New analytical methods for evaluating the degradation of polymeric materials

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1. INTRODUCTION

Rubber and plastics, paint films and allied polymer materials have many advantages over other materials, notably low weight, low cost and good formability. They are therefore increasingly used in place of metals and natural materials such as wood, leather or clay in a significant part of most home furnishings, domestic electrical goods and motor vehicles. However, they also have a drawback - compared with other materials, polymers are susceptible to degradation under the action of environmental factors like heat, light and water.

The degradation of a polymer material generally leads to a decline in physicochemical properties as both the chemical structure of the polymer itself and the chemical composition of the material change. Research on the degradation of polymer materials in this way has a long history: the underlying degradative mechanisms have largely been elucidated and much work has been done on individual polymers. In practice, however, the relationship between decline in properties and the complex changes in chemical structure that occur in the course of degradation are not understood in any detail, and the actual decline in properties must still be evaluated by measuring the properties themselves.

Nevertheless, almost all methods of polymer analysis [1] can be applied to the evaluation of changes in chemical structure and chemical composition. The methods most commonly used for studying the degradation of polymer materials are perhaps attenuated total reflection-infrared (ATR-IR) spectrometry, which gives a wealth of information on chemical structure including surface composition and state, and X-ray photoelectron spectrometry (XPS), which gives information on surface functional groups. Since the degradation of polymer materials often commences at the surface of the material, these methods can identify the initial changes in chemical structure, allowing evaluation of short-term degradation. In practice, however, surface fouling can interfere with the examination of parts or products, and surface information must be supplemented with information on the interior. Moreover, degradation in the interior may differ from surface degradation.

The techniques of “oblique cutting-IR” and “derivatisation-XMA (X-ray microanalysis)” are useful in this situation. The former was designed for analysis in the depth direction in polymer materials of thickness of the order of several tens of μm, as in coatings and plastic film, and a depth resolution of 1 μm was attained. The latter was designed to overcome the problem of low sensitivity, a weakness of IR methods, and permits examination of the distribution of trace functional groups of 0.1% order that form in polymer materials: the spatial resolution is around 3 μm and the limit of detection is ca. 0.05%. This article reviews the principles and performance of the two techniques, along with some examples of their application to evaluation of degradation in polymer materials and analysis of degradation mechanism.

2. OBLIQUE CUTTING-IR ANALYSIS

2.1 Principle

The principle of the method is shown schematically in Figure 1. The specimen is cut obliquely with a microtome...
at an angle of several degrees to prepare slices several
μm thick; a line analysis proceeding from the surface into
the interior is made by micro-IR examination of the slices
or cut section. The intention here is to enlarge the depth-
profile information by a factor of 50 or more. The method
allows analysis of the individual layers in a thin multilayer
film such as a paint film, and analysis of composition
profile near the surface of a resin material.

2.2 Performance

The method is characterised by high depth resolution.
The theoretical depth resolution was estimated as
2.4 μm for a slice thickness (t) of 2 μm, an infrared slit
width (L) of 25 μm and cutting angle (θ) of 1°. When
the interface in an actual resin bilayer in which epoxy
resin was bonded to PET was examined under the same
conditions (Figure 2), the observed thickness resolution
was 2.4 μm, agreeing with theory. Although thickness
resolution increases if the slice thickness or infrared slit
width is reduced, the sensitivity of infrared absorption
then falls. The cutting and measurement conditions must
thus be chosen to suit the purpose of measurement.

2.3 Applications

The utility of the method was confirmed in application to
analysis of the degradation of coatings in weatherability
tests, evaluation of the level of degradation of the lower
layer in a bilayer coating, and analysis of the behaviour
of plasticiser in polyvinyl chloride (PVC).

1) Analysis of the degradation of coatings in
weatherability tests

The Sunshine Weather-O-Meter (SWOM) has long
been used for the accelerated weatherability testing of
plastics and coatings but the results of evaluation are
considered inconsistent with outdoor exposure, and tests
have more recently used a xenon light source or other
source closer to sunlight. We compared the degradation
profiles of a white amino-alkyd paint film in the depth
direction (Figure 3) in tests by three different methods:
outdoor exposure (2 years), SWOM (6 months) and a
new accelerated weatherability test using a source close
to sunlight (6 months). The coatings degraded in the
three tests had comparable gloss retention rates, and the
degree of degradation evaluated from the surface was
assessed as equal. The vertical axis shows the percentage
of residual benzene rings, representing degradation of
alkyd resin, and the percentage of residual triazine rings,
representing degradation of amino-resin.

The following is clear from Figure 3.
1. Although the coatings have a similar decrease in
surface gloss, the depth of degradation is large in
the SWOM test and small in outdoor exposure.
2. The pattern of disappearance of benzene rings and
triazine rings is different in SWOM and outdoor
exposure tests.
3. Degradation in the new accelerated weatherability test with a light source approximated to sunlight is similar to that in outdoor exposure. Such results are one of the reasons evaluation by SWOM does not match outdoor evaluation and suggest that matching the light source to sunlight is a prerequisite for accelerated weatherability testing. Since it explores the composition profile in the depth direction, oblique cutting-IR can thus be applied to the evaluation of weatherability tests.

2) Evaluation of degree of degradation of the lower layer in bilayer coatings

Oblique cutting-IR can provide information on depth profiles near interfaces as well as in the vicinity of the surface. We examined the degradation of the lower layer in a bilayer coating degraded for 4000 hours by SWOM (Figure 4). The top-coat used was a blue amino-alkyd coating, while the undercoat was an anionic electrodeposition coating. The vertical axis in the graph is the absorbance of the oxidation product (1740 cm⁻¹) formed by degradation of both coatings.

The following was clear from Figure 4.
1. Degradation proceeds from the surface in the upper film in SWOM testing.
2. The lower film itself undergoes oxidative degradation by the light transmitted through the upper film.
3. The lower film is already degraded somewhat by the baking process when the coating is new.

Thus, when a coating of high optical transmission is used for the top-coat, or when the upper film is thin, the undercoat film may degrade, and since this can result in film peeling, evaluation of durability in this way seems necessary when a coating is being designed.

3) Analysis of plasticiser migration from flexible PVC [3]

Although the use of PVC has been declining because of environmental problems, it is now being re-evaluated on account of its low utilisation of fossil fuels. We examined the depth profile of plasticiser (Figure 5) when two kinds of PVC with different stabilisers were tested by heating (120°C, 100 hours), SWOM (600 hours) and outdoor exposure (2 years). The PVC-A used incorporated dioctyl phthalate (DOP) as plasticiser and dibutyl tin dilaurate (DBTDL) as stabiliser; PVC-B incorporated DOP as plasticiser and dibutyl tin maleate (DBTM)/DBTDL as stabiliser. The vertical axis in the graph represents the percentage of DOP remaining, found from the absorption due to ester groups (1740 cm⁻¹).

The following is clear from Figure 5.
1. The behaviour of DOP in the heating test differs with the stabiliser incorporated in the PVC: PVC-A gives a diffusion rate-determined migration profile, while PVC-B gives a volatilisation rate-determined profile.
2. PVC-B gives a volatilisation rate-determined profile in the heating test but a diffusion-rate determined profile in SWOM and outdoor exposure.
3. The results in (2) are similar to those from immersion for 600 hours in water at 60°C.

It follows from (3) that the diffusion rate-determined profile in PVC-B in SWOM and outdoor exposure testing is attributable to extraction of plasticiser by water. Other analyses showed that degradation products of DBTM accumulate near the surface in the heating test on PVC-B, preventing volatilisation of plasticiser. It is thus possible to evaluate the migration of additives of relatively high formula content by oblique cutting-IR spectrometry.

4) Analysis of degradation in chloroprene rubber

Rubber products are difficult to cut because of their pliability but they can be cut when frozen with liquid nitrogen. We exposed chloroprene rubber to heat and ozone and compared the respective patterns of degradation (Figure 6). The thermal degradation test ran.
for 168 hours at 100°C, without the specimen extended; the ozone degradation test ran for 168 hours at 40°C at an ozone concentration of 50 pphm (parts per hundred million). The vertical axis in the graph is the absorbance of the oxidation products (1600 cm⁻¹) that form as the rubber degrades.

The following was clear from Figure 6.

1. Thermal degradation proceeds more or less uniformly from the surface through to the interior.
2. The ozone test produces degradation to a depth of about 40 μm below the surface; beyond this point the rubber remains completely free of degradation.

Since the degradation depth profile thus differs with the test conditions, it should be possible to deduce which factors are responsible when examining the degradation profile of rubbers exposed in the market environment.

As illustrated by these examples, we were able to confirm that the oblique cutting-IR technique allows evaluation of weatherability test methods, evaluation of degradation at the interface in resin bilayers, and analysis of additive migration behaviour, making it useful for evaluating degradation and analysing the degradation mechanism in polymer materials.

3. DERIVATISATION-XMA

3.1 Principle

The principle of the derivatisation-XMA method [4] is shown schematically in Figure 7. The functional groups in the polymer material are chemically modified (derivatised) with a reagent that contains a labelling element highly sensitive to XMA and highly selective for functional groups; the distribution of the labelling element is then determined by XMA to examine the distribution of the original functional groups. Sensitivity is boosted by derivatisation and resolution is boosted by the use of XMA. Functional groups are derivatised under appropriate conditions (detailed in 3.4 below), e.g. reaction with bromine if the functional groups are double bonds formed by degradation of PVC as shown by the example at the top of Figure 7.

3.2 Performance

Spatial resolution and detection sensitivity were examined as basic performance parameters in the analysis of polymer materials by XMA. The spatial resolution was found by line analysis (Figure 8) of the chlorine atoms or bromine atoms at the resin bilayer interface when a conventional epoxy adhesive was bonded to PVC or brominated epoxy resin (Br-epoxy). The vertical axis in the diagram is the X-ray intensity in XMA determination of Cl or Br atoms in PVC or Br-epoxy. The spatial resolution in PVC was 2.4 μm and the resolution in hard Br-epoxy was 1.8 μm, showing that a spatial resolution of better than ca. 3 μm is available.

The detection sensitivity was determined by mixing Br-epoxy with conventional epoxy resin to prepare resins with different concentrations of bromine and then analysing the Br atoms in the resin by XMA. The detection
sensitivity was found to be about 0.05% \((S/N \text{ ratio} = 2)\). Thus, compared with the preceding oblique cutting-IR method, the spatial resolution was at least 4 times higher and the detection sensitivity at least 10 times greater.

### 3.3 Reliability

To confirm the reliability of the derivatisation-XMA method, the depth profile of double bonds in PVC sheet subjected to degradation by exposure to amine vapour was determined by oblique cutting-IR and derivatisation-XMA (Figure 9). The vertical axis in the upper diagram represents the absorbance of double bonds \((1670 \text{ cm}^{-1})\) formed in the PVC; the vertical axis in the lower diagram represents the concentration of Br atoms after derivatisation of the double bonds with bromine.

In PVC sheet heated 5 hours at 110°C a large number of double bonds was formed at the surface exposed to amine, the number tending to decrease with depth. These observations were closely consistent with the results from oblique cutting-IR analysis. It was hence confirmed that the distribution of double bonds could be reliably determined by this method.

In the case of PVC sheet thermally degraded under the milder conditions of 20 hours at 80°C, oblique cutting-IR investigation was completely unable to identify the pattern of degradation owing to a large dispersion in the data. However, derivatisation-XMA clearly identified the depth profile of double bonds and generated a far more stable profile than oblique cutting-IR. Note in this connection that the sensitivity of the XMA method for detection of double bonds was around 30 times that of oblique cutting-IR.

### 3.4 Derivatisation conditions

Since derivatisation is the key to the whole analysis, the optimum conditions for derivatisation were explored [5-9]. Five functional groups were chosen: the double bond, carboxyl group, keto group and hydroxyl group important in studies of polymer degradation; and the epoxy group important in studies of the hardening process. The conditions affording the highest conversion and selectivity were determined for each functional group. The derivatisation reagents used contained the chlorine or bromine atom giving high sensitivity in XMA. The optimum conditions obtained are listed in Table 1.

### 3.5 Applications

The utility of the method was confirmed in application to analysis of degradation in flexible PVC sheet backed with polyurethane foam (PUF) as used for automotive interior trim, and polyethylene (PE) sheet exposed outdoors.

1) Analysis of degradation of flexible PVC sheet backed with PUF (automotive interior trim material) [10]

Although less use has recently been made of flexible PVC sheet backed with PUF because of environmental problems, it was formerly much used for automotive interior trim. We examined the depth profile of double bonds forming in the PVC (Figure 10) when the sheet was subjected to heat resistance testing (110°C, 400 hours). The flexible PVC sheet was material made by powder slush moulding (powder particle size ca. 100 μm).

The following was clear from Figure 10 and allied experiments.

1. Double bonds do not form at the surface in the PVC sheet under heat resistance testing; formation of double bonds is prominent at the interface with the PUF layer.
Double bonds form owing to migration of residual amine catalyst from the PUF layer to the PVC sheet where the catalyst promotes dehydrochlorination of the PVC.

Heating PVC sheet made by powder slush moulding generates numerous double bonds at the particle boundary in the powder, and the sheet is thus susceptible to degradation at the particle boundary.

It follows that to prevent degradation of the PVC sheet the amine in the PUF must not be allowed to migrate to the PVC or else the migrating amine must be deactivated.


General purpose plastic PE sheet was exposed outdoors for 18 months and the distribution of carboxyl, keto and hydroxyl groups forming in the PE was examined at 6 month intervals (Figure 11). The vertical axes in the graphs are the concentrations of Cl or Br atoms in the PE from derivatisation of the respective functional groups under appropriate conditions.

The following was clear from Figure 11.

1. During initial exposure all functional groups began to increase proceeding from the surface, but at 12 months the concentrations of keto and hydroxyl groups increased at a depth of 200-300 μm and then progressively decreased up to a depth of around 500 μm, beyond which they remained constant.

2. At 18 months the carboxyl group concentration likewise increased in the interior as though following on from (1). A similar trend was seen on the reverse of the sheet, suggesting that the ease of diffusion of oxygen into the PE sheet contributes greatly to degradation.

3. After 18 months of exposure all functional groups decreased at the outermost surface. This phenomenon was attributed to the extraction and removal by rainwater of superficial oxidation products of reduced molecular weight.
3) Evaluation of degradation in rubber sheet exposed outdoors

Owing to the softness of rubber, it was anticipated that substantial damage by the electron beam would make XMA measurements difficult. However, some measurements were possible. Styrene-butadiene rubber (SBR) was exposed outdoors for 12 months and the distribution of double bonds and carboxyl groups in the SBR was examined at 6 month intervals (Figure 12). The vertical axes in the graphs are the concentrations of Br in the SBR after derivatisation of the respective functional groups under the appropriate conditions.

The following was clear from Figure 12.

1. The double bond concentration decreases up to a depth of ca. 200 μm from the rubber surface during outdoor exposure.
2. In the same region as double bonds decrease with outdoor exposure, carboxyl groups increase and the rubber thickness diminishes. The results suggest that the butadiene component of the rubber undergoes oxidative degradation in response to outdoor exposure; examination by the foregoing oblique cutting-IR method is needed to ascertain whether the styrene component is degraded.

As illustrated above, it was possible to analyse the degradation of flexible PVC sheet for automotive interior trim and PE sheet in outdoor exposure, and to evaluate degradation in rubber sheet subjected to outdoor exposure, confirming the usefulness of the technique for evaluating polymer degradation and analysing the mechanism of degradation.

4. CONCLUSIONS

Analysis by oblique cutting-IR and derivatisation-XMA has been reviewed. Both techniques provide information on the chemical structure of polymer materials in the direction of depth. Along with analysis by ATR-IR and XPS to obtain information on chemical structure at the surface, the new tools should be useful for evaluating degradation and elucidating degradation mechanism in polymer materials.

REFERENCES