## Life and Death of Plastics

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The European industrial demand for plastics summed up to 46.3 million tons in 2013, with the most demanding industries being packaging, construction and automobile.[1] For all these users, one of the biggest challenges is to predict how the material will withstand the test of time. Indeed, extremely diversified applications expose the base polymers to strong temperatures variations, sunlight, air, or even aggressive chemicals, all of which contribute to their degradation.[2]

Base materials suppliers provide indications of ageing based on standardized tests: for instance, they expose their compounds to a constant temperature for long periods, and then propose target temperature windows and conservative lifetimes to the application industries.[3] The problem here is that these application industries are producing final objects that will be exposed to non-constant environmental stresses (like short periods of high, out-of-specifications temperatures), and often for much longer times than advised by the base material suppliers.

In order to solve this problem, a team of chemists from the University of Applied Sciences Western Switzerland in Fribourg (HES-SO) has launched a research program in collaboration with four major industrial partners producing final polymer-based products and partially funded by the Canton of Fribourg (PST-FR).[4] These companies, namely Geberit Fabrication (composite water tubes), Jesa (plastic overmolding elements), Johnson Electric (automotive components) and Wago (electric connectors), came with their own environmental target conditions on their respective base materials, and the research team led by Prof. Dr. Pierre Brodard selected the most appropriate characterization methods.[5]

The first year of the program, called POLYAGE (2014-2015), was dedicated to chemical ageing. Two classes of plastics, based on polyethylene (PE) and polyamide (PA), were first characterized to obtain their whole thermal, structural, topographic and oxidation properties. For this purpose, we used differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), infrared and Raman spectroscopy, scanning electron microscopy (SEM) and chemiluminescence, respectively. Then, the samples were exposed to various temperature programs to force their degradation, and compared to aged products provided by our industrial partners.

As expected, PE-based materials are chemically decomposed by oxidation, which was easily confirmed by spectroscopy. Hence, we quantified their kinetics by chemiluminescence, a method that measures the weak light emission generated by oxidation following the Russell's mechanism.[6] By performing several isothermal measurements in a precise oxygen-containing atmosphere, we could extract the empirical Arrhenius parameters (activation energy and pre-exponential factor) of the degradation, thus allowing an exact prediction of the lifetime of the samples at any temperature.[7]

On the other hand, PA-based materials did not seem to change their chemical composition: even though their mechanical integrity was strongly fading during ageing, their infrared and Raman spectra were almost unaffected. Indeed, the fracture toughness measured by tensile tests was reduced by 40% in the hardest conditions (20 days at 200 °C), but the composition remained the same. We then found out that the structure of the material seems to change: SEM images revealed a highly inhomogeneous dispersal of the glass fibers in the reinforced PA-based samples after thermal ageing, which probably accounts for their apparent fragility (Fig. 1).[8]

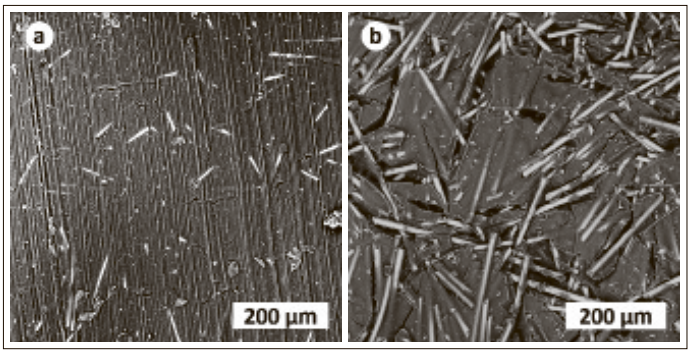


Fig. 1. SEM images of PA before (a) and after (b) thermal ageing at 200 °C for 20 days.

As a logical next step, we decided to concentrate on physical ageing in the second year of the program (POLYLIFE, 2015-2016). By physical ageing, we mean no change in the chemical composition but a modification of the structure, like the above-mentioned alteration of the glass fibers distribution in the PA

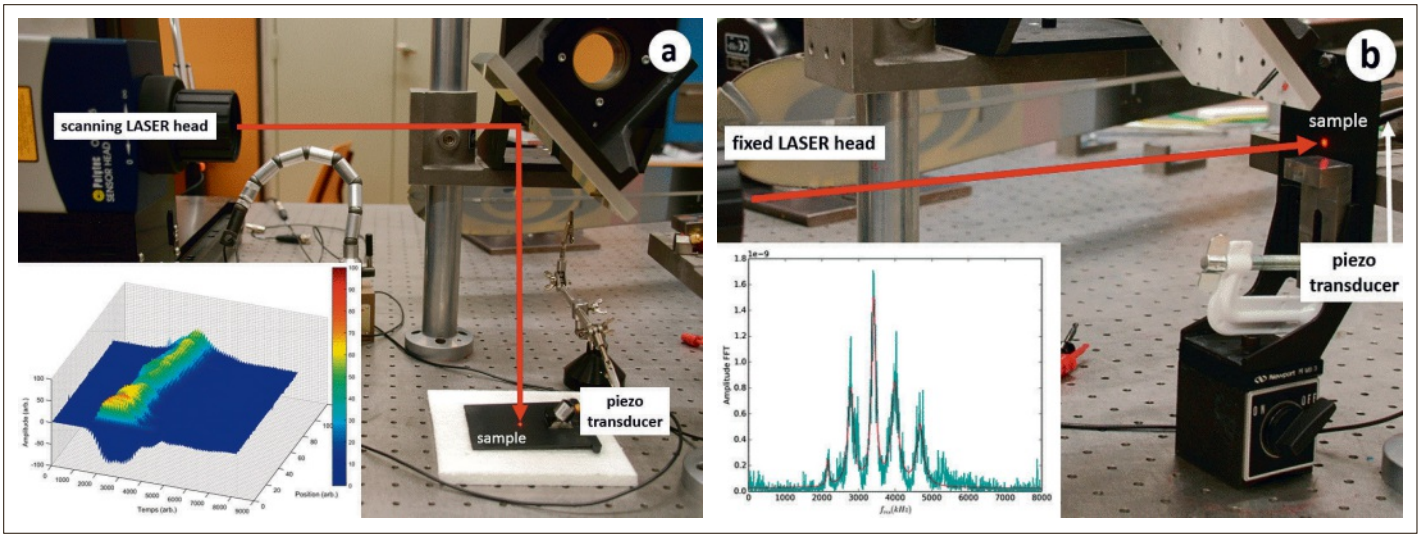


Fig. 2. Ultrasonic characterization method, with waves propagating in the plane (a) or through the sample (b).

matrix. For this purpose, and with the strong support of our mechanical engineering department, a new method based on ultrasound was developed: a piezoelectric transducer generates ultrasonic waves in the sample, and an interferometric laser head is used for detection. Two implementations have been devised: ultrasonic Lamb waves propagating in the plane of a thin flat sample and mapped by the scanning laser head, allowing determination of the elastic modulus of the material in different directions, and resonance of ultrasonic frequencies through the sample, enabling to measure more complicated, non-flat objects (Fig. 2).

These two non-destructive techniques are sensitive to any modification of the physical structure, even on final industrial products. Both approaches have already been validated, first on model aluminium samples and then on polybutylene terephthalate (PBT) objects: excellent correlation with mechanical properties obtained by macroscopic (tensile test) and microscopic (nanoindentation) methods prove their potential. We then started to measure pure and glass-fibers reinforced PBT samples having been exposed to high temperatures, as well as final manufactured objects, with interesting results in progress.

In addition, we extended the study beyond the initial PE- and PA-based samples under thermal exposition: polyethylenimine (PEI) was exposed to UV light, as well as various high-performance polyphthalamide (PPA) and polyphenylene sulfide (PPS) aged at high temperature, not to forget a high-temperature PE-based material exposed to water. For the PEI samples, we found no detectable degradation under constant UV-illumination for two months. On the contrary, for various PPA samples exposed to several temperature programs (160 °C to 270 °C, 30 h to 3000 h), tensile tests revealed a temperature-dependent exponential decay of the fracture toughness with time. Based on these results, we are now calculating the Arrhenius parameters in order to predict their lifetimes. Moreover, SEM images combined with TGA investigations of these glass fibers-reinforced PPA indicate an evaporation of the base polymer (up to 20% mass loss), whereas ageing temperatures (240 °C max) are still well below the melting point (approx. 320 °C). For the PE-based samples, first results suggest a different and faster oxidation mechanism in water than in air. Finally, the campaign of thermal ageing has just started for the PPS samples.

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