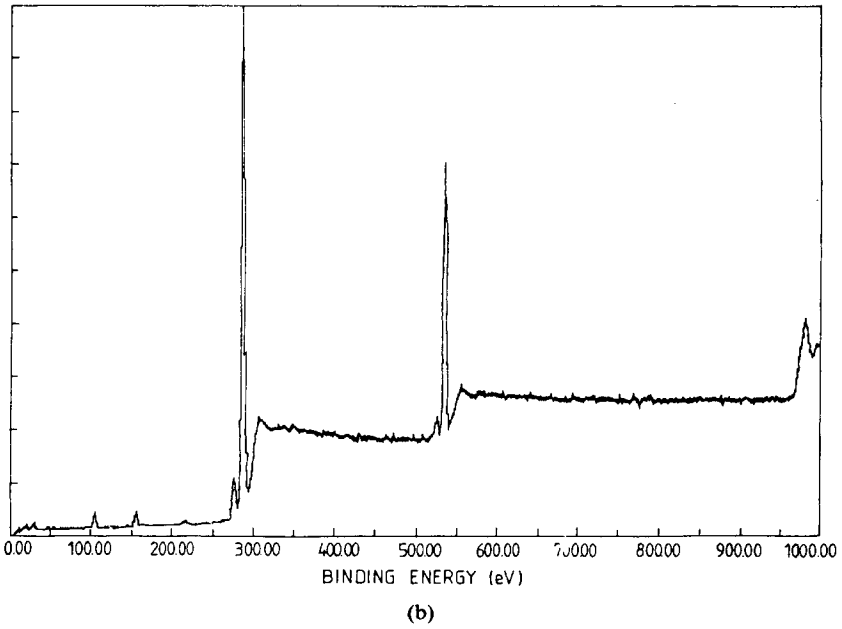
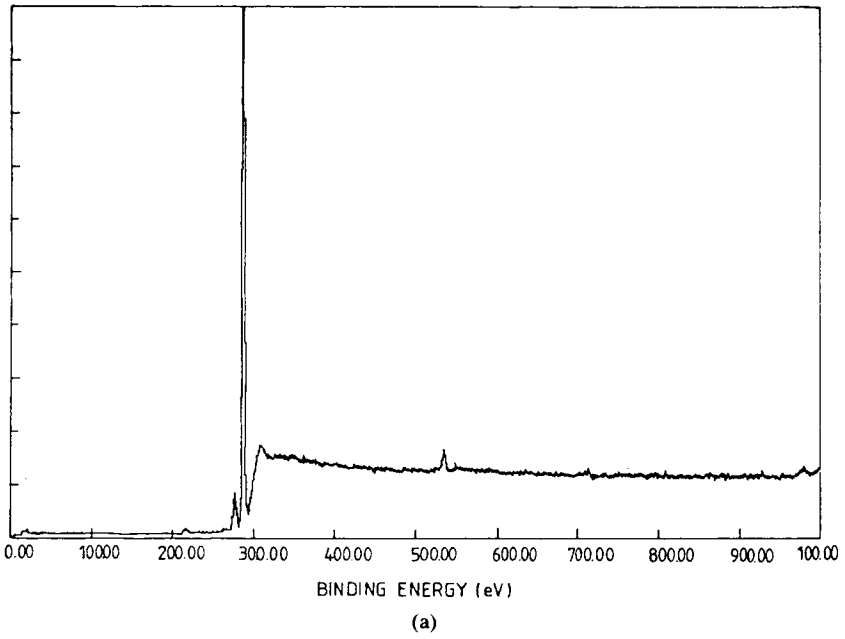


Fig. 2. (a) XPS spectrum of the interior of the milk-crate wall; (b) XPS spectrum of the surface of the milk crate.

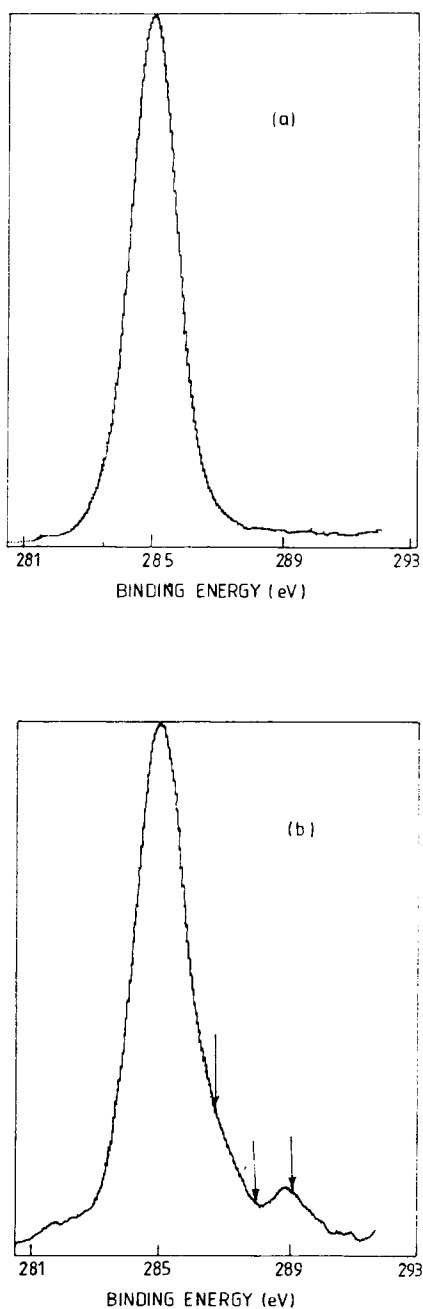


Fig. 3. Carbon region of (a) bulk and (b) surface layer of the weathered HDPE milk crate.

the surface layer contributes a bimodal endotherm. The bimodal character of the thermogram of the surface layer arises from its biphasic structure, which itself is a consequence of the rejection of crosslinks from the crystalline phase.¹⁴ According to this explanation, the 121°C peak corresponds to bulk HDPE whereas the 119.5°C peak corresponds to crosslinked HDPE phase

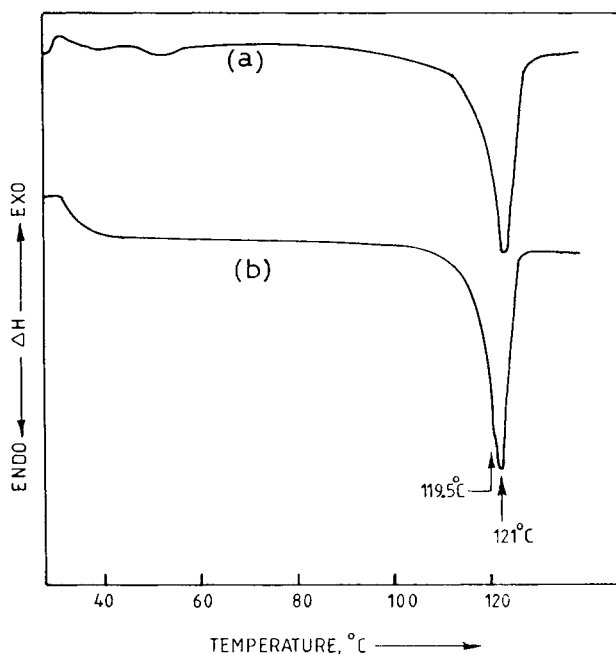
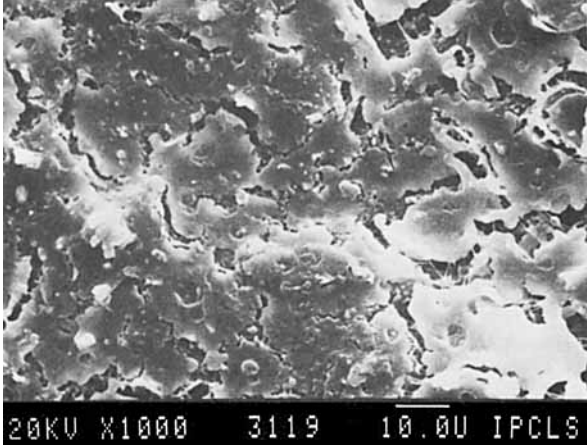


Fig. 4. DSC scans of microtomed sections of the milk crate: (a) bulk; (b) surface layer.

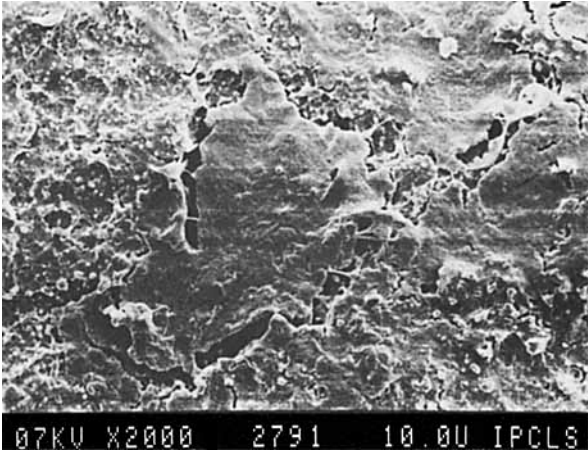
(Fig. 4). An alternative explanation for bimodal thermograms of the surface layer can be provided in terms of a segregation of low molecular weight and high molecular weight phases,¹ each phase giving rise to a different peak. It is difficult to choose any one of the two explanations offered from DSC data because both incorporate a phase that can be *brittle*, namely, the crosslinked phase and the low molecular weight material, respectively.

SEM photomicrographs illustrated in Figure 5 support the formation of a brittle surface layer^{12,14} on the fracture surface of the milk crate. Micrographs reveal a large number of cracks spread all over the fracture surface. These cracks are rather wide and have few "tie fibrils" connected across their width. Because the surface layer resembles a skin and has a finite thickness, it is very brittle. As a consequence, it gets easily detached from the fracture surface [e.g., the portion at the left in Fig. 5(b)], revealing the inner subsurface lying beneath the surface layer. This region underlying the fracture surface also exhibits a large number of cracks, shows very little fibrillation, and reveals a very large concentration of polymer additives (micro- and submicroparticles) which are migrating to the surface, resulting in their loss and depletion. Figure 5(c) shows two large pigment particles, one located near the top left and the other located near the top middle, the sizes of both particles exceeding 10 μm . On the other hand, the sizes of polymer additives are usually less than 1 μm . Summarizing the present SEM data, it can be concluded that the fracture of the milk crate is brittle. The surface layer has a structure which is nonspherulitic.

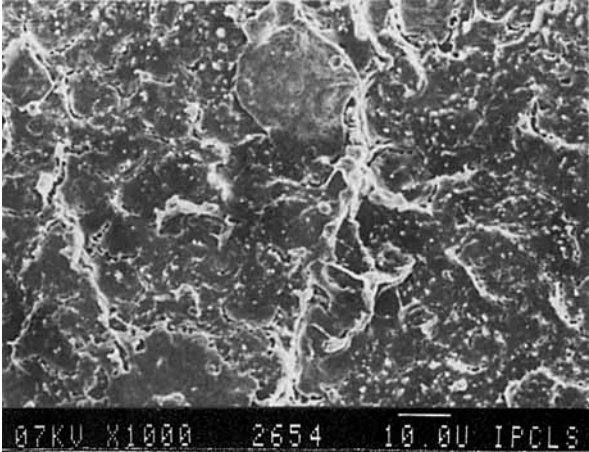
The elongation to rupture of bars cut from the weathered milk crate was determined to be 75% which is roughly 10 times smaller than the corresponding parameter for undegraded HDPE.



(a)



(b)



(c)

Fig. 5. SEM micrographs of the fracture surface of the milk crate.

DISCUSSION

Aggressive environmental factors to which a milk crate is usually subjected to during its service life include its exposure to internal (frozen) and external (dynamic) stresses, impacts, temperature, sunlight, detergent, etc. After the milk crate has been in service over a substantial period, it becomes unprotected and vulnerable to degradation. The effects of accelerated aging and destabilization are maximum in the surface layer where the degradation is very pronounced. As a consequence of degradation, structural and morphological changes (crosslinking, embrittlement, loss of elongation) occur in the surface layer which reduce its resistance towards fracture initiation and eventually cause a failure of the milk crate (Fig. 6). Oxidative crosslinking of HDPE and a low number of tie fibrils^{13, 21} contribute to the brittleness of the oxidation skin. At low stress levels, a series of sharp cracks form on the surface which tend to propagate through the crate wall in a brittle way. A brittle failure of HDPE can also occur due to detergent-induced ESC.^{7,13} A catastrophic failure of the milk crate ensues, terminating its useful service life rather prematurely.

In order to prevent a premature failure of plastic articles, which are subject to aggressive handling when in service, the following precautions seem to be necessary:

(a) Since the protective agents (e.g., antioxidants, stabilizers, etc.) are consumed much more rapidly in plastics subjected to dynamic stress than in plastics aged in absence of stress,²² it is necessary to boost stabilizer levels in plastics or use more effective stabilizers in conjunction with mobilizing additives.²³

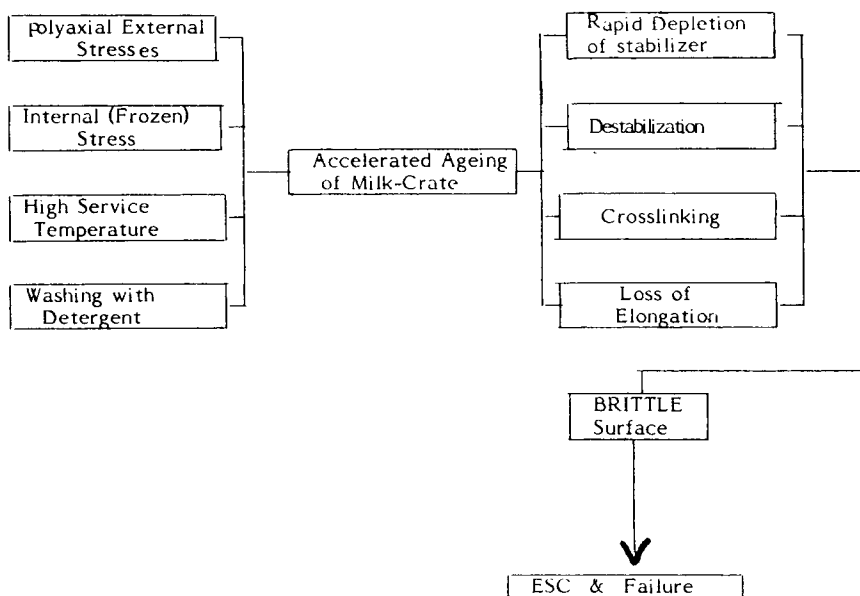


Fig. 6. A model of the probable mechanisms operating during the service life of the milk crate, resulting in its premature failure.

(b) Rapid cooling of a molded plastic leads to development of fine spherulitic structure and the lowest practical crystallinity in the material. Formation of impurity-rich, brittle spherulitic boundaries is prevented by rapid cooling.¹ Low matrix crystallinity and small spherulitic sizes ensure a better acceptance of stabilizers,²³ on the one hand, and improved crack resistance, on the other.^{24,25}

(c) Crack resistance of plastics can be enhanced by increasing their molecular weight²⁵ and by removal^{1,4} of brittle low molecular weight material (i.e., by narrowing the molecular weight distribution²⁶). The resistance to failure of plastic will depend on the number of tie molecules,²⁷ and this has been shown to depend on molecular weight.²⁵ Low content of tie molecules contributes to brittleness.

CONCLUSIONS

Stress and environmental factors accelerate the destabilization and aging of milk crates. Application of repeated stress accelerates the transfer of anti-degradants and stabilizers to the surface, resulting in their depletion inside the milk crate. The presence of oxygen, especially on the surface, causes accelerated oxidation and crosslinking of HDPE. Oxidative degradation begins at the surface and penetrates from there (via a diffusion controlled mechanism). A brittle surface layer is formed as a consequence of degradation which is devoid of any spherulites and has a low fracture strain. Cracking of milk crate is governed by (a) degradation-induced morphological changes and (b) the inability of the degraded surface to withstand frozen and cyclical stresses. Oxidative degradation of HDPE thus shortens the life cycle of the milk crate considerably, resulting in its failure by cracking.

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