BRIEFING NOTE

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Environmental and thermal aging of plastics: Studies on changes in chemical structure and emissions of volatile organic compounds (VOCs)

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KEY FINDINGS

The main aim of this study is to study the effects of thermal and environmental aging on mechanical and thermal properties of recycled plastics and biopolymers [polylactic acid (PLA), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT)]. For recycled plastics, it was observed that after aging there is an increase in tensile stress at break which was attributed to the occurrence of crosslinking processes in polymer matrix which can lead to strengthening of the structure and recrystallization processes in the polymer. In the case of biopolymers, tensile properties declined with PLA samples exhibiting the highest reduction in mechanical properties after 1000 hours of UV exposure. VOCs analysis revealed that no toxic emissions such as benzene or toluene were emitted from the recycled plastics after aging. Low levels of benzene were emitted from PBAT samples after aging for 1000 hours. Thermal analysis revealed that recycled plastics exhibited thermal stability up to 400^{o}C and the main degradation products from recycled plastics were observed to be alkanes and alkenes.

INTRODUCTION

The plastics industry is growing at a rapid pace with the global plastics market projected to grow from $457.73 billion in 2022 (plastics production reached a peak of 475 million tons in 2022[1]) to $643.37 billion by 2029, at a compounded annual growth rate (CAGR) of 5.0%[2]. This growth can be attributed to the rising demand for materials from the food & beverage industry, as well as other industries such as consumer goods, automotive, biomedical and electrical and electronics. The common plastics used in the above industrial sectors include polyethylene, polypropylene, polyvinyl chloride and polystyrene.

This burgeoning growth of plastics has also resulted in an increased generation of plastic waste; reports indicate that global plastic waste generation has more than doubled in the last decade and recorded a high of 350 million tons in 2019. Of this plastic waste, only 9% is being recycled, 50% is dumped in landfills, 19% is incinerated and more than 22% leaked into terrestrial or aquatic environments. These plastic wastes can disintegrate to form micro and nano plastics which can be ingested by marine life leading to contamination of food supply chain and create irreparable damage to human health.

A multi-pronged solution approach is required for reducing plastics pollution which includes increasing recycling rates, designing products for circularity and developing environmentally friendly alternatives. As part of increasing recycling rates, there has been a rise in the development of recycled products for outdoor applications such as plastic timber products [outdoor furniture (benches in school playgrounds), decking] and use of plastic waste in asphalt to improve durability of roads. This is considered as a promising strategy as it converts waste plastics into value-added durable products and large quantities of waste plastics are diverted from landfills. However, when these products are exposed to dynamic outdoor conditions (influence of sunlight, temperature and humidity) for long durations it can lead to photo-degradation which can result in surface changes (loss of color, cracking) and loss of mechanical properties. In many applications, these products will be exposed to a combination of two

[1] https://ourworldindata.org/grapher/global-plastic-production-projections

[2] https://blog.gitnux.com/plastic-industry-statistics/

or more factors (e.g. temperature and humidity), often resulting in complex synergistic degradation of the material.

Apart from decline in mechanical properties, the degradation of polymers results in generation of volatile organic compounds (VOCs). The released volatile compounds can undergo further complex photochemical reactions and produce oxidized compounds. Additionally, some VOCs are toxic and can have adverse short-term and long-term effects on human health. Several studies have dealt with analysis of mechanical and physical properties of plastics when subjected to degradation processes, however, reports on emissions of VOCs from degradation of plastic products is limited.

The other strategy to tackle plastic pollution is the use of bio-based materials for niche products. A major portion of the generated plastic wastes are single-use products which are not recycled due to economic reasons or contamination with soil (much), food waste (e.g., food cartons) and biomedical waste (e.g., syringes, surgical aprons, diagnostic kits) and can be replaced using biobased materials. While biopolymers possess environmental advantages over conventional plastics in terms of sustainability of raw materials and embodied energy in production processes, there are limited studies on the environmental impact of degradation products that are formed when biopolymers are subjected to weathering. The tracking of degradation products is necessary towards ensuring sustainability of biopolymers and making sure that toxic chemicals/additives/plasticizers if used in the production stages are not generated as byproducts.

The main aim of this study is to study the effects of thermal and environmental aging on properties of recycled plastics (sourced from local companies) and biopolymers [polylactic acid (PLA), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH), polybutylene succinate (PBS) and polybutylene adipate terephthalate (PBAT). The emission of VOCs from the samples before and after aging was also analysed.

METHODOLOGY

Samples were subjected to environmental aging in a weathering chamber (Model: QUV Xe-3, Q-Lab Corporation, USA) and as per ISO 4892-3 for a duration of 1000 hours and the changes in surface and mechanical properties before and after aging was determined. The analysis of emissions of VOCs from control and weathered samples were also performed using pyrolysis-gas-chromatograph coupled with mass spectrometer (Py-GC-MS). Additionally, the iso-thermal degradation components from aged and unaged samples were evaluated from Thermogravimetric - Fourier transform infrared (TG-FTIR) spectroscopy analysis.

MAIN RESULTS

Mechanical studies

For recycled plastics, it was observed that there is an increase in tensile stress at break and decrease in elongation at break values as aging time increases. The recycled samples are majorly polyolefins and the increase in strength could be attributed to the occurrence of crosslinking processes in polymer matrix which can lead to strengthening of the structure and recrystallization processes of the polymer.

In the case of PLA samples, it was found that tensile stress decreased by 71% and strain at break increased by 19%; PBS samples exhibited a 25% decrease in tensile stress and 46 % decrease in strain at break with aging; PHBH samples demonstrated a 12 % decrease in tensile strength and 62% reduction in strain at break. Among the different biopolymers, based on the tensile test results, PLA samples exhibited the highest decline in mechanical properties after 1000 hours of UV exposure (Figure 1).

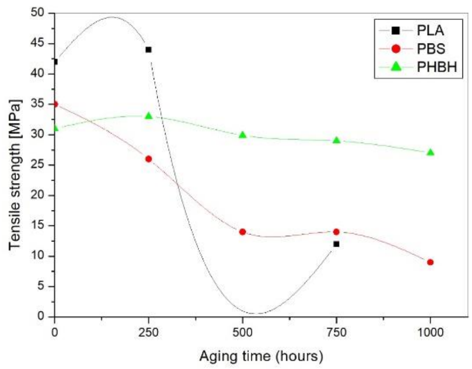

Figure 1: Variation of tensile strength of biopolymers after aging

VOCs analysis

For recycled plastics, it was observed that 1-Nonadecane is present in highest concentration after aging. The emitted VOCs could originate from various factors such as presence of additives like antioxidants and stabilizers used in plastic manufacturing. No toxic VOCs such as benzene or toluene were emitted from the recycled plastics after aging. Amongst biopolymers, emissions of methyl ethyl ketone and benzaldehyde was observed for PBS and PBAT respectively. Low levels of benzene were emitted from PBAT samples after aging for 1000 hours.

TG-FTIR studies

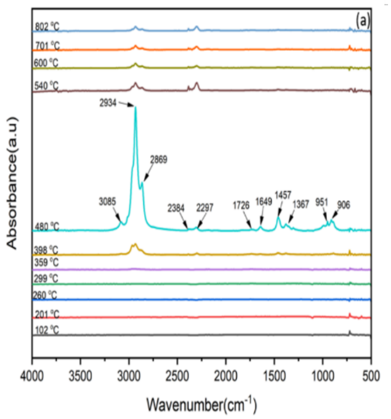

Figure 2: FTIR spectra of recycled plastics during thermal degradation

Thermal studies (Figure 2) showed that the recycled plastic samples exhibited a peak degradation temperature of 480°C indicating thermal stability up to 400°C and the main degradation products from recycled plastics were observed to be alkanes and alkenes. In the case of biopolymers, PBAT and PBS exhibited high peak degradation temperatures of 423°C and 452°C which is attributed to the presence of benzene rings in its molecular structure. The maximum degradation temperature of PLA was determined to be 410˚C. At temperatures above 200◦C, intramolecular trans-esterification and fragmentation processes occurs resulting in the final formation of acetaldehyde and CO_2. The final degradation products in biopolymers include oligomers, unsaturated carboxylic acids, CO_2, CO and H_2O.

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