Universidade Federal de São Carlos (UFSCar) – câmpus Sorocaba
Centro de Ciências e Tecnologia para a Sustentabilidade (CCTS)
Programa de Pós-Graduação em Planejamento e Uso de Recursos Renováveis (PPGPUR)
Grupo de Pesquisa em Poluição Plástica (GPPP)

Glaucia Isabel de Andrade Sebastião

Efeito da interação entre microplásticos de filme *mulching* e pesticida tebuconazol no desenvolvimento do tomate-cereja (*Solanum lycopersicum* L.)

Projeto de mestrado FAPESP nº 2024/17526-0 vinculado ao Projeto Temático nº 2022/12104-4 “Destino e impacto de microplásticos e pesticidas em matrizes aquáticas e terrestres em contextos agrícolas”

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Defesa de mestrado apresentada ao Programa de Pós-Graduação em Planejamento e Uso de Recursos Renováveis da Universidade Federal de São Carlos. Área de concentração: Ciências Ambientais.

Orientação: Walter Ruggeri Waldman

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Profa. Dra. Adriana de Oliveira Delgado Silva (UFSCar)

Prof. Dr. Felipe Klein Ricachenevsky (UFRGS)

Profa. Dra. Luciana Camargo de Oliveira (UFSCar)

Dr. Luan de Souza Leite (UNICAMP)

Prof. Dr. Walter Ruggeri Waldman (UFSCar)

O Relatório de Defesa produzido pelos membros da Comissão Julgadora encontra-se arquivado junto ao Programa de Pós-Graduação.

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“Devo minhas flores às minhas raízes.”

-Autor(a) desconhecido(a).

RESUMO

A crescente utilização de filmes *mulching* de polietileno de baixa densidade (PEBD) na agricultura tem contribuído para o aumento da contaminação dos solos por microplásticos, levantando preocupações quanto aos seus efeitos ecotoxicológicos e à sua interação com pesticidas. Neste estudo, investigamos quatro filmes de PEBD com diferentes formulações e níveis de degradação, onde detectamos que a fotodegradação por UV-C alterou propriedades estruturais e químicas dos filmes de maneiras distintas, modificando sua capacidade sortiva, com destaque para o filme prata degradado, que apresentou maior remoção de um fungicida (tebuconazol) da solução e se mostrou mais suscetível a degradação para as condições aqui testadas. Além disso, observamos que a incorporação de microplásticos prístinos e degradados no solo influenciou o desenvolvimento inicial do tomate-cereja (*Solanum lycopersicum* L.), promovendo alterações significativas nos padrões de alocação de biomassa (SLA, SMF, RSR e LMR), embora sem afetar de forma consistente os parâmetros de crescimento total. Nossos resultados apontam que, além do tipo de polímero, a formulação e o nível de degradação são fatores determinantes nas interações entre os microplástico e a planta. Ao integrar as dinâmicas de degradação, sorção e efeitos biológicos, este estudo amplia a compreensão sobre a complexidade dessas interações no ambiente e reforça a necessidade de considerar a diversidade química e o envelhecimento dos plásticos em avaliações ecotoxicológicas e modelagens ambientais.

Palavras-chave: Microplástico; Ecotoxicologia; Degradação de polímeros; Filme mulching; Fungicida.

ABSTRACT

The increasing use of low-density polyethylene (LDPE) mulching films in agriculture has contributed to rising microplastic contamination in soils, raising concerns about their ecotoxicological effects and their interactions with pesticides. In this study, we investigated four LDPE films with different formulations and degradation levels and found that UV-C photodegradation altered their structural and chemical properties in distinct ways, thereby modifying their sorption capacity. Notably, the degraded silver film showed the highest removal of the fungicide tebuconazole from solution and proved to be the most susceptible to degradation under the conditions tested. In addition, we observed that the incorporation of pristine and degraded microplastics into the soil influenced the early development of cherry tomato (*Solanum lycopersicum* L.), promoting significant changes in biomass allocation patterns (SLA, SMF, RSR, and LMR), although total growth parameters were not consistently affected. Our findings indicate that, beyond polymer type, formulation and degradation level are key factors governing microplastic–plant interactions. By integrating degradation dynamics, sorption processes, and biological effects, this study advances the understanding of the complexity of these interactions in the environment and highlights the importance of considering chemical diversity and plastic aging in ecotoxicological assessments and environmental modeling.

Keywords: Microplastics; Ecotoxicology; Polymer degradation; Mulching film; Fungicide.

SUMÁRIO

PRÓLOGO

Este trabalho se insere nas linhas de pesquisa que estão sendo desenvolvidas sob o "guarda-chuva" do projeto temático da FAPESP nº 2024/17526-0: Destino e impacto de microplásticos e pesticidas em matrizes aquáticas e terrestres em contextos agrícolas. Este projeto é chefiado pela Dra. Cassiana Carolina Montagner (UNICAMP) e coordenado pelos pesquisadores principais Dr. Walter Ruggeri Waldman (UFSCar), e Dr. Evaldo Luiz Gaeta Espíndola (USP). O contexto agrícola trabalhado no presente trabalho é o efeito da interação entre microplásticos de filme *mulching* e pesticida tebuconazol no desenvolvimento do tomate-cereja (*Solanum lycopersicum* L.).

O filme *mulching* é um dos principais filmes utilizados na agricultura moderna e pode beneficiar economicamente os produtores ao reduzirem a necessidade de rega, herbicidas e fertilizantes. Os benefícios, entretanto, mascaram um grande problema ambiental, que é o acúmulo de fragmentos de *mulching* no solo devido a dificuldade na retirada do material após o plantio. A consequência direta da falta de gestão após o ciclo de vida útil do material se reflete no acúmulo de microplásticos no solo, formados a partir da degradação destes fragmentos. Mesmo em locais onde a coleta é feita seguindo regulações a fim de evitar o rasgo do material, a sua fina espessura e alta degradação tornam a reciclagem técnica e economicamente inviável.

Uma das preocupações associadas à presença destes microplásticos no solo ainda pouco explorada está relacionada ao papel dos microplásticos como sorvedores de poluentes ambientais. Neste trabalho, buscamos compreender não somente o impacto de microplásticos de filmes *mulching* sobre o desenvolvimento do tomate, como também a interação do fungicida tebuconazol com os microplásticos de *mulching*.

Uma outra lacuna que o trabalho se propõe a responder se baseia no seguinte contexto: ao analisar diversos estudos da área de ecotoxicologia de microplásticos, vários trabalhos se debruçam na investigação dos efeitos de diferentes polímeros (ex.: PP, PE, PVC, etc) sobre os organismos, e embora tenhamos informação sobre sua toxicidade, ainda não compreendemos bem a toxicidade particular de suas formulações. Em nosso estudo, selecionamos quatro filmes de mesma composição polimérica - polietileno de baixa densidade (PEBD) - mas de diferentes cores e valores na tentativa de variar as formulações.

As perguntas que nortearam a criação deste projeto de pesquisa são: 1) qual a natureza química e física dos filmes selecionados e quais são seus comportamentos diante da degradação?; 2) a degradação e os aditivos influenciam de que maneira a sorção de um fungicida?; 3) diferentes formulações podem mudar a toxicidade de um

microplástico? Se sim, há diferença entre os impactos de microplásticos prístinos e degradados?

Uma vez que trabalhar com quatro filmes de PEBD de diferentes formulações é a premissa essencial para todas as etapas seguintes, o Artigo 1 foi elaborado somente para caracterização desses polímeros. Após, no Artigo 2, o estudo se voltará à verificação de potencial tóxico para o tomate-cereja, para a microbiota do solo e para as propriedades do solo na forma de microplásticos.

Para responder às perguntas mencionadas e também introduzir a temática ao leitor, esse documento se divide em três capítulos: Capítulo 1) Introdução geral; Capítulo 2) Caracterização dos filmes *mulching* e capacidade sortiva com tebuconazol; Capítulo 3) Efeito de microplásticos de filme *mulching* em tomate-cereja. Os artigos constituem os últimos dois capítulos.

Os artigos foram escritos na língua inglesa não somente para que eu pudesse desenvolver essa habilidade científica, como também visando deixar o material mais próximo do seu estado final para publicação. Compreendendo que a divulgação do documento em inglês pode não ser acessível para todos, me proponho, ao fim do mestrado, a realizar a divulgação dos resultados dessa pesquisa através do meu canal no YouTube (canal: https://www.youtube.com/@glauciaisabeldeandradeseba8106), entendendo a importância de retribuir à sociedade os investimos por ela feitos e também considerando o maior alcance desse tipo de divulgação quando comparado à da linguagem acadêmica.

Enfim, para organizar a bibliografia, utilizei o gerenciador Zotero. Como o mesmo artigo é citado múltiplas vezes em capítulos diferentes, a numeração automática gerada pelo software ficou não sequencial ao longo do texto. Por isso, para garantir uma lista de referências única, optei por agrupar todas as citações em uma única bibliografia geral no final do documento. Ao leitor, desejo uma leitura proveitosa.

CAPÍTULO 1: INTRODUÇÃO GERAL

Em todo o mundo, a produção de plásticos cresce de forma acelerada a cada ano. Em 2022, a produção global atingiu 400,3 megatoneladas, um aumento de 2,5% em relação ao ano anterior.[1] O mesmo acontece no setor agrícola, onde estima-se que a procura global por filmes para estufas, *mulching* e silagem aumente em 50% até 2030, de 6,1 milhões de toneladas em 2018 para 9,5 milhões de toneladas até o final desta década.[2] Isso se deve às extensas melhorias que os plásticos agrícolas proporcionam ao setor agroalimentar,[3] dentre elas a proteção contra doenças e pragas, a regulação do microclima e facilidade no transporte de insumos.[4]

Contudo, essas melhorias também acarretam problemas relacionados ao uso intensivo de plásticos, especialmente devido ao descarte inadequado desses materiais nos solos, onde se degradam, gerando microplásticos (MPs), fragmentos que variam de 5 mm a 1 µm, e nanoplásticos, que variam de 1 a 1000 nm.[5,6] Para além disso, os solos agrícolas também recebem grande carga de MPs provenientes de outras fontes, tais como: compostos fertilizantes que, durante seu processamento, retém grandes quantidades desse poluente,[7] e deposição proveniente de locais externos ao plantio, via ar e água de irrigação.[8,9] A título de exemplo, ao analisar a distribuição de microplásticos provenientes da irrigação de culturas com águas residuais pelo mundo, o Brasil se encontra na sétima posição de maior quantidade desse poluente, com 61 quilotoneladas de microplásticos estimados.[10]

A crescente concentração de microplásticos nos solos tem sido associada a prejuízos para a biota, tanto pela obstrução do trato digestório causada pela absorção de particulados como pela toxicidade gerada pela lixiviação de aditivos intencionalmente e não intencionalmente adicionados (IAS e NIAS, dos acrônimos em inglês para *intentionally added substances* e *non-intentionally added substances*), que são liberados da matriz polimérica para o meio.[11] Além disso, estudos ecotoxicológicos têm investigado como diferentes tipos de plásticos afetam organismos-teste, revelando dessemelhanças na toxicidade em detrimento da diversidade química dos diferentes polímeros e das substâncias neles presentes.[12–14]

Ademais, vale destacar que os microplásticos são conhecidos por sorver outros poluentes orgânicos persistentes (POPs), devido às dinâmicas propiciadas pelas interações hidrofóbicas, interações π-π, forças eletrostáticas, ligações de hidrogênio, forças de Van der Waals e preenchimento de poros,[15] sendo um vetor dessas substâncias para os organismos presentes no solo.[16] Essas substâncias podem adentrar células e causar, dentre outros, prejuízos ao desenvolvimento das plantas de interesse agrícola,[17] da fauna presente no solo e da microbiota.[18,19]

Um dos plásticos agrícolas mais utilizados é o filme *mulching*, geralmente formado por polietileno de baixa densidade (PEBD), por possuir boa durabilidade, flexibilidade e relação custo-benefício.[20] No mundo, estima-se que 20 milhões de hectares de terras agrícolas são cobertas por esse filme.[21] O *mulching* é vendido como uma prática sustentável, já que poupa o solo e a água através da criação de uma barreira protetora entre o solo e a atmosfera, favorecendo o microclima do solo e diminuindo a necessidade de irrigação, fertilização e aplicação de pesticidas.[22] Não obstante, devido a seu uso intensivo na agricultura e pela dificuldade de remoção completa ao fim da colheita, os filmes *mulching* contribuem significativamente para a poluição plástica nos solos,[5] correspondendo a uma massa de contaminação que pode estar entre 0,5 a 2,3 milhões de toneladas de plástico nos solos agrícolas.[10]

Os microplásticos gerados pela fragmentação dos filmes *mulching* podem se incorporar, acumular no solo e, com o passar dos anos, modificar suas características fisiológicas e biológicas.[23,24] Segundo uma revisão realizada por Kedzierski e colaboradores (2023), que analisou 442 locais, aqueles cujas terras estavam sujeitas a contaminação por *mulching* possuíram, em média, 5.692 mg de microplásticos por m³, podendo alcançar 10.347 $mg.m^{-3}$ em terrenos mais contaminados.[10] Em testes realizados em plantas de interesse econômico, a contaminação por resíduos de *mulching* no solo podem influenciar negativamente o crescimento de raízes, da parte aérea, afetando a biomassa vegetal, o teor de clorofila e até mesmo rendimento final de frutos e grãos.[17,18,25,26]

Assim como outros microplásticos, os filmes *mulching* possuem a capacidade de sorver poluentes orgânicos, tais como pesticidas, o que leva a redução da lixiviação de pesticidas pelo solo, decorrente tanto da capacidade sortiva que o polietileno (PE) possui,[27] quanto das mudanças que os particulados causam na estrutura do solo, aumentando sua porosidade, e diminuindo a conectividade.[23] Um exemplo é a interação que ele possui com o tebuconazol, um fungicida utilizado em plantações de tomate para combate de pragas como Septoriose (*Septoria lyopersici*) e Pinta-preta (*Alternaria solani*)[28]. O tebuconazol é autorizado pela Agência Nacional de Vigilância Sanitária (ANVISA) para uso em mais de 90 culturas[29] e pode ser sorvido por microplásticos de PE por particionamento, aumentando seu tempo de persistência na água.[27]

O tomate é uma das culturas beneficiadas pelo uso do filme *mulching*, podendo inclusive apresentar maior rendimento da produção em ocasião da aplicação de filmes.[30] Seus frutos estão entre os de maior importância comercial[31] e, em 2022, sua produção alcançou 186 milhões de toneladas.[32] Contudo, há evidências suficientes que apontam o uso de filmes por um período prolongado de tempo como causador do aumento gradual de microplásticos no solo, o que, no longo-prazo, pode acarretar em

danos para a estrutura do solo, para os organismos nele presentes e por fim para a própria cultura de interesse.[17,19,33,34]

Diante do exposto, embora haja evidências suficientes dos efeitos negativos dos microplásticos em solos e seres vivos, ainda não está claro como diferentes formulações de um mesmo polímero (PEBD) podem promover diferentes níveis de toxicidade para as plantas. Também há pouca investigação no que tange como diferentes formulações afetam a degradação e a capacidade sortiva dos plásticos com um pesticida.[35]

CAPÍTULO 2: CARACTERIZAÇÃO DOS FILMES MULCHING E CAPACIDADE SORTIVA COM TEBUCONAZOL

Artigo 1: Characterization of four LDPE mulching films of different formulations before and after degradation and their sorption behavior with the fungicide tebuconazole

Glaucia Isabel de Andrade Sebastião, Mariana Amaral Dias, Luan de Souza Leite, Adriana de Oliveira Delgado Silva, Marcia de Almeida Rizzutto, Cassiana Carolina Montagner, Elias Ricardo Durango Padilla, Alice Pita Barbosa, Walter Ruggeri Waldman

ABSTRACT

Mulching films are widely used in agriculture for their economic and agronomic benefits, but incomplete removal from soils makes them a significant source of microplastics. Although plastic degradation and pesticide sorption have been studied, the influence of film formulation on degradation and physicochemical properties remains unclear. This study evaluated four mulching films (two black, one silver, and one white), examining their physicochemical properties before and after photodegradation and their interaction with the fungicide tebuconazole. Scanning electron microscopy revealed crack formation in the Silver film and additive migration in the White film after degradation. Tensile tests showed increased fragility in the Silver film, while blacks were the most stable, results supported by spectroscopy. Hydrophobicity generally decreased with degradation, except for Silver. Sorption tests indicated greater tebuconazole retention after degradation, with the Silver film removing up to 53% in its most degraded state. The elemental analysis showed heterogeneous distributions of elements among the films, both in presence and quantity. Overall, formulation was proved to be a key factor controlling film resistance and contaminant interaction, highlighting the need to consider formulation when comparing degradation and environmental effects of the same polymer.

INTRODUCTION

Mulching films are agricultural plastics used to cover soil and are sold as a sustainable practice since it helps to reduce the need for watering, herbicides, labour cost, among other benefits.[22] These characteristics provide not only greater profits for farmers but can also increase the vegetable production. Despite having lots of benefits, its problems start by the end of its useful life. These films are very thin (10-32 μm) and by the end of its life-time they are seriously degraded by weathering, which makes them easily torn during its removal, leaving lots of fragments behind.[4,33] Even when collected in

accordance with regulations that include previous cleaning and removal without dragging, the unfeasibility of recycling remains.[36] To follow these regulations is expensive and does not reflect the reality of most farmers, so in practice, the removed films are often dirty and mixed with other colors.[4] For this reason and due to its wide application, mulching films has become a huge problem and an important source of microplastic (MP) to agricultural fields.[2] It is also worth noting that these films are also exposed to pesticides sprayed on the crops,[35] which raises concerns, since plastics have the ability to sorb persistent organic pollutants.[15]

Mulching films, as well as any commercial plastic product, contains not only the polymer structure, but also a series of substances that impart specific characteristics to the plastic, called additives. Conventional mulching films, i.e., non-biodegradable, are usually made of low-density polyethylene (LDPE). LDPE is included in a polymer class called polyolefin. Photodegradation - the process where materials breakdown by light's energy - of polyolefins is a well-established process.[37] In order to happen, photodegradation requires chromophore groups to absorb light. Polyolefins, like polyethylene, are theoretically immune to photodegradation because they don't have natural radiation absorbing groups.[37] However, the photodegradation in polyethylene products still happens because of additives added to films together with manufacturing defects that degrade the plastics, generating carbonyl and carbon insaturations that are able to absorb UV light.[37–39] According to Reay et al. (2025), LDPE mulching films commonly contain antioxidants and lubricants as intentional additives, in addition to non-intentionally added substances (NIAS)[40]

Photodegradation of polyolefins starts with the absorption of UV light by chromophore groups, leading to the formation of a radical. In contact with oxygen in the air that penetrates the polymer, this radical forms hydroperoxide. This reaction depends on the amount and nature of light energy and also the amount of oxygen that permeates the surface. After hydroperoxide is formed, homolytic cleavage occurs in alkoxy and hydroxy radicals.[41] This mechanism is an autocatalytic degradation and once started, cannot be stopped.

Mulching films are exposed to sunlight for months straight and, by the end of the season, they undergo severe degradation reactions. This process is driven especially by photodegradation, but thermal[42] and physical degradation can also contribute to polymer chain scission. As a result, mulching films can exhibit increased carbonyl group content and changes in surface roughness, wettability and crystallinity.[43,44] Noteworthy that these films are exposed to pesticides, which raises concerns since plastics have the ability to sorb persistent organic pollutants[45] and their sorption capacity may be further modulated by degradation processes.

Even though there are some early studies investigating degradation of mulching films in specified conditions,[43,44] it is not clear how different formulations affect their degradation. A study by Nerín *et al*. (1996) assesses the sorption capacity of four mulching LDPE films (normal, black, thermic and extra-LDPE) and one EVA film to absorb eight pesticides. They observed differences in absorption depending on the polymer structure, since LDPE films behaved in similar ways.[35] However, literature still lacks understanding how different formulations, especially in their degraded state, influence the sorption capacity of mulching films. This comprehension is important, since the fragments left in the field are often highly degraded, which in turn modulates how mulching-derived MPs interact with pesticides and potentially affect their transfer into organisms.

In this study, we aim to understand how four different formulations of LDPE mulching films behave in face of degradation and how they modulate the plastic to interact with a pesticide. The chosen pesticide is the fungicide tebuconazole, authorized in several countries and used in various crops to combat pests such as Septoria leaf spot (*Septoria lyopersici*) and early blight (*Alternaria solani*)[28].

METHODOLOGY

Selection criteria

Criteria such as color and price were used to guide the selection of these films to ensure different formulations. The color criteria is related to the fact that certain pigments have different elements in their composition, while the price is often determined by the additives added to the polymers, as well as the care with raw materials and industrial processing, which might influence NIAS. These differences can be indicative of variation in formulation. Considering it, we chose two black/black mulching films, one of which was cheap and the other expensive. The other two films were silver/black and white/black. The code color/color refers to side A/side B. The cheap black/black film is black brand 1 and will be called “BB1” and the expensive black/black “BB2”. The average thickness of the films is 19 µm.

Degradation

In order to evaluate the degradation evolution of four types of mulching film, we exposed them for 7 and 18 days of degradation. To speed up the process, films were exposed to three 36W UV-C lamps (Osram) positioned 49 cm above the sample in a lab-made photodegradation chamber[41] and to ensure uniform exposure, the degradation sample holders were rotated 180º and switched positions daily. These holders were borrowed from a UV accelerated weathering tester.

Optical and chemical characterization

The degradation was first analysed by visual aspects using both a Nikon (D3200) camera and Scanning electron microscope (SEM) (Thermo Fisher Scientific Inspect F50) with secondary electron detectors Everhart-Thornley Detector (ETD). Prior to SEM analysis, the films were carbon-coated using a sputter coater (Leica EM ACE600). Fourier Transform Infrared (FTIR) was applied to inspect polymer composition and degradation level. The spectra of films were collected by transmission accessory on a Thermo Scientific Nicolet Summit spectrometer and were measured from 400 to 4000 cm^{-1} at 18 ºC, 32 scans and spectral resolution of 4 cm^{-1}. Analyses were performed on the side exposed to UV-C light.

Elementary composition

To evaluate elementary composition of films, X-ray fluorescence (XRF) was used and results were processed through WinQxas software. The calibration was established using Ar from air and a Pb plate as standards, measured at 100 s per point under 30 kV and 5 μA. X-ray spectra of plastic samples were obtained at 30 kV and 80 μA, using Mo (25 μm) and Al (250 μm) filters. The Zn (Kα)/Fe (Kα) peak area ratio was used to compare the relative abundances of these elements across the films. XRF is a crucial analysis, as plastic manufacturers do not share the formulation for reasons of intellectual properties.[46] Measurements were taken on the side exposed to UV-C light. XRF results were processed in WinQXAS software.

Wettability

A goniometer (Ramé-Hart) was used to inspect changes in hydrophobicity of films in different degradation levels, where 30 scans were performed for each film with a time interval of 0,001s using the circle method. Measurements were taken on the side exposed to UV-C light.

Mechanical characterization

Mechanical characterization of the LDPE mulching films was performed through tensile tests using an Emic DL10000 Universal Testing Machine (UTM), equipped with a 200 N load cell at a speed of 5mm/min, and Tesc 3.04 software, following ASTM D882 guidelines. For each treatment, five rectangular specimens (10 mm x 100 mm, 20 μm thickness) were used, from which the means and standard deviations of maximum stress (MPa) and elastic modulus (MPa) were determined. Maximum stress was calculated as the ratio between the maximum force and the cross-sectional area, while the elastic modulus was obtained from the slope of the linear region of the stress-strain curve.

Sorption analysis

For the sorption analysis, fragments measuring 3.8 × 1.5 cm were cut, and their edges were rolled with the colored/degraded surface facing outward, then secured with a galvanized staple using a stapler. The stapling step was necessary to standardize surface exposure, since the more degraded the plastic, the greater its tendency to curl due to internal stresses in the material, which could reduce the surface area in contact with the solution.

For the test, each fragment was placed in 4 mL of an aqueous solution containing tebuconazole (TEBUCO 430 SC NORTOX) at a concentration of 1 μg L^{-1} in 10 mL glass tubes capped with polytetrafluoroethylene (PTFE) caps. The tubes were placed on a roto-torque shaker (Marconi MA161/ROTO) at room temperature (20 °C) and 80 rpm.[47] All experiments were performed in triplicate. Control samples containing only the tebuconazole solution and tebuconazole + staple were also prepared and the presence of the staple proved negligible.

Tebuconazole quantification was performed by direct injection. Samples were filtered through hydrophilic regenerated cellulose syringe filters (13 mm diameter, 0.22 μm pore size) (Filtrilo, Colombo, Brazil). After filtration, 200 μL of each sample were transferred to a vial containing 560 μL of H_2O:MeOH (70:30, v/v) solution and 40 μL of the internal standard tebuconazole-trimethyl-$^{13}C_3$ at a concentration of 50 μg L^{-1}, resulting in a dilution factor of 4. Analyte determination was carried out using a Thermo Vanquish liquid chromatograph coupled to a Thermo Fortis triple quadrupole mass spectrometer equipped with electrospray ionization (ESI). Chromatographic separation was achieved using a Zorbax SB-C18 column (2.1 × 30 mm, 3.5 μm particle size). The analytes were determined in selected reaction monitoring (SRM) mode under positive ionization.

Calibration curves were constructed over a concentration range of 1 to 500 μg L^{-1}, with an instrumental limit of quantification (IQL) of 1 μg L^{-1} for tebuconazole and a method limit of quantification (LOQ) of 1 μg L^{-1} for tebuconazole.

RESULTS AND DISCUSSION

Although UV-C radiation is mostly absorbed by the ozone layer[48] and, therefore, it is not environmentally representative, it is commonly used for degradation in experiments, including in industry,[44] due to its high energy and consequently higher rate of degradation. Despite having different mechanisms and photochemical yields, this strategy was adopted since UV-A and UV-C radiation produce some similar final results, including the production of volatile organic compounds (VOCs),[49] and reactive oxygen species (ROS).[50] In addition, both produce wavelengths capable of ultimately breaking

polymer chains,[49,51] producing oxygenated species,[52,53] forming cracks in the surface,[52,54] and yielding a brittle material.[55]

Visual aspects

All four films showed stretching in the UV-C protected area (the edges) from the first week of exposure to UV-C light, indicating that degradation processes were already taking place in the exposed area (Figure 1). This stretching results from molecular changes that involve the breaking of polymer chains in the exposed area,[56,57] which releases pre-existing internal tensions and increases the free volume of the material. The increased free volume can foster chain mobility, promoting crystallinity of the material and since crystals occupy a smaller volume than the previous amorphous chain, the material becomes tensioned, leading to internal stress and stretching.[56]

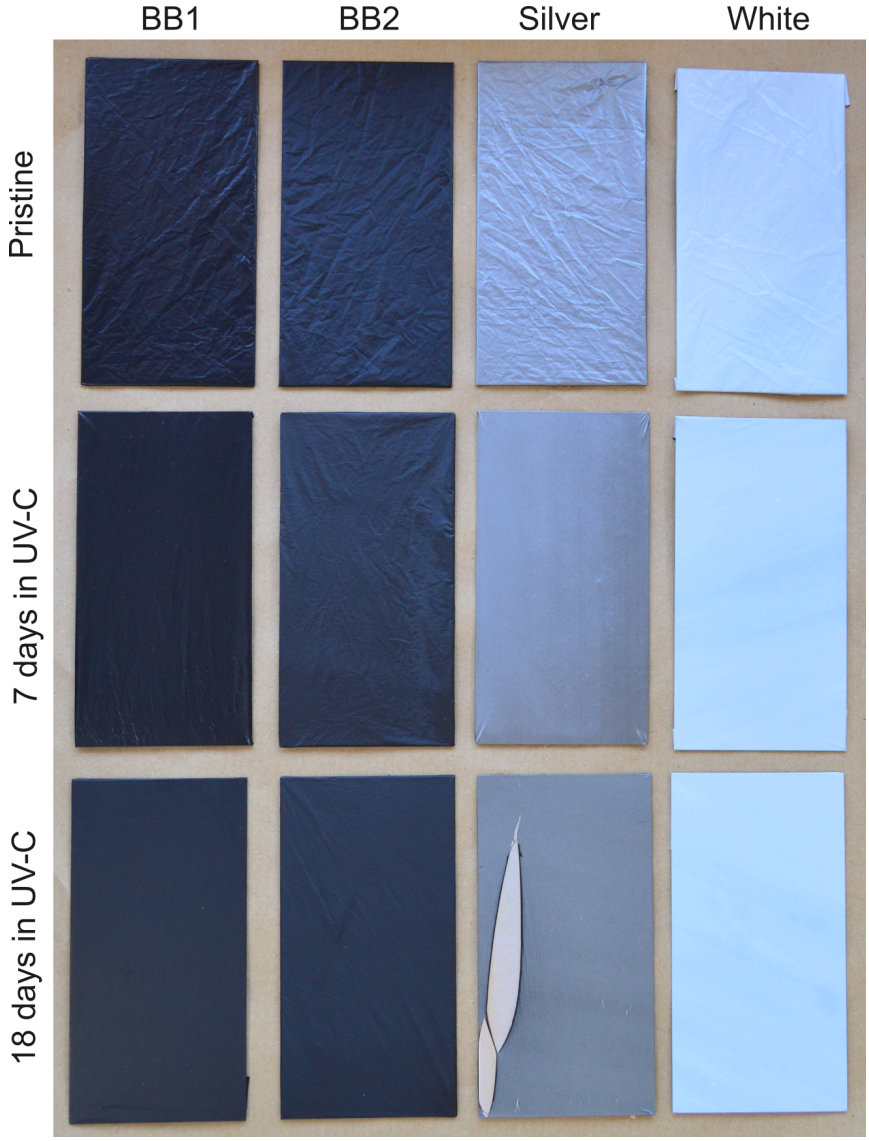


Figure 1. Degradation evolution of four mulching films (BB1, BB2, Silver, and White).

Degradation, however, evolved differently among the films. BB2 and BB1 were the ones that presented the least amount of stretching after 7 days, while Silver and White presented more pronounced stretching. Silver, in particular, was the film that showed the greatest change in roughness and tension, while BB1 and White seemed to lose the gloss (Figure 1). Loss of gloss is a common sign of polymer degradation and it reflects loss of surface mechanical properties.[54,58] Increased opacity arises from the formation of voids with dimensions close to the wavelength of visible light.[59] These voids scatter incident light more diffusely when compared to pristine films, thereby enhancing the visual opacity of the surface and by losing surface mechanical properties.[58]

After 18 days, the trends presented in the first week were the same and the effect of degradation have intensified as the films kept becoming more opaque. Silver is the film that resists photodegradation the least under the conditions of this study as it has become extremely fragile and tearable. This is due to break of molecular chains caused by UV-C radiation, causing the material to be more brittle.[60] All of the films kept losing the gloss. BB2 (the most expensive film) seemed to be the most resistant to degradation, just by changing a little bit its color and by showing the least amount of stretching. The gloss is not a very useful parameter for this film in particular, since it is opaque even when pristine because of its different texture. This film also showed minimal stretching, proving to be more resistant than the other films in the exposed area. Given this result, Silver appears to be the least resistant film among the four and the most prone to fragmenting into MPs.

X-Ray Fluorescence

Among all films, Zn had the highest number of counts, except for Ti, the predominant element in White film (Figure 2). Zn compounds are added in plastic formulations as a UV stabilizer,[71,72] and also as lubricant,[73] while Ti probably comes from the pigment TiO_2, used as a light blocker (and what gives the color white).[74]

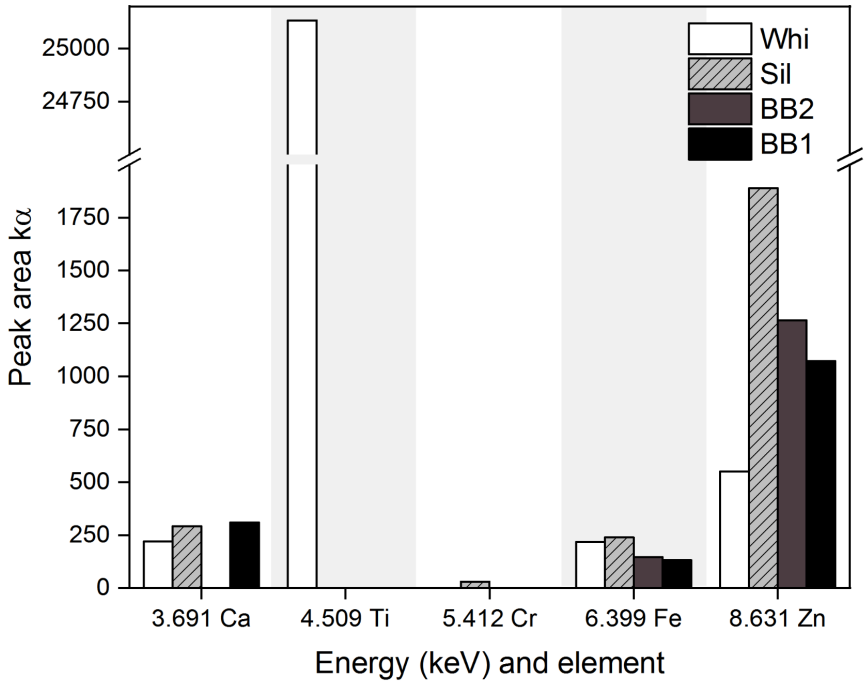


Figure 2. Counts of elements for four mulching films (BB1, BB2, Silver, and White).

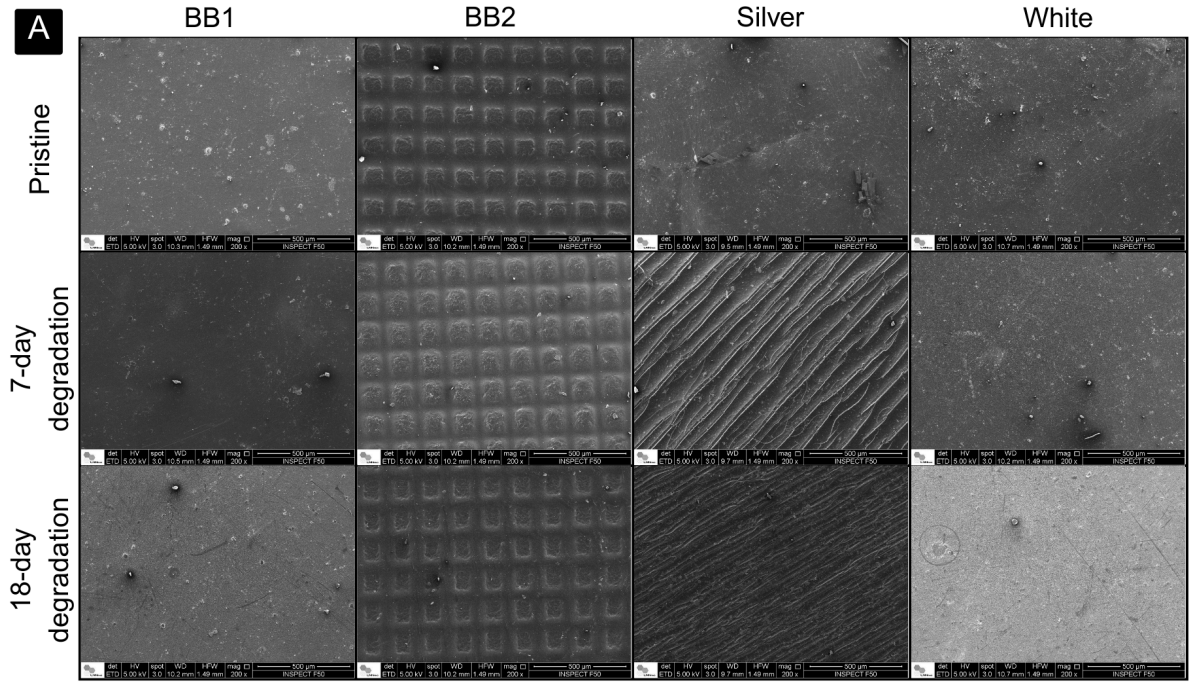
Fe is also an element present in all films. The abundance of Zn and Fe observed in this study reflects the rest of the LDPE film market, where these elements represent the majority of heavy metals added.[77] It also in accordance with Reay *et al*. 2025,[40] that investigated dozens of mulching films and found that the most abundant heavy metal additives were the same due to the pigments added to films.

Except for BB2, Ca is another common element found in films. Salts such as $CaCO_3$ are commonly added to mulching films as an inert filler, for being cost-effective,[40,78] and is used to improve characteristics like impact resistance and stress cracking.[78] BB2 is an expensive material compared to the other films and probably uses another type of additive to extend the lifetime of the film in the field. Finally, Cr was found in small quantities in Silver film.

In order to compare the proportion of common elements among the films, we propose a Zn/Fe ratio comparison. To do that, we adopted the Kα peak area for both of these elements. BB1, BB2 and Sil present a similar Zn/Fe ratio, ranging from 7.9 to 8.6, while White had the most different one: 2.5. In XRF analysis, relative intensity is measured, so the more Ti, the lower the fraction of Zn relative to Fe, even if the amount of these elements are similar.

Scanning Electron Microscope

The surface morphology analysis performed with SEM (Figure 3) indicates some differences between the films. Comparing pristine films among each other, BB2 has a different texture from the rest, with a pattern of dots. By analyzing the progressive change over the course of degradation, a change in the surface of all films can be detected, especially after 18 days of degradation (Figure 3B). The BB1 and BB2 films differ from their less degraded counterparts in the roughness of the material, which increases progressively after UV-C exposure, reflecting the loss of cohesion of the material. Meanwhile, the silver film shows the most prominent changes in texture. After 7 days of degradation, it is possible to observe the formation of cracks that intensify after 18 days.



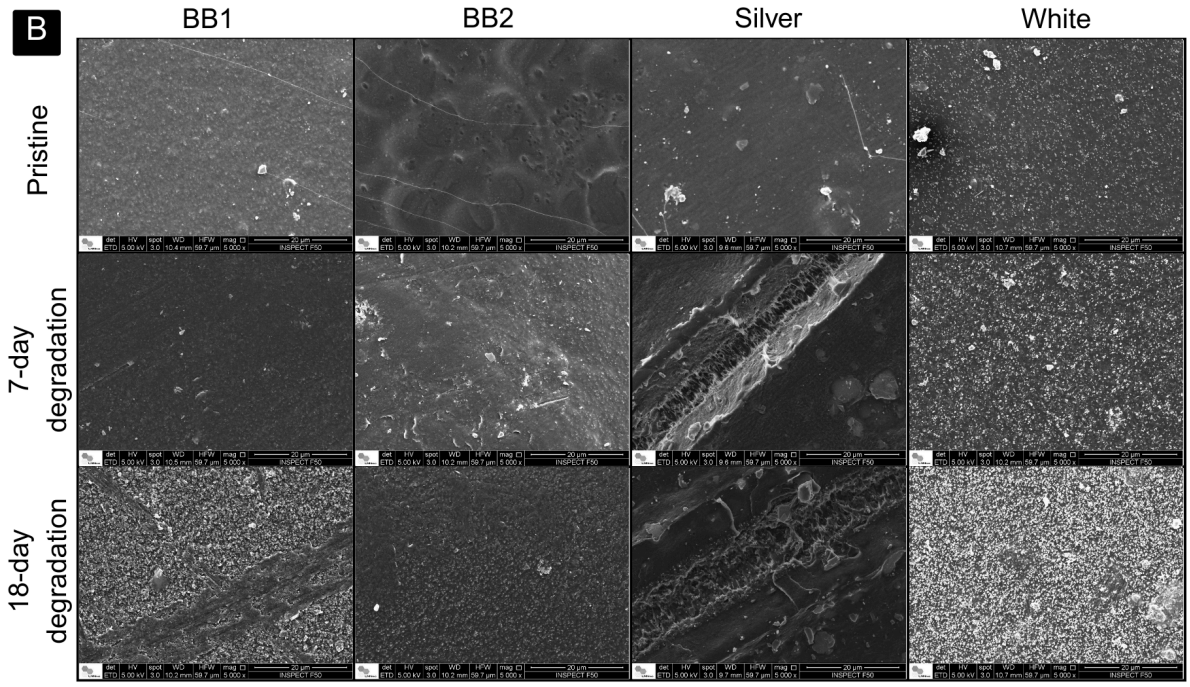


Figure 3. Progression of degradation through Scanning Electron Microscopy of four mulching films (BB1, BB2, Silver, and White) in pristine and degraded forms (for 7 and 18 days). SEM image at 200× magnification in (A) and 5000× magnification in (B).

The cracks presented in “Silver” film are oriented in the same direction, suggesting a single tension direction.[58] They originate from the development of microvoids, which trigger a fibrillation process, which consists of the formation of supporting fibrils between walls in the process of breaking.[61] This rupture process is known as craze and is responsible for weakening the material.[54] When the fibrils break, cracking occurs. When analyzed at higher magnification, it is possible to see the formation of the fibrils (Figure 4) and their nanometric dimensions (Figure 4B). This result indicates the potential of this film at this stage of degradation to form nanoplastics, pollutants whose toxic effects are still poorly understood due to the challenges of analysis resulting from their size limitations.

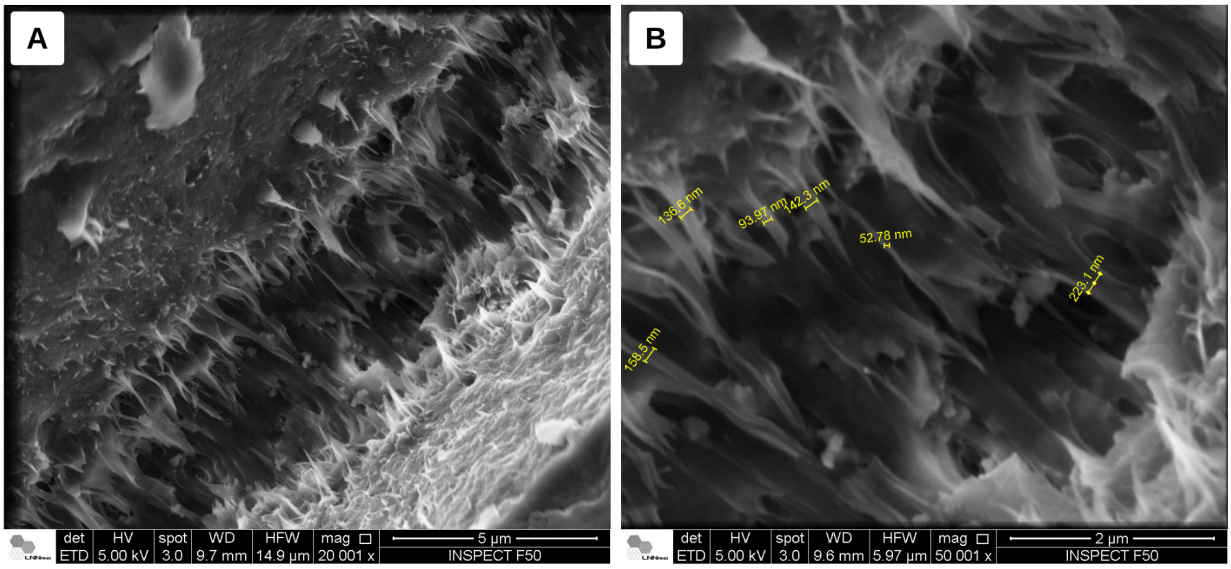


Figure 4. Craze phenomena taking place in Silver film with 7-day degradation with formation of nano fibrils.

Meanwhile, the white film shows the highest intensity of secondary electrons after 18 days of degradation (Figure 3A and B), which probably indicates an increase in the concentration of TiO_2 on the surface. We have two hypothesis for this phenomena: 1) this contrast difference was caused by a phenomenon known as blooming, when additives (in this case TiO_2) present inside the polymer chain migrate to the surface as a result of polymer degradation;[62] 2) a degradação In the specific case of this film, there is likely migration of titanium dioxide , an additive with a high molecular weight that is widely present in the sample.

From an environmental standpoint, the blooming phenomenon is concerning because it can lead to the leaching of additives previously protected in the polymer matrix into surrounding ecosystems.[62]

Fourier Transform Infrared Spectroscopy

The analysis made through transmission-FTIR spectra enables us to investigate not only the degradation level, but also to confirm the type of plastics. All of them were indeed LDPE films due to the presence of the following absorption bands (cm^{-1}): 2914 (CH_2 asymmetric stretch), 2847 (CH_2 symmetric stretch), 1462 (CH_2 bend), 1376 (CH_3 symmetric bend) and 719 (CH_2 rock).[63] What allows differentiation between High-Density Polyethylene (HDPE) and LDPE is the presence of the band at 1376 cm^{-1} in LDPE,

present in all of four films (Figure 5).[63] This difference is due to the higher degree of chain branching in LDPE, which results in a higher content of methyl (–CH_3) groups.

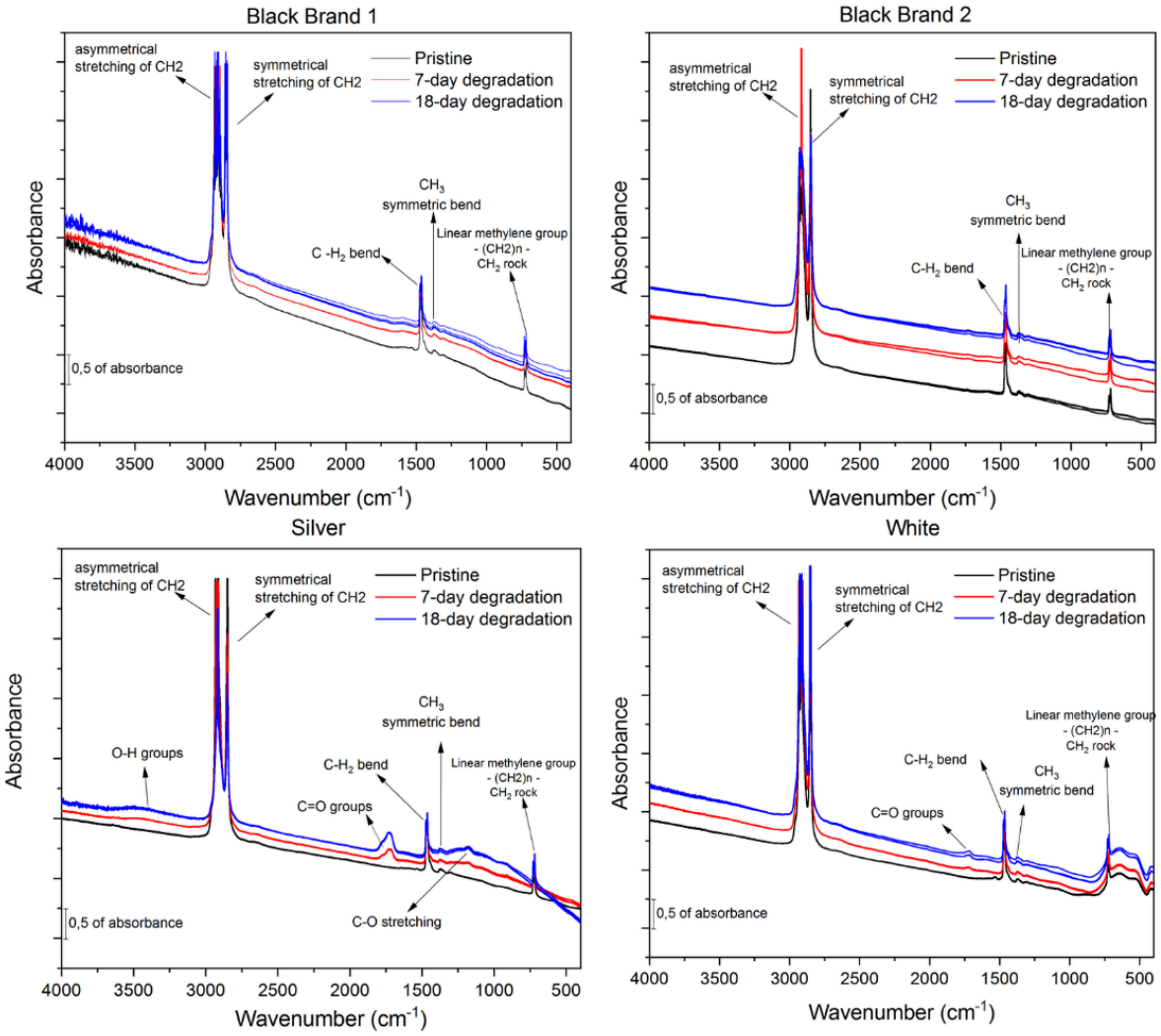


Figure 5. FTIR spectra (transmission mode) of four mulching films (BB1, BB2, Silver, and White) in pristine and degraded forms (for 7 and 18 days).

We studied the degradation evolution of different films over time by analysing the formation of indicator groups of degradation, like carbonyl (C=O) and hydroxyl (OH) groups. Differences between the films started to appear from the first week and have intensified after 18-day exposure to UV-C radiation. BB1 and BB2 films did not show signs of degradation or modifications, while Silver presented signs of carbonyl and hydroxyl formation (around 1808-1673 cm^{-1} and 3618-3319 cm^{-1}, respectively), as well as White, with a carbonyl band around 1756-1692 cm^{-1} (Figure 5). However, the

carbonyl groups formed in Silver are more intense compared to White, indicating that this film is degrading faster than any other. In addition, the band shape in Silver is broader than the one in white, which may reflect an overlap of different types of carbonyls, like acids (1716 cm^{-1}), esters (1740 cm^{-1}), and lactones (1772 cm^{-1}).[64] A new peak emerged in the fingerprint region of Silver after degradation in the region of 1000-1200 cm^{-1} (Figure 6), indicating the presence of C-O stretching, showing a new product of degradation in this particular film.[65,66] In addition to that, White also presented an important difference in the fingerprint region (<700 cm^{-1}) even before degradation, characterized by a broader and more intense baseline. This aspect suggests the presence of inorganic additives, such as TiO_2 detected through XRF analysis.

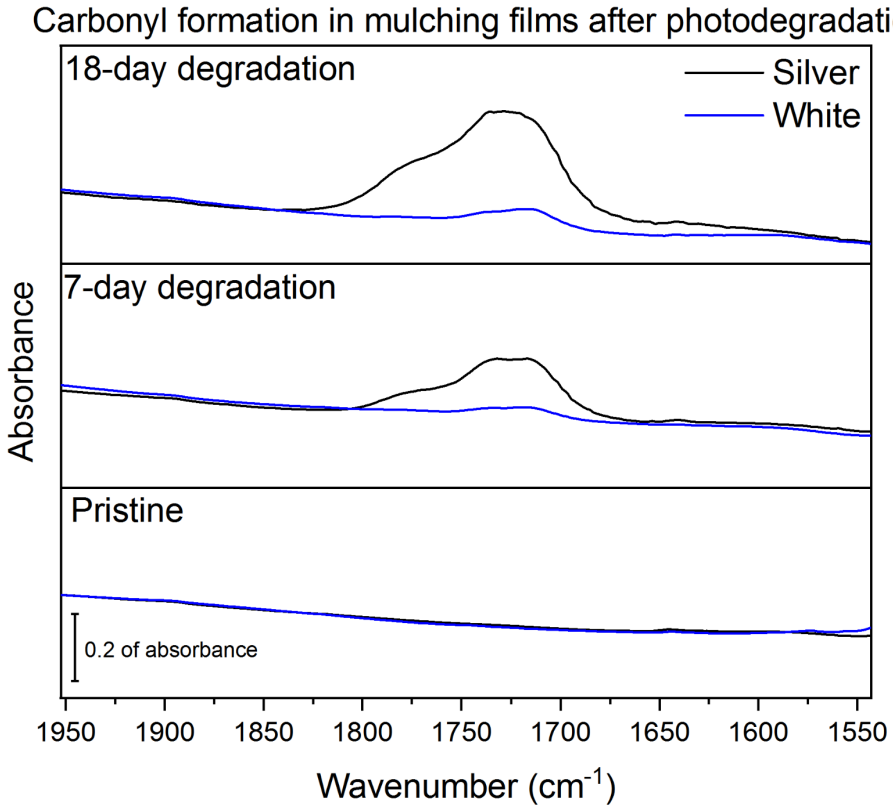


Figure 6. Carbonyl formation in mulching films (silver and white) after photodegradation acquired with transmission-FTIR.

After degradation, another difference was detected. Before exposure, White had a peak around 1530 cm^{-1} probably related to a nitro compound[67] that was later lost (Figure 5). This degradation is probably related to TiO_2, a result that will be presented in the next topic. Once exposed to UV light, TiO_2 acts as a photocatalyser, generating reactive

oxygen species capable of degrading organic compounds,[68] which explains the disappearance of this band.

As mentioned before, the BB1 and BB2 films appear to show no signs of degradation, which contradicts visual observation. Visually, the BB1 film shows stretching and loss of gloss since the first week, while the BB2 film shows a color difference in the exposed area that intensifies after 18 days. We attribute this result to the mechanism of degradation, the transmission mode and additives. When exposed to UV-C, the surface of the material is more prone to suffer degradation compared to the bulk because photodegradation relies on both light and oxygen to occur.[37,69] In contrast, when using this FTIR technique, the infrared light will cross and measure the entire thickness of the sample,[70] so the signal will be diluted by inner layers that were still not very affected by degradation. Another possibility is that black films contain carbon black in their composition, masking the signal.

Contact angle

When degraded, plastics can become MPs and can pose a threat due to their capacity to sorb pollutants already disposed of in the environment.[79] This interaction is mediated by factors such as plastic polymer type, size of the plastic, chemical properties of pollutants, degree of weathering of plastic and environmental factors.[80] Once absorbed, MPs can act as a “trojan horse” by carrying pollutants when consumed by an organism.[45]

Surface wettability, i.e., the angle measured between the line tangent to the surface of a liquid drop and the solid surface on which it rests, is another characteristic subject to degradation, by introducing polar functional groups or changing surface roughness. These changes can, in turn, influence the affinity of MPs for pollutants.[81,82]

In light of this, contact angle measurements were taken to analyse possible differences in wettability caused by degradation to the plastics (Figure 7). Before degradation, BB1 and Silver presented hydrophilic surfaces (θ> 90°) while BB2 and White were relatively hydrophobic surfaces (close to 90º). Thus, all films showed similarity in surface wettability (Figure 7).

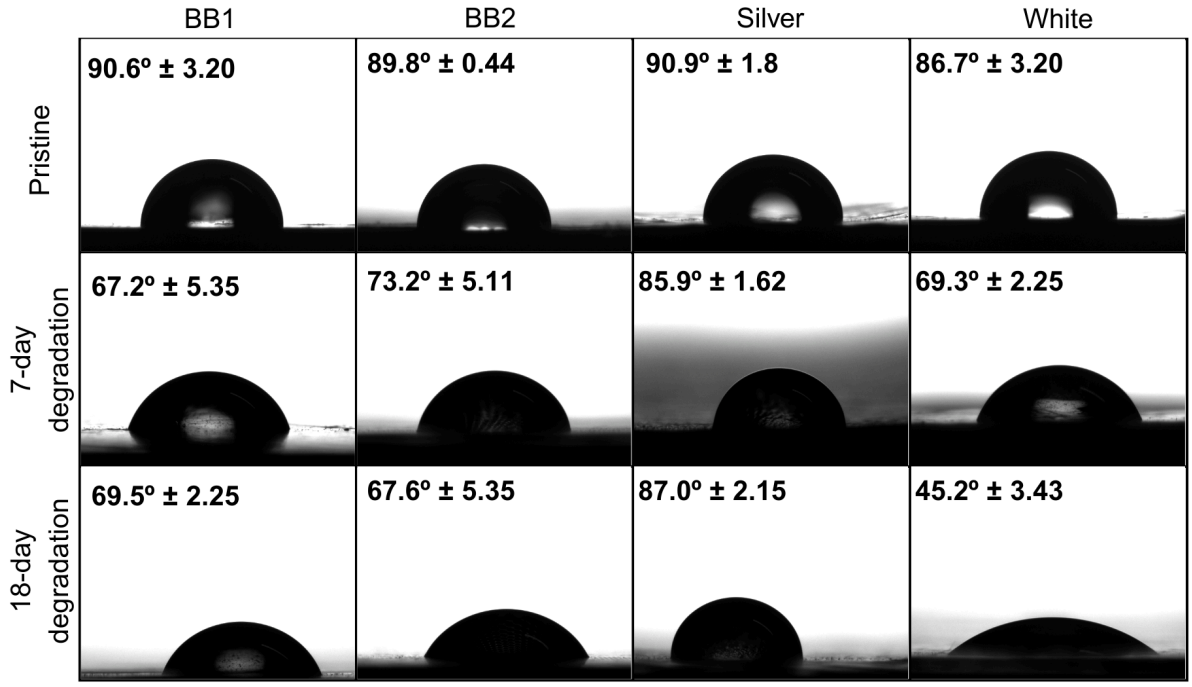


Figure 7. Pictures of deionized water drops above the surface of four mulching films (BB1, BB2, Silver, and White) in pristine and degraded forms (for 7 and 18 days). The measurements are the mean ± SD.

After degradation, it's possible to see the water drops progressively interacting more with the films by decreasing the contact angle, except for Silver (Figure 7). This happens because photodegradation produces polar groups (e.g., carbonyls), making the structure more hydrophilic.[81] The most notable hydrophilicity was exhibited by the White film (45º).

Despite being the most degraded film of all, the Silver film maintained its contact angle close to 90°, even after degradation (Figure 7). This apparent contradiction may be explained by the characteristics of surface roughness. Through SEM, it is noteworthy that Silver has a lot of cracks on its structure (Figure 3). These cracks may have caused the Cassie-Baxter Effect, when trapped air pockets create an apparent hydrophobicity by preventing full liquid-solid contact.[82] After seven days, the cracks were probably insufficient to stabilize air layers, but after 18 days, the material's roughness likely reached a threshold where air entrapment compensated for chemical changes.

Mechanical characterization

Photodegradation affected the mechanical strength of the polymers heterogeneously (Figure 8). No significant variations were observed in terms of degradation time for films BB1 and BB2. BB2, however, has lower elasticity than all the other plastics (Figure 8).

The Silver film, on the other hand, showed an abrupt drop in both properties (maximum stress and elastic modulus) after degradation, an effect that occurred due to the deepening of cracks (Figure 3), while the White film showed a decrease in maximum stress and an increase in elastic modulus. A reduction in the maximum stress can be attributed to the cleavage of the polymer chains and consequent reduction in molar mass, compromising the material's ability to withstand stress.[83]

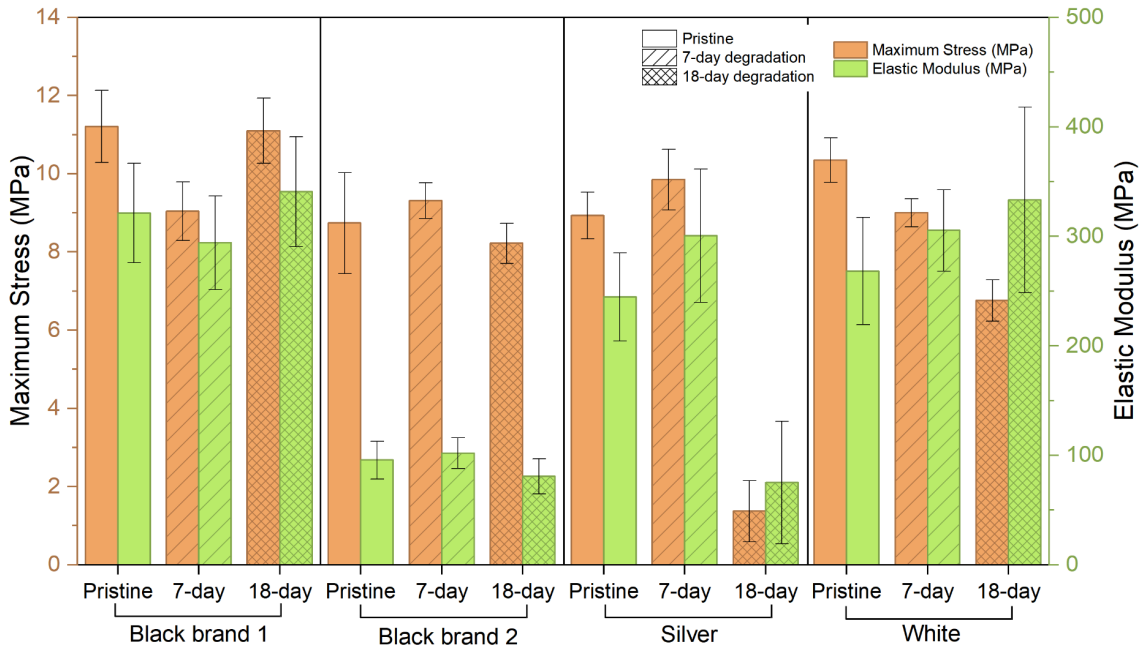


Figure 8. Maximum stress (MPa) and elastic modulus (MPa) of four mulching films (BB1, BB2, Silver, and White) in pristine and degraded forms (for 7 and 18 days).

Cracks observed in degraded Silver film acted as stress concentrators, causing a drastic drop in maximum stress and modulus of elasticity, at which point the breakdown of the chain prevented mechanical resistance. In contrast, the black films (BB1 and BB2) maintained greater stability and consistency in their tensile properties. This resilience can be attributed to the probable presence of carbon black additive, added to various plastics, which acts as a colorant and UV filter, delaying chain scission from progressing to the cracking stage observed in the Silver film. This result reinforces the influence of plastic formulation on photodegradation.

Tebuconazole sorption

In order to explore the potential influence of formulation into the sorption dynamics of mulching films, we selected the fungicide tebuconazole. The first criteria for selecting

tebuconazole was its application in several economically important crops, such as tomatoes, soybeans, and sugarcane.[84] The second criteria considered the high value of octanol/water partition coefficient (log K_{ow}) of the fungicide to ensure sorption efficiency between the films (hydrophobic) and the substance.

The differences between the plastic formulations observed in the previous analyses were also reflected in their sorption capacity with tebuconazole (Figure 9). After degradation, the Silver film exhibited the highest sorption capacity for tebuconazole, removing more than half of the solute from the solution. The BB2 and Whi films also showed a tendency toward increased sorption after degradation, whereas the BB1 film maintained consistent behavior.

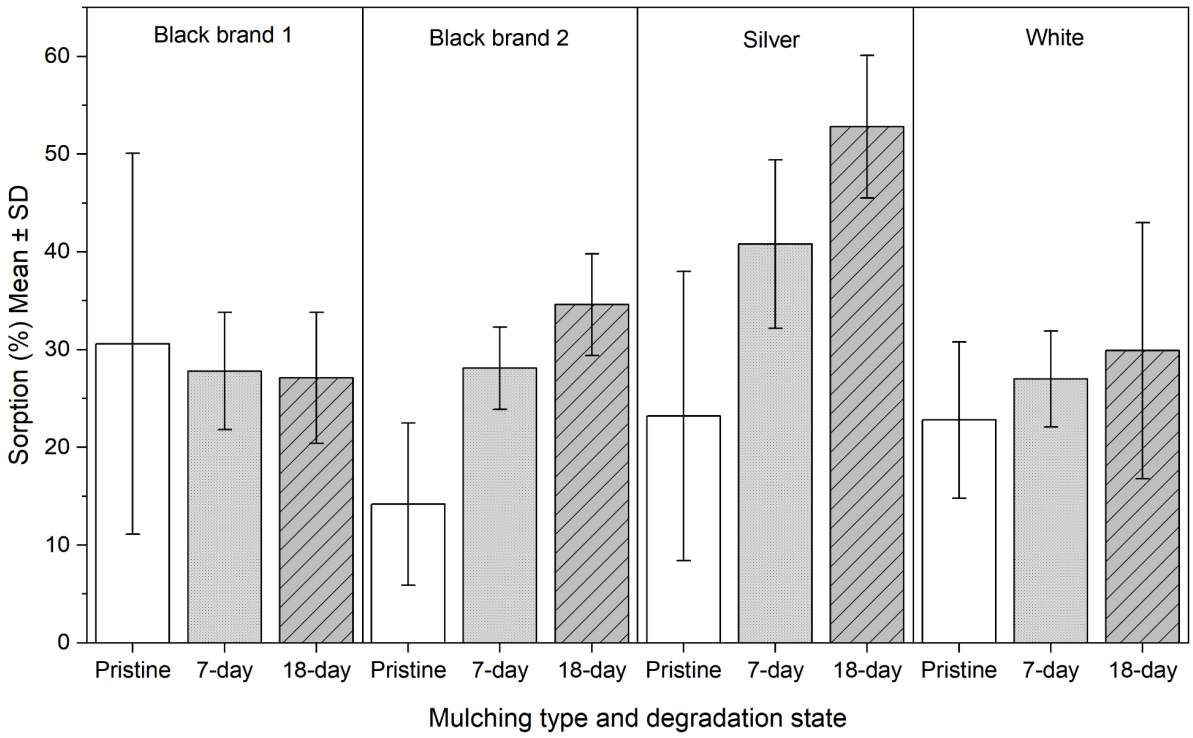


Figure 9. Sorption dynamics of the fungicide tebuconazole on four mulching films at different levels of photodegradation.

Although degradation reduces the hydrophobicity of films (Figure 8) by forming hydrophilic groups,[85] the trend toward increased sorption of tebuconazole, a hydrophobic substance (log K_{ow} of 3.7),[86] can be explained more by structural changes generated in the degradation process than by chemical changes. In addition, for the Silver film, the formation of cracks was observed, an additional element that provides

more surface area for plastic-pesticide interactions. The increase in the sorption capacity of plastics after degradation corroborates similar studies in the literature.[87]

The results obtained here complement the work of Nerín et al. (1996)[35], who investigated the sorption of several pesticides onto four types of LDPE films, among other polymers. In their study, no significant differences in sorption were detected among films composed by the same polymer, despite differences in formulation.[35] In contrast, our findings demonstrate that formulation can influence the resistance of plastics to degradation, thereby altering their structure and composition after weathering. This suggests that when degradation is incorporated as a factor, an additional level of complexity is introduced into pesticide–microplastic interactions, highlighting the importance of considering both formulation and aging processes in sorption studies.

The aspects of formulation and degradation level addressed in this study are environmentally relevant, as alterations in sorption directly affect the fate and mobility of pesticides across different environmental matrices. By demonstrating that formulation and degradation introduce additional levels of complexity, our study provides important insights not only for risk assessment but also for environmental modeling studies that rely on sorption parameters in the development of predictive transport models.[88]

CONCLUSION

The analyses showed that the four LDPE mulching films have intrinsic differences in their physical and chemical properties before and after degradation. The black film from the most expensive brand was the most resistant to degradation, followed by the cheapest black film. Silver film degraded the most during the analyzed period, to the point of tearing, being the one that resisted the least in the stress test. SEM analyses also revealed that Silver film had many cracks, which distinguished its hydrophobicity from the other films after degradation. These cracks most likely contributed to the higher sorption capacity for tebuconazole observed in this film. The white film interacted most with the water and was also the only one that showed signs of additives predominating on the surface. XRF analyses also showed important differences between the four films, highlighting the presence of Ti in the white film, Cr in the Silver film, and the absence of Ca in the BB2 film. These results highlight the need to include the formulation variable in experiments with microplastics in order to allow comparisons between different materials, as well as reinforcing the importance of adopting weathered plastics.

Acknowledgments

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CAPÍTULO 3: EFEITO DE MICROPLÁSTICOS DE FILME *MULCHING* EM TOMATE-CEREJA

Artigo 2: Impact of four formulations of microplastics from LDPE mulching films on the development of cherry tomatoes (*Solanum lycopersicum* L.), both pristine and degraded

Glaucia Isabel de Andrade Sebastião, Mussa Issufo, Febriana Amaral Tefa, Bruna Natalina de Souza Martins, Rafael Vinicius de Oliveira, Alice Pita Barbosa, Walter Ruggeri Waldman

ABSTRACT

Microplastic pollution is ubiquitous worldwide, and in agricultural systems it is estimated that 12.6 million tons of plastic are produced annually. Among the main sources of microplastics in agricultural soils, mulching films, commonly composed of polyethylene, stand out. It is already known that microplastics derived from this material can impair the development of several plant species. However, the ecotoxicological effects arising from different formulations of the same polymer remain poorly understood. To address this knowledge gap, we investigated the effects of four microplastics derived from low-density polyethylene (LDPE) mulching films with different prices and colors (two black, one silver, and one white) on the early development of cherry tomatoes (*Solanum lycopersicum* L.). The films were processed in the laboratory and incorporated into the soil in both their pristine form and after UV-C degradation. Our results showed that microplastics with different formulations and degradation levels altered biomass allocation patterns, particularly affecting specific leaf area, shoot mass fraction, root dry mass, root/shoot ratio, and leaf mass ratio. Among the tested materials, the degraded Silver film induced the most pronounced changes compared to the others and also exhibited the fastest photodegradation under the conditions evaluated in this study. These findings open new perspectives in the field of microplastic ecotoxicology by demonstrating that polymer formulation, beyond polymer type alone, plays a critical role in determining biological effects. Moreover, our results reinforce the importance of incorporating weathered plastics into experimental designs to better approximate realistic environmental conditions.

INTRODUCTION

Global plastic production breaks new records every year and reached the milestone of 430.9 Mt in 2024.[89] The high industrial demand for this material stems from the cost-effectiveness and versatility of plastics compared to various materials previously used traditionally, such as metal, wood, and glass.[90] In the agricultural sector, the scenario is no different. Various types of plastics have emerged in recent decades to meet specific market demands that reflect needs ranging from the germination stage (such as seed coating and seedling plug trays), through plant growth (such as mulching film, greenhouse plastic, silage films and pipes), to the final transportation of products (such as woven polypropylene bag sacks).[2]

It is estimated that the plasticulture sector is responsible for the production of 12.6 million tons of plastic per year.[91] In this context, mulching films, used for soil covering, are among the most widely used due to their ability to increase productivity, control weed occurrence, retain soil moisture, and regulate the microclimate.[22] However, although they reduce the demand for herbicide application and irrigation, the sustainability of this practice may be questioned when considering the product's full life cycle.[92]

Mulching films can last from one growing season to several years, and their durability depends on their thickness, field conditions (temperature, humidity, radiation), and formulation.[4] At the end of their service life, the films become extremely brittle and require special protocols for removal, including prior cleaning, avoiding dragging, and separation by color.[36] However, in practice, complete removal of the film is unfeasible, which results in the remaining fragments in the field continuing to degrade until they reach the size of microplastics (MPs), defined as particles smaller than 5 mm.[4,93]

The presence of MPs originating from mulching films can generate several negative impacts on the development of agricultural species, such as alterations in root and shoot growth, nutrient uptake, and crop water consumption.[18,94–97] In soils, these MPs can also modify field capacity and induce physiological and reproductive changes in earthworms.[94,98] Biodegradable films are often marketed as a sustainable alternative; however, studies warn of deleterious effects that may, in some cases, be even greater than those caused by conventional MPs due to the faster release of MPs and additives.[17,95]

In this context, the type of polymer emerges as a relevant factor in determining the materials toxicity.[99] In addition, the level of degradation has also been identified as a crucial factor in determining plastic toxicity.[85] More degraded plastics undergo changes in surface roughness and crystallinity, as well as an increase in the formation of polar carbonyl groups, which tends to enhance hydrophilicity.[43,44] Furthermore, with polymer chain scission, there is a tendency for additive leaching,[100] which, once released from

the matrix, may become bioavailable to biota, causing structural and functional cellular damage.[101–103]

In the context of mulching films, the literature regarding the impacts of UV-weathered plastics on organisms is still very scarce.[94] The available studies report that weathered mulching MPs may exhibit effects different from their pristine counterparts—being, in some cases, more harmful[104,105] and, in others, potentially mitigating toxic effects.[94,106] Thus, this is an area that requires greater attention from researchers, especially considering that studying aged plastics brings experimental conditions closer to the real environmental scenarios to which plastics are exposed.[85] This also applies to the context of the present study, in which we identified a lack of such investigations aimed at understanding the effects of weathered MPs on agricultural species.

Within the scope of this study, there are works investigating the impacts of MPs from different plastic polymers (e.g., polyethylene vs. polylactic acid) on agricultural species.[94,105] However, we observe that, for our specific scope and for the broader literature on MP ecotoxicology, there is still a lack of understanding regarding the diversity of responses that may arise from different formulations of the same polymer. Many studies focus on understanding the effects of different types of plastics, without addressing the variability of formulations within a single polymer type.

Thus, in light of the identified knowledge gap, this study aims to investigate the impact of MPs derived from four low-density polyethylene (LDPE) mulching films with different formulations (additives), in both pristine and degraded forms, on the early development of cherry tomato (*Solanum lycopersicum* L.).

METHODOLOGY

Selection criteria of mulching film

Criteria such as color and price were used to guide the selection of these films to ensure different formulations. The color criteria is related to the fact that certain pigments have different elements in their composition, while the price is often determined by the additives added to the polymers, as well as the care with raw materials and industrial processing, which might influence NIAS (Non-Intentionally Added Substances). These differences can be indicative of variation in formulation. Considering it, we chose two black/black mulching films, one of which was cheap and the other expensive. The other two films were silver/black and white/black. The code color/color refers to side A/side B. The cheap black/black film is black brand 1 and will be called “BB1” and the expensive black/black “BB2”. The average thickness of the films is 19 µm.

Manufacture of MPs

To verify the effects of different films on the initial development of cherry tomatoes (*Solanum lycopersicum* L.), MPs were prepared by manually cutting mulching films. This was done by cutting pieces of film with a back-and-forth movement using a 45 mm circular blade on a bamboo cutting board (Figure 1A). Granulometric sieves were used for size separation, and the average length of the fragments was 710 µm. Measurements were made on a stereomicroscope (Leica S8APO) to check size distribution (all data available in Supplementary Material, file mulching_film_size). Part of the MPs was separated and taken to a photodegradation chamber (Figure 1B) with three 36W UV-C lamps (Osram) positioned 49 cm above the sample for 14 days to emulate moderate weathering sufficient to generate degradation products and conditions of greater leaching.[85] In order to homogenize degradation in the samples, the MPs were stirred with a spatula daily. The incubation time is essential to allow sufficient time for: stabilization of the microbial community;[107] interaction of this community with MPs;[55] and leaching of additives and NIAS into the soil.[108] Unlike substances added intentionally to impart technical properties to polymers, NIAS are by-products of the degradation and manufacturing process and can generate toxicological responses in organisms.[109,110]

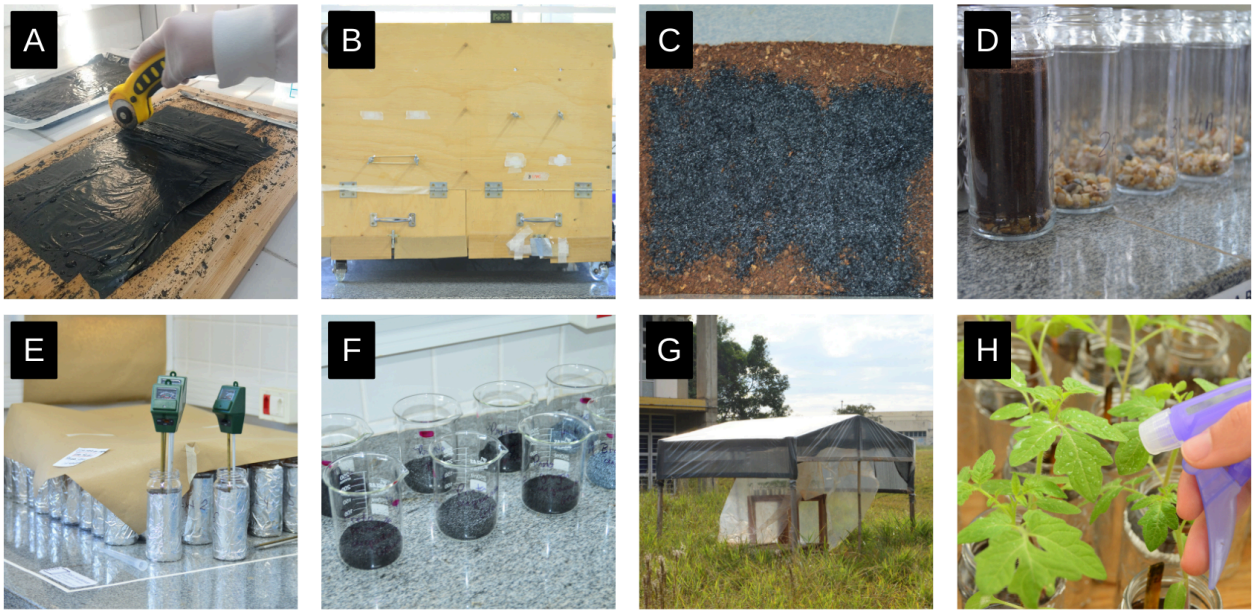

Figure 1. Stages of the experiment. A) cutting the film to generate microplastics; B) photodegradation chamber; C) mixing soil with microplastics; D) glass containing soil and pebbles; E) soil incubation; F) mulching microplastics; G) rain-protected tent; H) application of milk and detergent-based fungicide.

Soil preparation

The substrate selected for growing tomatoes was purchased from a local flower shop and sieved through a 2 mm pore size. Its composition consists of 35% total sand, 13% silt, and 52% clay, with an organic matter content of 9%, classified as a clay soil highly rich in organic matter (original report available in supplementary material). Suppliers reported that the soil is enriched with limestone, bone meal, and castor bean powder. MPs were added to the soil at a ratio of 1% (w/w) and homogenized in a container (Figure 1C) before being transferred to 350 mL glass pots (Figure 1D), totaling 110g of soil per pot. The same soil manipulation was performed in the control without MPs in order to cause the same level of disturbance in the media.[55] It is worth noting that some modifications were made before the experiment in the glass pots, such as: a hole in the bottom of each pot with a 2 mm diamond drill bit; covering the hole with micropore tape to prevent MPs from escaping during watering; adding 50 g of #2 pebbles to prevent water accumulation at the bottom (Figure 1D); covering the side surface with aluminum foil to prevent the roots from coming into contact with light (Figure 1E). Finally, a liquid fertilizer NPK 10-10-10 (nitrogen, phosphorus, and potassium in proportion) (Dimmy) was added in the proportions recommended by the manufacturer to ensure all the nutrients necessary for the plants.

After receiving the MPs and fertilizer in the aforementioned concentration, the substrate was kept in incubation (Figure 1E) at room temperature under shade for two weeks before sowing. Humidity was maintained at around 70% and monitored with a manual humidity meter (MFL). By the end of the preparation, there were nine treatments, with eight replicates each (totaling 72 samples), including: control, BB1 P (Pristine Black Brand 1), BB1 D (Degraded Black Brand 1), BB2 P (Pristine Black Brand 2), BB2 D (Degraded Black Brand 2), Sil P (Pristine Silver), Sil D (Degraded Silver), Whi P (Pristine White), and Whi D (Degraded White) (Figure 1F).

Plant cultivation

After incubation, three previously disinfected[111] cherry tomato seeds (*Solanum lycopersicum* L., Samambaia variety, TopSeed, Brazil) were sown per pot at a depth of 1 cm. Thinning was performed randomly after seedling establishment, keeping only one plant per pot. The plants were kept in the laboratory at room temperature for the first four days after germination. Then, they were then transferred to an outdoor location protected from direct solar radiation and, after three additional days, moved to a rain-protected tent, where they remained until the end of the experiment (Figure 1G).

Each experimental unit was monitored and kept exposed for 31 days after germination. The position of the pots was randomized once a week. Due to the appearance of powdery mildew on the 22nd day from germination, a fungicide based on milk and

detergent was applied (Figure 1H).[112] After this period, the roots were carefully removed using running water. Each plant was divided into roots, stems, and leaves. The stems were measured to obtain their final height with a ruler, and the fresh leaves were photographed for area analysis using ImageJ software. The roots were stored in a 54º GL alcohol solution until we could measure their volume, which was done by immersing each root in a 10 mL test tube and observing the displaced volume. Each part of the plant was then dried in an oven for 48 h at 50 ºC and weighed on an analytical balance.

The variables controlled in this ecotoxicological test were: substrate (composition, quantity, and incubation time), irrigation, container size and type, planting method, exposure time, MP mass within each treatment, and seeds of the same species, supplier, and batch. Temperature and humidity were recorded with a thermohygrometer from the beginning of incubation until the last day of planting, and the results are available in the Supplementary Material, file experiment_monitoring.xlsx.

Assessed parameters

Plant growth and biomass allocation were assessed through the parameters of relative growth rate in height (RGR) (eq. 1), leaf mass ratio (LMR) (eq. 2), stem mass ratio (SMR) (eq. 3), root mass ratio (RMR) (eq. 4), shoot mass fraction (SMF) (eq. 5), root/shoot ratio (RSR) (eq. 6), root density (RD) (eq. 7), leaf area ratio (LAR) (eq. 8) and individual leaf area (ILA) (eq. 9), and specific leaf area (SLA) (eq. 10).

RGR was calculated as:

$$RGR = \frac{ln(H_2) - ln(H_1)}{t_2 - t_1} \quad \text{(eq.1)}$$

where H_1 and H_2 are the initial and final heights, respectively, and t_1 and t_2 are the corresponding times (days).

Biomass allocation parameters were calculated on a dry mass basis:

$$LMR = \frac{DW_{leaf}}{DW_{total}};\ SMR = \frac{DW_{stem}}{DW_{total}};\ RMR = \frac{DW_{root}}{DW_{total}};\ SMF = \frac{DW_{shoot}}{DW_{total}} \quad \text{(eqs. 2, 3, 4, 5)}$$

The root/shoot ratio was calculated as:

$$RSR = \frac{DW_{root}}{DW_{shooot}} \quad \text{(eq. 6)}$$

where DW_{shoot}, DW_{leaf}, DW_{stem}, DW_{root} are the dry masses of each organ (g), and DW_{total} is the total plant dry mass (g).

Root density was determined as:

$$RD = \frac{DW_{root}}{V} \quad \text{(eq.7)}$$

where V is the volume.

Leaf area parameters were calculated as:

$$LAR = \frac{LA}{DW_{total}}; \; ILA = \frac{LA}{N}; \; SLA = \frac{LA}{DW_{leaf}} \quad \text{(eq.8, 9, 10)}$$

Statistical analysis

The data were submitted to two-way analysis of variance (Two-Way ANOVA) to evaluate the effects of the factors: type of plastic (BB1, BB2, Sil, and Whi) and level of degradation (pristine and degraded), as well as the possible interaction between them. Shapiro-Wilk and Levene tests were applied to verify the assumptions of ANOVA, such as normality of residuals and homogeneity of variances. When the assumptions were not met, outliers present in the samples were identified and removed (Grubbs test) or logarithmic transformation was applied. In cases of persistent non-normality after transformation, the non-parametric Kruskal-Wallis test was used followed by Dunn's post-hoc test. When significant effects were detected in ANOVA followed by Tukey's post-hoc test. The control groups were analyzed separately from the factorial structure, and one-way ANOVA was used for comparison. In cases of violation of the assumption of homogeneity of variances, Welch's ANOVA followed by Games-Howell post-hoc test were applied. For all analyses, a significance level of 5% ($p < 0.05$) was adopted. The analyses and graphs were done in OriginPro 2026 software.

RESULTS

Relative growth rate

Growth in height was constant across all treatments, with no statistically significant differences, as demonstrated by the similarity in RGR (Figure 2). The mean RGR value across all treatments was 0.068 cm cm^{-1} day^{-1}.

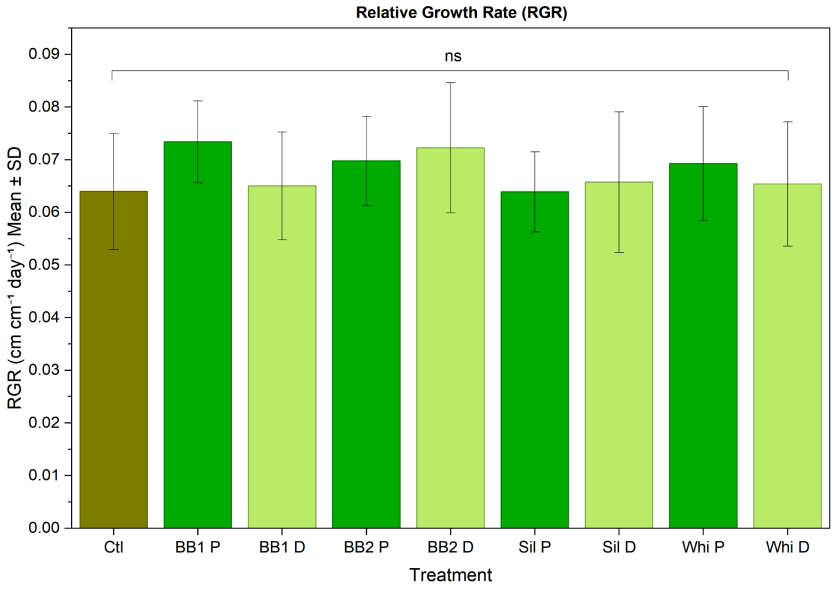

Figure 2. Relative growth rate of *Solanum lycopersicum* cultivated in the presence of different microplastics of mulching film (n=8). Statistics performed by two-way ANOVA and one-way ANOVA for comparison with the control ($p>0.05$).

Leaf morphology and shoot biomass allocation

Similarly to the previous parameter, the number of leaves did not vary significantly between treatments with different types of plastics and at two levels of degradation (Table 1). The same was observed for the variables LA, ILA, and stem length (SL) (Table 1). However, a difference was detected for the SLA parameter between the Whi P x Sil D and Whi P x Whi D treatments, with plants grown in Whi P exhibiting values 14% lower than those recorded for both treatments (Figure 3). Among the treatments with MPs, Sil D and Whi D had the highest SLA: 756 ± 31 and 757 ± 43 $cm^2\ g^{-1}$, respectively. The Whi P treatment had the lowest SLA value, with 664 ± 38 $cm^2\ g^{-1}$. The control had a higher mean value (795 ± 156 $cm^2\ g^{-1}$) than all treatments, but did not differ from any of them due to high variation in data distribution (Figure 3).

Parameter	Black Brand 1		Black Brand 2		Silver		White		Control
	Pristine	Degraded	Pristine	Degraded	Pristine	Degraded	Pristine	Degraded	No microplastics
Number of leaves	5.5 ± 0.8[a]	5.8 ± 0.5[a]	6.1 ± 0.6[a]	5.6 ± 0.5[a]	5.8 ± 0.5[a]	5.8 ± 0.5[a]	5.6 ± 0.5[a]	5.5 ± 0.5[a]	5.4 ± 0.5[a]
RD (g/mL)	0.026 ± 0.007[a]	0.02 ± 0.004[a]	0.02 ± 0.008[a]	0.02 ± 0.005[a]	0.02 ± 0.01[a]	0.03 ± 0.01[a]	0.02 ± 0.004[a]	0.02 ± 0.004[a]	0.02 ± 0.005[a]
ILA (cm^2/ leaf)	15.0 ± 2.1[a]	15.8 ± 1.8[a]	16.1 ± 3.1[a]	16.8 ± 4.0[a]	16.9 ± 3.9[a]	16.9 ± 3.1[a]	15.3 ± 2.4[a]	15.1 ± 1.6[a]	14.4 ± 3.7[a]
SL (cm)	17.8 ± 1.9[a]	17.7 ± 1.2[a]	18.4 ± 1.1[a]	17.5 ± 0.9[a]	17.8 ± 1.7[a]	17.7 ± 1.6[a]	16.3 ± 1.8[a]	17.7 ± 1.05[a]	16.4 ± 1.9[a]
DW leaves (g)	0.1 ± 0.03[a]	0.1 ± 0.03[a]	0.1 ± 0.04[a]	0.1 ± 0.05[a]	0.1 ± 0.03[a]	0.1 ± 0.03[a]	0.1 ± 0.03[a]	0.1 ± 0.03[a]	0.1 ± 0.03[a]
DW stems (g)	0.06 ± 0.01[a]	0.06 ± 0.01[a]	0.06 ± 0.01[a]	0.06 ± 0.02[a]	0.06 ± 0.02[a]	0.07 ± 0.01[a]	0.06 ± 0.01[a]	0.06 ± 0.01[a]	0.05 ± 0.01[a]
DW shoot (g)	0.2 ± 0.04[a]	0.2 ± 0.03[a]	0.2 ± 0.05[a]	0.2 ± 0.1[a]	0.2 ± 0.05[a]	0.2 ± 0.04[a]	0.2 ± 0.04[a]	0.2 ± 0.04[a]	0.1 ± 0.04[a]
LAR (cm^2/g)	447.0 ± 41.7[a]	434.9 ± 52.6[a]	449.9 ± 24.9[a]	446.8 ± 47.6[a]	467.2 ± 33.3[a]	444.1 ± 45.8[a]	413.7 ± 22.3[a]	449.1 ± 17.6[a]	73.6 ± 69.8[a]
SMR (g/g)	0.3 ± 0.02[a]	0.3 ± 0.05[a]	0.3 ± 0.03[a]	0.3 ± 0.03[a]	0.3 ± 0.05[a]	0.3 ± 0.03[a]	0.3 ± 0.03[a]	0.3 ± 0.02[a]	0.3 ± 0.03[a]
RMR (g/g)	0.06 ± 0.01[a]	0.08 ± 0.01[a]	0.06 ± 0.02[a]	0.1 ± 0.02[a]	0.06 ± 0.02[a]	0.09 ± 0.02[a]	0.07 ± 0.02[a]	0.09 ± 0.01[a]	0.08 ± 0.04[a]

Table 1. Morphological attributes of *Solanum lycopersicum* cultivated in the presence of different microplastics of mulching film (n=8). Mean ± standard deviation. Means that do not share a letter are significantly different ($p<0.05$).

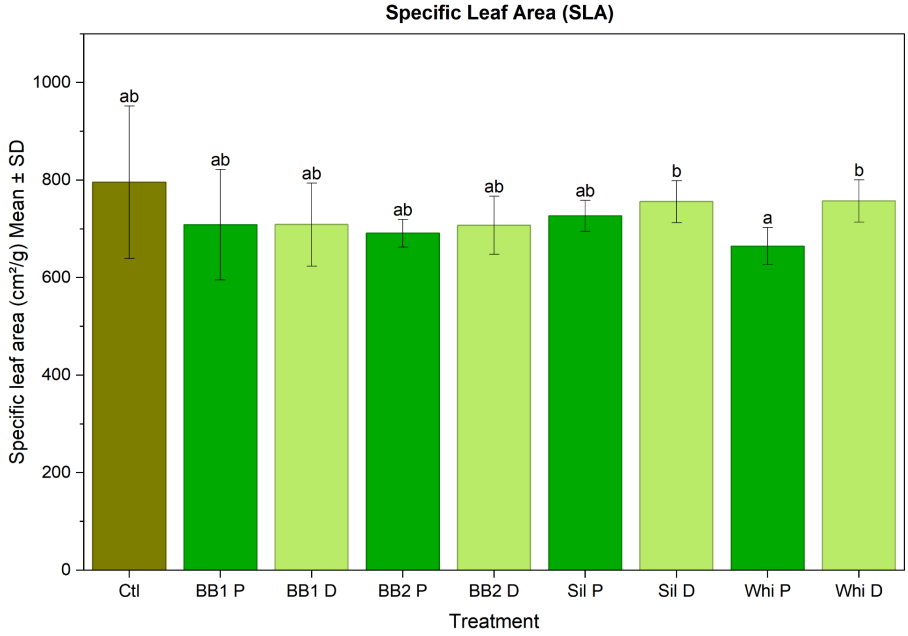

Figure 3. Specific leaf area of *Solanum lycopersicum* under different treatments with microplastics from mulching film (n=8). Statistics performed with Welch ANOVA ($p=0.003$) followed by Games-Howell post hoc test ($p<0.05$).

For the shoot mass fraction parameter, the two-way ANOVA showed a significant effect for the stage of degradation ($p<0.0001$) (Figure 4), resulting from a difference between the Sil D and the BB1 P, BB2 P, and Sil P treatments. The BB1 P, BB2 P, and Sil P films resulted in a higher shoot dry biomass fraction compared to the Sil D treatment. Even without a significant difference, there is a slight upward trend in SMF for the pristine groups compared to the control and their peers.

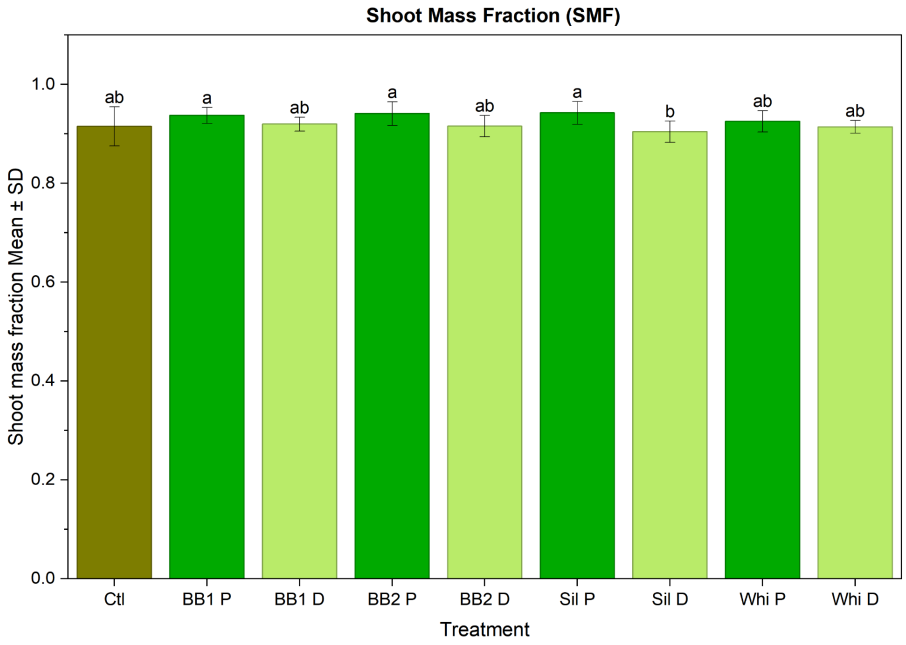

Figure 4. Shoot mass fraction of *Solanum lycopersicum* under different treatments with microplastics from mulching film (n=8). Statistics performed with two-way ANOVA followed by Tukey's HSD post hoc ($p<0.05$) and one-way ANOVA for comparison with the control ($p<0.05$).

Dry weight and physiological ratios

Through the analysis of dry biomass, it is possible to note that among the different treatments, the plants maintained 59-65% of investment in leaves, 28-33% in stems, and 6-9% in roots (Figure 5). When analyzing the dry weight of each organ among the treatments, no significant difference was detected in the mass of leaves, stems, and shoots. However, a highly significant difference ($p<0.001$) was detected for roots dry biomass between the Sil D and BB1 P groups (Figure 6), where the Sil D group had the highest average dry mass among all treatments (0.02 ± 0.001) and BB1 P had the lowest (0.012 ± 0.003). Although these were the only statistically significant differences, it is worth noting that there was a tendency for root dry biomass to increase after degradation for all treatments, except for the Whi group. Despite this difference, root density was not influenced by the treatments (Table 1).

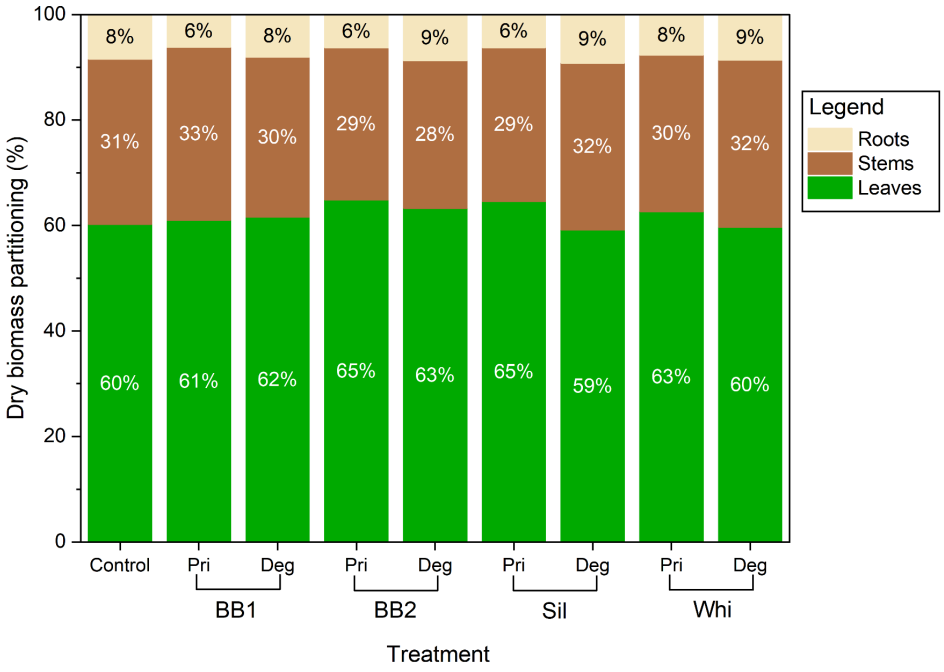

Figure 5. Dry biomass partitioning (%) de *Solanum lycopersicum* under different treatments with microplastics from mulching film (n=8).

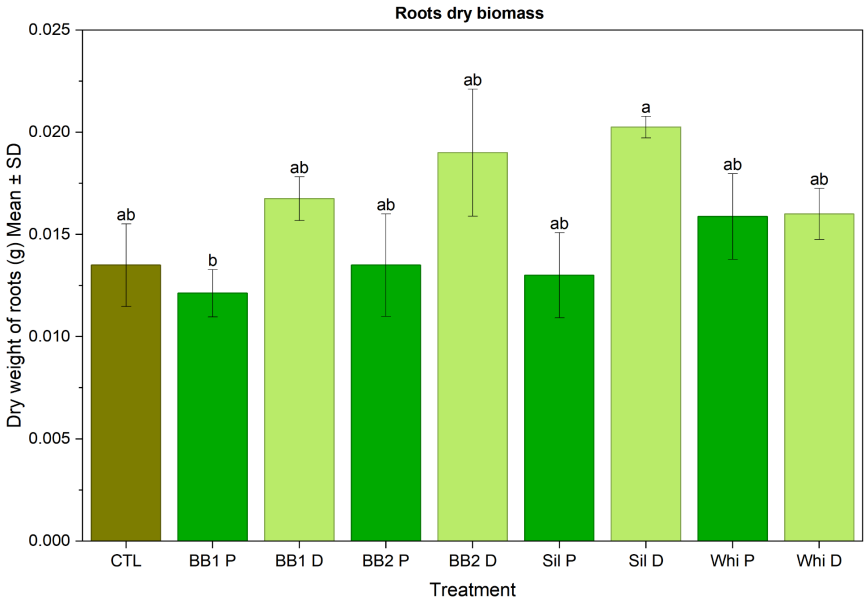

Figure 6. Root dry biomass of *Solanum lycopersicum* under different treatments with microplastics from mulching film (n=8). Statistics performed with Welch ANOVA ($p<0.001$) followed by Games-Howell post hoc test ($p<0.05$).

The degradation state of the plastics was a relevant factor in terms of the RSR ($p<0.0001$). The Sil D film showed a significant increase in resource allocation to the root system (0.106 ± 0.026) compared to three pristine plastics: BB1, BB2, Sil, where BB2 P had the lowest value (0.063 ± 0.026) (Figure 7).

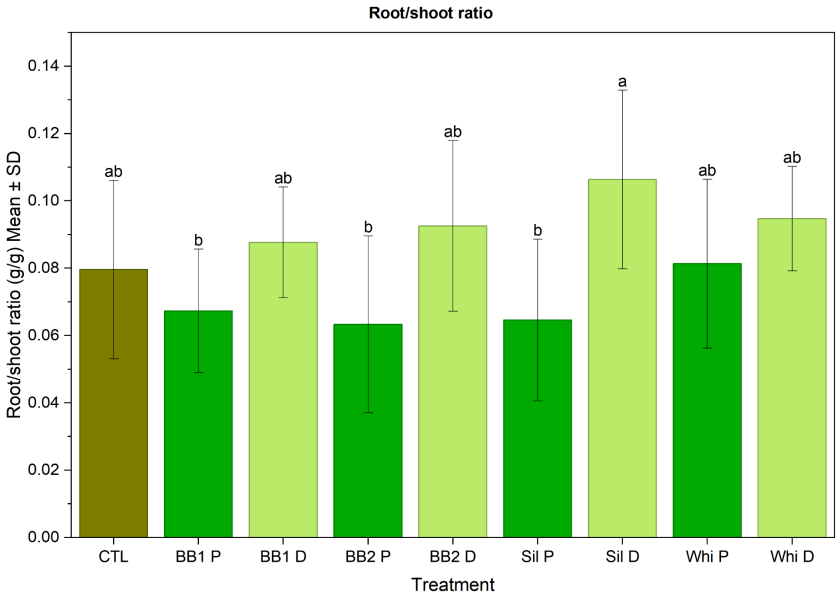

Figure 7. Root/shoot ratio of *Solanum lycopersicum* samples under different treatments with microplastics. Statistics performed with two-way ANOVA followed by Tukey's HSD post hoc ($p<0.05$) and one-way ANOVA for comparison with the control ($p>0.05$).

The LMR was significantly different between treatments BB2 P and Sil D ($p=0.01$) (Figure 8). The lowest LMR was found for plants in the Sil D group (0.58 ± 0.039), indicating that this was the treatment with the lowest investment in leaves compared to the others.

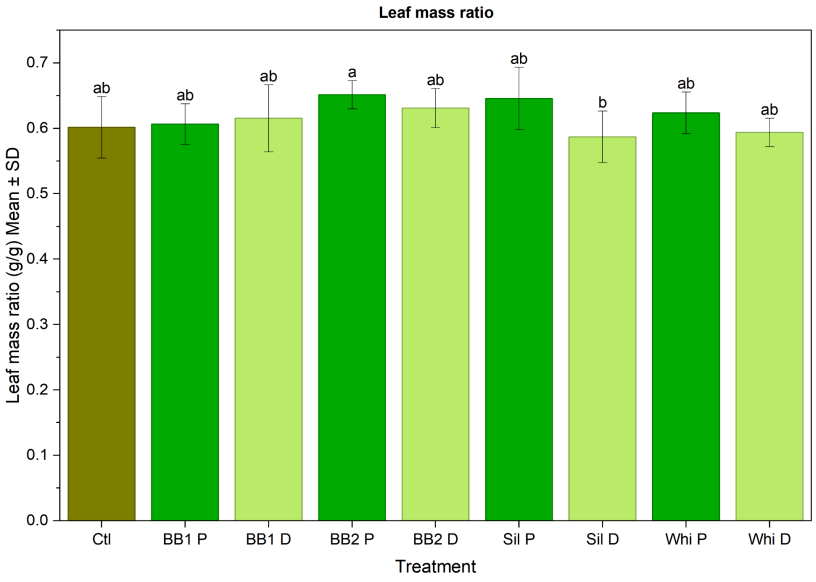

Figure 8. Leaf mass ratio of *Solanum lycopersicum* under different treatments with microplastics from mulching film (n=8). Statistics performed with Kruskal-Wallis test followed by Dunn's post hoc ($p<0.05$).

For root mass ratio, although the Kruskal-Wallis test indicated overall differences among groups (*p=0.0056*), post hoc Dunn's test did not remain significant after correction for multiple testing. The LAR and SMR were not significantly different between the treatments with MPs and the control (Table 1).

DISCUSSION

In this study, we investigated how different formulations of pristine and degraded mulching films can affect the initial development of cherry tomatoes (*S. lycopersicum*). Through the results obtained, we show that in addition to the type of polymer, the level of degradation and additives are important factors in determining the growth alterations caused by a plastic. To the best of our knowledge, this is a novel approach in the field of ecotoxicology.

Structures development

Regarding the development of shoot structures, the Whi P treatment presented the lowest SLA values among all treatments, whereas its degraded version (Whi D) and the Sil D film exhibited the highest. This is the first evidence herein discussed to suggest that the level of degradation may interfere with leaves' development and also that not all

films behave in the same way when degraded. A reduction in SLA is generally related to stress response, especially water deficit.[113] When this occurs, cell walls can become thicker, the intercellular spaces become smaller, the number of cells in the mesophyll can increase, increasing leaf thickness and improving water use efficiency.[114] Increased SLA, on the other hand, has been reported in the presence of PE MPs (0.2%, 0.1%, and 0.2%), PVC (0.1% and 0.2%),[115] PES (0.40%) and PP (0.40%).[116] However, the literature still lacks studies addressing the effects of MPs on leaf anatomy, such as analysis of the effects on leaf micromorphometry.

The presence of mulching film particles in the soil is known to alter porosity, field capacity, bulk density, and water repellency, affecting the availability of water and air to the roots.[98,117] In this experiment, watering was standardized across all treatments, which leads us to believe that the primary effect of the difference between the two levels of degradation on SLA lies in the chemical formulation of the plastics. The stress suffered by the presence of MPs, whether due to changes in the physical structure of the soil and/or the effect of leachate, was reflected in the allocation of plants' resources.

The SMF was another parameter altered due to the level of plastic degradation, where, once again, Sil D differed from Sil P, and also from BB1 P and BB2 P treatments. The lower SMFs, obtained in the former, reflect a reduced investment in shoot production. This result is consistent with the variation presented between treatments for dry root mass, in which the plants exposed to Sil D MPs stands out as having the highest production of this organ, differing from the BB1 P treatment. In addition, the increase in root production for the Sil D treatment is also reflected in the low LMR and high SLA and RSR presented by plants exposed to this film.

When polymers photodegrade, greater leaching of additives and migration of NIAS can occur, which can intensify the toxic effects of degraded MPs compared to their pristine form. In addition to the release of these substances, degraded polymers tend to exhibit greater hydrophilicity due to the appearance of oxygenated groups,[85] leading to greater water absorption[118,119] and shaping interactions with the microbiota that make up the rhizosphere, interfering with plant development.[55,102]

Based on degradation tests for the same plastics presented in Chapter 2 of this dissertation, silver plastic (Sil) was found to be the most sensitive to UV-C treatment under the conditions used in this study. This film exhibited a higher degree of chemical signs characteristic of degradation, such as: formation of surface cracks associated with loss of mechanical strength; increase in the carbonyl band (around 1808-1673 cm^{-1}); and decrease in hydrophobicity. As the most degraded film, it is expected to exhibit a greater trend to leach additives, which may, in turn, affect the soil-plant system, including changes in the composition of the soil microbiota.

Overall, the differences caused by MPs on cherry tomatoes influenced biomass allocation patterns, not total plant growth parameters, highlighting the importance of evaluating allocation patterns (ratios) rather than working solely with absolute values. More specifically, we observed that for a set of parameters (RGR, RD, number of leaves, LA, SH, ILA, DW of leaves, DW of shoot, DW of stem, LAR, and SMR), no significant differences were found between the groups with MPs and the control group. Our findings are partially in line with previous studies that tested MPs in soil at a concentration of 1% w/w.[99,120,121] The study by Zantis et al. (2024)[95] reported reduction in the growth of patterns like roots, stems, and biomass accumulation of carrot and lettuce species exposed to MPs from mulching film. In another study by Liang et al. (2024),[122] mulching MPs modified the root and shoot biomass of strawberries (□shoot and root), cabbage (□shoot and root), cucumbers (□shoot and root), and adzuki beans (□shoot and □root). For tomatoes, the same dose of mulching MPs increased root biomass, but did not had no significant effect on shoot biomass.[122] In the experiments by Saha et al. (2024)[123] also conducted with tomatoes, a reduction in shoot length was observed for treatments with polyethylene terephthalate and polystyrene (PS) MPs and a reduction in root length for treatments with PS and nylon. This makes it clear that the effects observed are not only dependent on the species, but also on the type of MP.[95,122]

The concentration of 1% is considered high when compared to the environmental relevant concentration of MPs from mulching film,[10] but it was adopted for being sufficient to cause significant reductions in plant growth parameters. Considering the above, a possible explanation for the absence of toxic effects on various parameters analyzed in tomatoes, even at a concentration commonly associated with morphological changes, may be related to the nutritional level of the soil used in this study. The soil used was composed of approximately 9% organic matter and received extra fertilization with nitrogen (N), phosphorus (P), and potassium (K). These elements are the three main macronutrients absorbed in large quantities by plants, as they constitute the amino acid, protein, chlorophyll, and various structures related to vegetative growth.[124]

Although we have not tested other soil types, the absence of effects on parameters that are generally sensitive (e.g., shoot DW, SL) at the same concentration of MPs applied to the soil may be an indication that the presence of high content of organic matter and essential nutrients during the seedling development phase may mitigate the toxic effects.

Organic-rich and clay soils are known to attenuate contaminant effects due to the high sorption capacity of amphiphilic constituents within the soil matrix, thereby reducing contaminant bioavailability.[125] Humic substances, derived from the decomposition of organic matter, can bind a range of organic and inorganic pollutants.[125,126] Additionally, hydrophobins (cysteine-rich proteins produced by soil fungi) also contribute to these

interactions.[119] This sorptive capacity may represent one of the mechanisms underlying the mitigation of effects induced by MP leachates.

We emphasize that, although in the short term the limitation of the bioavailability of contaminants seems beneficial, this is a transitory process, which may result, in the longer term, in the exposure of living organisms to the contaminants retained there. This aspect is particularly relevant in areas under recurrent cultivation, where the continuous addition of inputs can progressively increase the total load of contaminants in the soil. In the case of pesticides, for example, there is evidence that their transformation products may be as toxic as or more toxic than the original molecule.[127]

Finally, the effects of climate change must also be taken into account, as they can alter the sorption and desorption processes of pollutants,[128,129] directly influencing the restoration of their bioavailability. In the case of MPs, higher temperatures associated with UV exposure can accelerate the degradation process of polymers,[130] accelerating the release of leachates.[55] Changes in rainfall, drought, and wind patterns could also alter the distribution of MPs throughout the ecosystems.[131]

Future prospects and limitations

The results here presented bring a new perspective to the ecotoxicology of MPs, showing that, in addition to the type of polymer, it is important that studies include the diversity of formulations of plastics with the same polymer composition in experimental designs. We also reinforce the importance of adopting weathered MPs in ecotoxicological studies, in an effort to conduct more environmentally relevant experiments.[55,85]

We identified that resource allocation parameters were sensitive depending on the degradation state and the type of mulching film used. However, the morphological responses observed were not correlated with cellular biomarkers. Therefore, it is important that future analyses explore the interface between exposure to MPs and the potential oxidative stress induced, elucidating the defense mechanisms at the cellular level. In addition, it is important for future research to examine the impact of different formulations on fruit development.

Beyond understanding the effects of MPs on plants, it is important to treat soil as a complex matrix,[132] which requires a greater degree of isolation of variables for a deeper understanding of soil-plant-microorganism interactions. To better understand this interaction, we suggest that further studies be conducted to understand how soil nutrition and composition influence the effects caused by MPs and their leachates on plants. Finally, we highlight the importance of applying techniques to analyze microbial diversity between treatments, since MPs can alter the soil microbiota.[107] These changes,

in turn, impact plant development, since plant-microorganism interaction is crucial for nutrient absorption and plant health.[133]

CONCLUSION

This study highlights that, beyond polymer type, formulation and degradation state play an important role in shaping plant responses to microplastics. Although total growth parameters of cherry tomato (*S. lycopersicum*) were largely unaffected by mulching film MPs, significant shifts in biomass allocation patterns (SLA, SMF, RSR and LMR) were detected. These findings indicate that formulation should be considered a critical parameter when comparing studies involving the same polymer type, as different additive compositions may lead to distinct biological outcomes. Furthermore, our results reinforce the importance of incorporating degraded plastics into experimental designs in order to better capture the range of responses that a single polymer can cause under environmentally realistic conditions.

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CONSIDERAÇÕES FINAIS

Os resultados apresentados nos capítulos anteriores demonstraram que os quatro filmes *mulching* selecionados apresentam diferenças significativas em sua formulação química, influenciando sua resistência à degradação e modificando suas interações com pesticidas. Observamos que a degradação altera propriedades estruturais e sortivas dos filmes *mulching*, resultando em comportamentos distintos frente à sorção do fungicida tebuconazol. Além disso, a presença desses filmes na forma de microplásticos, tanto prístinos quanto degradados, promoveu alterações no desenvolvimento do tomate-cereja (*Solanum lycopersicum*), evidenciando que a formulação, e não apenas o tipo de polímero, é um fator determinante nos efeitos ecotoxicológicos.

Nossa abordagem contribui para um campo ainda pouco explorado ao incorporar simultaneamente a formulação e a degradação nos experimentos, oferecendo subsídios para o aprimoramento de desenhos experimentais e para interpretações menos generalistas ao comparar estudos que testam efeitos de plásticos de mesma composição polimérica sobre os organismos. Por fim, ao ampliar a compreensão sobre as interações entre microplásticos, pesticidas e plantas, este trabalho contribui para discussões alinhadas aos Objetivos de Desenvolvimento Sustentável 12 (Consumo e Produção Responsáveis) e 15 (Vida Terrestre), especialmente no contexto da sustentabilidade dos sistemas agrícolas.

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