Chapter III

Techniques and hypothesis of the techniques used for studying effect of metal salt on metal salt containing PVA films.

Ultraviolet spectrophotometry

1. Introduction

The use of ultraviolet absorption measurements as an analytical tool has been greatly extended during the past 10 years, primarily because of the rapid improvements in instrumentation. Probably the most important single advance has been that of electronic components to provide means for precise and sensitive recording to spectra.

Although UV-visible spectroscopy is a common routine analytical technique in organic chemistry it is not capable alone of completely identifying an unknown compound, requiring other information, or measurements using other techniques. Its use in polymer analysis is still more restricted, though it performs certain tasks with great efficiency. It has the advantage of using very small samples, though the preferred state is in dilute solution, and with many polymers this cannot be conveniently arranged. Modern instrumentation permits very fast analyses to be performed with good accuracy and minimal training as long

as a few simple rules relating to clean handling of the sample and all components in the optical path are carefully observed. The rapid analysis capability of the technique means that it can be adapted to make measurements online on following systems (Cambell and White, 1989).

In addition to providing information about polymer molecules, the UV-visible technique may also be of value in studying additives in polymers. Pigments and UV stabilizers are two classes of additive which depend on their response to radiation within this range to provide the very property for which they are included. In such applications the choice of additive may be guided by reference to UV-visible studies, though the technique can be used equally in a diagnostic manner to indicate the concentration of such an additive and, possibly, to identify it. It is important to realize that such compounds may be present in any com-mercial plastic presented for analysis and that the spectrum obtained may contain large contributions from relatively small amounts of additive, a hazard unlikely to be met when analyzing the product of a carefully controlled laboratory polymer preparation (Gordon, 1962).

2. Principles

The absorption of one quantum of visible or ultraviolet radiation by a molecule causes an electronic transition from one energy state to a higher energy state. In the spectral region of 200-700 nm., these transitions involve, almost entirely, the π electrons in conjugated systems. The absorption in the far ultraviolet region, wavelengths shorter than 200 nm., involve the σ bonds and π electrons in nonconjugated

double bonds. Research in the far ultraviolet region maybe vary fruitful in the analysis of polymers such as polybutadiene, polyisoprene, etc. (Gordon, 1962).

Since the absorption bands in the ultraviolet region are the result of a shift of electrons to more excited states, it seems obvious that such absorptions are not so specific for molecular structure, but rather are characteristic of the atom themselves. Hence, correlations of absorption spectra in this region with molecular structure are very suspect without other evidence to verify the conclusions made from the spectral observations alone.

3. Instrumentation

The usual light source for absorption spectrometry in the ultraviolet region is the hydrogen lamp. This grow discharge lamp emits a nearly continuous spectrum of wavelengths over the region 160-600 nm., which includes the ultraviolet region normally used for absorption measurements.

Most of the commercially available instruments today use prism optics in the monochromator. Quartz is most commonly used it give good dispersion over the region from 185 nm. to about 1300 nm.

3.1. Spectrometers

There are two basic designs of instruments, each of which has desirable and undesirable properties. The first is the single-beam, point-measuring instrument; coupled with a null-balancing bridge measuring circuit, it is unsurpassed for precise quantitative measurements. The major disadvantage is the time-consuming operation required for determining spectra rather than single wavelength values of absorption.

The double-beam recording instrument, on the other hand, is ideally suited for qualitative inspection of the spectrum, but is less precise than the single-beam instrument for quantitative use. In the double-beam recording instrument the spectrum is obtained directly in either per cent transmittance or absorbance depending on the recorder design. Compensation for atmospheric or solvent absorption is automatically made by using one beam for the reference and the other beam for the sample. The recorder plots the ratio directly. Either methods of compensation with the single-beam instrument required that both the light source and the measuring circuit be highly stable in the measurements.

3.2. Detectors

The most generally useful detector in the visible and ultraviolet regions is the photoemissive type of photoelectric cell. For the measurement of absorption spectra, where the ration of the sample that of the reference is the important quantity, the nonuniform spectral sensitivity

of the photocell is of no important except as it may require excessive slit widths and hence broaden absorption bands in same regions. Given adequate sensitivity and stability, the quality required of a photocell for spectrophotometric use is linear response with intensity of illumination.

4. Sample preparation

4.1. Solutions

Due to the fact that absorption spectra in the region of 200-700 nm. require some degree of conjugation in the molecule, many substances are relatively transparent in the ultraviolet. This allows a rather wide selection of liquids for use as solvents for materials to be studied in this region.

Among the advantages to be gained by solution work is the ease of establishing precise concentrations and therefore the ease of quantitative calculations by means of the Beer-Lambert law (Gordon, 1962).

Among the disadvantages is the limited solubility of many of the polymeric materials and the difficulties encountered with polymers containing opaque fillers such as carbon black or zinc oxide.

4.2. Films

A technique for solid materials such as polymers that offers great advantages in many cases is the use of the material as a thin film.

Advantages of the use of films are the elimination of correlation for solvent absorption and the ease of storage of samples. It is also possible to use films for a series of treatments with the initial and subsequent spectra all observed on the same specimen. One limitation of the method is the problem of reproducibly preparing films of a desired known thickness.

5. Applications to analysis

5.1. Qualitative analysis

The general interpretation of ultraviolet absorption spectra in terms of structure is difficult and often suspect. A comparison of the spectrum of the unknown with spectra of known systems using the frequency and intensity of absorption maxima, widths of absorption bands, and the changes or shifts in absorption maxima in different solvents, are valuable aids in establishing the structure.

5.2. Quantitative analysis

In order to make quantitative analyses from spectral absorption data it is necessary to have a quantitative relationship between concentration or thickness and the amount of absorbed energy. If a sample of thickness d is exposed to monochromatic radiant energy of initial intensity Io, an amount of transmitted energy of intensity I is observed on the other side.

This can also be expressed as

$$\frac{I}{I_o} = e^{-kd} \qquad \text{for solids}$$

$$\frac{I}{I_o} = e^{-\alpha cd} \qquad \text{for liquids}$$

where k is the proportionality constant for solid samples and is known as the absorption coefficient, d is the thickness of the specimen or the cell, and α is the proportionality constant for solutions and is known as the molar absorption coefficient if the concentration, c, is expressed in moles per liter. These equations express the Beer–Lambert law. Examination of the above equation reveals that for very dilute solutions the absorption is directly proportional to the concentration.

6. Application to polymers

The measurement of the conjugation length is an important application of UV–visible spectroscopy that follows directly from the theoretical analysis. One of the commonest conjugated systems is the six–

membered carbon ring, as found in benzene or as a phenyl group (a constituent in many polymer molecules). This gives a characteristic family of absorptions, though overlap with other absorptions produced by other structures on the polymer molecule may sometimes obscure it or cause unambiguous identification to be impossible. Other groups of atoms may give characteristic absorptions that may be used to establish their presence, and, if the spectrum is not cluttered with absorptions from other sources, may be used to measure the abundance of the groups in question. A group giving rise to such a characteristic absorption is known as a 'chromophore' and an example is the carbonyl group, C=O.

Another application of UV-visible spectroscopy is in the analysis of copolymer. If the two or more monomers posses characteristic absorptions that do not overlap then the relative intensities of the absorptions measured on the copolymer formed from them can be used to estimate composition. It is not important whether the absorption bands correspond to conjugated backbone structures or to pendant chromophores, merely that they are distinguishable in the copolymer absorption spectrum.

Infrared spectrophotometry

1. Introduction

The infrared absorption spectrum of a material is highly characteristic of that substance led to the development of infrared absorption spectrometry as an analytical tool. Such a spectrum is in reality a multiparameter measurement and so may give as much information as a large number of single measurements, such as density, refractive index, solubility, and the like. It is possible for two materials to have nearly the same values for the above mentioned parameters, but the chance that they will have identical fingerprints. Further advantages are that spectra are easily and quickly obtained, only small quantities of the substance are needed.

The infrared region of the spectrum most widely used for analytical work is that from 5000 to 650 cm.$^{-1}$ wavenumbers. The wave number is defined as the reciprocal of the wavelength in centimeters and the relationship between wavelength and frequency is

$$\lambda \nu = c \qquad \text{or} \qquad \nu = c / \lambda$$

where λ is the wavelength, ν is the frequency, and c is the velocity of light. Since the velocity and wavelength of light vary as they pass through different media, it is the frequency that is the more fundamental property. Further, the frequency is related to the energy of the photon by the relationship.

$$E = h\nu$$

where h is Planck's constant.

2. **Principles**

The frequencies of the absorptions of a given system are the frequencies of vibrations of the atoms within the molecule together with combinations and harmonics of these vibrations. Using the theory of harmonics oscillation, theoretical expressions can be derived for a given system of masses as an atomic weights and force constants for bond as a spring constants. An example of an idealized case will serve to illustrate the use of this theory in the calculation of absorption frequencies.

Since the atoms of an organic molecule are restricted to oscillate about their equilibrium positions by the forces of the valence bonds connecting the atoms, as a first approximation these oscillations may be considered to obey Hooke's law. If this assumption is made, then a mechanical model of the molecular group can be used in which springs replace the valence bonds, and simple masses in the ratio of the atomic weights replace the atoms. The C−H group can be approximated by two masses, m_1 and m_2, of relative weights 12 and 1, respectively, and a spring of modulus k connecting these.

The frequency of vibration of such a system in simple harmonic motion is described from Hooke's law by

$$\nu = (1/2\pi c) \, [k \, (1/m_1 + 1/m_2)]^{1/2}$$

where ν Is the frequency in cm^{-1}., c is the velocity of light, m_1 and m_2 are the masses of the atoms which are expressed as gram–atomic weights, and k is the modulus of the spring or the force constant of the valence bond. Substituting the values of π and c and the unit factors so that k is in units of 10^5 dynes/cm., from the literature, the value of k for C–H in methane in 10^5 dynes/cm. is approximately

$$\nu_{C-H} = 1307 \, [5 \, (1/12 + 1/1)]^{1/2} = 3040 \;\; cm.^{-1}$$

This calculation assumes also that the other substituents attached to the carbon atom are so heavy that they are unable to follow the vibration of the C and H atoms. An example is the chloroform molecule, $CHCl_3$. The infrared spectrum of the chloroform shows a strong absorption band at 2915 $cm.^{-1}$, which is in remarkable agreement with the calculated value considering the assumptions and approximations used (Gordon, 1962).

3. Instrumentation

3.1. Infrared light sources

The energy used in infrared absorption spectrometry is usually obtained by resistance heating of filament or rod such as silicon carbide rod. The ideal source would radiate energy according to the Planck's equation for black body radiation where the radiant energy is a function of wavelength in microns at absolute temperature. The fact that wavelength of maximum intensity is a function of temperature of source, as can be described by Wien's displacement law. This expression shows that the general infrared peak emission at room temperature occurs at maximum around 9.7 μ wavelength. Further, the over-all intensity of the source diminishes as the source temperature is reduced. Increasing the temperature greatly increases the total energy emitted, but only slightly increases the amount available to the infrared spectroscopist. This Theoretical amount of available energy is reduced further by the fact that no actual source is a true black body radiator.

3.2. Monochromators

Prisms and gratings are two means for dispersing the radiation emitted from the source.

3.2.1. Prisms

The aperture of a prism is defined as the resolving power divided by the dispersion. Obviously, prisms showing high apertures, high resolving power, and good dispersion are desirable, particularly for use in the infrared where low energies are used and numerous absorption bands need to be resolved. High dispersion simplifies the mechanical problem of precise selection of wavelengths.

The advantages in the use of prisms as the means of selecting the wavelength in monochromator are the relatively high speed of scan of wavelengths, the freedom from astigmatism and spurious lines, and availability of high quality materials. The disadvantages are the limitations of aperture and dispersion, difficulties in minimizing stray light, and nonlinear dispersion over the usable wavelength range. The alkali and alkaline earth halides, in general, are the types of materials best suited for infrared use.

3.2.2. Gratings

The general dispersion of a grating is derived from Bragg's law where the ratio of the angle of reflectance to the wavelength is a function of distance between the grating and the detector for the linear dispersion.

Among the advantages in the use of gratings are the wide spectral range possible, particularly when a series of

reflectance gratings are used, in which case the nature of the support for the grating does not limit its usefulness; the wide apertures possible since large gratings can be made; the linear dispersion and high degree of dispersion possible by fine rulings; and the freedom from stray light. Among the disadvantages are the relatively slow scanning speeds, problems in restricting the spectrum to a single order of reflectance, and the possible appearance of spurious absorption due to imperfections in the ruled lines on the grating.

3.3. Detectors

Photographic emulsions properly treated may be used to detect radiation. However, photographic techniques are not generally suitable for the usual infrared analytical procedures because the more characteristic vibration of organic molecules occur at wavelengths beyond the sensitivity of emulsions.

Recently, semiconductor detectors made of lead sulfide, lead selenide, or lead telluride have been made available. However, more sensitive devices are needed to allow the detection of the extremely small energies available at longer wavelengths. At present, evacuated thermocouples treated to absorb the radiation with high efficiency, coupled with high gain amplifiers, are widely used.

3.4. Photometers

The signal received from the detector may be measured in a number of ways. In single-beam instruments highly sensitive galvanometers have been used as directreading instruments. Usually, however, a bridge circuit is used which is balanced either manually as in point-by-point operated instruments or mechanically as in direct-recording instruments. The bridge-circuit type of balancing instrument is desirable for quantitative analysis.

The use of a single-beam instrument requires a measurement of the transmission both with the sample in the beam and without the sample so that the per cent transmission of the material under observation can be calculated as a ratio these two measurements.

There are two categories of double-beam systems presently being used:

(1) ratio-recording instruments, which measure the ratio of the amount of energy in the reference beam and the sample beam .

(2) null-point instruments, in which the differences in energy between the reference beam and the sample beam is used to actuate a servomechanism to reduce the reference to zero by manipulating a calibrated shutter in the reference beam, the position of the shutter being a measure of the percentage absorption of the sample. Both types of double beam instruments record the spectra directly in per cent

transmission or absorbance, and so obviate the need for calculating ratios and replotting the curves.

Both single-beam and double-beam methods allow the use of compensation, such as a correction for solvent absorption of solutions or correction for atmospheric absorptions. However, the double-beam instrument records the ratio directly, and, in instances where strong absorption bands occur in the reference solvent or air, the energy in both beams may be so small as to give insufficient signal to the recorder for proper function.

3.5. Fourier transform spectrometers

Interferometry was first used to investigate the otherwise inaccessible far infrared (FIR) region of the spectrum. Developments in Fourier transform spectroscopy (FTIR) have extended applications of interferometry to the whole IR region particularly for rapid sampling.

The light source is a high intensity mercury lamp or heated wire which emits an approximately continuous spectrum. The light from the source passes into the interferometer which is at the heart of the spectrometer. The essential components of the interferometer are the two mirrors, one fixed and the other moveable and the beam splitter which is set at an angle 45° to the path of the collimated beam. The beam is partially transmitted and partially reflected at the thin dielectric beam splitter. The transmitted and reflected beams are incident normal to the two mirrors and following reflection, are recombined at the beam splitter

where they produce interference effects. The beam is then passed through the sample and on to the detector. If the mirrors are located equidistant from the beam splitter or when the optical path difference is and integral number of wavelengths, the reflected beams are in phase and so produce constructive interference. Conversely when the optical path difference is an odd number of half wavelengths, destructive interference will occur. When the moveable mirror is moved axially, relative phase displacement occurs resulting in an oscillatory pattern or interferogram, which is a representation of the spectral distribution of the absorption signal, reaching the detector. The Fourier transformation is usually carried out by means of a built-in dedicated microprocessor, enabling the absorption spectrum to be produced in a relatively short time.

3.6. Raman spectrometers

The essential components of a Raman spectrometer are shown in Figure 3.1. The very low intensity of a Raman scattering necessitates the use of high intensity monochromatic light. Most spectrometers now employ laser light sources. Both grating and prism monochromators find use in Raman spectrometers. Great care is essential in setting up the instrument to ensure efficient collection of the Raman scattered light. The intensity of the scattered light is measured using very sensitive photomultiplier tubes. A photomultiplier consists of a photosensitive cathode which emits electrons when photons strike it. The electrons are accelerated by an applied electric field and cause the emission of secondary electrons in the from of a cascade by striking an assembly of dynodes. The electrical pulses are amplified and when the

spectral range is scanned the variations in pulse light constitutes the Raman spectrum. The slit settings are fixed so that there is no compensation of the instrument varies continuously with wavelength.
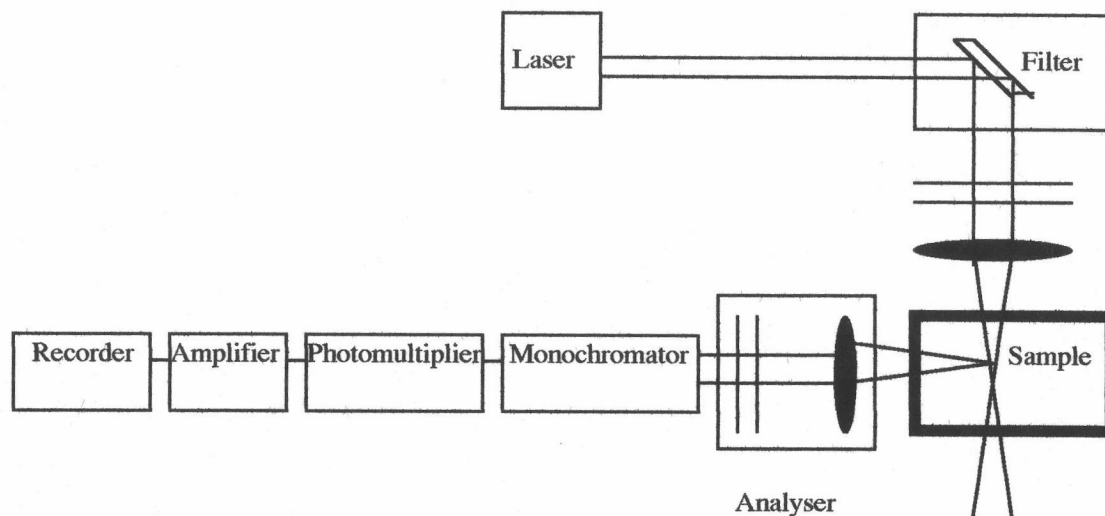

Figure 3.1 : The essential components of a Raman spectrometer

3.7. Attenuated total reflectance (ATR)

The depth of penetration depends both on the wavelength of the light, increasing with increasing wavelength, and on the relative values of the reflective indices and is typically of the order of several microns. As a consequence, light having wavelengths corresponding to the absorption spectrum will be absorbed in proportion to the depth of penetration. This implies that there will be greater absorption of the longer wavelength light. The spectral distribution of the reflected light is then representative of the surface regions of the material. The effect can

be used to examine in particular the surface layers of polymeric materials and so provide information on, for example, surface oxidation, or to obtain spectral of samples having very high absorptivities not readily examinable by transmission spectroscopy.

In order to obtain measurable absorption spectra, it is normal practice to use multiple reflection prisms and these are available as standard spectrometer accessories.

4. Sample preparation

4.1. Films

One method of sample preparation particularly adaptable to polymer studies is the film technique. The advantage in the use of films are that no corrections need be made for solvent or cell absorptions and that the sample is in a form particularly suitable for storage or further treatment. Some of the disadvantages may not be so obvious, however.

4.2. Solutions

The use of solutions in infrared spectroscopy is limited because all organic compounds exhibit absorption bands in the infrared. However, for careful study of portions of the spectra or for quantitative analysis requiring only absorption values at a few wavelengths, proper selection of the solvent makes this technique quite practical. In some

cases slight absorption bands in the solvent can be overcome by the use of correction factors using the single-beam instruments or direct compensation can be made using the double-beam instruments.

The major advantages gained by the use of solutions are the precise control of the concentration, the freedom from effects of crystallization and strain, the ease of protecting the sample from oxidation and contamination, and the relative ease in adjustment of the intensity of absorption bands by dilution or change in the cell thickness. Among the disadvantages are the restriction to only certain parts of the spectrum due to solvent absorption bands, the effect of solvent-polymer interactions on the spectrum (shifts due to hydrogen bonding, etc.).

4.3. Mulls (suspensions)

Probably the most commonly used method for preparing insoluble materials for infrared examination is the mulling technique. This method involves converting the material to a fine powder and grinding or mulling this powder in a suitable suspending liquid. The suspending medium must not have strong absorption bands in the region of interest for the polymer. Nujol and hexachlorobutadiene are two commonly used suspending liquids that allow a fairly complete spectrum to be obtained because the absorption bands of Nujol are missing in hexachlorobutadiene, and vice versa.

Difficulties arise with this technique also, although in many cases the relative ease of preparation and the availability of many published spectra obtained by this method for comparison often outweigh

some of the objections. Consideration must be given to the possibility of degradation of the polymer in the rather severe grinding operation.

5. Applications

5.1. Qualitative analysis

As mentioned earlier, the use of fundamental absorption frequencies calculated from theory is too complex to be practical for molecules larger than just a few atoms, and impossible in the case of high polymers. However, many correlations between characteristic frequencies and structure of functional groups have been established; these permit the identification of such groups as OH, C≡N, NH, SH, C=O, C–N, and larger groups such as olefinic substituents, carboxyl and ester groups, amides, imides, aromatic nuclei, and many others.

The characteristic frequencies are not absolute frequency values, but rather narrow regions of frequencies over which these groups have been found to absorb in a large number of chemical compounds. Some caution must be exercised in the use of such data because of shifts of position of absorption frequencies due to solvent interaction, hydrogen bonding, crystallization, or a high degree of ordering caused by internal strains in solid samples.

5.2. Quantitative analysis

5.2.1. Using Lambert's law

The theoretical quantitative relationship between energy transmitted by a material at a single wavelength and the thickness of the material is given by Lambert's law

$$T = \frac{I}{I_o} = e^{-kL}$$

where T is defined as the transmittance or the ratio of the intensity of the transmitted radiation, I, to the incident radiation, I_o; e is the natural logarithm base; k is the absorbance coefficient per centimeter and is a constant specific for each absorber at the specified wavelength; and L is the thickness in centimeters. Frequently this expression is used in its logarithmic form and log 1/T is defined as the absorbance, A. The constant converting natural logarithms to common logarithms is usually included in the value of the absorbance coefficient, k. Hence

5.2.2. Using Beer's law

A modification of Lambert's law, known as Beer's law, can be applied to solutions

$$T = \frac{I}{I_o} = e^{-KLC}$$

where C is the concentration in grams per liter and K is absorbancy coefficient per gram per liter. Again, the absorbancy, A, is the sum of the absorbancies of all absorbing substances and all the absorbancy coefficients should be known or deviations from this law may occur.

6. Applications to polymers

Although IR and Raman spectroscopy are not widely used in qualitative and quantitative analysis of analysis of polymers and additives, the potential these techniques offer in producing information on chain conformations, stereochemical structure, crystallinity and orientation of polymers render them more generally useful in polymer characterization. Infrared spectroscopy is the more readily available of the techniques and it is likely that Raman spectroscopy will remain a specialized technique for some time to come (Bark and Allen, 1982).

Thermal analysis : dynamic mechanical thermal analysis ; DMTA

1. Introduction

These techniques measure mechanical properties on samples under an oscillatory load and are extremely useful technically in considering the overall performance of polymers, since the mechanical properties are measured as a function of temperature and frequency. These properties are also very sensitive to molecular structure, and changes with temperature have been useful in determining glass temperature region, the presence of crystallinity, phase separation and cross-linking. Polymer blends, block copolymers and copolymerisation have also been analyses by dynamic thermomechanical analysis.

There are many types of instruments available, commercial and research, which differ in the type of measurement made and the frequency of the loads applied. Some measure of Young'modulus, other shear and even the bulk modulus. Each technique has its own limitations and restrictions in use, and also range of applications, and is best considered separately under the different headings, but only a few can be considered.

2. The DMTA technique

The dynamic mechanical method assesses the structure and properties of solids and viscoelastic liquids via their dynamic moduli and damping. In particular, changes in these parameters are studied as a

function of measurement temperature (dynamic mechanical thermal analysis – DMTA) and impressed frequency (dynamic mechanical spectrometry).

The method has great sensitivity in detecting changes in internal molecular mobility and in probing phase structure and morphology. Secondary relaxations in the glassy state can be easily studied as well as the glass transition (T_g) relaxation process.

2.1. Principles of the technique

When a sinusoidal stress is applied to a perfectly elastic solid the deformation (and hence the strain) occurs exactly in phase with the applied stress. A completely viscous material will respond with the deformation lagging $90°$ behind the applied stress.

When a sinusoidal stress is applied to a viscoelastic material it will behave neither as a perfectly elactic nor as perfectly viscous body and the resultant strain. The magnitude of the loss angle is dependent upon the amount of internal motion occuring in the same frequency range as the imposed stress.

The complex dynamic modulus (E^* for bending or tensile measurements, G^* for shear measurements) is defined as

E^* = stress amplitude / strain amplitude

The complex modulus, however, does not take into account the phase and it is therefore convenient to define completely elastic and completely viscous components of the deformation.

The storage modulus, E' (or G' in shear) is defined as

E' = amplitude of in phase stress component / strain amplitude

The loss modulus, E'' (or G'') is defined as

E'' = amplitude of out phase stress component / strain amplitude

The storage modulus is the elastic respond and corresponds to completely recoverable energy whereas the loss modulus is the viscous respond corresponding to energy lost through internal motion.

The tangent of the loss angle, tanδ, is dimensionless and is equal to the ratio of energy lost (dissipated as heat) to energy stored per cycle.

tanδ = loss modulus / storage modulus = E'' / E'

A material may be scanned over a range of temperature and at various imposed frequencies. A loss maximum in the temperature scan is observed when the frequency of a motional process coincides with the impressed (measurement) frequency. With increase in measurement frequency the loss process is found at higher temperatures, where the molecular motion is faster.

The DMTA imposes a sinusoidal stress on a sample in the bending, shear or tensile mode and determines the sample modulus and tanδ as a function of temperature and/or frequency.

In the bending mode the sample is usually in the form of a rectangular bar clamped rigidly at both ends and with its central point vibrated sinusoidally by the drive clamp. This arrangement is extremely versatile and may be used to accommodate a huge range of sample types, from films to composites.

Soft materials such as rubbers, adhesives, or fats may be measured in the shear sandwich geometry. Here a disc or plate is affixed to the drive clamp and the sample sandwiched between this and studs mounted on the fixed clamps. The faces of this arrangement may be horizontal or vertical.

The tensile mode utilizes additional control of the static stress in the sample and can accommodate samples which relax with temperature, such as films and fibres. In this mode the sample is mounted such that its length is parallel to the drive direction.

The environment within the temperature enclosure is controllable. The coolant circulates in a separate jacket and an inert gas or controlled humidity air may be introduced from pipes in the rear bulkhead.

Temperature is sensed and controlled by a blackened platinum resistor lying immediately behind the sample.

2.2. General construction

The mechanical spectrometer head consists of a demountable temperature enclosure, an electromagnetic drive assembly, a displacement transducer and demountable sample clamping configuration. There are three types of mechanical head ; bending/shear, power, and tensile. All three heads are constructed in a similar manner.

A composite drive shaft is driven by supplying current to an electromagnetic vibrator; the resultant displacement of the shaft is determined using a noncontacting eddy current transducer consisting of a static components both lie in a compartment between two bulkheads and are maintained at ambient temperature. A knob situated at the rear of the bulkhead allows adjustment of the gap between the transducer probe and target. A black 'U' shape cover protects all components between the bulkheads.

The sample is clamped between the stationary clamps and drive clamp and is thus mounted horizontally within the temperature enclosure.

2.3. Operating principles of the analyser

A sample undergoing analysis in the DMTA is subjected to a sinusoidal force of known magnitude and the resultant displacement in the sample is measured. The DMTA dynamic analyser generates and controls the sinusoidal signal applied to the sample whilst monitoring the resultant displacement. It then analyses both signals to give results relating to the dynamic behavior of the sample.

Optical microscopy techniques

1. Introduction

Microscopy investigations have provided much of the detailed information on polymer morphology. Whereas scattering methods are statistical averages over the bulk samples, microscopy permits the examination of features from the micron to the atomic scale.

In general the practice of polymer microscopy (as compared to that of metals and ceramics) is hindered by the radiation sensitivity of the specimens and the difficulty of obtaining thin samples with sufficient contrast from bulk material. It is further hindered by from practitioners who display insufficient regard for the influence of radiation damage and electron optical conditions on their resultant images and on an overly subjective approach to image interpretation.

2. Principles

There exist many excellent references on microscope theory and practice. Their emphasis is largely towards metals and biological materials and towards amplitude contrast (diffraction contrast for metals and mass thickness contrast for strained biological sections).

To aid in our critical discussion of polymer microstructural studies it is first necessary to define briefly the standard transmission

electron optical techniques. The normal situation of a beam incident at 90 ^{o}C to a thin specimen. Bright field (BF) imaging utilised the light scattered in the forward direction, which are selected by the objective aperture, whereas for dark field (DF) imaging the objective aperture is set to collect a portion of the scattered light. DF imaging by simply displacing the objective aperture off the optic axis is very convenient, but for high resolution the resultant image shift and image aberration of the displaced aperture technique can be prevented by using tilted incident illumination, (Hall, 1984).

3. Image interpretation

The incident light, after interacting with the specimen, carry information in both the amplitude and phase of their wave function. The usual way to extract information from the electrons is to use the squared amplitude of the wave function to produce amplitude contrast (mass thickness contrast or diffraction contrast). The phase part of the electron wave function may also be used to produce changes in intensity (phase contrast). In order to produce a change in intensity from phase differences in the electron wave functions by the object, the microscope system. In a light microscope, this shift can be produced by a phase plate that uniformly changes the phase of selected photons (Zernike contrast). In an electron microscope this phase shift is produced by spherical aberration and defocusing the objective lens. However, defocusing shifts the phases of the electrons in a complicated manner and makes image interpretation more complex.

For polymer specimens, which may consist of complex arrays of quite small structural units, it should be emphasises that the image is a two-dimensional projection of the three-dimensional specimen. If the structural unit size and the film thickness are similar, the projected object function is uncomplicated and correct interpretation of the image is possible, however, the units are randomly distributed and much smaller than the film thickness so that the resulting projection will be complex and hard to distinguish from and otherwise homogeneous film with small random fluctuations. For this reason very thin specimens must be prepared to study small scale structures. Moreover, determination of the volume fraction of an image feature requires careful consideration of the size of the feature with respect to the film thickness (Manson, 1976).

Mechanical properties

1. Introduction

Mechanical properties are associated with the reaction that results when a force or load is applied to a material. These properties are sometimes referred to as physical properties ; however, the term mechanical properties is preferred.

Mechanical properties include compressive strength, tensile strength, shear strength, fatique and flexing, hardness, indention, and friction.

The crystalline axes of crystalline polymers generally produce a slightly anisotropic material. The crystallinity of a material provides relatively rigid regions in the molecular structure, something similar (not the same) to crosslinks. When stretched, a crystalline polymer tends to orient itself so that its crystals are stretched in the direction of the applied stress, which may be desirable in fiber production or some product designs.

In linear polymers, the chains tend to pack closely, increasing density with the percentage of crystallinity. The bulky side groups in branced polymers keep the polymer chains farther apart, thus decreasing the tendency to crystallize.

Amorphous materials have the long-range disorder of liquids and are isotropic. Remember that a portion of all polymers have amorphous regions. As the molecular mass and crystallinity increase, there is generally an increase in softening temperature, strength, stiffness, hardness, creep resistance, and impermeability to gas and liquids. *There is less space between molecular chains in crystalline materials for moisture and gases to permeate.* Short molecular chains are more easily attached by reactants. It is also important to have a relatively narrow distribution of molecular chain lengths for best properties. Short molecular mass chains are more easily attacked and may act as plasticizers, softening the material. Increasing molecular mass reduces creep because the long chain length tends to entangle, thus resisting slippage. As you know, melt viscosity increases rapidly as the molecular mass increases. It takes much more energy to break the large molecular chains.

Thermosetting materials begin as low molecular mass materials but increase dramatically in molecular mass during processing and curing. There are three direct kinds of stress (force) which may be applied to materials : compression, tension and shear. The rate (time) at which all three types are applied is specified in standard procedures. Forces applied too rapidly or slowly during testing yield false values. Most tensile and compressive testing equipment operates at constant crosshead speed.

Polymers are considered to be viscoelastic. They behave something like elastic metals and viscous oils. For some tests, the rate (time) at which the polymer is stressed may be measured in microseconds, minutes, days, or longer periods. Polymer subjected to a

load (stress) for a period of time tends to deform (strain). The degree of deformation depends on the load duration. Impact strength measures the polymer's resistance to a quick blow and constitutes a much faster experiment. Most stress–strain studies are relatively slow, in the order of millimeters per second or inches per minute. There is viscoelastic deformation of the polymer chains in stress–strain and impact tests.

2. Tensile strength

If stress is applied to a material by pulling it until broken, tensile strength may be calculated. Tensile strength is calculated by dividing the maximum load (force) by the original cross–sectional area.

Pulling stress usually causes material to deform by thinning and stretching in length. The change in length, is called strain which is measured in millimetres per metre, inches per inch of length and in percent of elongation.

Strain is evident in testing of most plastics. Plastics that are not reinforced deform in cross–sectional area before breaking. The breaking strength may be less than the greatest tensile strength, which occurs when strain has reduced the cross–sectional area of the specimen.

Stress–strain diagram are convenient means of expressing and plotting the strength of plastics.

A certain amount of strain is called elastic strain. As the name indicated, the molecules return to the original position once the stress is removed. Plastic strain, however, occurs when the molecules begin to slip and slide past each other in permanent (irreversible) deformation. The point where elastic strain end and plastic strain begins is referred to as the proportional limit of the material.

3. Stress-strain properties

In stress-strain tests the build up of force (or stress) is measured as the specimen is being deformed at a constant rate. This method is the most popular and universally used of all mechanical tests (Nielson, 1974). Following illustrated the great variation in stress-strain behaviors. The first is for hard, brittle material. It shows an initial steep slope rising to a break or failure point at relatively low strain. The second is typical of ductile material which may show a curved line characteristic of uniform extension or a yield point where in the stress may remain constant or even decrease as the strain (elongation) increses. This type of behavior is typical of a necking-down or reduction of sample cross section at the yield point due to cold-drawing of the specimen. A leveling of stress often occur after the yield point until the break point is reached. The final is typical of elastomeric materials which may show a smooth increses in strain or elongation well beyond a 100% change in length at relatively constant stress.

Temperature and stress-application rate greatly influence the stress-strain result. A material that shows tough, ductile behavior when

stress is applied slowly often behaves as if it were brittle when a large stress is applied. Similarly, when the temperature at which the stress is applied is lowerd, the tough ductile specimen often becomes brittle even if the stress-application rate is low.

4. <u>Modulus of elasticity (tensile modulus)</u>

The modulus of elasticity, also called Young's modulus, is the ratio between the stress applied and the strain, within the elastic range. It is calculated by dividing the stress (load) in pascals by the strain in millimetres per millimetre.

Young's modulus has no meaning at stress above the proportional limit. Plastic strain and permenent deformation cannot be allowed in the design of products. The ratio of the tensile force to elongation is useful in learning how far a plastics specimen will stretch under a given load. A large tensile modulus indicates that the plastic is rigid which would be resistant to stretch and elongation.

The area under the stress-strain curve represents the energy required to break the plastics sample. This area is an approximate measure of toughness.

<u>**Environmental endurance**</u>

1. <u>Introduction</u>

Plastics are found in nearly every environment. They are used for containing chemicals, storing food in the freezer, and even inside the human body. Before a product is designed, plastics must be tested for endurance under the expected environmental extremes. The environmental endurances of plastics include solvent resistance, chemical resistance, weathering, ultraviolet resistance, permeability, water absorption, biochemical resistance, and stress cracking.

2. <u>Solvent resistance</u>

During the polymerization process, there is a breaking and recombining of chemical bonds. The types of bonds, the distance between bonds, and the energy needed to break these bonds are important in considering the chemical reactivity and solubility of plastics. Chemical deterioration is usually undesirable in plastics products.

The chemical resistant of the polyolefins and fluorocarbons is due to the C-C and C-F bonds. These bonds are very stable. As a result these plastics are exceptionally inert, non-reactive, and resistant to chemical attack.

The hydroxyl groups (-OH) attached to the carbon backbone of cellulose and polyvinyl alcohol are very reactive. Water or other chemicals may break these bonds.

The statement that "most plastics resist weak acids, alkalies, moisture, and household chemicals" must be used only as a broad rule. Any statement about the response of plastics to chemical environments must be only a generalization. It is best to test each plastics to determine how it can be specifically applied and what chemicals is expected to resist.

Temperature, fillers, plasticizers, stabilizers, colorants and catalysts can affect the chemical resistance of plastics.

3. Water absorption

Some plastics, especially polyamides, tend to absorb moisture. After a sample is dried and weighed, it is immersed in water for period of time. The sample is then reweighed and the percentage of additional mass is calculated.

Some plastics swell and lose optical and electrical properties when moisture is absorbed.

Water absorped epoxy and polyamide polymers results to decreases of short-term elevated-temperature strength. The moisture acts as a plasticizer, lowering the glass transition temperature. The swelling

must be considered in designs with close tolerance dimensions and in composite designs. Moisture lowers the matrix and reinforcement bond. During processing and molding, moisture will vaporize to give gas bubbles in the melt. Appearance and mechanical properties may be greatly poor with bubbles in the molded parts.