CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Mechanical properties of a material such as strength, hardness and elasticity or stiffness are measures of a materials ability to carry the application of mechanical forces or energy. They are expressed in terms of the input (load, stress or energy), output (elongation or ductility) and ratio between input and output (modulus of elasticity). These properties will be discussed in this chapter.

2.2 Tensile and flexural properties

Tensile properties often used to predict the behaviour of a material under loading other than uniaxial tension. A tensile test is a fundamental mechanical test where a moulded specimen is loaded in a very controlled manner while measuring the applied load and the elongation of the specimen over some distance. Tensile tests are used to determine the modulus of elasticity, elastic limit, elongation, tensile strength, yield point, yield strength and other tensile properties.

The strength of a material is measured in terms of either the stress necessary to cause appreciable plastic deformation or the maximum stress that the material can withstand. Ductility which is a measure of how much materials can be deformed before it fractures is usually used to ensure quality and toughness of the materials. Low ductility in a tensile test often is accompanied by low resistance to fracture under other forms of loading.

A stress-strain curve may be plotted when load-elongation data are converted to engineering stress and strain. The advantage of dealing with stress versus strain rather than load versus elongation is that the stress-strain curve is virtually independent of

specimen dimensions. The stress-strain curve relates the applied stress to the resulting strain and each material has its own unique stress-strain curve.

Stress, σ, is defined as a mechanical force or energy that produces deformation in the material and usually has the dimensions of force per unit area. It refers to the internal inter-atomic forces that react to an externally applied force. Since it is difficult to measure these internal forces, stress is usually expressed as an externally applied force. While strain, ε, is commonly referred to the deformation of a material subjected to mechanical energy forces. It also defined as the change per unit of length in a linear dimension of the material body. There are two types of strain i.e. elastic strain and plastic strain. Elastic strain is reversible which recovered immediately upon unloading. In this situation, stress and strain are usually proportional to each other. However, plastic strain is a permanent deformation which the atomic structure does not return to its original state when the stresses are released. Hence, the material will remain deformed [19]. Many materials exhibit elasticity under limited conditions of stress, but are plastic under heavy stresses, such as polyamide.

The flexural strength is the ability of a material to resist combined tensile and compressive stresses developed under a bending load. These properties is expressed in terms of the maximum stress a material can sustain without fracture under loading parallel to the longitudinal axis for the test specimen [20]. It shows how the material will react when force is required to bend a beam under three or four point loading conditions.

The specimens may be loaded in either three-point bending or four-point bending. The major difference between four point and three point bending modes is the location of the maximum bending moment and maximum axial fibre stress. In four-point bending the maximum axial fibre stress is uniformly distributed between the loading noses. In three-point bending the maximum axial fibre stress is located immediately under the loading

nose. These tests are most meaningful for brittle materials that have linear stress-strain behaviour up to the point of fracture.

2.2.1 Reinforcement theory of discontinuous fibre composites

The simplest expressions governing the stiffness and strength of continuous and uniaxially aligned fibre reinforced composites are given by the following simple rule of mixture (Equation 2.1) where E_c is moduli of the composite, E_f is the moduli of the fibre, E_m is the moduli of the matrix and V_f is the fibre volume fraction.

$$E_c = E_f V_f + E_m\left(1 - V_f\right) \qquad (2.1)$$

Many theories have been proposed on the longitudinal stress distribution along the fibre-matrix interface. The theory that considered both the fibre and the matrix in the elastic state has been reviewed by Cox [21]. Two assumptions were made in this theory:

a) a perfect bond exists between the fibre and the matrix
b) no load transfer through the end of the fibre which means lateral contraction of the fibre and matrix are equal

The fibre length, l embedded in a matrix under a general strain, ε. A point distance, x from the end of the fibre is considered to obtain expressions for stress distribution. Thus, the load transfers from the matrix to the fibre maybe defined by the equation below.

$$\frac{dP}{dx} = \mathrm{H}\,(u\text{-}v) \qquad (2.2)$$

Where u is the displacement if fibre is present, v is displacement of same point if fibre is absent , P refer to load in the fibre and H is constant depends on the fibre and matrix properties and their geometrical arrangement.

Differentiating Equation 2.6

$$\frac{d^2P}{dx^2} = H\left(\frac{du}{dx} - \frac{dv}{dx}\right) \qquad (2.3)$$

where

$$\frac{dv}{dx} = \text{strain in the matrix } (\varepsilon)$$

$$\frac{du}{dx} = \frac{P}{A(E_f - E_m)} = \text{strain in the fibre}$$

A is the cross sectional area of the fibre.

Strain in the fibre is due to the transfer of load as the fibre and matrix have different physical properties. The differences in moduli should be used in expressing strain in terms of load.

Substituting in Equation 2.3

$$\frac{d^2P}{dx^2} = \mathrm{H}\left(\frac{P}{AE} - \varepsilon\right) \qquad (2.4)$$

Solving this differential equation:-

$$P = EA\,\epsilon + R\sinh\beta x + S\cosh\beta x \qquad (2.5)$$

where R and S are constants of integration. $P = 0$ when $x = 0$ and $x = l$ if the broken fibre has a total length, l. By dividing the area of the fibre the expression for stress σ_f in the fibre is obtained for general strains provided by an applied stress σ_c :

$$\sigma_f = \frac{(E_f - E_m)}{E_m}\left[1 - \frac{\cosh\beta\left(\frac{l}{2} - x\right)}{\cosh\beta\frac{l}{2}}\right] \qquad (2.6)$$

where β is given by :-

$$\beta = \left[\frac{H}{E_f A_f}\right]^{\frac{1}{2}} \qquad (2.7)$$

By considering the total force in the fibre, the average stress in the fibre is obtained as:

$$\overline{\sigma}_f = \left(E_f - E_m\right)\varepsilon\left[1 - \frac{\tanh\beta\frac{l}{2}}{\beta\frac{l}{2}}\right] \qquad (2.8)$$

The average longitudinal stress in a composite containing fibre with volume fraction, V_f can be calculated as a weight average of the stress developed separately in the fibre and matrix, i.e.:-

$$\sigma_c = \overline{\sigma}_f V_f + \left(1 - V_f\right)\sigma_m \qquad (2.9)$$

where σ_m is the stress in the matrix. Since σ_m is equal to ϵE_m, where E_m is Young's modulus of matrix, applied stress σ_c :-

$$\sigma_c = V_f E_f \varepsilon\left[1 - \frac{\tanh\beta\frac{l}{2}}{\beta\frac{l}{2}}\right] + \left(1 - V_f\right)E_m\varepsilon \qquad (2.10)$$

The effective longitudinal modulus of the composite is given by:-

$$E_c = \frac{\sigma_c}{\varepsilon} = V_f E_f \left[1 - \frac{\tanh \beta \frac{l}{2}}{\beta \frac{l}{2}} \right] + \left(1 - V_f\right) E_m \qquad (2.11)$$

The efficiency of reinforcement of fibres is associated with both fibre orientation and fibre length which is reviewed by Krenchel [22] and the Equation 2.11 can be rewritten as:-

$$E_c = \eta_o \eta_l E_f V_f + E_m \left(1 - V_f\right) \qquad (2.12)$$

where η_o η_I are the correction factor due to fibre orientation and fibre length respectively. η_I is equal to :-

$$\eta_l = 1 - \frac{\tanh \beta \frac{l}{2}}{\beta \frac{l}{2}} \qquad (2.13)$$

It was also shown that if a fibre is misaligned by an angle θ to the stress axis, it supports a load proportional to $\cos^4\theta$. For n groups of fibre with total cross-sectional area a_i, aligned at an angle θ_i to the stress axis, the orientation efficiency factor, η_o of the fibres is given by [4]:

$$\eta_o = \frac{1}{a_n} \sum a_i \cos^4 \theta_i \qquad (2.14)$$

For unidirectional laminae η_o = 1 and 0 when tested parallel and perpendicular to the fibres respectively. η_o = 1/3 for in-plane random fibre distributions and η_o = 1/6 for three-dimensional random distributions [27].

Kelly and Tyson [23] have developed a theory to predict the strength of such composites where the matrix is ductile. Two important parameters involved in this theory are the

critical fibre length, l_c, and the shear flow stress of the matrix, τ_f. The relationship between these two properties is:-

$$l_c = \frac{\sigma_f d}{2\tau_f} \qquad (2.15)$$

Kelly [24] argued that high shearing stresses in the matrix near the fibre ends cause yielding of the matrix so that, at failure, the stress distribution has the form shown in Figure 2.1. General distribution of stress in the fibre is given by Equation 2.16 where z is the distance from the centre of the fibre. A constant shear flow stress, τ_f, occurs along the fibre end which is equal to the yield shear stress of the matrix.

$$\sigma_f = \frac{2\tau_f\left(\frac{l}{2} - z\right)}{r_f} \qquad (2.16)$$

Kelly and Tyson's approach for the tensile strength of the composite is based on the following simple equilibrium equation [23]:

$$\sigma_c = \bar{\sigma}_f V_f + \bar{\sigma}_m V_m \qquad (2.17)$$

which relates the tensile stress applied to the composite, σ_c, to the average stresses σ_f, and σ_m in the fibres and matrix respectively. V_f and V_m are the volume fractions of fibres and matrix respectively in the composite. The average stress ($\overline{\sigma_f}$) is related to the maximum stress in the fibres ($\sigma_{f(max)}$) by the relation

$$\bar{\sigma}_f = \lambda \sigma_{f(\max)} \qquad (2.18)$$

where λ is a factor to be determined and depends primarily on the lengths of the fibres, l.

Figure 2.2 shows the variation of the stress distribution, relative to the ultimate strength of the fibre, with the length of the fibre. Critical fibre length, l_c is the length of fibres that allows the ultimate strength of the fibre to be reached. The ultimate strength of the fibre ($l > l_c$) and the ultimate strength of the matrix achieve ($l < l_c$) must be considered in studying the ultimate strength of the composite. Equation 2.19 is modified from Equation 2.17 of external and internal stresses because the ultimate strength of the fibres ($l > l_c$) is utilised the fibres and carry the majority of the load where σ_f is average stress in the fibre, σ_m is stress in the matrix for a general strain, ε and σ'_m refer to stress in the matrix at fibre breaking strain [25]. The composite will fail by fracturing of the fibres when the maximum stress in the fibres equals their breaking strength. Relationship between average and ultimate strength by considering the total force in the fibre is shown in Equation 2.20

$$\sigma_c = \overline{\sigma}_f V_f + \sigma'_m V_m \qquad (2.19)$$

$$\sigma_c = \sigma_f \left(1 - \frac{l_c}{2l}\right) V_f + \sigma'_m \left(1 - V_f\right) \qquad (2.20)$$

For fibres shorter than the critical length, ($l < l_c$) the ultimate strength of the fibre is not achieved so that failure occurs and the average stress in the fibre is:-

$$\overline{\sigma} = \frac{\tau_f l}{2r_f} \qquad (2.21)$$

Significantly, discontinuous fibres have lengths less than l_c which the matrix deforms around the fibre such that there is virtually no stress transference and little reinforcement by the fibre.

2.2.2 Tensile and flexural properties of single fibre composites

Hassan *et al*. [26] have studied the structure property relationship of injection moulded carbon fibre reinforced PA 6,6 composites in terms of the effect of compounding routes. Extrusion and pultrusion techniques were used in this study and they found pultrusion-compounded composites show increment in tensile strength and tensile modulus. However, the fracture strain is reducing. In addition, tensile strength and tensile modulus were increased with an increase in volume fraction; V_f. Fibre length characteristics support the improvement in tensile properties.

The mechanical properties of thermoplastics has been reported by Bader and Bowyer [27] using a commercial glass fibre reinforced nylon containing short glass fibres and polypropylene containing glass and carbon fibres with different length. Longer fibres are found to be more effective in improving strength compared to the same fractions of short fibres especially at higher values of strain. The stiffer carbon fibres are more effective than glass for reinforcing nylon. Since the minimum fibre length for effective reinforcement is related to the strain in the composite and to the strength of the fibre/matrix interface, a critical length effect has been proposed. They also found that the failure in nylon based composites reinforced with carbon or glass was initiated by fibre fracture while failure occurs in the polypropylene/glass system matrix.

2.2.3 Tensile and flexural properties of hybrid fibre composite

Determination of flexural properties have been done by Pike and Novak [28] using both three and four point bending test rigs with a span to depth ratio of 32:1. All the specimens in four point flexure failed in shear to give a low value of flexural strength while specimens in three point flexure exhibited a bending mode failure. Longitudinal results indicated insensitivity to the ply system in load transfer but the dispersed construction proved slightly stronger. Carbon and S glass, tow by tow lay ups, showed no

decrease in flexural strength or modulus up to 25% V_f of glass fibre, and interplay HMS graphite or intraply AS graphite resulted in the highest modulus for a lay up system.

Marshall [29], using hybrid tapes in a vinyl ester matrix, found an increase in flexural properties with increasing carbon fibre content, and also discovered that the rule of mixtures underestimated the first fracture stress. The author suggests that the retardation of failure of the hybrid composite is due to the stiffer glass fibre resin matrix relative to all resin matrices. Hence, the resin matrix was reported to have equivalent or better performance than conventional epoxy resins, with good adhesion to both fibres.

Miyairi *et al.* [30,31] has reported a substantial increase in the flexural strength of GRP when laminated with CFRP and has developed a beam theory approach which predicts these flexural properties. The fracture modes of hybrid composites was differ from those single glass fibre composites, with brittle failure across the carbon fibres in glass mat core hybrids, and zig-zag fracture surface in glass cloth core fibres.

2.3 Impact properties

The impact testing techniques measures the energy necessary to fracture a standard notched bar by an impulse load and as such are an indication of the notch toughness of a material under shock loading. Impact test conditions were chosen to represent those most severe relative to the potential for fracture such as deformation at a relatively low temperature, a high strain rate, and a tri-axial stress state which is introduced by the present of a notch. The reason of introducing a notch with the accompanying stress concentration is to break the ductile materials.

Two standardized tests [32], the Charpy and Izod, were designed and are common tests to measure the impact energy i.e. notch toughness. The Charpy V-notch (CVN) technique is most commonly used in the United States. For both Charpy and Izod, the

specimen is in the shape of bar of square cross section, into which V-notch is machined. Charpy impact specimen is supported at the ends and struck in the middle. The impact weight, *W* is struck on the side apposite the notch, with certain velocity and Izod impact specimen is a cantilever beam with a notch on the tension side to insure fracture when the impact load is applied on this side of specimen. Specimens and loading configurations for these are illustrated in Figure 2.3.

A swinging pendulum which acts as an impact weight *W* is used for applying the impact load in both cases. The energy required to break the sample is determined from a height of pendulum swings after breaking the sample. The disadvantage of pendulum impact tests is that energy in excess of that to cause failure is stored in the specimen and hence the impact energies measured are too high. Dynamic tear test is another test used as impact testing technique. Specimens for this test have a centre notch and they are impacted in three-point bending by a falling weight [20]. The energies obtained in these notch-impact tests are depending by numbers of factors. The details of the specimen size and geometry, the support and loading configuration, mass and velocity of pendulum will naturally modify the test results. The shape and size of the notch influence the impact toughness, and a decrease in toughness occurs with increased sharpness of notch [33].

2.3.1 Fracture toughness

From the theory of fracture mechanics, a quantity called the stress intensity factor; *K* can be defined that characterizes the severity of the crack situation as affected by crack size, stress and geometry. The stress intensity factor is related to the applied stress and the crack length by the following equation [4]:

$$K = Y\sigma\sqrt{\pi a} \qquad (2.22)$$

where Y is a constant related to the sample's geometry, a is a crack length and σ is the stress applied to the material (Figure 2.4).

The material is assumed to behave in a linear-elastic manner hence; linear-elastic fracture mechanics (LEFM) theory is being used. The compliance of the specimen, C is the displacement per unit load, i.e. the reciprocal of stiffness. Thus, when the crack has length a, the specimen is less compliant. In general, the concept of compliance as a ratio of deformation to applied load is:-

$$C = \frac{\delta}{P} \qquad (2.23)$$

Energy is stored as strain energy when the material is under stress. Since the material response to the deformation is entirely elastic, the absorbed energy, W is given by:-

$$W = \frac{P\delta}{2} = \frac{P^2 C}{2} \qquad (2.24)$$

The total strain energy, U for a specimen with uniform thickness, B can be written in terms of this compliance as:

$$U = \frac{W}{B} = \frac{CP^2}{2B} \qquad (2.25)$$

When a crack of length, a is grown into the specimen by a small amount of ∂a, the material become more compliant thus, it stores less elastic energy at a fixed displacement, but elastic energy stores more at a fixed load. The rate of change of elastic energy with increase in crack area can be defined as the strain energy release rate, G [20]:

$$G = \frac{\partial U}{\partial a} = \frac{P^2}{B}\frac{\partial C}{\partial a} \qquad (2.26)$$

The energy release rate relates to the stress intensity factor as:

$$G = \frac{K^2}{E} \qquad (2.27)$$

Where E is Young's modulus and K is given by Equation 2.22. Substituting Equation 2.22 for K^2 in Equation 2.27, the new equation for G is:-

$$G = \frac{Y^2\sigma^2 a}{E} = \frac{P^2}{2B}\frac{\partial C}{\partial a} \qquad (2.28)$$

$$\frac{\partial C}{\partial a} = \frac{2BY^2\sigma^2 a}{P^2 E} \qquad (2.29)$$

In three-point bend test, the load P is given by simple bending theory as:-

$$P = \frac{4BD^2\sigma}{6S} \qquad (2.30)$$

Substituting the expression for P in Equation 2.29 gives:-

$$\frac{\partial C}{\partial a} = \frac{9aY^2S^2}{2EBD^4} \qquad (2.31)$$

Thus, the compliance, C can be determined by:-

$$C = \frac{9S^2}{2EBD^4}\int Y^2 a.\partial a + C_\circ \qquad (2.32)$$

Substituting Equations 2.30 and 2.31, for P and C respectively in Equation 2.24 gives:-

$$W = \frac{B\sigma^2}{E}\left[\int Y^2 a.\partial a + \left(\frac{SD}{18}\right)\right] \qquad (2.33)$$

The σ^2 term in Equation 2.33 can be eliminated by means of Equations 2.22 and 2.27 gives:-

$$W = \frac{GB}{Y^2 a}\left[\int Y^2 a.\partial a + \left(\frac{SD}{18}\right)\right] \qquad (2.34)$$

$$W = GBD\phi \qquad (2.35)$$

where B and D are refer to the width and depth of the specimen, respectively. The parameter ϕ is a geometrical correction factor determined as a function of a/D is given by [16]:

$$\phi = \frac{1}{2}\left(\frac{a}{D}\right) + \frac{1}{18\pi}\left(\frac{S}{a}\right) \qquad (2.36)$$

where a and S are crack length and span of the specimens, respectively. At fracture, the energy release rate, G enhances a critical value, G_c:-

$$W = G_c BD\phi \qquad (2.37)$$

A plot of W against $BD\phi$ produced a straight line, where its slope is equal to the G_c of the materials. The method of G_c and K_c determination has been employed by Carling and Williams [34] in most of their work.

2.3.2 Impact properties of single fibre composites

Laura *et al.* [35] have done research on the effect of glass fibre and maleated ethylene–propylene rubber content on impact properties of polyamide 6. Materials containing 0–20 wt% glass fibre and 0–20 wt% EPR-*g*-MA were formulated. The modulus and yield strength of the unreinforced materials decreased as EPR-*g*-MA content increased. This effect can be completely counteracted by the addition of more

than 10 wt% glass fibre, regardless of rubber content, with blends containing 20 wt% glass fibres showing substantially higher modulus than that of polyamide 6. Izod impact strength of super-tough blends was reduced by 50% with the addition of small amounts of glass fibre; however, these glass fibres reinforced, rubber-toughened blends still retain high impact strength.

Leach and Moore [36] investigated the failure and fracture behaviour of a range of reinforced nylon compounds. A good resolution of initiation and propagation mechanisms have provided by instrumented falling weight impact tests. Total impact energy to fracture showed a decrease with fibre content up to approximately 15% w/w, thereafter it increased and reached a plateau at a fibre loading of approximately 33% w/w. Difference in matrix used found to influence both the energy to initiate and propagate cracks. Nylon 6,6 appeared tougher than nylon 6, although as glass content increased the variations almost disappeared. Greater energy absorption was exhibited in using toughened unfilled Nylon 6,6 as expected.

Hashemi and Mugan [37] studied fracture behaviour in terms of influences of specimen position from nylon 6,6 plaque mouldings, notch direction, notch sharpness and the rate of testing on fracture toughness of short glass fibre reinforced nylon 6,6. This composite was under static loading using compact tension specimens and under impact loading using single-edge notch (SEN) charpy specimens. Fracture toughness was highest for the cracks perpendicular to the mould fill direction and was lowest for cracks parallel to the mould fill direction. The fracture toughness was not affected by the sharpness of the initial notch for notches perpendicular to the mould fill direction. In contrast, sharpness of the initial notch had a significant effect upon the measured value of the fracture toughness for cracks in the mould fill direction. This study also indicated that the fracture toughness is rate insensitive over the crosshead speed ranging from 0.5-50 mm/min. The

specimen position, as taken from plaque mouldings had no significant effect on the measured value of the fracture toughness.

2.3.3 Impact properties of hybrid fibre composite

Studies of impact behaviour have been made by several authors [38-42] using instrumented Charpy, slow bend work of fracture, or ball impact test. Impact energy of CFRP by adding GRP or ARP is increase for all tests. The glass and aramid fibres modify the failure characteristics and lead to extra energy absorption by debonding, fibre pull-out, etc. Dorey *et al.* [40] reported on the considerably greater energy required for damage initiation in ARP/CFRP hybrid plates compared with similar all CFRP. Harris and Bunsell [41] note that varying the intimacy of mixing of CFRP and GRP is not important in determining the impact energy of the hybrid. In contrast, Mallick and Broutman [42] state that the proper placement of plies is important in maximising energy absorption.

The study of impact and fracture mechanics has been reviewed by Rybicki and Kanninen [43] who believed that static and dynamic test only good for ranking but do not provide an inherent material parameter independent of geometry. They also believe the fracture processes are difficult to understand in hybrids because of our imperfect understanding of them in ordinary composites.

2.4 Dynamic mechanical properties

Dynamic Mechanical Analysis (DMA) is widely used to characterise dynamic mechanical properties of polymers such as modulus, stiffness and damping. It measures changes of rheological behaviour under dynamic conditions as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. The stiffness of materials depends on the mechanical properties of the material and its dimensions. It is

frequently converted to a modulus to enable sample inter-comparisons. Damping is expressed in terms of tan δ and is related to the amount of energy a material can store. The properties of materials are deformed under a sinusoidal or other periodic stress or forces [44]. These dynamic parameters have been used to determine the glass transition region, relaxation spectra, degree of crystallinity, molecular orientation, crossing, phase separation, chemical composition in polymer blends, etc.

2.4.1 Analysis of dynamic mechanical properties

In a dynamic mechanical test, an oscillating strain (sinusoidal waveform) is applied to a sample and the resulting stress developed in the sample is measured using Equation 2.38 where $\sigma(t)$ is the stress at time, t, σ_{max} is the maximum stress and ω is the angular frequency of oscillation.

$$\sigma(t) = \sigma_{\max} \sin \omega t \qquad (2.38)$$

The applied stress produces a strain, ε which is measured according to how the stress is applied (e.g. compression, tension, bending, shear etc.). For elastic materials, Young's modulus, E is measured and normally the test is carried out in tension or bending. For a soft or liquid material the measurement is carried out in shear mode, thus a shear modulus (G) is measured.

According to ISO 6721-1 [45], the storage modulus, E' represents the stiffness of a visco-elastic material and is proportional to the energy stored during a loading cycle. It is roughly equal to the elastic modulus for a single, rapid stress at low load and reversible deformation. The loss modulus, E'' is defined as being proportional to the energy dissipated during one loading cycle which represents energy lost as heat. It is a measure

of vibration energy that has been converted during vibration and that cannot be recovered.

The ratio between the loss and storage modulus, E''/E' gives the useful quantity known as the mechanical damping factor, tan δ which is a measure of the energy lost, expressed in terms of the recoverable energy, and represents an internal friction in a visco-elastic system. Tan δ is expressed as a dimensionless number. Material that has a high, non-elastic strain component has a high tan δ value, while the elastic material gives a low value of tan δ.

2.4.2 Dynamic mechanical properties of composites

The thermo mechanical and dynamic mechanical properties of films and fibres in vapour laden atmospheres and simulated dye baths were investigated by Price [46] in order to understand their processing behaviour. Thermo mechanical and dynamic mechanical measurements (TMA and DMA) were used to monitor the behaviour of polymers in liquids or saturated vapours because they can avoid problems due to condensation or evaporation which plague calorimetric studies. Acetone and water vapour acted as plasticisers for cellulose acetate film. 2-phenoxyethanol was found to penetrate poly(ethylene terephthalate) film above its glass transition temperature and consequently depress its glass-rubber transition temperature, T_g. The use of 'carriers' to enhance the rate of dyeing of acrylic fibre was investigated. The increase in colouration was found to be proportional to the degree of plasticisation caused by the candidate compounds.

Aitken *et al.* [44] described a method for determining the glass transition temperature for both dry and wet acrylic filament. Dynamic mechanical analysis and a novel method of mounting the test specimen were used in their study. The presence of water was found to reduce the T_g of dry acrylic fibre by 20^{o}C, thus demonstrating the plasticising action of water upon the polymer. Dynamic mechanical analysis is shown to be a suitable technique for determining glass-rubber transition temperature of acrylic filament when immersed in water by means of the use of a novel method of mounting the fibres.

Meldrum & Ward [47] measured the compressibility of a pack of wet acrylic fibre as a function of temperature as part of a study of their dyeing behaviour and thermoplastic properties in relation to practical dyeing operations. The data indicates a glass-rubber transition temperature, T_g in the region 70-80ºC as opposed to the normal dry T_g of 90-100ºC. Murayama & Armstrong [48] and Desai & Wilkes [49] appear to have independently developed methods for measuring the dynamic mechanical properties of fibres and films in liquid environments using a modified Rheovibron Viscoelastometer. This was used to study Nylon 6,6 filaments in deionised water, tetrachloroethylene & dry air and poly(ethylene terephthalate) (PET) film in the presence of various solvents. Ingamells & Yanumet [50] used the same technique on PET to support the claim that aromatic and cyclic solvents solvate the aromatic part of the repeat unit and aliphatic solvents solvate the aliphatic part.