International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 08 Issue: 01 | January - 2024 SJIF Rating: 8.176 ISSN: 2582-3930

Comparative Analysis of the Properties of High- and Low-Density Polyethylene Polymers: Examining the Effects of Surface Modification Methods, Raman Spectroscopy, and ATR-FTIR

[1]Vipual Sharma, [2]Dr. Sumit Kumar Gupta

1. Research scholar University of Technology, Jaipur

2.Professor, Department of Physics

University of Technology, Jaipur

Abstract:

Polyethylene polymers, widely utilized in various industries, exhibit distinct characteristics based on their density. This study presents a comparative analysis of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) to understand the influence of polymer structure on material properties. The investigation employs analytical techniques, including Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), Raman spectroscopy, and surface modification methods. The ATR-FTIR analysis provides insights into the molecular structure and chemical composition of LDPE and HDPE. Spectral differences are examined to identify variations in functional groups and crystallinity, shedding light on the distinct properties arising from differences in polymer chain packing. Raman spectroscopy is employed to delve deeper into the molecular vibrations and crystalline phases present in LDPE and HDPE. The results offer a comprehensive understanding of the polymer morphology, crystallinity, and the presence of any structural defects, contributing to the differentiation of the two polyethylene types. Surface modification techniques, including plasma treatment and chemical functionalization, are explored to alter the surface properties of LDPE and HDPE. The impact of surface modification on wettability, adhesion, and mechanical properties is investigated, providing valuable insights into enhancing the performance of these polyethylene materials for specific applications.

The comparative study aims to contribute to the optimization of polyethylene materials by correlating their molecular structure and surface characteristics with performance attributes. The findings from ATR-FTIR, Raman spectroscopy, and surface modification techniques offer a comprehensive understanding of the distinct properties exhibited by LDPE and HDPE, guiding potential applications in areas such as packaging, medical devices, and polymer blends.

Introduction:

Polyethylene polymers, classified into low-density polyethylene (LDPE) and high-density polyethylene (HDPE), constitute two major players in the polymer industry due to their diverse applications and distinct properties. LDPE is known for its flexibility, transparency, and excellent impact resistance, making it suitable for packaging materials, films, and various molded products. On the other hand, HDPE, characterized by its high strength, rigidity, and chemical resistance, finds applications in containers, pipes, and industrial products.

The inherent differences in molecular structure and properties between LDPE and HDPE stem from variations in their polymer chain arrangement, crystallinity, and processing conditions. Understanding these distinctions is crucial for optimizing the performance of polyethylene materials in specific applications. Consequently, this study aims to conduct a comprehensive comparative analysis of LDPE and HDPE, focusing on their molecular characteristics and surface properties.

Significance of the Study:

The significance of this research lies in the practical implications of distinguishing LDPE and HDPE properties. The ability to tailor these polyethylene materials to specific applications relies on a detailed understanding of their molecular structures, crystalline phases, and surface behaviors. By elucidating these aspects, we can enhance the design, processing, and performance of polyethylene-based products, leading to improved efficiency and functionality.

Objectives of the Research:

1. **Characterization of Molecular Structure:** Utilize ATR-FTIR spectroscopy to analyze the molecular structure of LDPE and HDPE. By examining infrared absorption bands, we aim to identify distinctive features related to functional groups, crystallinity, and chain conformations.
2. **Investigation of Crystallinity and Morphology:** Apply Raman spectroscopy to delve into the crystalline phases and molecular vibrations present in LDPE and HDPE. This objective aims to uncover differences in polymer morphology, providing insights into the mechanical and thermal properties of these materials.
3. **Surface Modification Techniques:** Explore the impact of surface modification techniques, including plasma treatment and chemical functionalization, on LDPE and HDPE. By altering the surface properties, we seek to enhance wettability, adhesion, and other surface-related characteristics, paving the way for improved compatibility in various applications.

Research Rationale:

The combination of ATR-FTIR and Raman spectroscopy, along with surface modification techniques, offers a holistic approach to understanding and manipulating the properties of LDPE and HDPE. This research is poised to contribute valuable knowledge that can inform material design, processing, and application strategies, advancing the versatility and efficiency of polyethylene materials in diverse industrial sectors.

Literature Review:

Polyethylene polymers, encompassing both low-density polyethylene (LDPE) and high-density polyethylene (HDPE), have been extensively studied due to their ubiquitous presence in various industries. Previous research has explored the distinctive properties of LDPE and HDPE, shedding light on their molecular structures, crystalline phases, and surface characteristics. Additionally, analytical techniques such as Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (ATR-FTIR), Raman spectroscopy, and surface modification methods have been applied to elucidate the unique features of these polymers.

1. Properties of LDPE and HDPE:

Numerous studies have investigated the mechanical, thermal, and chemical properties of LDPE and HDPE. LDPE, with its branched structure and lower density, exhibits enhanced flexibility and impact resistance, making it suitable for applications like packaging and films. In contrast, HDPE, with its linear and more densely packed structure, boasts superior strength, rigidity, and chemical resistance, rendering it ideal for containers and industrial products.

2. ATR-FTIR and Raman Spectroscopy Applications:

ATR-FTIR spectroscopy has been widely employed to analyze the molecular structure of polymers, including polyethylene. Researchers have utilized this technique to identify specific functional groups, determine crystallinity, and understand chain conformations. Similarly, Raman spectroscopy has been applied to investigate the crystalline phases and molecular vibrations of polyethylene, providing insights into the polymer's morphology and structural variations.

3. Surface Modification Techniques:

Studies have explored surface modification techniques to alter the surface properties of polyethylene. Plasma treatment and chemical functionalization have been employed to enhance wettability, adhesion, and other surface-related characteristics. These modifications aim to improve the compatibility of polyethylene in applications such as adhesion to other materials, printing, and biomedical devices.

Gaps in Knowledge:

Despite the wealth of information available, there exist gaps in our understanding that this research aims to address:

- **Limited Comparative Studies:** While individual studies on LDPE and HDPE properties are abundant, there is a lack of comprehensive comparative analyses that systematically explore the molecular distinctions and surface behaviors of these polymers.
- **Integration of Spectroscopic Techniques:** Many studies have focused on either ATR-FTIR or Raman spectroscopy separately. There is a need for integrated analyses using both techniques to provide a more comprehensive understanding of the molecular characteristics of LDPE and HDPE.
- **Holistic Examination of Surface Modifications:** Previous research on surface modifications has often been application-specific. This study seeks to provide a more holistic examination of surface modification techniques and their impact on various surface properties of both LDPE and HDPE.

By addressing these gaps, this research aims to contribute to the comprehensive knowledge of LDPE and HDPE properties, offering valuable insights for material design, processing, and application across diverse industries.

. Materials and Methods:

a. Material Selection:

The selection of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) for the study is grounded in the distinct properties and applications of these two polyethylene polymers. Several factors contribute to the rationale behind choosing LDPE and HDPE for the investigation:

1. **Widespread Use and Importance:**
    - LDPE and HDPE are among the most commonly used polymers globally, finding applications in various industries such as packaging, agriculture, automotive, construction, and healthcare.
    - The ubiquity and importance of these materials make them crucial subjects for in-depth studies aimed at optimizing their properties for specific applications.
2. **Diverse Properties:**
    - LDPE and HDPE exhibit divergent mechanical, thermal, and chemical properties due to differences in their molecular structures and processing conditions.
    - LDPE is known for its flexibility, transparency, and impact resistance, while HDPE is characterized by its higher strength, rigidity, and chemical resistance. Understanding these differences is fundamental for tailoring materials to specific needs.

3. **Versatility in Applications:**
    - The versatility of LDPE and HDPE in a wide range of applications necessitates a nuanced understanding of their properties. This study seeks to uncover molecular distinctions and surface behaviors that can influence and enhance their performance in diverse industries.
4. **Challenges in Material Optimization:**
    - While both LDPE and HDPE are extensively used, there are challenges in optimizing their properties for specific applications. A comprehensive comparative study provides insights into the unique characteristics of each polymer, aiding in the development of tailored solutions.
5. **Analytical Techniques Compatibility:**
    - The analytical techniques chosen for this study, namely ATR-FTIR, Raman spectroscopy, and surface modification techniques, are well-suited for the analysis of polyethylene polymers. These techniques offer detailed insights into molecular structures, crystallinity, and surface properties.
6. **Research Gap Addressing:**
    - There is a gap in the literature regarding comprehensive comparative studies that investigate both LDPE and HDPE simultaneously, particularly using multiple analytical techniques.
    - This research aims to address this gap by providing a holistic understanding of the molecular and surface properties of LDPE and HDPE, offering valuable insights for future material design and applications.

Infrared Spectroscopy

Figure 1 displays the infrared spectra of LDPE, HDPE, PE-BIO, and PE-OXO that were not exposed to UV-B radiation. These spectra illustrate the IR bands characteristics of PE, which include the wagging and rocking vibration of methylene (CH_2) at 700–750 cm−1 and the stretching vibration of the Carbon-Hydrogen (CH) group of the main chain at 2772–3038 cm−1. Because HDPE and PE-BIO are linear polymers, their IR spectra exhibit a single peak at 700–750 cm−1 and at 1440–1490 cm−1, respectively; however, because LDPE and PE-OXO are branched polymers, these same bands are bifurcated.

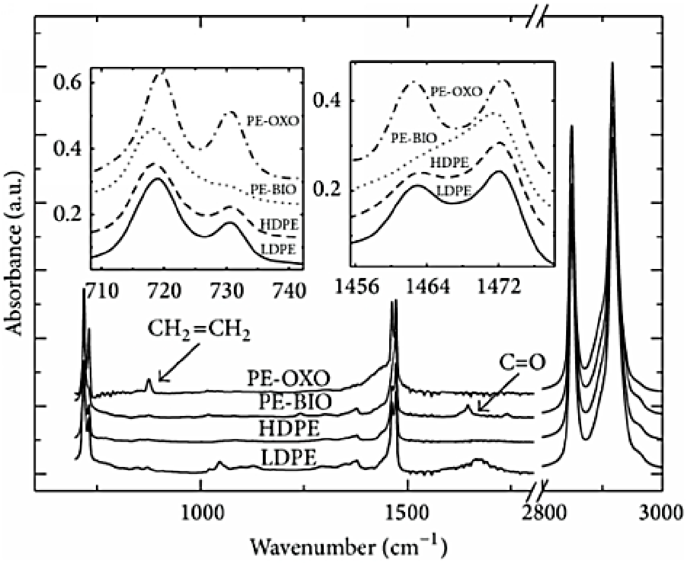

Figure-1 IR spectrum of the LDPE, HDPE, PE-BIO, and PE-OXO films without exposure to UV-B radiation.

Carbonyl Index:

According to the Norrish Type II reaction mechanism, which is thought of as a homolytic process with four steps—initiation, propagation, chain branching, and termination—the photooxidation of the PE films subjected to UV-B light develops. The hydroperoxides produced during PE polymerization processes are primarily responsible for the initiation step. When UV-B radiation breaks down these hydroperoxides, functional groups like hydroxyls, anhydrides, and carbonyls are created. Vinyl groups are created when UV-B radiation doses rise and react with reactive chemical groups like tertiary carbons. Because the degree of branching affects how much more labile hydrogen is bonded to the tertiary carbon atoms, a PE with more tertiary carbons on its molecular structure exhibits a higher degree of photooxidation .The carbonyl and vinyl groups on PE films can be examined as a sign of polymer backbone scission when the UV-B radiation exposure is increased . Since the carbonyl and vinyl groups are thought to be the primary photooxidation products of PE .the UV-B radiation's impact on PE films is assessed using the carbonyl index (I_{CO}) and vinyl index (I_V) metrics

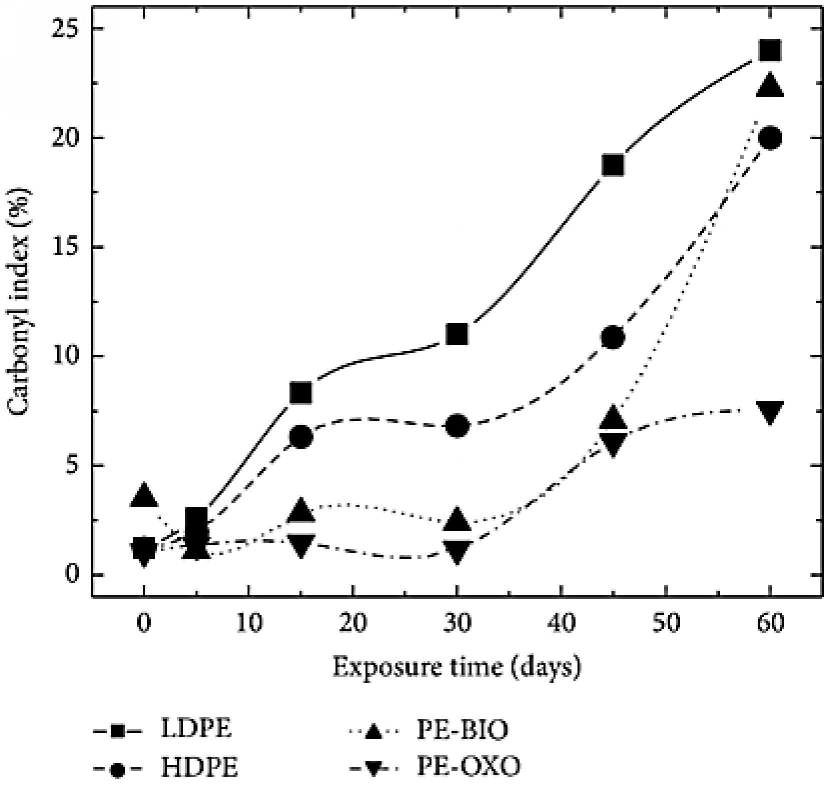

Figure -2 Carbonyl index (I_{CO}) of the LDPE (■), HDPE (▲), PE-BIO (▼), and PE-OXO (●) films exposed to UV-B radiation.

Vinyl Index:

The vinyl index (I_V) for PE-BIO, PE-OXO, LDPE, and HDPE is displayed in Figure 3. LDPE, HDPE, and PE-BIO tend to increase with an almost linear tendency from 0 to 60 days of exposure to UV-B radiation; this is because of the embrittlement process and the breaking of the bonds of the tertiary carbons of the polymer backbone branches, which result in the formation of the vinyl group

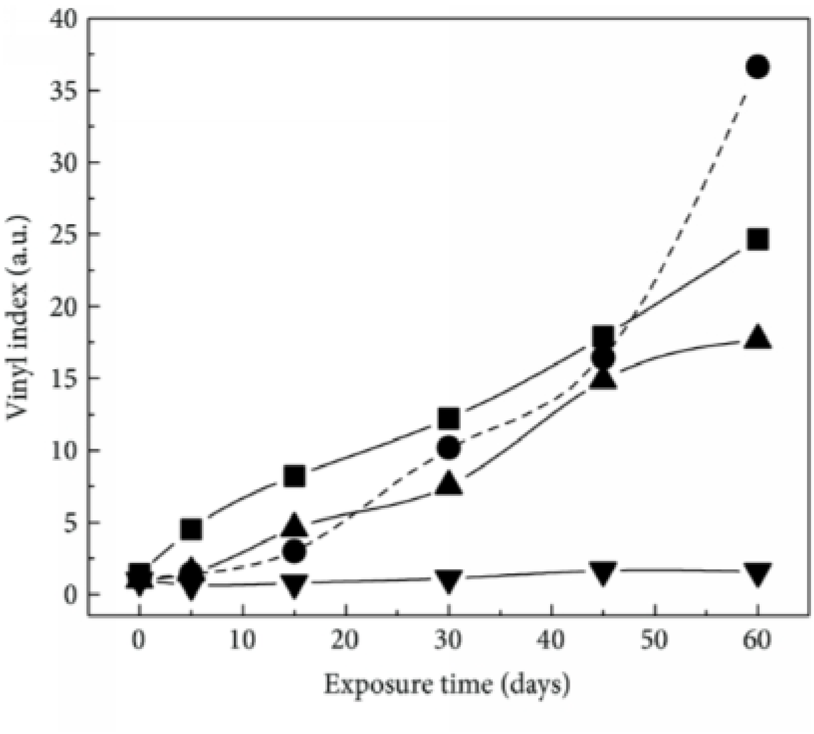

Figure 3 Vinyl index (I_V) of the LDPE (■), HDPE (▲), PE-BIO (▼), and PE-OXO (●) films exposed to UV-B radiation.

Conclusion: This paper shows that when exposed to the same conditions of UV-B radiation, PE with modified structures, PE-BIO and PE-OXO, which include organic and prooxidant agents in the molecule, respectively, to increase their biodegradability, show a lower degree of photooxidation than PE with unmodified structures, LDPE and HDPE.

Both PE-BIO and PE-OXO have reduced levels of UV-B radiation exposure up until 45 days after exposure to UV radiation, both I_{CO} and I_V ; PE-BIO and PE-OXO are lower than those of LDPE and HDPE after 45 to 60 days, PE-BIO tends to have the same levels as LDPE and HDPE. These indices have grown, which suggests that these polymeric materials are more biodegradable. After 30 days of exposure to UV-B radiation, the crystalline phase fraction of LDPE and HDPE grows even more, influencing their physical characteristics like stiffness, dissolving resistance, and dimensional stability. Furthermore, all varieties of polyethylene exhibit an increase in the dichroic ratio during the first thirty days after UV-B radiation exposure, suggesting that branches scission from the polymer backbone are rearranged parallel to the stretch direction of the films. Thus, we draw the conclusion that UV-B radiation causes the chains' orientation and crystallinity to increase, both of which have a significant impact on the physical characteristics of polyethylene

References

1. P. K. Roy, P. Surekha, R. Raman, and C. Rajagopal, "Investigating the role of metal oxidation state on the degradation behaviour of LDPE," *Polymer Degradation and Stability*, vol. 94, no. 7, pp. 1033–1039, 2009.
   View at: Publisher Site | Google Scholar
2. T. F. M. Ojeda, E. Dalmolin, M. M. C. Forte, R. J. S. Jacques, F. M. Bento, and F. A. O. Camargo, "Abiotic and biotic degradation of oxo-biodegradable polyethylenes," *Polymer Degradation and Stability*, vol. 94, no. 6, pp. 965–970, 2009.
   View at: Publisher Site | Google Scholar
3. A. Valadez-Gonzalez, J. M. Cervantes-Uc, and L. Veleva, "Mineral filler influence on the photo-oxidation of high density polyethylene. I. Accelerated UV chamber exposure test," *Polymer Degradation and Stability*, vol. 63, no. 2, pp. 253–260, 1999.
   View at: Publisher Site | Google Scholar
4. M. Koutny, J. Lemaire, and A.-M. Delort, "Biodegradation of polyethylene films with prooxidant additives," *Chemosphere*, vol. 64, no. 8, pp. 1243–1252, 2006.
   View at: Publisher Site | Google Scholar
5. J. V. Gulmine, P. R. Janissek, H. M. Heise, and L. Akcelrud, "Degradation profile of polyethylene after artificial accelerated weathering," *Polymer Degradation and Stability*, vol. 79, no. 3, pp. 385–397, 2003.
   View at: Publisher Site | Google Scholar
6. F. Khabbaz, A.-C. Albertsson, and S. Karlsson, "Chemical and morphological changes of environmentally degradable polyethylene films exposed to thermo-oxidation," *Polymer Degradation and Stability*, vol. 63, no. 1, pp. 127–138, 1999.
   View at: Publisher Site | Google Scholar
7. M. Liu, A. R. Horrocks, and M. E. Hall, "Correlation of physicochemical changes in UV-exposed low density polyethylene films containing various UV stabilisers," *Polymer Degradation and Stability*, vol. 49, no. 1, pp. 151–161, 1995.
   View at: Publisher Site | Google Scholar
8. H. Xingzhou, "Wavelength sensitivity of photo-oxidation of polyethylene," *Polymer Degradation and Stability*, vol. 55, no. 2, pp. 131–134, 1997.
   View at: Publisher Site | Google Scholar
9. A. Ammala, S. Bateman, K. Dean et al., "An overview of degradable and biodegradable polyolefins," *Progress in Polymer Science*, vol. 36, no. 8, pp. 1015–1049, 2011.
   View at: Publisher Site | Google Scholar
10. S. Bonhomme, A. Cuer, A.-M. Delort, J. Lemaire, M. Sancelme, and G. Scott, "Environmental biodegradation of polyethylene," *Polymer Degradation and Stability*, vol. 81, no. 3, pp. 441–452, 2003.
   View at: Publisher Site | Google Scholar