A comparison of rheology and FTIR in the study of polypropylene and polystyrene photodegradation

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Abstract

Rheology and FTIR spectroscopy are compared as methods to study the degree of photodegradation in polypropylene (PP) and polystyrene (PS) sheets. The materials are hot pressed, artificially photo-aged with fluorescent lights for 4-2048 h and then measured with a rotational rheometer and FTIR. Both materials show a tendency for chain scission which can be seen as a reduction in viscosity. Changes in PP can be observed with both methods after 256 h of irradiation. Changes in PS become significant in rheology after 64 h but in FTIR only after 1024 h of irradiation. Due to the different chemical nature of the materials, the degradation of PS is rather linear with exposure, whereas the degradation of PP is more exponential. By using the zero shear viscosities obtained through extrapolations of the Cole-Cole and Carreau-Yasuda models, relative molecular weights are estimated with the aid of the power-law relationship between these two. These results are compared with the carbonyl indices determined from the FTIR spectra. Rheology is found to be a viable alternative for FTIR in certain situations.

Keywords: Rheology, FTIR, photodegradation, UV, polystyrene, polypropylene

Introduction

Fourier transform infrared spectroscopy (FTIR) is probably the most common technique for analysing polymer ageing caused by UV irradiation. It is fast, accurate, and widely used.[1-3] The IR spectrum reveals the presence of functional groups, such as carbonyl groups, which are formed from the polymer radicals generated during the degradation process. Polymer rheology, on the other hand, is typically used to estimate processability and the properties of materials. The use of rheology in the study of polymer photodegradation is based on the fact that rheology is sensitive to changes in molecular weight, and it is a less frequently used method than FTIR.

Polymer radicals can induce crosslinking and chain scission reactions,[4] which are the two main competitive reactions that affect molecular weight during photodegradation. Chain scission reduces the average molecular weight of a polymer, whereas crosslinking raises it by increasing the bonding between polymer chains. Chain scission generally dominates over crosslinking and, therefore, a decrease in the molecular weight is a common consequence of photodegradation. The primary means to obtain information concerning the molecular weight of a polymer is gel permeation chromatography (GPC). However, GPC has many drawbacks such as long operation times, expensive equipment, and the need to dissolve the polymer in a solvent, which in some cases needs to be performed at high temperatures that can induce thermal ageing.

In ageing studies, rheology is typically used to analyse thermal degradation caused by heat or multiple extrusions.[5-8] However, rheological testing has been increasingly utilized in the study of photodegradation.[9-15] Many of these studies have been made by one research group, and they are rarely focused on the comparison of these two methods. Studies where a limited comparison between FTIR and rheology is possible have been made on materials such as polybutene-1,[9] elastomers,[10] biodegradable polymers,[11] PE/feather composites,[12] gamma-irradiated high melt strength polypropylene,[13] and polyetheretherketone.[14] The polybutene-1 study[9] indicates that rheology could be a more accurate method than FTIR in detecting the early signs of photodegradation. The results of the rheological studies show a very different behaviour between the materials, some of them being highly crosslinkable, and others showing a tendency for chain scission. These kinds of photodegradation studies of conventional PP and PS samples were not found in the literature, but thermal degradation studies indicate a large reduction in molecular weight for both materials. This reduction can be seen as decreased viscosity, and the research hypothesis of this study is that this behaviour is observed under UV irradiation as well. Thermal and photodegradation are similar as long as the degradation occurs by the generally acknowledged hydroperoxide mechanism, as is the case for PP.[18, 19] There is evidence that a majority of PS degrades through a different chain scission mechanism, resulting in depolymerisation and release of gaseous styrene monomers, dimers, and trimers[20] as well as complete oxidation products CO_2 and H_2O.[21] This mechanism should lead to noticeable changes in molecular weight, and should thus be observable with rheology.

The goal of this study is to evaluate the suitability of rheological measurements for detecting changes in the polymer structure caused by photodegradation. The linear viscoelastic properties of photodegraded PP and PS samples are determined by means of small amplitude oscillatory shear measurements. The results of the measurements are compared with the corresponding results provided by FTIR spectroscopy.

Experimental

Materials

Two materials, Lyondellbasell polypropylene Moplen grade HP501L (Rotterdam, Netherlands) and BASF Polystyrol 143 E polystyrene (Ludwigshafen, Germany) were used. HP501L is a homopolymer grade with a melt flow rate of 6.0 g/10min. Polystyrol 143 E is a medium strength, easy flowing general purpose grade with a melt volume-flow rate of 10 cm^3/10 min (200 °C, 5 kg). Neither of the materials have inherent UV-stability. According to a DSC test (Netzsch DSC 204 F1, N_2 atmosphere, 10 °C/min) the T_g of PP was 8 °C, T_m 172 °C, and the T_g of PS was 84 °C. Molecular weights (M_w) and polydispersity indexes (PI) were 307900 g/mol and 2.28 for PS,[8] and 325000 g/mol and 5.9 for PP.[22]

Materials were hot pressed between aluminium plates using a temperature of 210 °C and force of 200 kN for 3 minutes. Force was increased slowly to minimize the formation of air bubbles. The sample thickness was 0.43 ± 0.03 mm and the sample size approximately 20*15 cm.

Photodegradation procedure

PP and PS samples were exposed to UV radiation using a self-built UV chamber. The chamber is equipped with four UVA-340 fluorescent tubes (Q-Panel Lab Products, Cleveland, USA) as the radiation source. The spectrum in the chamber is close to sunlight in the critical short wavelength UV region, and the solar cut-off is 295 nm. To compensate the decrease in light intensity with time, a simple tube rotation and replacement system was adopted. This involves replacing the oldest of the four tubes every 400 h and rotating the remaining three lamps. This results in 1600 h of use time for each lamp.

The UV irradiation chamber was characterized using a Bentham DM150 double-monochromator spectroradiometer equipped with measurement head UV-J1002 from CMS Schreder. The chamber was symmetrically divided into nine measuring points and their average was used. The focal plane of the measurement head was approximately 16 cm from the bottom of the chamber. The dose rate at the UVB range (290-315 nm) was 0.7 W/m^2, at the UVA range (315-400 nm) 12.1 W/m^2, and at the visible range (400-600 nm) 3.1 W/m^2. The samples were irradiated for 4-2048 h; 2-1024 h from both sides, one hour of irradiation corresponding to a 57 kJ/m^2 dose.

Rheological measurements

Oscillatory shear measurements within the linear viscoelastic range were carried out for the samples using an Anton Paar Physica MCR 301 rheometer. All the experiments were performed under a nitrogen atmosphere using a 25 mm plate-plate geometry and a gap size of approximately 0.4 mm. The measurement temperature was 200 °C for PP and 220 °C for PS. The measuring points in the angular frequency range of 0.1 – 562 rad/s were recorded with decreasing frequency.

FTIR measurements

FTIR measurements were made with Bruker optics tensor 27 using ATR (attenuated total reflectance) mode. Spectra were measured between 400-4000 cm^{-1}, using 64 scans and a resolution of 4 cm^{-1}.

Results and discussion

Rheological measurements

The rheological testing was performed on all samples but there are no visible changes in samples irradiated for 4-32 h. In PP the changes become visible between 256 h and 512 h (Figure 1) and in PS between 64 h and 128 h of irradiation (Figure 2). The observed degradation behaviour is different between the materials. In PP the degradation initiates later than in PS but at a more rapid rate so that the viscosity of the 2048 h irradiated samples is approximately only 0.01 % of the 1024 h sample viscosity. To measure the 2048 h PP sample, special arrangements had to be made: a larger plate and a smaller gap were used. In PS the changes are visible earlier but the degradation rate is slower so that even the 2048 h irradiated samples were easily measurable. The degradation in the 2048 h irradiated samples was observable without any equipment, since the colour of PS had turned yellow and PP cracked with minimal force.

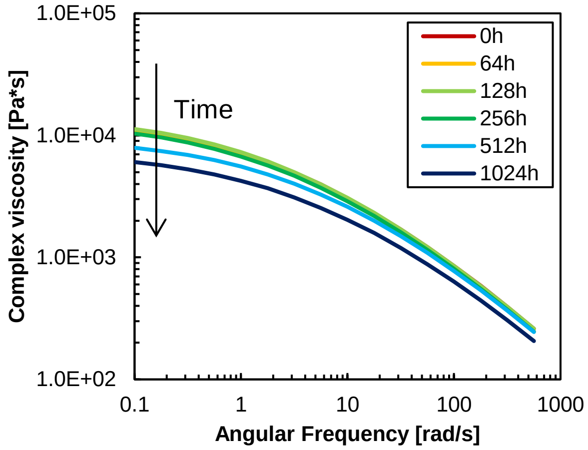

Figure 1. Complex viscosity of the PP samples measured at 200 °C.

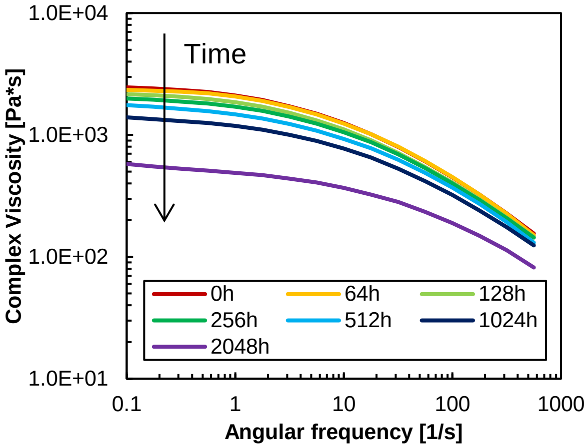

Figure 2. Complex viscosity of the PS samples measured at 220 °C.

Previous studied have shown that in the photodegradation of PP approximately one crosslink occurs per ten chain scissions, depending on the ageing time and the sample thickness.[16] In PS the probability of chain scission is initially higher than the probability of crosslinking, but it decreases during the ageing.[17] This indicates that a higher reduction in viscosity should be seen for PP. PP degrades through the general hydroperoxide mechanism, which is similar to thermal degradation, except for the fact that the degradation is initiated by photoexcited extrinsic carbonyl groups.[18, 19] This mechanism is well known and has been extensively studied since the late 1960's. On the other hand, as little as 10 % of photoexcited PS hydroperoxide radicals go through the general hydroperoxide mechanism.[21] Nevertheless, the photodegradation in PS is initiated by chain scission reactions resulting in large changes in the molecular weight although the probability of chain scission decreases with ageing.[17, 20] The differences in degradation mechanisms causes the different rheological properties for PP and PS.

It is possible to estimate the changes in the molecular weight (M_w) by using the power-law relationship between the zero shear viscosity (η_0) and M_w: [23]

$$\eta_0 \propto M_w^{3.4} \tag{1}$$

Equation 1 presumes that M_w is above a critical limit where molecular entanglements begin to resist the flow. Zero shear viscosity can be estimated by using the imaginary component (η'') and the real component (η') of the complex viscosity, the equation known as the Cole-Cole equation (2):

$$\eta^*(\omega) = \frac{\eta_0}{1+(i\omega\lambda_0)^{1-h}} \tag{2}$$

where η^* is the complex viscosity, ω angular frequency, η_0 zero shear viscosity, λ_0 average relaxation time and h parameter of the relaxation-time distribution. This often used experimental rheological model predicts that the η'' versus η' curve is an arc of a circle in the complex plane and that the extrapolated crossing point of the arc and the real axis is zero shear viscosity η_0. The use of this model has been extensively reviewed in several photodegradation publications.[10, 15, 24]

As previously mentioned, chain scission reactions are dominant in PP and PS. This is evident in the Cole-Cole plots, Figure 3 for PP and Figure 4 for PS, as the arc radiuses are reduced during the irradiation. The reduction in PS is steadier compared to PP. The 2048 h PP curve was not plotted since the arc radius was less than 1 Pa*s.

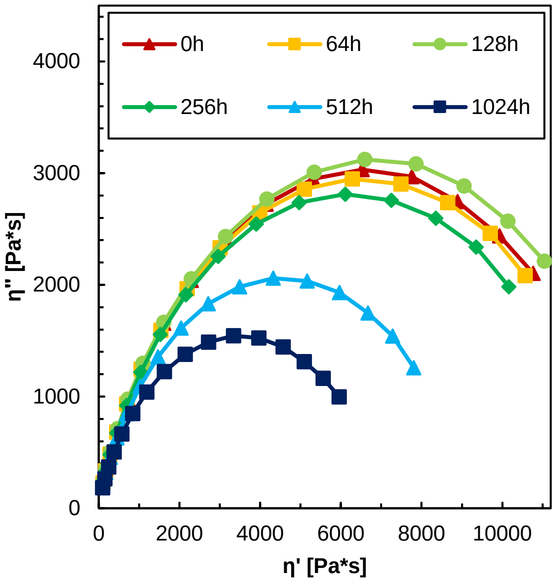

Figure 3. Cole-Cole plot of the PP samples measured at 200 °C.

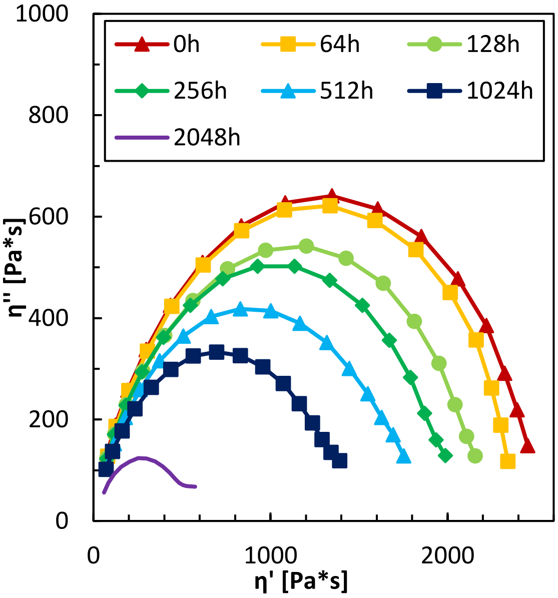

Figure 4. Cole-Cole plot of the PS samples measured at 220 °C.

The relative molecular weights were estimated by using η_0 obtained from the Cole-Cole curves' polynomial 2nd extrapolated X-axis crossing points and equation 1. The results can be seen in Figure 5. According to the results, the relative M_w decreases rather linearly up to 1024 h, after which the decrease accelerates. In PS the relative M_w of the 2048 h sample is 65% of the 0 h sample, whereas in PP it is only 6 %. This is plausible considering that the 2048 h PP sample is very fragile, but the accuracy of this value may be poor. A different measuring setup was used due to the very low viscosity, and equation 1 is valid only above a certain critical limit, as mentioned before.

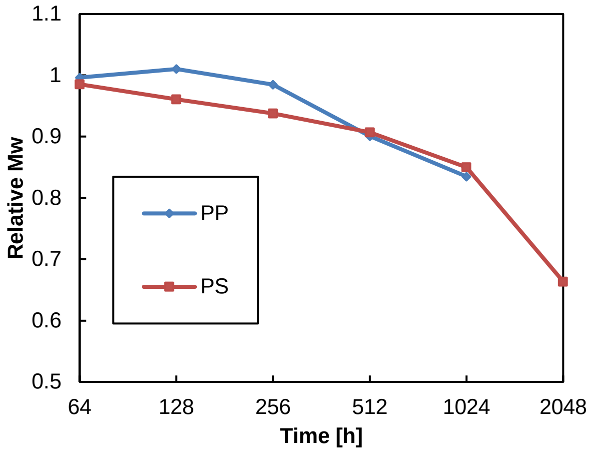

Figure 5. Relative molecular weights of the PP and PS samples calculated from the extrapolated Cole-Cole plots.

Another way to estimate the zero shear viscosity is derived from the complex viscosity curves. Since the angular frequencies used in this study were not low enough to provide the zero shear viscosities directly, extrapolations had to be used. This was done in equation 3 by fitting and extrapolating the Carreau-Yasuda model:[24]

$$\eta = \eta_0[1 + (\lambda\omega)^a]^{(n-1)/a} \tag{3}$$

where η_0 is the zero-shear rate viscosity, ω the angular frequency, and λ, n and a are the other fitting parameters. The results, calculated using equation 1 and presented in Figure 6, are consistent with the Cole-Cole inspections. Among these two methods, the Carreau-Yasuda extrapolations were significantly more complicated and time-consuming so, based on these results, the use of Cole-Cole plots is recommended.

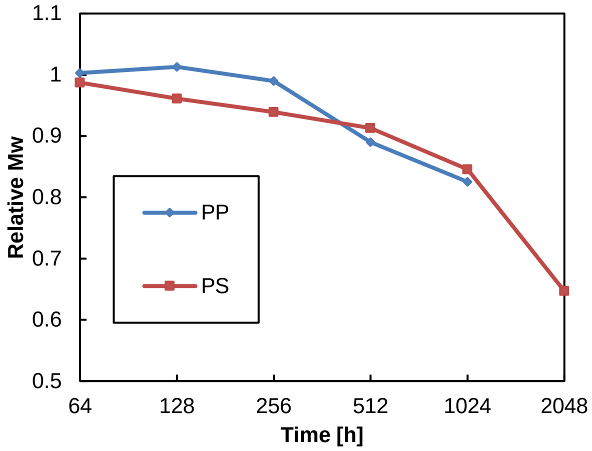

Figure 6. Relative molecular weights of the PP and PS samples calculated using the Carreau-Yasuda model.

FTIR

Numerous different chemical groups are formed in the photodegradation of polymers, mainly different carbonyl and hydroxyl groups. In this study we concentrate on the carbonyl groups, which cause the most apparent changes in the IR-spectra. Ketones, aldehydes, carboxylic acids, and esters contain the carbonyl group (C=O) and absorb IR-radiation in the wavenumber region 1870–1540 cm^{-1}. The carbonyl absorption band's constant position, high intensity, and freedom from interfering bands make it an excellent candidate to follow the progress of photodegradation.[25]

Carbonyl index (CI) is calculated as a measure of the progress of photodegradation. The CI is defined, in this case, as the ratio of the absorbances of the carbonyl band maximum and the reference band. The reference bands used are the CH_3 rocking band at 972 cm^{-1} for PP (equation 4) and the symmetric CH_2 stretching band at 2851 cm^{-1} for PS (equation 5):

$$\mathrm{CI_{PP}} = \frac{\mathrm{Abs}(1713\ \mathrm{cm}^{-1})}{\mathrm{Abs}(972\ \mathrm{cm}^{-1})} \tag{4}$$

$$\mathrm{CI_{PS}} = \frac{\mathrm{Abs}(1726\ \mathrm{cm}^{-1})}{\mathrm{Abs}(2851\ \mathrm{cm}^{-1})} \qquad (5)$$

Linear baseline corrections are applied to all measured absorbances, since the baselines shifted during photodegradation. The baseline correction regions are listed in Table 1.

Table 1. Linear baseline correction for the PP and PS samples.

Polymer	Absorption band [cm^{-1}]	Baseline correction [cm^{-1}]
PP	972	1070–926
	1713	1825–1531
PS	2851	2876–2820
	1726	1840–1630

FTIR tests show a totally different behaviour between these two materials than rheology. In the case of PP the changes become visible roughly at the same time as in rheology, between 256 h and 512 h (Figure 7). In the case of PS (Figure 8), the changes are small compared to PP, and do not become clearly visible before 1024 h. The CI of PP starts rising rapidly after 256 h so that the 2048 h sample has almost 40 times higher CI than the 0 h sample (Figure 9). The rise in the CI of PS is smaller and more linear compared to PP. The first signs of degradation are visible around 256 h of irradiation, where the CI has risen 10% from the 0 h sample. At 512 h the rise is 22%, at 1024 h 48%, and at 2048 h 240%. Among these two materials, the FTIR results are more consistent in PS. The variation in the surface of PP is estimated to be a material related property which makes the early detection of photodegradation difficult with FTIR.

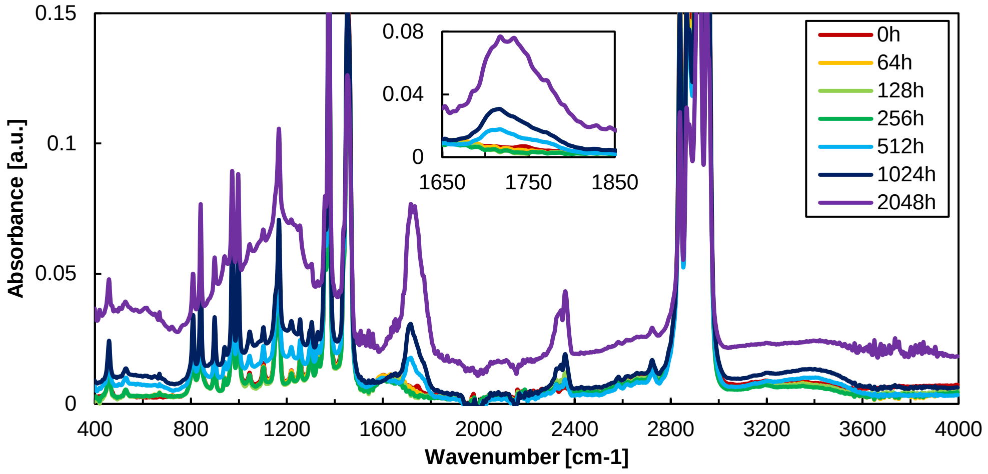

Figure 7. FTIR curve of the PP samples.

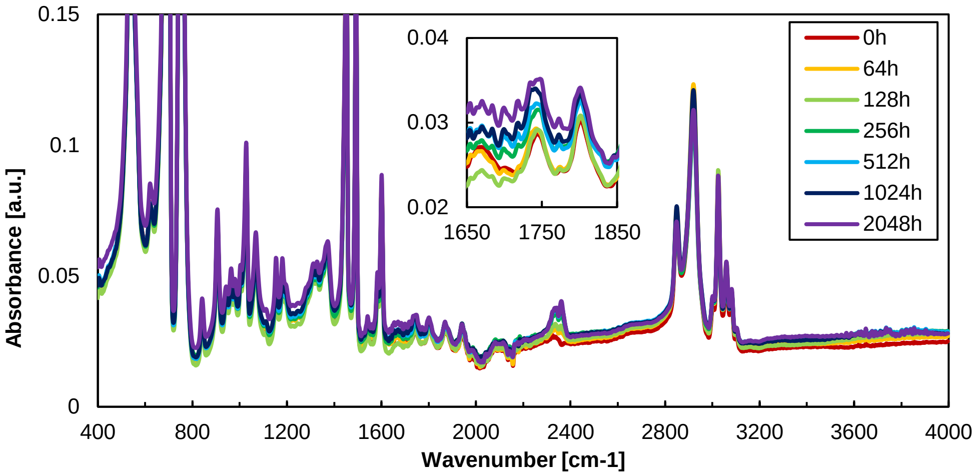

Figure 8. FTIR curve of the PS samples.

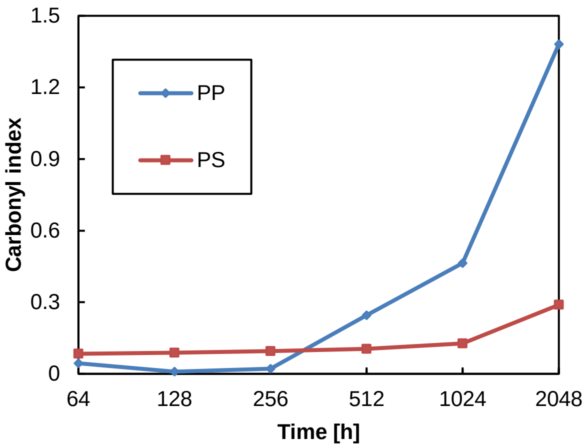

Figure 9. Carbonyl index of the PP and PS samples.

Conclusions

In the case of PP, rheology and FTIR were determined to be equally efficient methods in detecting the early signs of photodegradation, observable after 256 h of UV irradiation. The photodegradation mechanism of PS differs from PP so that the changes in PS can be seen much earlier in rheology than in FTIR. The first signs of degradation were clearly visible in rheology after 64 h of irradiation but the FTIR measurements did not show any changes before 256 h and no significant changes before 1024 h of ageing. This result is important because FTIR is the most commonly used method to estimate the first signs of photodegradation. The use of rheology could improve the detection of photodegradation in many cases, including situations where the surface is nonhomogeneous, dirty, or flaky. In addition, rheology could be better utilized in samples like textiles or fibers where FTIR has limitations.

Chain scission reactions were dominant over crosslinking which could be seen as reduced viscosity for both materials. The curves of the Cole-Cole-plots were almost perfectly circular arcs as suggested by theory, which provided a good basis for the relative molecular weight estimations. These results were consistent with Carreau-Yasuda estimated molecular weights

It is important to notice that rheology reflects the changes in the whole sample whereas ATR-FTIR shows only the chemical changes very near the material surface. This is a clear advantage of rheology but it is also limited by the sample size requirements. Even though it is possible to prepare samples from complex objects to be measured with rheology, this would be too time-consuming to compete with FTIR. A typical rheological measurement takes only a few minutes but sample preparation can multiply the time needed. Nevertheless, the results show that rheological measurements have the potential to replace FTIR in certain situations in the study of UV degradation, essentially in the early detection of degradation.

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Graphical abstract