Raman Spectroscopy of irradiated and non-irradiated plastics

Jessica Dipold[1], Allan Bereczki[1], Gustavo Pinheiro[2], Kamilla Vasconcelos[2], Anderson Zanardi de Freitas[1], Niklaus U. Wetter[1]
[1] IPEN/CNEN, Av. Prof. Lineu Prestes, 2242, Sao Paulo – SP – Brasil
[2] Laboratório de Tecnologia de Pavimentação, Escola Politécnica da USP, Av. Professor Almeida Prado, 83, São Paulo - SP, Brazil
Author e-mail address: jessica.dipold@gmail.com

Abstract: Understanding radiation damage to plastic is of great interest for possible construction applications. Two different plastics were gamma irradiated and their property changes were studied with micro-Raman spectroscopy, showing promising results in increasing its toughness. © 2022 The Author(s)

1. Introduction

It is of much interest of practical and theoretical nature to study radiation damage to plastics caused by gamma or neutron irradiation due to possible applications in civil and road construction. The understanding of the contribution of chain splitting and crossing to the damage mechanisms is of fundamental importance for their usage in concrete and asphalt mixes and influences important factors such as rigidity, stability and many others.[1]

One of the important applications is the reuse of plastic waste in asphalt road construction, since a large volume of materials would be used each year [2].

The biggest difficulty for this application is the fusion temperature of the polymers, which varies depending on the composition. If the plastic melts, the viscosity of the asphalt produced may vary, which would disrupt its usual fabrication, therefore, a previous study of melting temperature is necessary to choose which plastics can be used and how it could be inserted into the pavement structure. For hot and warm mix asphalt concretes, the temperature of fabrication ranges from 110 to 170ºC, so plastics such as polyethylene (PE), which melts at 110 – 135 ºC and polypropylene (PP), which melts at 160ºC, are promising types of polymers for this kind of application. However, since plastics present some elasticity, they make a softer base than what is necessary for the asphalt deposition process, needing a solution to allow further applications.

In 2018, Schaefer et. al[3] proposed the addition of gamma-irradiated plastic to Portland cement concrete in order to increase the compressive strength comparing to non-irradiated plastics. They demonstrated that by irradiating a polyethylene terephthalate (PET) sample with 100 kGy, there was an increase in the crystallinity of the material, which made it more resistant and adequate for use. This kind of study has not been made for asphalt concrete yet.

Here, we study the changes caused by gamma-irradiation of 100 kGy in two different polymers, a bio-oriented polypropylene and a high-density polyethylene, by using micro-Raman spectroscopy. The objective is to characterize the polymers to verify the possibility of adding them to asphalt concrete, making it more resistant and assisting in the plastic reuse.

2. Materials and methods

Two kinds of plastic were studied. The first one is a bio-oriented polypropylene (BOPP), which is a mixture of leftovers from industrial production of plastic BOPP films that were turned into ~4 mm pellets in order to find applications for them. The second one is a high-density polyethylene, which are leftovers from plastic recycling with other applications. In this process, the company makes pellets, and our studied samples are shreds that come from them.

Both were irradiated at the Centro de Tecnologia das Radiações from IPEN, using a gamma-ray irradiator with a 60Co source with a dose level of 100 kGy. This dose level was chosen due to the previously mentioned results in [3], which also used 100 kGy and obtained good results.

The micro-Raman measurements were done using a LabRam Evolution – HORIBA system. The laser source wavelength was 785 nm of 100 mW maximum output power, where we used a 25% neutral density filter to reduce it to 25 mW and avoid polymer burning. The objective lens magnification used was 100x, which allowed precise measurements in a 0.8 µm spot size. The grating used had 300 lines/mm.

3. Results

The high-density polyethylene sample was measured with an integration time of 960 seconds with one accumulation, while the bio-oriented polypropylene was measured with 4 seconds of integration time with ten accumulations. The obtained spectra are shown in Figure 1. Both present some fluorescence, which shall be removed during further studies.

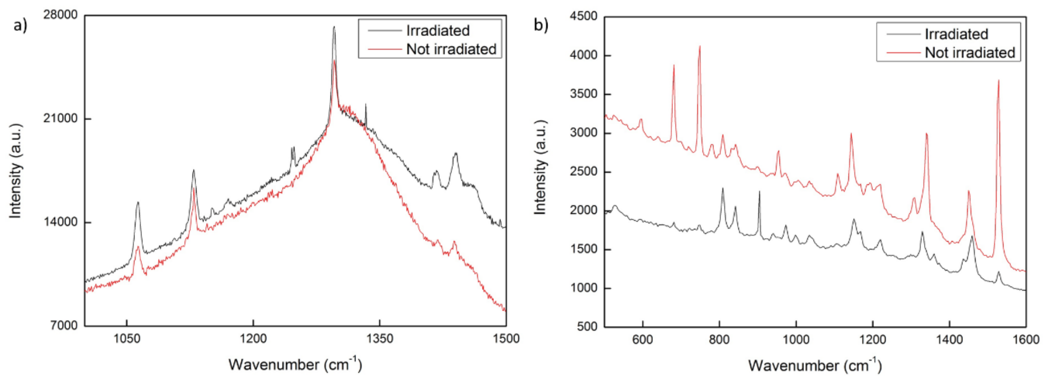

Figure 1: Raman spectra of a) PE irradiated and not irradiated; b) PP irradiated and not irradiated.

From the PE spectra shown in Figure 1a, there is no difference between the spectra except for the peak sizes. We can also see that the peak sizes after irradiation are larger than before irradiation, which is not common since the irradiation process usually breaks bonds and eliminates elements from the exposed material. The peaks between 1400 and 1500 cm^{-1} are related to the CH_2 bending vibration. In particular, at 1417 cm^{-1} and 1440 cm^{-1} we see two bands that increase largely in size. These are related to a crystalline band present in PE [4, 5], and, therefore, demonstrated an increase in crystallinity of this sample due to irradiation. This can mean that the polymer became more resistant, which will be tested in later measurements.

The PP spectra shown in Figure 1b presents more differences. The peak around 1528 cm^{-1} shows that there was contamination of an NH ligand in the polymer structure, which was greatly reduced by the irradiation. The peaks at 681 and 748 cm^{-1}, which also became much smaller, are related to CH_2 o-disubstituted and m-disubstituted, and were also removed in the process. The peak of 1143 cm^{-1} also became slightly smaller and shifted to 1150 cm^{-1} after irradiation. As it is related to the CC bond, it shows that the chain was stretched in the irradiation process. This blue shift of the peak is related to hardening effects. The peak at 1339 cm^{-1}, related to the CH bond, shifted to 1329 cm^{-1}, which shows a contraction of the bond. This red shift effect is related to softening effects. Therefore, to arrive at a conclusion if the irradiation process made this polymer harder, other studies will be necessary, such as XPS measurements and resistance measurements, which are the next steps to be carried out for these materials.

4. Conclusions

Two kinds of plastic were irradiated with 100 kGy and had their properties studied with micro-Raman measurements having asphalt mixing applications. The polyethylene showed promising results by having an increase in the intensity of its crystalline Raman bands, which probably made it harder than before irradiation. The polypropylene showed both, hardening and softening effects, which will need further studies to arrive at a conclusion.

This work was possible thanks to FAPESP projects 2017/50332-0, 2019/06334-4 and 2021/04334-7.

5. References

[1] S. G. Prasad, A. De, and U. De, "Structural and Optical Investigations of Radiation Damage in Transparent PET Polymer Films," International Journal of Spectroscopy, 2011, (2011).

[2] B. P. Grady "Waste plastics in asphalt concrete: A review," SPE Polymers, 2(1), 4-18 (2021).

[3] C. E. Schaefer, K. Kupwade-Patil, M. Ortega *et al.*, "Irradiated recycled plastic as a concrete additive for improved chemo-mechanical properties and lower carbon footprint," Waste Management, 71, 426-439 (2018).

[4] D. Barron, and C. Birkinshaw, "Ultra-high molecular weight polyethylene - Evidence for a three-phase morphology," Polymer, 49(13-14), 3111-3115 (2008).

[5] G. R. Strobl, and W. Hagedorn, "RAMAN-SPECTROSCOPIC METHOD FOR DETERMINING CRYSTALLINITY OF POLYETHYLENE," Journal of Polymer Science Part B-Polymer Physics, 16(7), 1181-1193 (1978).