

Man-made fibres from polypropylene to works of art

Thea van Oosten, Ineke Joosten and Luc Megens

Abstract While the potential of man-made fibres was realised when the first completely synthetic polymers were developed in the early part of the 20th century, many of these materials were not widely used until the 1960s and 1970s. From the early 1960s, polypropylene (PP) became increasingly common, due to the new polymerisation catalysts developed by Ziegler and Natta in 1954. PP possesses excellent properties that make it well suited to use as a fibre; however, it is also prone to oxidative degradation, accelerated by light, particularly in the ultraviolet (UV) region of the spectrum. A book published in 1962, entitled *Welche Chemiefaser Ist Das?* ('Which Synthetic Fibre is it?'), contains 126 samples of reference fibres, including polyester, polyamide, polyethylene, polypropylene and polyurethanes (Driesch 1962). At the time of writing this paper, all fibres in the book have been aged naturally for 43 years; some of them are discoloured and others have degraded entirely. The aim of this study is to investigate changes that may have occurred in the structure of the PP polymer in these reference samples and in PP fibres from two works of art and a relining fabric. Fourier transform infrared (FTIR) spectroscopy, microscopy and scanning electron microscopy (SEM) were used.

The first of the works of art, 'Fête II', is a wall tapestry constructed from PP and PP/polyethylene (PE) copolymer fibres. It has hung for more than 34 years on open display and the component fibres exhibit degradation. The second piece, 'The Knot', has suffered damage due to both display conditions and conservation treatments; freezing, as a measure against possible insect infestation, resulted in the embrittlement of some of the white fibres. The relining fabric was heavily degraded. FTIR analysis of these fibres identified them as isotactic PP. While the normal version of the polymer can withstand temperatures of $-30\text{ }^{\circ}\text{C}$, the isotactic form becomes brittle at $-20\text{ }^{\circ}\text{C}$ when under stress.

Keywords: polypropylene, synthetic fibres, freezing, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM)

Introduction

The work in this paper is based around a book published in 1962 entitled *Welche Chemiefaser Ist Das?* ('Which Synthetic Fibre is it?'), describing the history, chemistry, microscopic examination, manufacturing processes, applications and trade names of synthetic fibres (Driesch 1962). In addition to this information, the book contains 126 reference samples of these fibres, including polyester (PET), polyamide (PA), polyethylene (PE), polypropylene (PP) and polyurethanes (PUR) (Fig. 1). At the time of writing this paper, the fibres have been aged naturally for 43 years; some of them are discoloured and others have degraded entirely.

In addition to the investigation of the fibres in this book, the research also focused on the degradation phenomena observed in PP fibres found in two works of art, 'Fête II' and 'The Knot', and on PP fabric used for the cold relining of paintings in the 1970s. The first of these works of art is the wall tapestry 'Fête II', made from PP rope by Will Fruytier, a Dutch designer, in 1969. This work was acquired by the University of Nijmegen, the Netherlands, in 1971. The tapestry has been exhibited for more than 34 years in the hall of the university and white fibres within it are particularly degraded and brittle, making the work look messy (Fig. 2).



Figure 1 *Welche Chemiefaser Ist Das?* (Driesch 1962) (Plate 29 in the colour plate section).

The second item is a tapestry made from natural fibres entitled 'The Knot'. It was made by the artist Herman Scholten in 1967 and acquired by the Rijksdienst Beeldende Kunst (RBK) (now the Netherlands Institute for Cultural Heritage (Instituut Collectie Nederland/ ICN)) in 1968. The history of

the work is not known. In 2001, the tapestry was suspected to be infested with moths and was put in a freezer at $-20\text{ }^{\circ}\text{C}$ for three weeks as a remedial measure. Natural fibres withstand this treatment without damage, but in this item white, opaque fibres, which were only present in a rather small area of the work, became embrittled (Fig. 3). It was not previously



Figure 2 'Fête II' (Will Fruytier, 1969): white fibres (Plate 30 in the colour plate section).



Figure 3 'The Knot' (Herman Scholten, 1968): degraded area of tapestry (Plate 31 in the colour plate section).

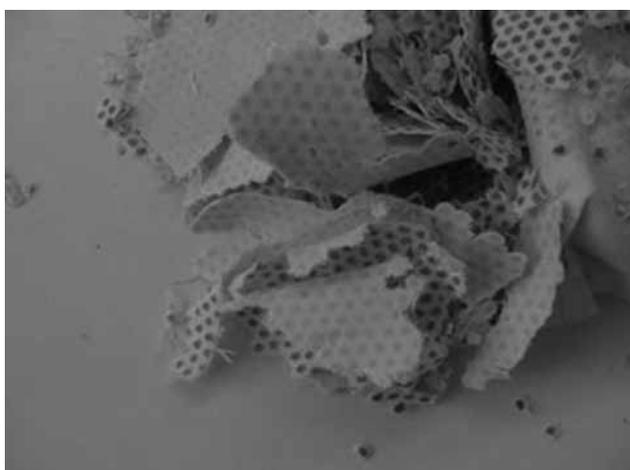


Figure 4 Relining fabric (1975) (Plate 32 in the colour plate section).

known that a small proportion of the fibres in the carpet were synthetic.

The third item studied is a relining fabric, which was used for the nap-bonded cold lining of a painting in 1975 at the Central Research Laboratory (now part of ICN). According to the relining method, the linen of the painting was pre-treated with diacetone-alcohol (4-hydroxy-4-methyl-pentan-2-one) and water, then dried on a vacuum table followed by the application of Plextol B 500, an acrylic methacrylate copolymer emulsion adhesive (Mehra 1975). The relining has become extremely brittle and is partly pulverised (Fig. 4).

Microscopy, scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy were used to compare the reference fibres from *Welche Chemiefaser Ist Das?* to the degraded fibres from the works of art and the relining fabric. FTIR analysis allows the composition and the degradation-related molecular changes of the samples to be studied. Birefringence colours, observed through polarised light microscopy (PLM), relate to variations in the crystallinity of the fibres, while SEM permits the examination of the fibre surfaces.

Polypropylene

The history of man-made fibres began at the end of the 19th century with the first semi-synthetic or regenerated materials (van Oosten 2002) and although the first completely synthetic polymers were developed in the early 20th century, many fibres that are now in common use were not fully exploited until the 1960s and 1970s. Currently, one of the most widely used fibres is polypropylene. The first commercially viable form of PP was developed in 1954 by the chemists Natta and Ziegler by using special catalysts (Gordon Cook 1993). Several different polymerisation methods can be used to produce PP, but all rely on exposing the propylene monomer to high temperatures and pressures in the presence of an active metal catalyst (Fig. 5). By selecting particular catalysts and polymerisation methods, the molecular configuration of the polymer can be directed to one of three forms: atactic, isotactic or syndiotactic (Fig. 6).

Atactic polymers are characterised by their tacky texture, amorphous behaviour and low molecular weights. Where present they act as a plasticiser by reducing the overall crystallinity of the PP. From a commercial viewpoint, isotactic PP is the most important form of the polymer. In comparison to the atactic and syndiotactic forms, isotactic PP has the greatest degree of stereo-regularity; as a result, a higher degree of crystallinity is achieved. Many of the mechanical properties and processing characteristics of PP are determined by the level of isotacticity and thus crystallinity.

The useful properties of the polymer, combined with its comparatively low price, make it suitable for a wide range of applications. PP is the lightest of all man-made fibres (0.91 g/cm^3) and has the lowest moisture absorption. Dirt will not penetrate the fibre and can easily be removed from the surface. Polypropylene fibres have the same tensile strength, wet or dry, and are also highly resistant to both acids and alkalis and to most organic solvents. The fibre does not rot and is not readily attacked by micro-organisms or moulds.

Production process

Most PP fibres are made by extruding the liquid material through the holes of a die plate, followed by spinning and stretching. The slit film method, however, in which the polymer is extruded through a small slit, was also used from the start of PP production. Slit film tape yarns were used principally in carpet backing and industrial sackings. Fibrillated yarns were developed in the 1970s. Nowadays, PP can be found as monofilaments, split or slit films, as either multifilament or staple forms. The polymer is usually pigmented before extrusion.

Modern PP comes in many varieties, ranging from tough rigid materials for outdoor furniture and car parts to soft, flexible fibres for clothing and babies' nappies. Some have good heat resistance, making them suitable for microwave food containers, while others melt easily and can be used for heat-sealable food packaging. Some are as clear as glass and others are completely opaque. Through research and development, the variety of materials available is increasing and polypropylenes are steadily replacing other polymers and traditional materials in many applications.

Degradation of polypropylene

The usefulness of polypropylene depends on the retention of its useful properties during a prolonged service life. Under mild conditions, unstabilised PP will retain these qualities for long periods of time. In most applications, however, exposure to heat and light will occur, accelerating oxidative degradation that results in a decrease in elastic properties, loss of flexibility, development of surface cracks and discoloration.

Photo-oxidation

Polypropylene readily suffers photo-oxidation, resulting in embrittlement, darkening and a decrease in molecular weight. It is considered that the induction period for these reactions represents the time necessary for the build-up of a sufficiently high concentration of peroxides, which subsequently decompose by a free radical mode and cause rapid oxidation (van Oosten and Aten 1996). The length of the induction period and the rate of subsequent oxidation depend upon the availability of oxygen. The induction time is inversely proportional to the square root of the oxygen pressure, the maximum rate of absorption increasing directly with the pressure.

Increasing the specimen thickness to the point where diffusion controls the availability of oxygen will prolong the apparent induction period. The presence of an antioxidant also prolongs this period by an amount directly proportional to its concentration within the polymer. An increase in temperature reduces induction periods and also increases the maximum oxidation rates. Both these functions give linear Arrhenius plots and have been used to determine apparent activation energies for the initiation and propagation stages of oxidation.

To retard oxidation and prolong service life, antioxidants and light stabilisers are normally added. These can be incorporated using any of the conventional thermoplastic compoun-

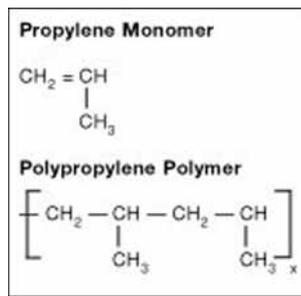


Figure 5 Monomer and polymer structure of polypropylene.

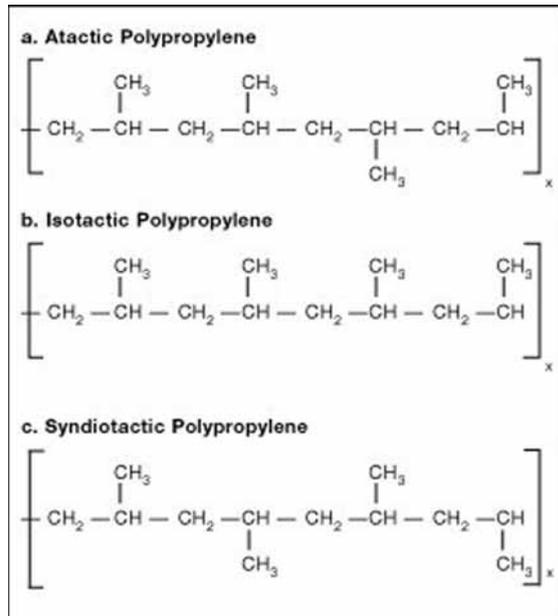


Figure 6 Three types of polypropylene.

ding techniques. Pigments are the most effective UV absorbers, however, and a concentration of 5% of various organic and inorganic pigments has been found to restrict the degradation of PP to surface oxidation, thus increasing the time to failure. It has been demonstrated that channel black and furnace black also act as mild antioxidants for PP. Their effectiveness increases with concentration and there is a correlation with the concentration of surface groups. But they have a deleterious effect on mechanical properties at concentrations greater than 5% and at this level there are no efficient stabilisers at processing temperatures so additional antioxidants may be required (Davis and Sims 1986).

Thermal degradation

Polypropylene tends to be stable to heat in the absence of oxygen; high temperatures are necessary to cause any significant decomposition. The activation energy, calculated from decomposition rates, is close to the value of 66.2 kcal/mol observed as the bond energy of a C-C single bond.

Photolytic oxidation

Although thermal oxidation at low temperatures is negligible, exposure to UV radiation in the presence of air can initiate

chain scission, cross-linking and the formation of polar groups such as peroxides, acids, ketones and aldehydes.

Catalysed oxidation

The presence of metallic contaminants such as copper, copper compounds or Ziegler catalysts accelerates the thermal oxidation by catalysing the breakdown of hydroperoxides, producing a much higher concentration of deleterious radicals in the polymer.

Reactive stability

The initiation process of reaction is believed to begin with the 'weak bonds' and structural imperfections (Tennent 1998). The weakest bonds present in PP are those between carbon and hydrogen. Atactic PP is slightly inferior to isotactic PP in its resistance to oxidation at 140 °C. The isotactic configuration is sterically favourable for the interaction of a peroxide radical on a tertiary carbon atom with an adjacent tertiary carbon atom on the same chain to form a hydroperoxide and leave a hydrocarbon radical at the attacked site. This hydrocarbon radical then reacts with molecular oxygen to give a peroxy radical which can attack the next tertiary carbon atom along the chain, the process repeating zipper fashion to leave hydroperoxide groups on alternate carbon atoms.

Other chemicals and solvents

Polypropylene is highly resistant to chemical attack from most solvents and chemicals in very harsh environments. Contact with certain chemicals, however, such as liquid hydrocarbons, chlorinated chemicals and strong oxidising acids, can cause surface crazing and the swelling of the material. In general, PP is not susceptible to environmental stress cracking and it can be exposed under load in the toughest conditions.

Analytical research

Fourier transform infrared spectroscopy (FTIR)

To verify chemical composition and study molecular changes, FTIR spectra of all 126 fibres in the book and the fibres of the two works of art and the relining material were recorded. Spectra were recorded using a PerkinElmer Spectrum 1000 FTIR spectrometer combined with a Golden Gate single reflection diamond ATR unit (sampling area 0.6 mm²), over the range 4,000–600 cm⁻¹, with 40 scans at a resolution of 4 cm⁻¹.

Polarised light microscopy (PLM)

The fibres were examined at 100 times magnification by PLM using a Zeiss Axioplan 2 imaging microscope equipped with an AxioCam MRC digital camera (1388 × 1040 pixels).

Scanning electron microscopy (SEM)

The samples were also examined by SEM, using a JEOL 5910 LV. The technique was used to study the surfaces of the fibres and to detect any deterioration phenomena. To avoid surface charging, the material was coated with gold using a JEOL JFC-1200 fine coater. The SEM was operated at an accelerating voltage of 2 kv.

Results and conclusion

FTIR

The infrared (IR) spectra of the three polypropylene samples from the book showed only isotactic carbon-hydrogen absorptions due to the backbone of the PP structure; no carbonyl absorption was present. It can be concluded that the PP fibres in the book are in perfect condition, probably due to the fact that they were never subjected to daylight. The book had been standing in the library, untouched, for more than 40 years. The IR spectra of the fibres from the tapestry 'Fête II' showed a carbonyl (C=O) absorption in addition to the carbon-hydrogen absorptions, indicating that degradation of the polymer has occurred within the timespan of 34 years. IR spectra of the white and blue fibres from this work showed the presence of a polypropylene/polyethylene copolymer, while the black- and orange-coloured fibres contained only polypropylene.

The spectra of the yellowed white fibres from 'The Knot' showed carbonyl (C=O) and C-OH absorptions as well as the expected carbon-hydrogen absorption of PP. Due to the oxidation of polypropylene, degradation products were formed and moisture absorption had occurred. This tapestry had then been put in a freezer at -20 °C for three weeks to prevent insect damage and therefore the C-OH absorptions were noticed. The IR spectrum of the relining fabric showed absorption bands of isotactic polypropylene. Carbonyl and water absorption bands are also present, indicating that the fibre is degraded and that oxidation has taken place.

PLM

The fibres from the artworks clearly show areas with varying birefringence colours. In addition, many cracks and tears are visible. The birefringence colours around a crack in a white fibre from 'Fête II' differ from those in the main body of the fibre (Fig. 7).

SEM

The surfaces of the three polypropylene fibres from the book are either smooth or generally smooth with striations running along the length of the fibre. Four samples from the tapestry 'Fête II' were examined. The white, blue and yellow fibres have a rectangular cross-sectional shape and appear to be very brittle. The surfaces show large cracks running parallel and perpendicular to the fibre axis. On a smaller scale, cracks running

perpendicular to the fibre axis are also seen in the middle of the fibre (Fig. 8). The black fibres appear to be degrading differently from the others – instead of cracking, the surface seems to be flaking off (Fig. 9).

The fibres of the tapestry ‘The Knot’ are rectangular in cross-section. There appears to be some degree of defibrillation at the edges of the fibres. Cracks can be seen running parallel to the length of the fibres and, in the surface striations, small cracks perpendicular to the fibre are visible. The relining material seems to be made up of short staple length fibres,

some of which are cracked (Fig. 10). The results of the FTIR analyses, visual observations and SEM images of the fibres are summarised in Table 1.

Conclusions

The three PP fibres from the book are all in good condition – neither degradation nor yellowing was observed, which was

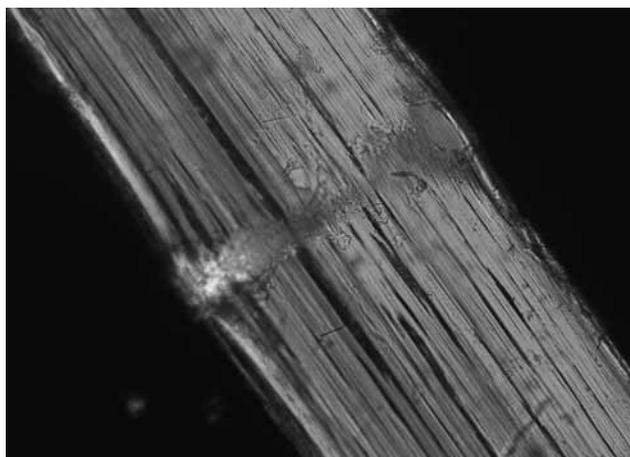


Figure 7 Polarisation microscope image of white fibre of ‘Fête II’ (100×) (Plate 33 in the colour plate section).

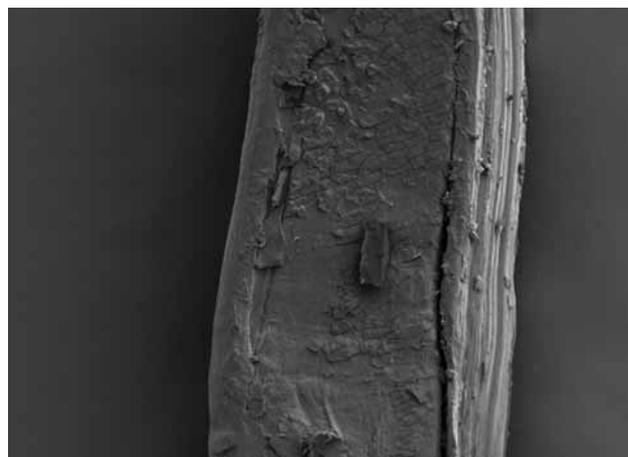


Figure 9 Secondary electron image of black fibre of ‘Fête II’.

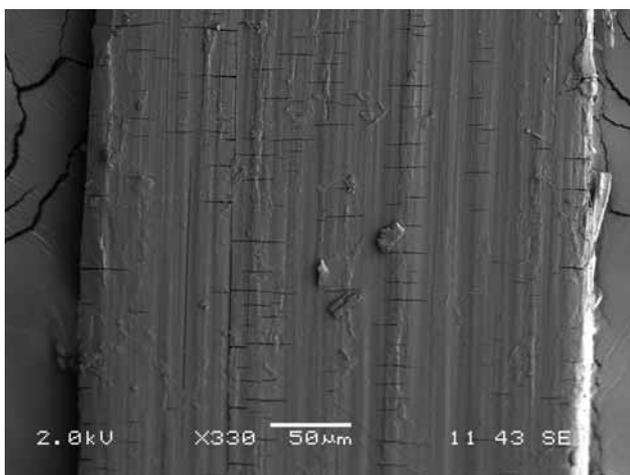


Figure 8 Secondary electron image of white fibre of ‘Fête II’.

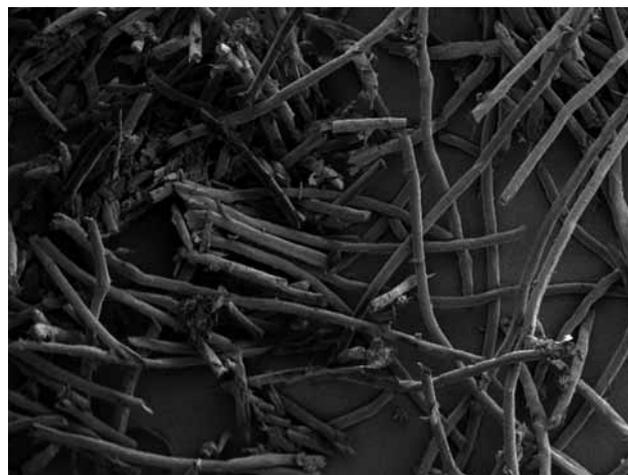


Figure 10 Secondary electron image from relining fabric.

Table 1 Visual examination of fibres and FTIR and SEM results.

| Sample | Polypropylene isotactic | Polyethylene | Carbonyl C=O | C-OH absorptions | Fibre or film | Yellowed/ brittle? | SEM |
|--------------------------|-------------------------|--------------|--------------|------------------|---------------|-----------------------|--------------------------------------|
| PP (book) | + | – | – | – | fibre | * | smooth surface |
| PP (book) | + | – | – | – | fibre | * | grooves |
| PP (book) | + | – | – | – | fibre | * | grooves |
| Fête II, white | + | + | + | – | film | brittle, not yellowed | cracks |
| Fête II, blue | + | + | + | – | film | brittle, not yellowed | cracks |
| Fête II, yellow | + | – | +/- | – | film | brittle | cracks |
| Fête II, black | + | – | +/- | – | film | brittle | surface flakes off |
| The Knot (yellowed area) | + | – | + | + | film | brittle, yellowed | cracks and fibres peel from the side |
| Relining fabric | + | – | + | + | fibre | brittle/not yellowed | cracks |

+ present; +/- small amount present; – not present; * no changes

to be expected as the PP fibres had been kept in the dark. In the tapestries 'Fête II' and 'The Knot', however, exposure to UV radiation/daylight and the freezer treatment have caused the serious degradation seen by yellowing and embrittlement of the PP. It is known that normal extruded PP can withstand temperatures of -30°C , but isotactic PP under stress becomes brittle at -20°C . The pulverised relining fabric was probably degraded by the solvent (diacetone-alcohol) that was not allowed to fully evaporate from the old linen before the PP relining fabric with the adhesive was applied.

Overall, it can be stated that photo-oxidation has occurred in all cases where exposure to UV radiation or daylight occurred; although it is known that this can happen, it was not expected for these works of art over a timescale of only 40 years. The other degradation phenomenon, due to freezing, was not anticipated, as PP was not supposed to be present in a tapestry believed to be constructed from natural fibres. This highlights the importance of fully understanding the composition of an object before conservation procedures are carried out.

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