IMAGING THE MOLECULAR ORIENTATION AT THE DISPERSE-CONTINUOUS INTERFACE OF A PP-PA6 BLEND BY THE FOUR-POLARIZATION FTIR METHOD

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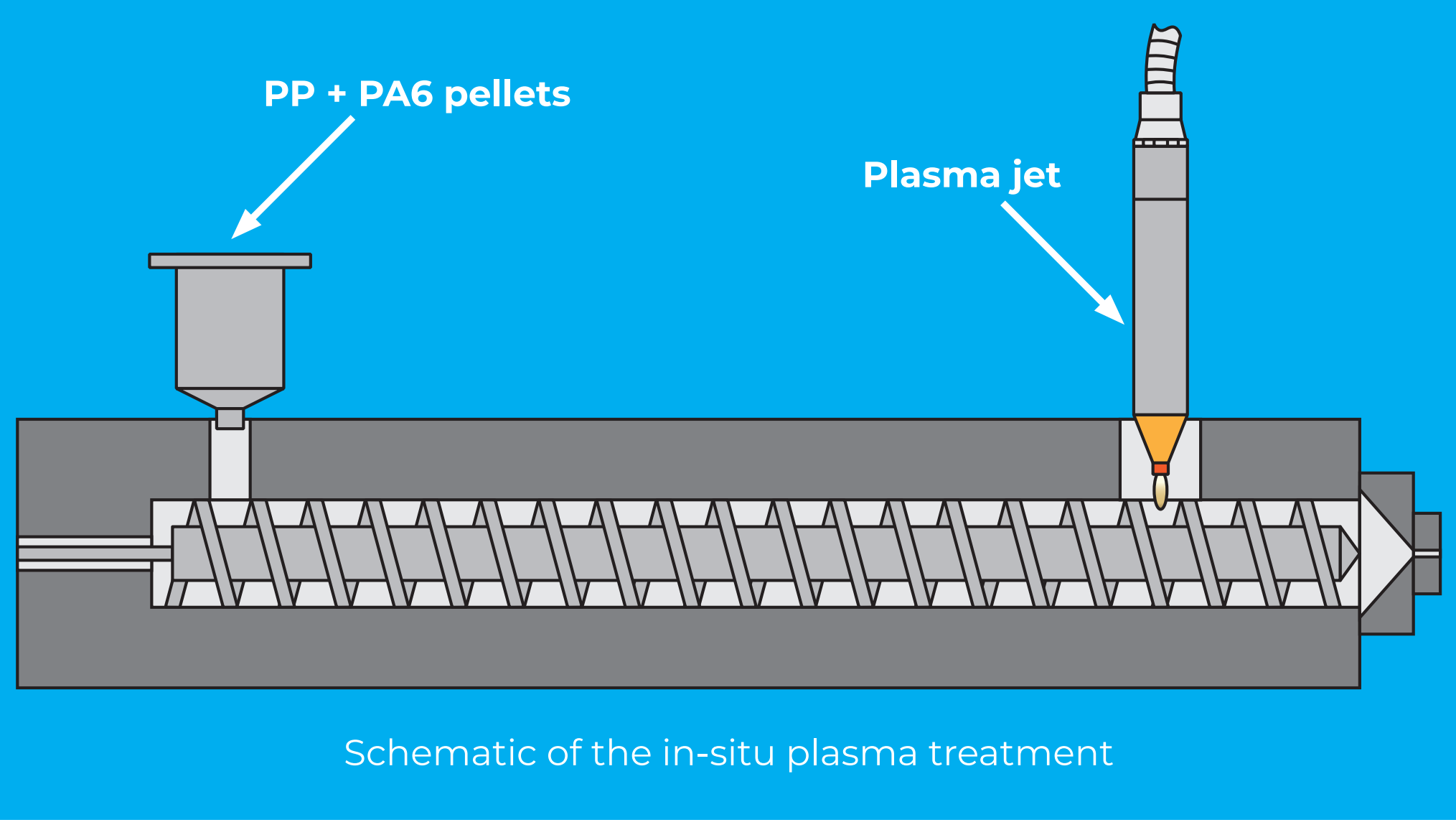
INTRODUCTION

Fourier-transform infrared spectroscopy (FTIR) is a well-known technique used to analyze the chemical composition of polymeric materials by measuring the absorption of infrared light over a range of wavelengths, where each absorption peak corresponds to a specific chemical bond. A chemical map image can be constructed by acquiring multiple IR spectra with a specified step distance over an area. Furthermore, it is possible to extract information about the molecular orientation by utilizing linearly polarized light [1], as the absorption intensity varies with the polarization angle of the incident radiation. Recently, a mathematical method was introduced which makes it possible to create a complete vector map of the average molecular orientation based on a selected vibrational mode by utilizing measurements of IR spectra in four different polarized orientations [2, 3]. This technique can provide immense insight into the molecular interaction between the different phases of a polymer blend.

BLEND PREPARATION

- 80% PP and 20% PA6 blends were prepared in a twin screw extruder.
- Blend A had no compatibilization, blend B had the substitution of 3% PP by PP-g-MAH to act as a compatibilizer, and blend C was plasma treated with an atmospheric pressure plasma jet.
- For blend C, the plasma jet was applied during the extrusion process by inserting the nozzle into a barrel opening near the die, as shown in the figure below.



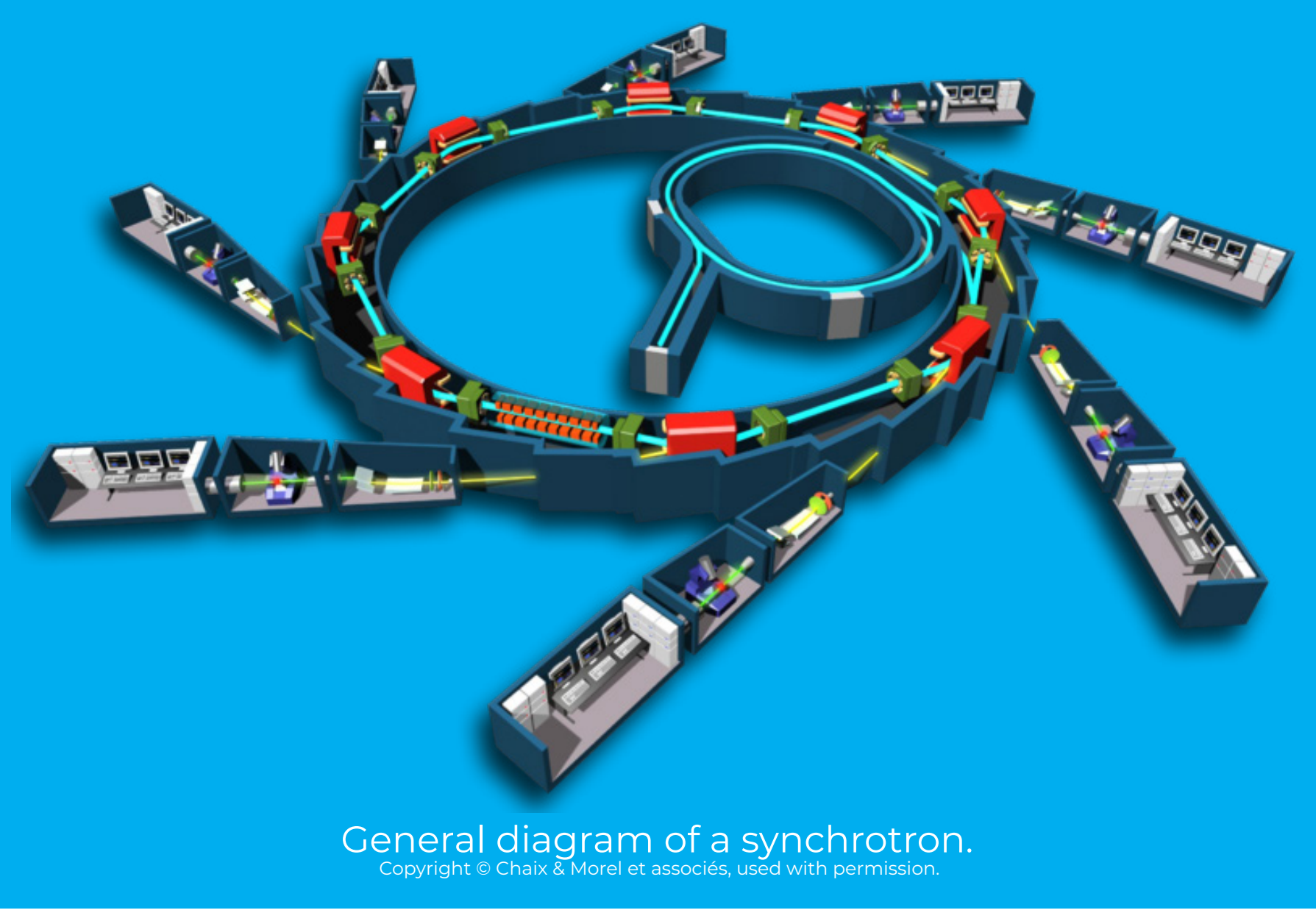
Schematic of the in-situ plasma treatment

OBJECTIVES

- Apply the four-polarization method to evaluate changes in the molecular orientation of the disperse phase and the continuous matrix of a polypropylene-polyamide 6 (PP-PA6) blend.
- Compare an uncompatibilized blend with a blend compatibilized with the addition of maleic anhydride grafted polypropylene (PP-g-MAH) and another with the application of a novel in-situ plasma treatment [4].
- Evaluate the efficacy of plasma treatment as a possible compatibilization method for polymer blends.

THE USE OF SYNCHROTRON LIGHT FOR FTIR

- Fast-moving electrons at 99.9997% of the speed of light generate concentrated beams of light more than a million times brighter than the sun.
- Highly collimated and highly polarised.
- Produces much higher signal-to-noise ratio measurements than traditional laboratory instruments.
- Can produce FTIR images with a diffraction-limited spatial resolution between 3-8 µm.



General diagram of a synchrotron.

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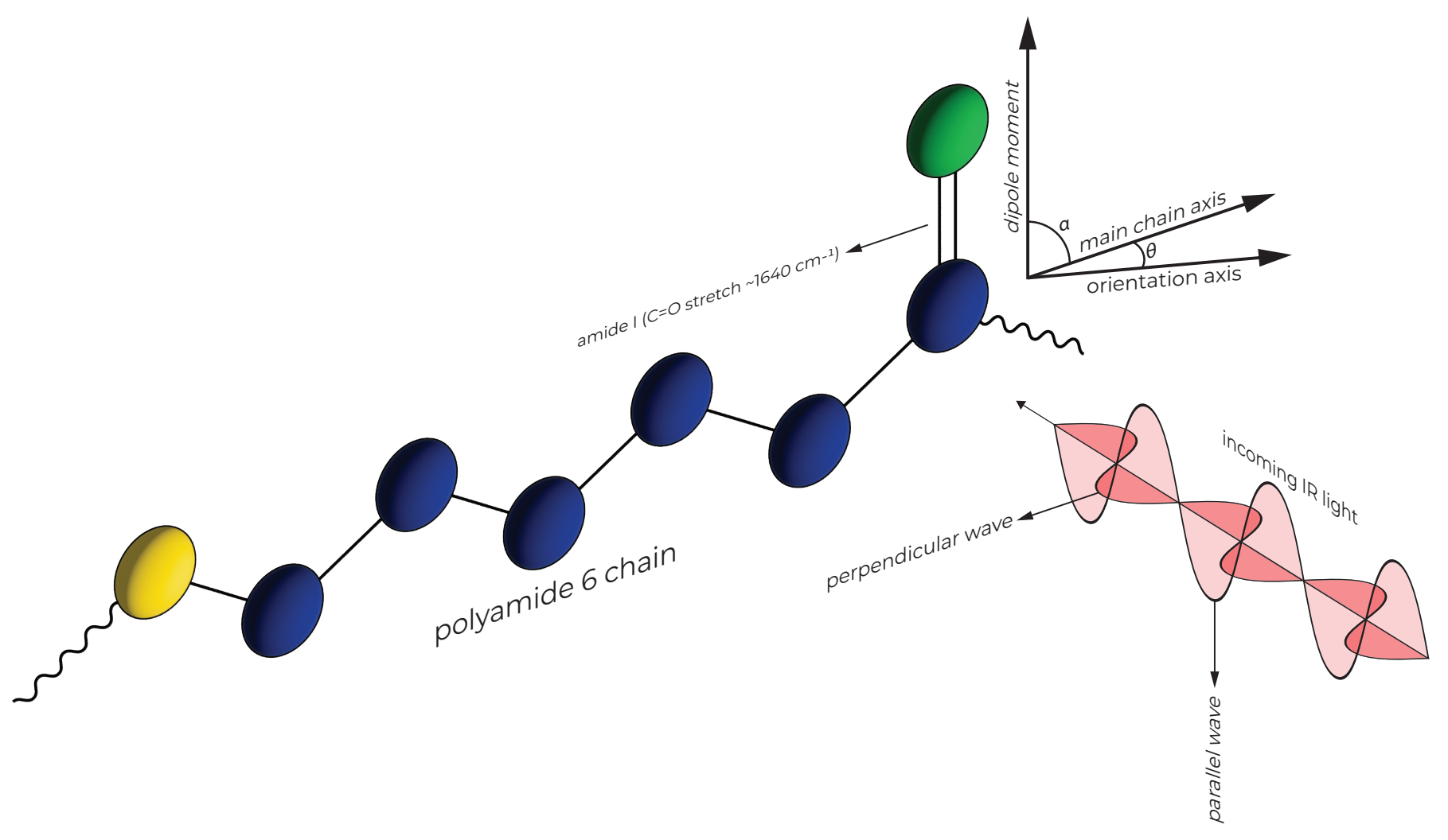
MATHEMATICAL PROCEDURE



In a partially oriented material, each chain forms an angle Θ between the main chain axis and the orientation axis, and for each molecular vibrational mode in polymers, there is an associated transition dipole moment at an angle α with the main chain axis. Infrared light is only absorbed by the material if the wavelength matches the frequency of said vibrational mode and has a component of the electric vector parallel to the dipole moment.

If the incident light is polarized parallel to the dipole moment, the absorption intensity will be highest, and the opposite is true for light polarized perpendicularly. The ratio between these two absorptions is called the **dichroic ratio** [5]:

$$D = \frac{A_{\parallel}}{A_{\perp}} \tag{1}$$

which can vary from 0 for isotropic materials to ∞ in perfectly oriented polymers, and it relates to the "Hermans orientation function" by[2]:

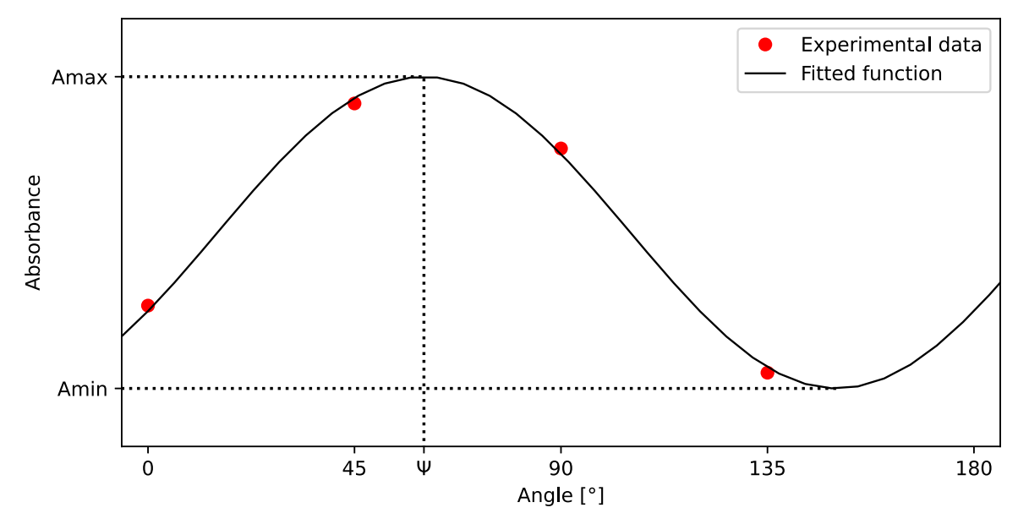
$$f = \frac{3\langle cos^2\theta\rangle - 1}{2} = \frac{D-1}{D+2}\frac{2}{3cos^2\alpha - 1} \tag{2}$$

Using only two perpendicular polarizations is satisfactory if the orientation axis is already known. However, to evaluate the relative orientation of spots adjacent to each, the use of at least four polarizations at 45° spacing is needed, allowing one to apply the Hermans orientation function independently of the chosen polarization axis. The absorbance at a polarization angle γ is derived as:

$$A_\gamma = \frac{A_{max} + A_{min}}{2} + \frac{A_{max} - A_{min}}{2} cos2(\gamma - \psi) \tag{3}$$

where A_{max} and A_{min} are the absorbances parallel and perpendicular to the average over the orientation distribution of transition dipole moments, respectively, and ψ is the "orientation azimuth angle", or the angle of maximum orientation, i.e., when $A_\gamma = A_{max}$.

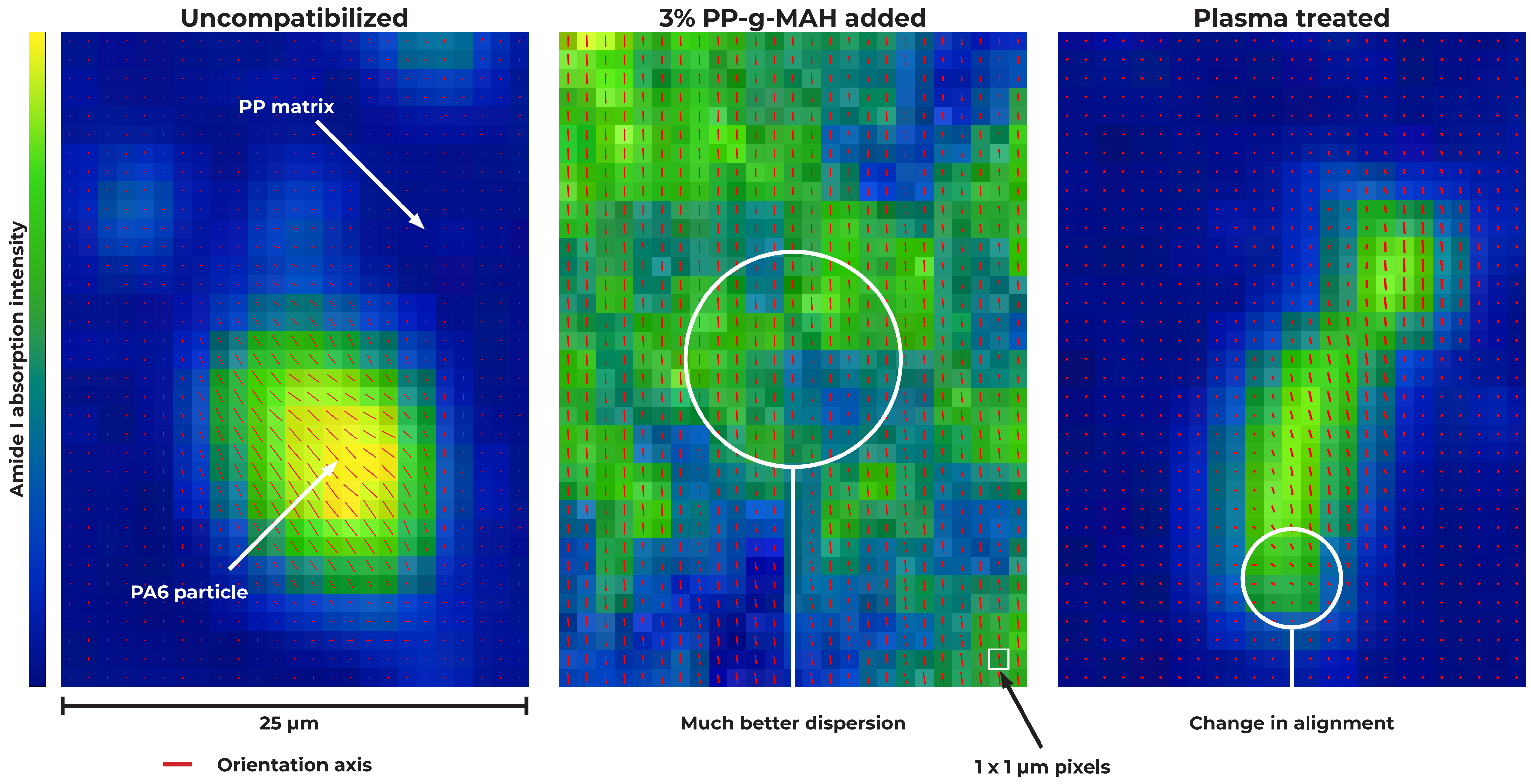
Thus, by measuring A_γ in four different polarizations, one can fit a sinusoidal curve to equation (3) and find A_{max}, A_{min}, and ψ for each image pixel, where ψ is given relative to the polarization axis chosen.



Fitted function for eq (3). This fitting is done for each pixel of the chemical map in order to find A_{max}, A_{min}, and ψ.

ANALYSIS

- FTIR measurements of 10 µm thick microtomed samples were taken under transmission with 16 averaged scans for each point.
- The chemical maps are generated by plotting the absorption intensity of the amide I band (C=O stretching at ~1640 cm^{-1}) for each image pixel. The images are composed of multiple measurements of an area of 25 x 35 µm with a 1 µm step per pixel.
- The red lines are vectors where the direction is the orientation azimuth angle ψ and the length is the respective value of the Hermans orientation function at ψ calculated for the amide I band.



CONCLUSIONS AND RECENT ADVANCEMENTS

- As expected, PP-g-MAH compatibilized blends have a much finer dispersion, where the resolution of these measurements is not fine enough to distinguish the two phases completely. The whole sample has a minor unidirectional alignment.
- PA6 particle in the uncompatibilized blend shows very high alignment and a relatively strong absorption intensity of the Amide I peak, while the plasma-treated has an overall reduced Amide I intensity and lower level of unidirectional alignment, more similar to the PP-g-MAH blend. Furthermore, a slight change in alignment can be noticed at one point near the interface, which might be attributed to the introduction of functional groups by the plasma treatment on that spot, changing the orientation of nearby chains.
- While the results are promising for our in-situ plasma treatment, drawing solid conclusions from a single particle is challenging.

The Australian Synchrotron IRM beamline team has developed a new Macro ATR-FTIR dispositive, demonstrating that the spatial resolution can be increased by a factor of 2 over transmission [6]. So far, it has yet to be tested under the 4 polarisation method, but if successful, it can provide even more detailed data when probing at such a small scale.

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