Carpathian Journal of Earth and Environmental Sciences
February 2027, Vol. 22, No. 1, p. 15 – 19;
https://doi.org/10.26471/cjees/2027/022/384

Oxidative degradation of agricultural polyethylene: FTIR evidence of early mulch film change in soil

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Abstract: Polyethylene (PE)-based agricultural plastics - mulch films, fertilizer sacks and pesticide packaging, are a major and growing source of microplastics in agricultural soils, yet it is unclear whether all three material streams degrade at comparable rates. In this work fragments of each material were incubated for four weeks in chernozem soil under a factorial range of temperature (20–40 °C), pH (7.0–9.0), moisture (20–60% water-holding capacity) and UV exposure (0–8 h day^{-1}) in the presence of the native soil microbiome, and compared Fourier Transform Infrared (FTIR) spectra before and after incubation. Fertilizer sacks and pesticide packaging showed no new absorption bands under any tested condition. Mulch films, by contrast, developed new bands at 3000–3600 cm^{-1}, ~1600 cm^{-1} and ~1000 cm^{-1}, consistent with early oxidative surface change, most pronounced under the combined stress of high temperature, alkaline pH, high moisture and intensive UV exposure. These findings indicate that, among common PE-based agricultural plastics, mulch films are disproportionately prone to early oxidative transformation and therefore warrant priority attention in soil microplastic monitoring and waste-management policy.

Keywords: polyethylene, microplastics, soil, FTIR, mulch film

1. INTRODUCTION

Microplastics (MPs) accumulate in agricultural soils primarily through the use of plastic mulch films, fertilizer sacks and pesticide packaging (Campanale et al., 2024; Huang et al., 2020). Global mulch film use alone is projected to rise from 4.5 to 5.6 million tonnes by 2030 (Campanale et al., 2024), and residues left after harvest fragment under UV exposure and tillage, increasing soil MP content by up to 30% (Ren et al., 2021). Beyond physical fragmentation, weathering of PE promotes leaching of embedded additives with documented ecotoxicological effects (Bridson et al., 2023). While PE is generally considered highly persistent in soil, it is not established whether the three principal PE-based agricultural plastic streams degrade at comparable rates under identical soil conditions. We addressed this directly by exposing mulch film, fertilizer sacks and pesticide packaging to a shared factorial range of abiotic and biotic soil conditions and comparing oxidative change by FTIR.

2. MATERIALS AND METHODS

Chernozem soil, a silty clay loam typical of the Vojvodina region (Galović et al., 2023), was collected near Subotica, Vojvodina, Serbia (Figure 1), from the 10-20 cm horizon using an Eijkelkamp core sampler (SRPS ISO 10381-2:2013), then air-dried and sieved to <2 mm (ISO 11464:2004). Soil pH was measured potentiometrically in distilled water and in 1 M KCl (ISO 10390:1994); free CaCO3 was determined volumetrically (ISO 10693:1995) and organic carbon by sulfochromic oxidation (ISO 14235:1998). Particle-size distribution (coarse sand 200-2000 μm, fine sand 20-200 μm, silt 2-20 μm, clay <2 μm) was determined by

https://doi.org/10.26471/cjees/2027/022/384

Figure 1. Soil and plastic material sampling locations.

combined sieving and the pipette method (Van Reeuwijk, 2002). Plant-available phosphorus was extracted with ammonium lactate (Egner et al., 1960) and quantified spectrophotometrically at 830 nm by the phosphomolybdenum-blue method (Murphy and Riley, 1962). The resulting soil was characterised as 5.17% organic matter, 2.27% $CaCO_3$ and pH 7.27 (water) / 6.86 (KCl). Fragments (<5 mm, 100 mg) of mulch film, fertilizer sack and pesticide packaging (active compound: thifensulfuron-methyl) were incubated separately in 4 kg soil planters for four weeks under a factorial combination of temperature (20, 30, 40 °C), soil pH (7.0, 7.8, 9.0, adjusted with elemental sulfur and $CaCO_3$, 40-day pre-incubation at 25 °C in the dark), moisture (20, 40, 60% of water-holding capacity) and UV exposure (0, 4, 8 h/day), in the presence of the native soil microbiome (*Pseudomonas, Bacillus, Streptomyces, Aspergillus, Penicillium, Fusarium*). Plastic residues were recovered, cleaned and analysed by diffuse-reflection FTIR (4000-400 cm^{-1}, 4 cm^{-1} resolution, 60 scans per analysis). Spectra were matched against reference polymer libraries (Aldrich Polymers, Aldrich Vapor Phase and Condensed Phase Sample Libraries, HR Spectra Polymers and Plasticizers by ATR, Hummel Polymer Sample Library) using a similarity-match threshold of >60% together with the presence of at least two characteristic bands, consistent with standard FTIR library-search practice for microplastic identification (Anshari et al., 2025).

3. RESULTS AND DISCUSSION

FTIR spectra of the unused materials confirmed the expected polymer identities: mulch film showed characteristic PE bands at 2914, 2847, 1470 and 718 cm^{-1}; fertilizer sack matched PET (2956, 1713, 1409, 1238, 1091, 1016 cm^{-1}); and pesticide packaging matched the formulated product (bands at 2921.5, 2852.3, 1743.7, 1458.4, 1357.7, 1268.3, 1160.6 and 716 cm^{-1}).

After four weeks of incubation, fertilizer sacks and pesticide packaging showed no new absorption bands under any of the tested temperature, pH, moisture or UV combinations, including the most extreme condition tested (40 °C, pH 9.0, 60% water-holding capacity, 8 h day^{-1} UV). This is consistent with reports that conventional PE-based products undergo only minimal chemical change during soil incubation (Huo et al., 2023) and that PE surface chemistry can remain largely intact even where soil biological and chemical properties are otherwise affected (Wang et al., 2022). Mulch film samples, in contrast, developed new absorption bands at 3000–3600 cm^{-1} and ~1000 cm^{-1} (Figure 2) - attributed to O–H stretching of hydroxyl-containing oxidation products and C–O stretching of the –C–O–C– functional group (Table 1), respectively-indicating early oxidative surface change (Heimowska, 2023). These signals were strongest under the combined high-stress condition (40 °C, pH 9.0, 60% water-holding capacity, 8 h day^{-1} UV), weaker but still detectable under moderate conditions (30 °C, pH 7.8, 40% water-holding capacity, 4 h day^{-1} UV), and absent under low-stress conditions (20 °C, pH 7.0, 20% water-holding capacity, no UV). This gradient points to a combined thermal, UV and moisture effect on oxidation onset, consistent with previous work showing that abiotic stressors act jointly with microbial activity to accelerate PE weathering in soil (Heimowska, 2023) and that PE surface oxidation can proceed without complete breakdown of the polymer backbone (Wahl et al., 2024).

The material-specific pattern observed here, oxidative change in mulch film but not in fertilizer sacks or pesticide packaging under identical exposure, suggests that film geometry (high surface-area-to-volume ratio, thin cross-section) rather than polymer chemistry alone governs early degradation susceptibility,

Table 1. FTIR bands used to identify oxidative change in mulch film after soil incubation, compared with bands present in unused (pre-incubation) material.

Spectral region (cm^{-1})	Assignment	Present before / after incubation
2914, 2847, 1470, 718	C–H stretching / CH_2 rocking (base PE structure)	Present before and after
3000–3600	O–H stretching (hydroxyl oxidation products)	Absent before / present after (mulch film only)
~1600	Unsaturated / oxidised C=C or C=O structures	Absent before / present after (mulch film only)
~1000	C–O stretching (–C–O–C–, atmospheric oxidation)	Absent before / present after (mulch film only)

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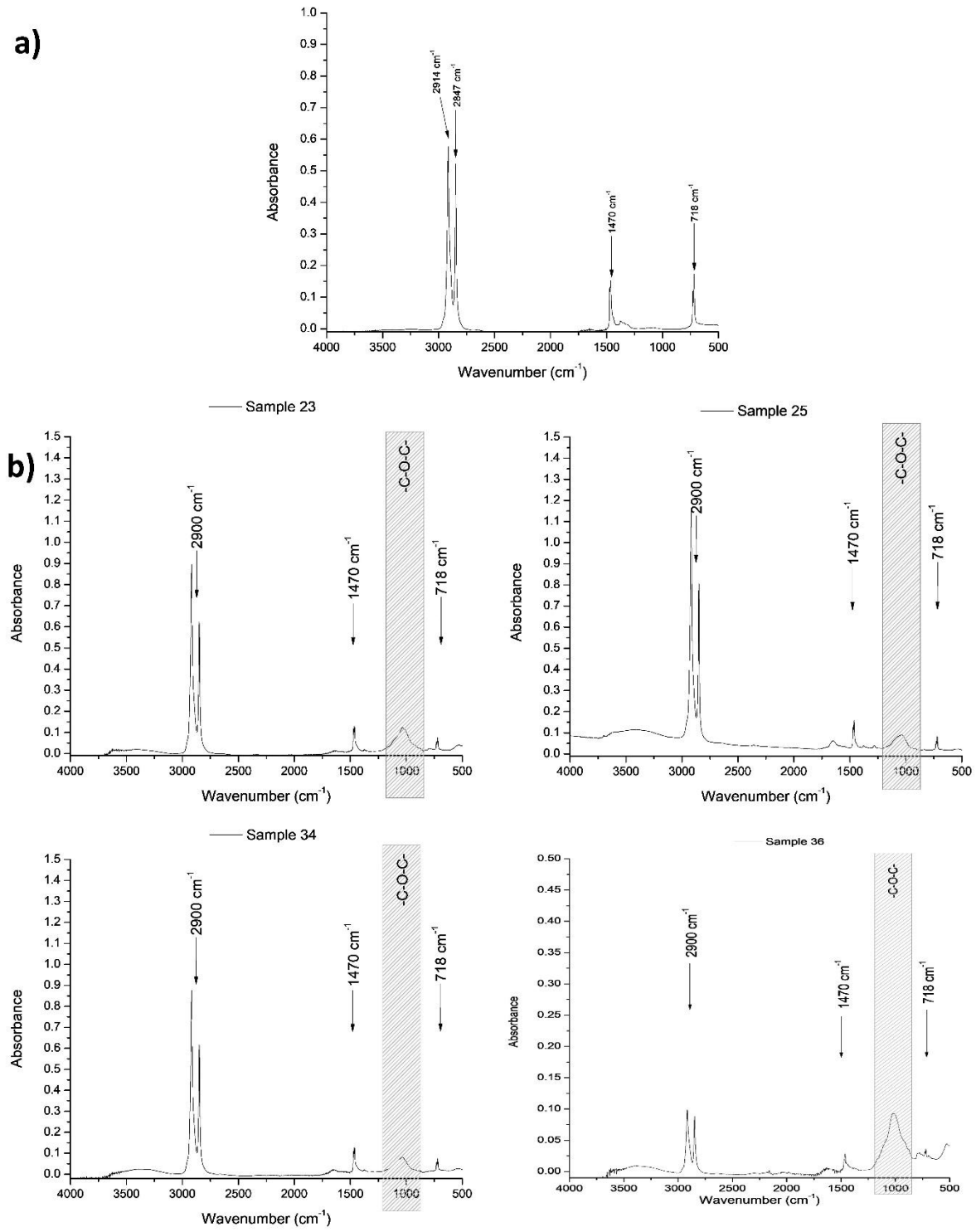

Figure 2. FTIR spectra of mulch film (a) before and (b) after four-week soil incubation, showing new absorption features in the 3000–3600 cm^{-1} and ~1000 cm^{-1} (–C–O–C–) regions not present before incubation.

since fertilizer sacks are largely PET rather than PE and pesticide packaging is a thicker HDPE-based product. This is consistent with the broader observation that PE remains among the more resistant agricultural polymers relative to PET and PP under comparable incubation (Dindar, 2025). Practically, it implies that soil microplastic monitoring and end-of-life management should not treat all PE-based agricultural plastic streams as equivalent: mulch films merit disproportionate attention given their thin geometry, large surface area and documented tendency toward early oxidative fragmentation.

https://doi.org/10.26471/cjees/2027/022/384

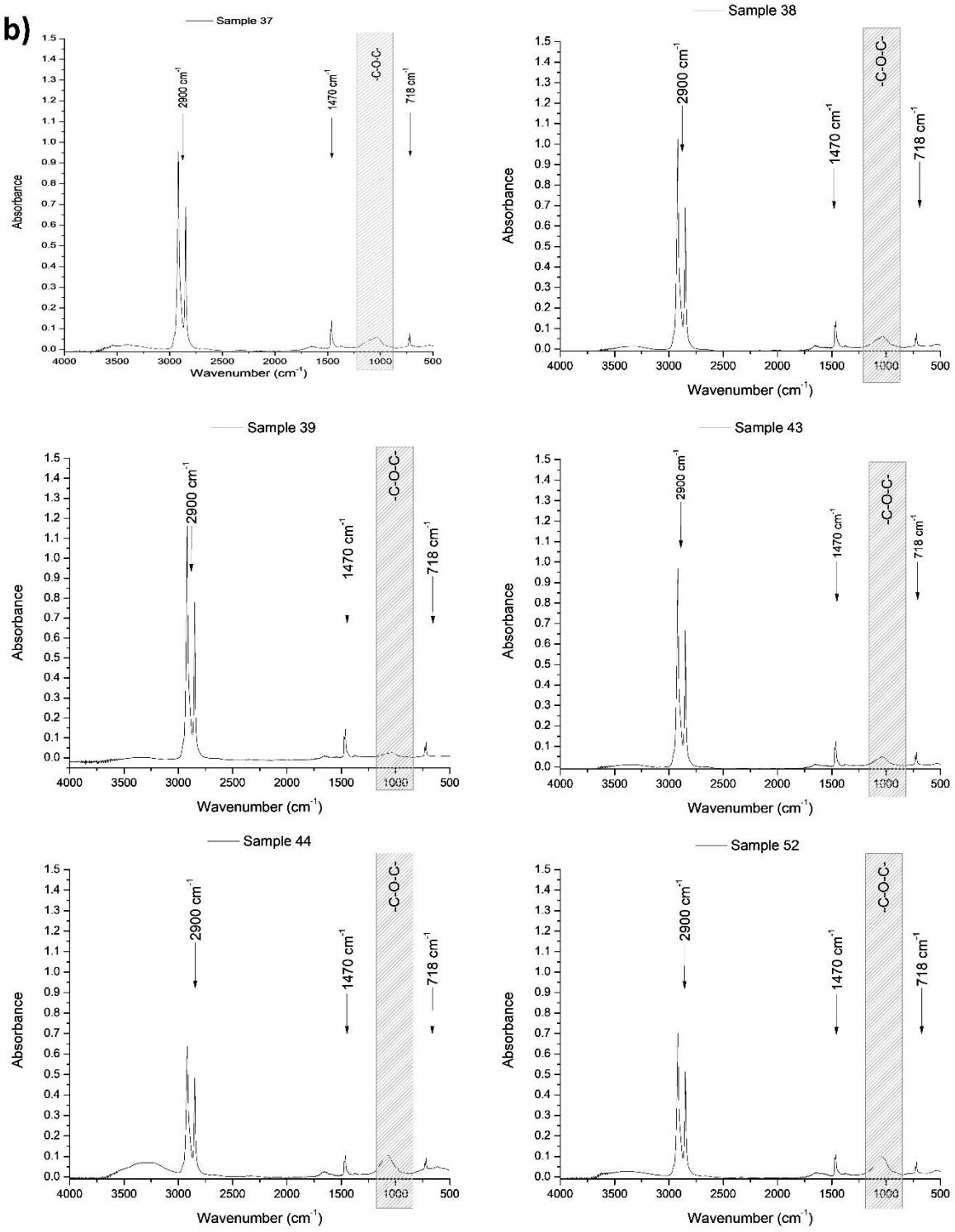

Figure 2. *(continued).*

4. CONCLUSIONS

Under controlled soil incubation, PE-based fertilizer sacks and pesticide packaging showed no detectable oxidative change over four weeks across a wide range of temperature, pH, moisture and UV conditions, whereas PE mulch film developed new FTIR absorption bands consistent with early-stage oxidation, most pronounced under combined high-temperature, alkaline, high-moisture and high-UV stress. These findings indicate that mulch films are disproportionately susceptible to early structural transformation among common agricultural PE plastics, supporting prioritisation of mulch-film

residues in soil microplastic monitoring and in the development of biodegradable alternatives and improved end-of-life management for this specific material stream. Given the controlled, single-soil-type design of this study, field-based validation across diverse agroecological conditions is recommended as a next step.

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Received: 21 July 2026
Revised: 17 September 2026
Accepted: 23 September 2026
Published: 22 October 2026