

Original Article

Investigation Of Optical and Thermal Behavior of Photodegraded Polystyrene/Polyisoprene Blend Thin Films

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Manuscript ID:
IJERSD-2026-020405

ISSN: 3067-2325

Volume 2

Issue 4

Pp. 23-29

August 2026

Submitted: 08 July 2026

Revised: 19 July 2026

Accepted: 12 Aug. 2026

Published: 31 Aug. 2026

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Quick Response Code:



Web: <https://rlgjaar.com>

DOI: 10.5281/zenodo.23101229

DOI Link:
<https://doi.org/10.5281/zenodo.23101229>



Abstract:

Pure Polystyrene (PS) and Polystyrene/Polyisoprene (PS/PI) blend thin films (20–30 μm) were fabricated via the solution evaporation technique and subjected to UV irradiation at 254 nm for exposure durations of 0, 30, and 60 days to investigate photodegradation-induced changes in their optical, structural, and thermal properties. UV-Vis spectroscopy revealed a progressive increase in absorbance along with a reduction in optical band gap, decreasing from 4.32eV to 4.28eV for unirradiated samples and further declining to 3.91eV after 60 days of exposure. FTIR analysis confirmed photo-oxidative degradation, evidenced by the emergence of carbonyl ($\sim 1740\text{ cm}^{-1}$) and hydroxyl ($\sim 3400\text{ cm}^{-1}$) functional groups, while the aromatic structure of PS remained strongly intact. The PS/PI blends show a higher degradation as compared to pure PS, linked to the presence of unsaturated double bonds in the polyisoprene material, which promote oxidative reactions. Thermogravimetric analysis (TGA) indicated a single-step degradation profile, with pure PS degraded within the range of 300–450°C, whereas PS/PI blends alter the degradation range to 150–400°C. A progressive reduction in onset degradation temperature and overall thermal stability with increasing irradiation time was noticed, attended by increased weight loss and reduced residual mass. These findings reveal that UV-induced photodegradation remarkably alters the physicochemical properties and thermal stability of PS/PI blend thin films.

Keywords: Polystyrene, Polyisoprene, UV-Vis, FT-IR, TGA

Introduction

Plastic pollution has become a severe environmental challenge with widespread adverse effect on ecosystems, wildlife, and human health. Over the past seven decades, the exponential growth in global plastic production has reshaped the modern society but also left a massive environmental burden [1]. Therefore, Plastic waste accumulation is the serious environmental challenge over worldwide. Due to the excessive dumping of plastic waste into the environment, natural water bodies worldwide are becoming increasingly polluted with plastic. Nevertheless, just 9 % of this plastic waste was recycled, with the remaining 79 % being dumped on land or dispersed into the environment. By 2050, 12,000 million tons of plastic wastes are prone to be released into the environment. The half-life of plastics generally takes several decades or even hundreds of years for their degradation [2]. Due to the high durability of plastics causes their deposition and prolonged existence in the environment with estimated rate of over 25 MT per annum [3].

Among the widely used polymers, PS is a petroleum-based polymer made from styrene monomer. Given that PS was first time synthesized in 1931. It has been used for broad range of commercial, packaging and building purposes and it has been world's most widely used polymer due to its excellent physical properties and low cost. When polystyrene is subjected to UV irradiation in the presence of air, it causes photodegradation which result in breaking of the polymer chains, leads to formation of free radicle and reduces the molecular weight [4, 5]. Polyisoprene exists in nature as a natural rubber but can also be produced synthetically which is called as isoprene rubber. Polyisoprene is used in many industrial fields, such as medical gloves, tires, coatings, adhesives, health care equipment, etc.

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How to cite this article:

Sharma, S. O., & Sangawar, V. S. (2026). Investigation Of Optical and Thermal Behavior of Photodegraded Polystyrene/Polyisoprene Blend Thin Films. *International Journal of Engineering Research for Sustainable Development*, 2(4), 23–29. <https://doi.org/10.5281/zenodo.23101229>

When Polyisoprene material is exposed to ultraviolet (UV) radiation, the composition and structure of polyisoprene has degraded progressively. UV Light, as a radical initiator. Can cleave the chemical bond and modify the performance of polymer materials at the time of photoaging.

In the presence of oxygen Free radicals are produced via the photo-initiated chain reaction based on the free radical mechanism. Particularly, the unsaturated bonds in the Polyisoprene backbone are more readily oxidized under the attack of oxygen and free radicals [6].

Blending PS with elastomeric polymers such as polyisoprene (PI) is an efficient approach to enhance flexibility, toughness, and impact resistance. The structure of PI contains carbon - carbon double bonds, which improve the degradation of blend thin films. The carbon - carbon double bonds in the blend thin films are more sensitive to oxygen attack, increases the rate of degradation and revising the reaction kinetics than pure polystyrene thin films. In spite of the existence of numerous studies in the literature on the photodegradation of polymer blends, to the best of author's knowledge, there are no published studies have investigated on the photodegradation of PS/PI blends thin films. Therefore, this work provided an opening to investigate the influence of photodegradation on PS/PI blends thin films [7].

In solid thin-film systems, mechanistic insight requires explicit support from complementary analytical techniques because degradation may dominate by surface-driven photooxidation rather than bulk hydrolysis or solution-phase free radical attacks. Fourier-transform infrared spectroscopy (FTIR) can demonstrate the evolution of oxygen-containing functional groups, UV-visible spectroscopy (UV-vis) can sensitively capture the photo-aging-related optical changes, including chromophoric evolution and aromatic disruption, and in addition with optical properties TGA analyze the thermal stability and thermal properties of the samples. Together, these techniques provide a spatially resolved a detailed understanding of degradation pathways in solid-state systems [8,9].

In this study, we therefore investigate the UV-induced degradation of PS/PI blend thin films under dry (air) conditions, representing an environmentally significant solid-state exposure scenario. We integrate UV-Vis, FTIR, and TGA analyses to systematically evaluate structural disorder, chemical bond modification, optical degradation, surface oxidation and thermal stability of PS/PI blend thin films. The analysis specifically aims to distinguishing surface-localized photooxidation from bulk polymer degradation through correlation between UV-Vis absorbance loss and reduction in optical band gap, FT-IR carbonyl indices and TGA parameters. On the basis of these multi - technique approach, we propose a photodegradation mechanism that highlights oxygen mediated surface reactions [9].

Materials and Methods:

Materials

Polystyrene (PS) and polyisoprene (PI) was purchased from Sigma – Aldrich Chemistry as a starting material. Toluene of analytical grade was used as the solvent for film preparation.

Preparation of PS and PS/PI Blend Thin Films:

Thin films of pure polystyrene (PS) and polystyrene/polyisoprene (PS/PI) blends were fabricated using the solution evaporation technique. For the pure PS sample, 2 g of polystyrene was dissolved in 20 mL of toluene. For the blend films, 7% polyisoprene (PI) was added to the pure PS solution. The resulting solution was heated to 70 °C and continuously stirred for approximately 1.5 hours to achieve complete dissolution and homogeneous mixture [10].

The homogeneous solution was then cast onto a flat glass plate and left to dry at ambient temperature for 6–7 hours to form uniform thin films. Subsequently, the prepared films were exposed to UV irradiation using an 8 W Philips tube light with a wavelength of 365nm in an UV cabinet chamber for different time intervals [11].

Characterization Techniques:

Characterization Techniques:

The optical properties of pure polystyrene (PS) and polystyrene/polyisoprene (PS/PI) blend thin films were interpreted using UV-Visible spectroscopy. The absorption spectra were recorded in the wavelength range of 200–800 nm using a UV-Vis spectrophotometer. Ultraviolet-visible spectroscopy was used for the evaluation of absorbance characteristics of the prepared thin films. Measurements were carried out for both unirradiated and UV-irradiated samples to access the effect of photodegradation. The absorption spectra were taken after each time interval [12].

Chemical composition and structural alteration in the films due to photodegradation were investigated using Fourier Transform Infrared (FTIR) spectroscopy. The working wavenumber range of the spectrophotometer was recorded from 4000–400 cm^{-1} . FTIR analysis was performed for both pure and UV-exposed samples is used for the detection of newly formed functional groups such as carbonyl (C=O), hydroxyl (–OH), and peroxide species. Variations in peak intensity and the formation of new absorption bands were used to confirm photooxidative degradation and chain scission processes in the polymer material [13].

Thermal stability and degradation behavior of the PS and PS/PI blend thin films were investigated using Thermogravimetric Analysis (TGA). The analysis was conducted under a controlled atmosphere (nitrogen or air) at a constant heating rate (typically 10 °C/min) over a proper temperature range. Weight loss as a function of temperature was recorded to determine degradation onset temperature, thermal stability, and decomposition patterns. Comparisons between unirradiated and irradiated samples were made to assess the impact of UV-induced photodegradation on thermal properties [14].

Result and Discussion:

UV-Vis Characterization:

The absorption spectra of Pure Polystyrene and Polystyrene/ Polyisoprene blends at 0 days, 30days and 60days are presented in figure 1. UV-visible absorption spectra of pure polystyrene (PS) and polystyrene/polyisoprene (PS/PI) blend thin films recorded

in the wavelength range of 200–1000 nm for different UV irradiation times (0, 30, and 60 days). An increase of absorbance is observed over the 200–1000 nm range in spectra of all the samples exposed to UV, which indicates that absorbing photoproducts are obtain in PS and PS/PI blend thin films. The spectra show strong absorption below 300nm dominated by PS aromatic rings and absorbance increases with PI content and increasing with UV exposure, indicating photodegradation and increased structural disorder [11, 13].

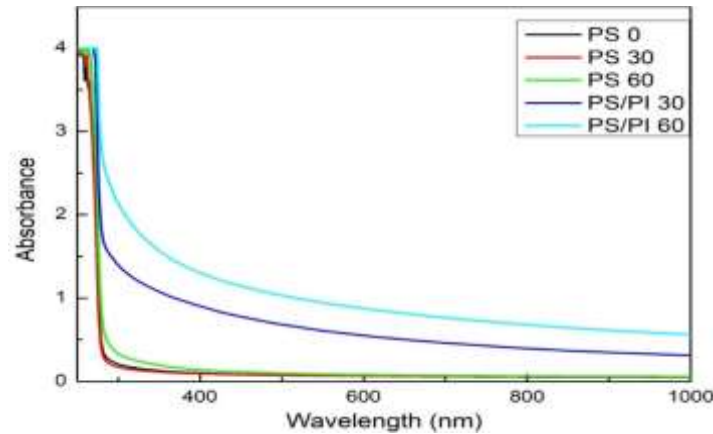


Fig 1: Absorption spectra of Pure Polystyrene and Polystyrene blend at 0 days, 30days and 60days exposure time.

Tauc plots $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for pure PS and PS/PI blend thin films at different UV irradiation durations (0, 30, and 60 days). The optical band gap E_g was determined by extrapolating the linear region of the curves to the energy axis. A systematic decrease in band gap with increasing UV exposure and PI incorporation is observed, confirming the formation of localized states and enhanced conjugation [11, 15]. The band gap of pure PS and PS/PI blend with different time exposure is shown in figure 2.

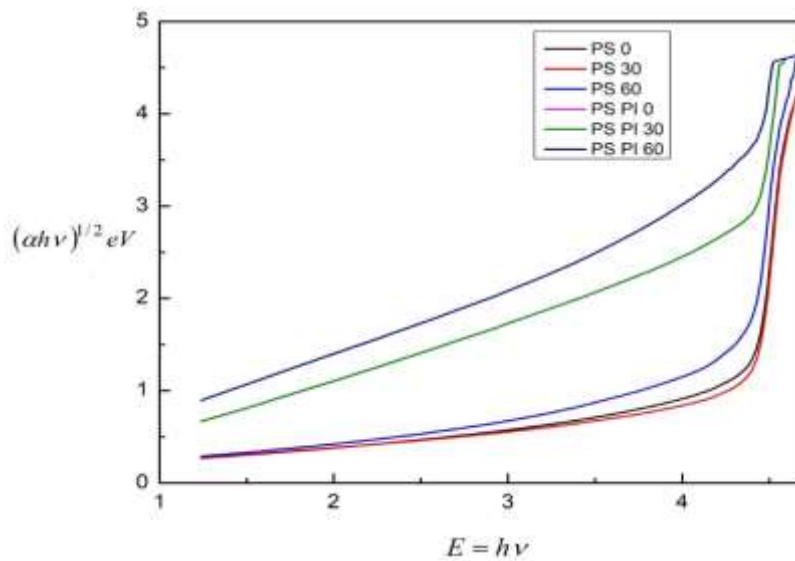


Fig 2: The band gap of pure PS and PS/PI blend thin films at 0 days, 30 days, 60days exposure time

The band gap values were obtained by extrapolating the linear region of each curve to the energy axis. The tabulated form of band gap energy is presented in table 1.

Samples	Band Gap Energy (eV)
PS 0	4.32
PS 30	4.28
PS 60	4.23
PS/PI 0	4.19
PS/PI 30	4.00
PS/PI 60	3.91

Table 1: Band gap energy values for Pure PS and PS/PI blend thin films for different time exposure

FT-IR Characterization:

The FT-IR spectra of pure PS at 0 days, 60days and PS/PI at 60 days irradiation time is presented in fig 3, 4, and 5 respectively.

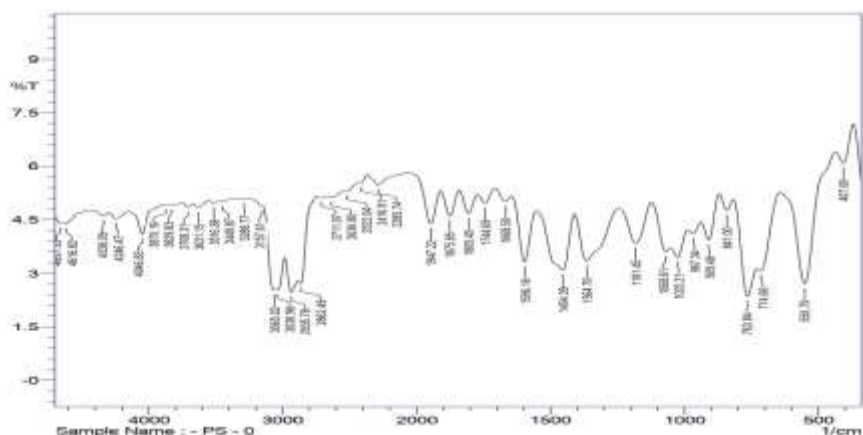


Fig 3: FT-IR spectra of Pure PS at 0 days exposure time

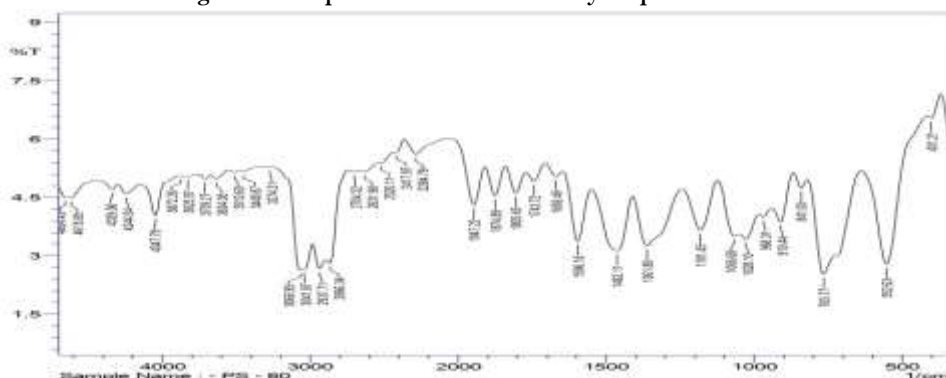


Fig 4: FT-IR spectra of Pure PS at 60 days exposure time

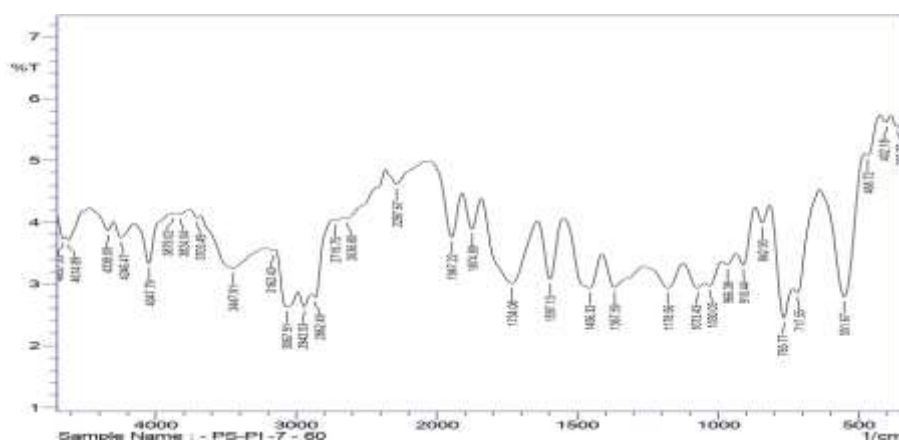


Fig 5: FT-IR spectra of Pure PS/PI at 60 days exposure time

The Fourier Transform Infrared (FTIR) spectra of pure polystyrene (PS-0), UV-irradiated polystyrene (PS-60), and polystyrene/polyisoprene (PS/PI, 7%) blend films after 60 days of exposure were analysed to investigate the structural modifications induced by photodegradation. The spectrum of pristine polystyrene (PS-0) exhibits characteristic absorption bands corresponding to its aromatic backbone, with prominent peaks observed around 3060–3030 cm^{-1} attributed to aromatic C–H stretching vibrations, and 2920–2850 cm^{-1} corresponding to aliphatic C–H stretching. The band at approximately 1596 cm^{-1} is assigned to aromatic C=C stretching, while peaks near 1454 cm^{-1} arise from CH₂ bending vibrations. Additionally, bands in the region of 1180–1025 cm^{-1} are associated with C–C stretching within the aromatic ring, and strong absorptions at around 760 and 700 cm^{-1} due to out-of-plane C–H bending of a monosubstituted benzene ring, confirming that structure of polystyrene remains intact [16, 17].

Upon UV irradiation for 60 days (PS-60), pronounced changes are observed in the FTIR spectrum, clearly shows the initiation of photodegradation in polystyrene. A remarkably increase in intensity of the absorption band near 1740 cm^{-1} is linked to the formation of carbonyl (C=O) groups, which are generally the products of photo-oxidative degradation. Furthermore, the emergence of a broad band in the region of 3400–3500 cm^{-1} indicate the formation of hydroxyl (O–H) groups due to oxidative processes occurs in polymer matrix. Further changes include the presence of weak bands in the range of 1660–1680 cm^{-1} , which may be associated with conjugated C=C structures generated during photodegradation. A slight reduction in the intensity of

aromatic C–H stretching bands is also observed, indicating structural modification in the polymer backbone. These spectral alterations confirm that UV exposure induces chain scission, free radical formation, and subsequent oxidation in polystyrene [18, 19].

The FTIR spectrum of the PS/PI (7%) blend after 60 days of UV exposure exhibits features corresponding to both polystyrene and polyisoprene, along with pronounced degradation-induced changes. The characteristic aromatic C–H stretching of polystyrene is retained around 3030 cm^{-1} , while the aliphatic C–H stretching bands appear within the spectral window of $2920\text{--}2850\text{ cm}^{-1}$. A pronounced increase in the carbonyl absorption band near 1734 cm^{-1} is observed, indicating higher degree of oxidation in the blend system. The broad hydroxyl band centred at 3447 cm^{-1} further confirm the generation of oxygen-containing functional groups. In addition, bands observed in the region of $910\text{--}990\text{ cm}^{-1}$ are ascribed to C=C bending vibrations related to the unsaturated polyisoprene structure. However, a decrease in the intensity of these unsaturation-related peaks indicated that the double bonds in polyisoprene progressively degraded under UV exposure. The presence of unsaturated bonds in polyisoprene increases the susceptibility of the blend to oxidative attack, thereby intensifying the photodegradation process [20, 21].

Overall, the FTIR results indicate that photodegradation gives rise to the formation of oxygenated functional groups such as carbonyl and hydroxyl groups, accompanied by structural transformation in both pure and blended thin films. The PS/PI blend displays a greater extent of degradation compared to pure polystyrene, which can be ascribed to the presence of unsaturated polyisoprene chains that improves the susceptibility to oxidative reactions. These findings confirm that the incorporation of polyisoprene enhanced the photodegradation process, resulting in more pronounced chemical transformations under UV exposure [21].

Intensity Correlation with functional group for Pure PS and PS/PI blend thin films for different time exposure are shown as tabulated form in table 2.

Wave Number (cm^{-1})	Functional Group	Vibrational Mode
3060–3030	Aromatic C–H	Stretching
2920–2850	Aliphatic C–H	Stretching
~ 1740	Carbonyl C=O	Stretching
1660–1680	Conjugated Double bond C=C	Stretching
~ 1596	Aromatic C=C	Stretching
~ 1450	CH_2	Bending
1180–1025	C–C, C–O	Stretching
3500–3400	Hydroxyl O–H	Stretching (Broad)

Table 2: Intensity Correlation with functional group for Pure PS and PS/PI blend thin films for different time exposure.

Thermogravimetric Analysis (TGA):

The TGA graph of pure PS thin films at 0 days and 60days and PS/PI blend thin films at 60 days irradiation time are presented in fig 6.

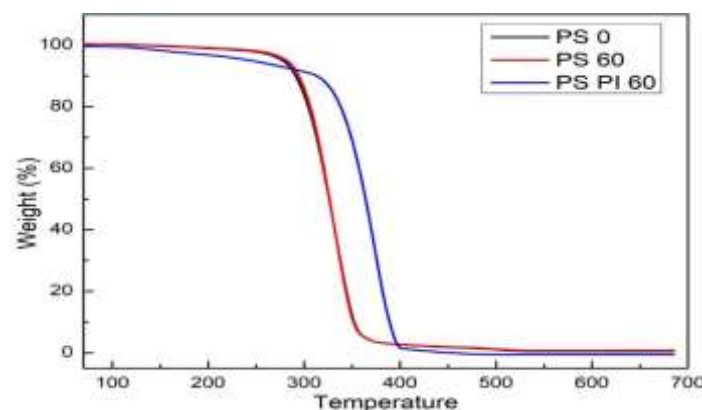


Fig 6: TGA spectra for Pure PS for 0 days and 60 days and PS/PI Thin films for 60 days exposure time.

The thermogravimetric analysis (TGA) of pure polystyrene (PS 0), UV-irradiated polystyrene (PS 60), and polystyrene/polyisoprene blend (PS/PI 60) reveals notable differences in thermal degradation behaviour and stability. All samples exhibit a single-step decomposition profile, characteristic of polystyrene undergoing thermal depolymerisation via random chain scission mechanisms, as widely reported in polymer degradation studies [22]. The pristine PS (PS 0) demonstrates high thermal stability, with an onset degradation temperature (T_{onset}) of approximately $\sim 315^\circ\text{C}$ and a maximum degradation temperature (T_{max}) around $\sim 355^\circ\text{C}$, followed by rapid weight loss within a narrow temperature range ($\sim 320\text{--}380^\circ\text{C}$), indicating uniform degradation behaviour.

In contrast, the UV-aged sample (PS 60) shows a clear shift in degradation toward lower temperatures, with T_{onset} decreasing to $\sim 300^\circ\text{C}$ and T_{max} to $\sim 345^\circ\text{C}$. This reduction in thermal stability is ascribed to UV induced photo-oxidative degradation which generate hydroperoxides, carbonyl groups, and chain scission defects that reduce the integrity of the polymer backbone [23,24]. Additionally, the marginally higher residual mass noted in PS 60 implies the generation of oxidized fragments or minor cross-linked structures during extended UV irradiation.

The PS/PI 60 blend exhibits enhanced thermal stability compared to UV-degraded PS, as evidenced by an increase in Tonset to ~325°C and Tmax to ~370°C. The temperature of photodegraded PS/PI blend, containing 7 wt% PI, shifts to higher temperatures, extended to ~400°C, indicating a more complex degradation mechanism involving both polystyrene and polyisoprene phases [25].

Overall, thermal stability is higher for PS/PI blend thin films is higher than the pure PS with 60 days irradiated and unirradiated pure PS thin films. It indicates that even though the thermal stability is slightly higher in PS/ PI 60 than PS 60 but unsaturated PI segment promote the photodegradation and contribute to limited cross linking or aromatic char formation which stabilizes the residue at higher temperature [26].

Conclusion:

The present study reveals that UV- induced photodegradation remarkably influences the optical and thermal properties of PS and PS/PI blend thin films. UV–Vi's analysis demonstrates a progressive increase the absorption intensity and reduction in band gap with increasing exposure time. IR spectra corroborated the formation of oxygen-containing functional groups such as carbonyl and hydroxyl groups, validating the occurrence of photo-oxidative degradation and chain scission. The PS/PI blend exhibited more remarkable chemical modifications, suggesting that the presence of unsaturated polyisoprene improving the degradation processes. Thermogravimetric analysis presented that UV exposure decreases the stability of pure PS, while blending of PI slightly enhanced the thermal stability but unsaturated fragment of polyisoprene improves the photodegradation process.

Acknowledgment

The authors express their sincere gratitude to the Department of Physics, KCES's Moolji Jaitha College, Jalgaon, and the Department of Physics, Government Vidarbha Institute of Science & Humanities, Amravati, for providing the academic environment and laboratory facilities required to carry out this research. The authors are thankful to their colleagues and faculty members for their valuable suggestions, technical assistance, and continuous encouragement throughout the course of this work. Appreciation is also extended to all those who directly or indirectly contributed to the successful completion of this study. Finally, the authors acknowledge the researchers whose published works have provided valuable guidance and scientific insights for the present investigation.

Financial support and sponsorship

Nil.

Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper

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