1.5. Characterisation of plastics

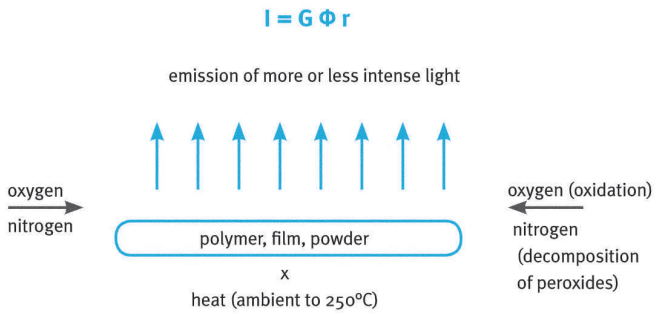


Figure 31. How we see the light emission from the degraded polymer surface

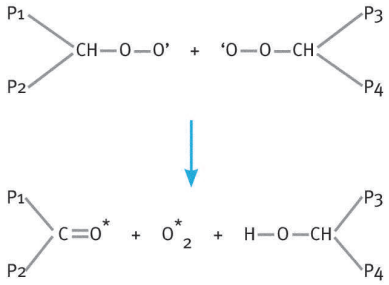
1.5.1. Chemiluminescence (CL)

Introduction

Chemiluminescence is light emission from the relaxation of electrons populating excited states in an elementary step of a chemical reaction. Since, the process of population of excited states is related kinetically to the kinetics of the given chemical reaction, the intensity of emission of chemiluminescence I over time will be related to the rate of the chemical reaction r. There are two proportionality constants, namely quantum yield of radiation which is typical for a particular polymer and geometrical factor G which sets the surface/volume ratio (Figure 31).

It has been established that chemiluminescence accompanies free radical reactions and that its observation is a function of oxygen concentration in the surrounding medium. A heat gain higher than 400 kJ/mol in an elementary reaction of oxidation is reported as being a necessary prerequisite for light emission if the light emission comes from excited triplet carbonyl groups. It may be significantly lower when the light emitter is singlet oxygen. This is also the reason why the most preferred elementary reaction considered as the potential light emitting process is disproportionation of secondary peroxy radicals (Figure 32).

In the above reaction, the excited triplet ketones and singlet oxygen may be formed simultaneously with released heat (450 kJ/mol). This is an optimum circumstance for the highest yield of the light emitted. One has to keep in mind, however, that deactivation of excited states occurs via the heat dissipated in collisions and that one photon is emitted per several millions or even billions of such deactivating procedures (Figure 33). Regardless



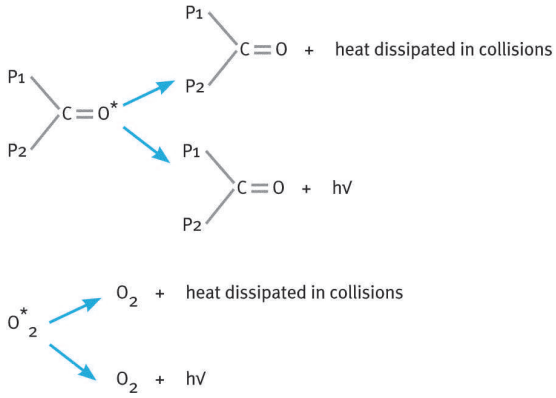


Figure 32 (left). The scheme of disproportionation of peroxyl radicals and formation of excited triplet ketones and singlet oxygen

Figure 33 (right). The scheme of conversion of excited molecules into their ground state (the emission of light)

of this, an extremely sensitive photomultiplier coupled with a photon counting unit is able to register it. This also pre-determines the extreme sensitivity of the chemiluminescence method. $6x10^{23}$ (Avogadro number) molecules or mers in one mole of a polymer indicates that the method is capable of successful monitoring of nano or even pico moles of compounds, which either oxidised or decomposed may provide the excited particles releasing fast quantum of the light.

The maximum of emission from excited triplet carbonyls occurs at 460 nm while that from singlet oxygen at 634 nm (dimol emission) and 1270 nm (monomol emission).

Instrument

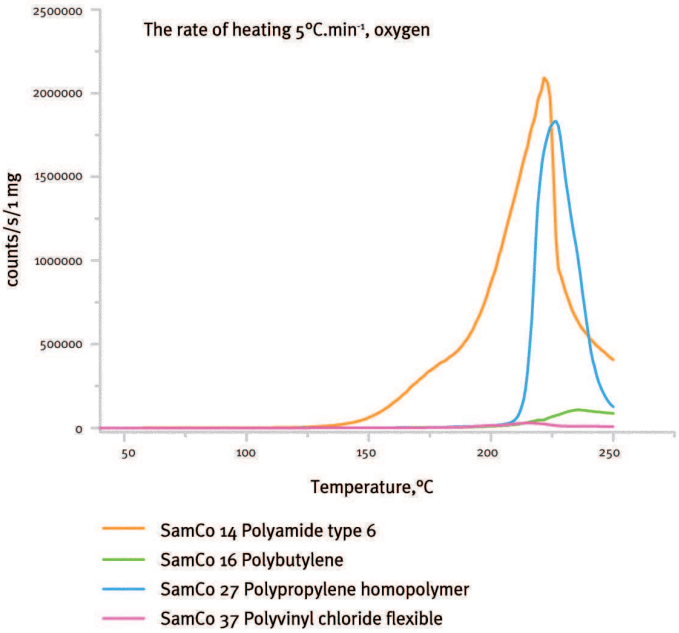
Spectrometer Lumipol 3, product of Polymer Institute, Slovak Academy of Sciences.

Sampling size

Milligram to 10 mg, films of maximum diameter 9 mm, powders, non-volatile liquids.

Examples and results

In the SamCo the plastics providing a relatively strong chemiluminescence signal may be differentiated well from those giving relatively weak light emission (Figure 34). Generally, polyolefins (except of polybutylene), polyamides and polyether urethanes which during oxidation provide statistically distributed carbonyl groups in recombination of secondary peroxyl radicals give strong chemiluminescence signals while polymers which depolymerize or crosslink give weaker signals poly(methyl methacrylate), polybutylene, polyester urethanes,



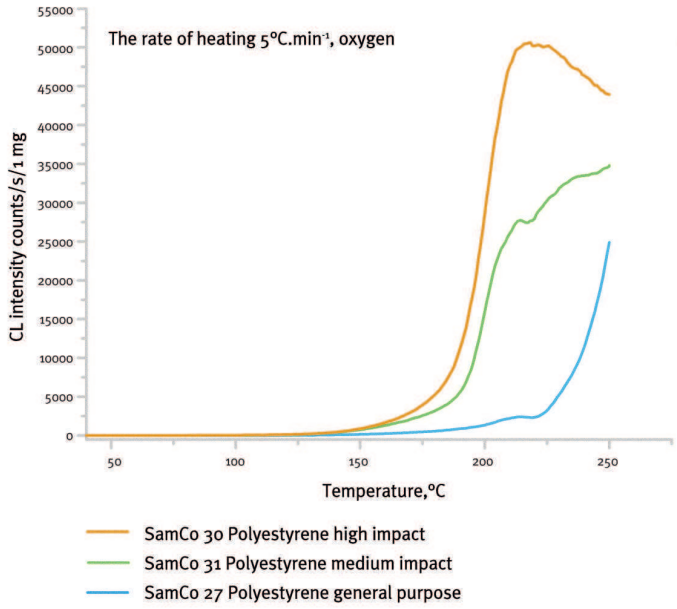


Figure 34 (left). Example of chemiluminescence runs on some typical plastics from SamCo collection

Figure 35 (right). Example of chemiluminescence differentiation of different polystyrene samples

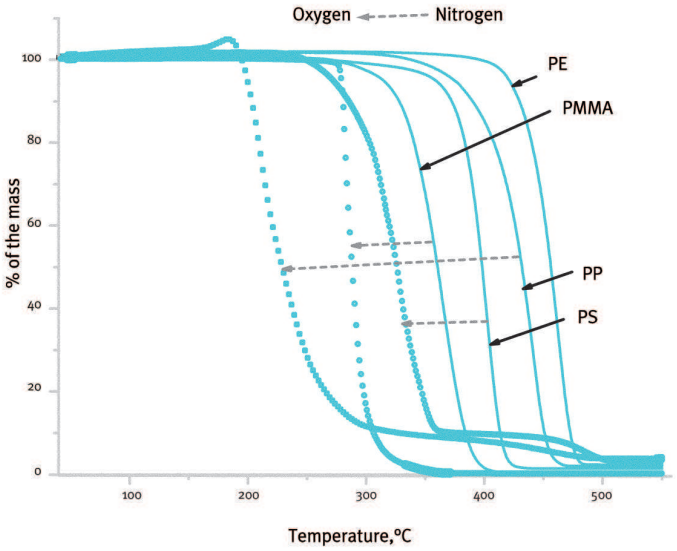
poly(vinyl chloride). Examining the chemiluminescence intensity vs. temperature signals we may also see which polymers are stabilised and which are not. In the Figure 34, e.g. polypropylene homopolymer contains a good stabiliser as the signal intensity starts to increase sharply when the stabiliser is consumed.

Chemiluminescence method allows also to differentiate between respective samples of one polymer containing chemically bound or additive hydrocarbon impact agents (See e.g. polybutadiene moieties in high impact polystyrene Figure 35).

1.5.2. Thermogravimetry (TGA)

Introduction

Thermogravimetry monitors the release of volatiles from the sample being formed by a simple evaporation or by decomposition of the material into low molar mass fragments. It may be used for quantitative estimation of total VOCs (volatile organic compounds), humidity and water or other products and other low molar mass additives present in the object. When increasing the temperature the products from the scission of chemical bonds are formed and non-isothermal experiment ends in complete conversion of a plastic into degradation products. At the same time the residue which remains may be either carbon containing char or inorganic additive (filler).



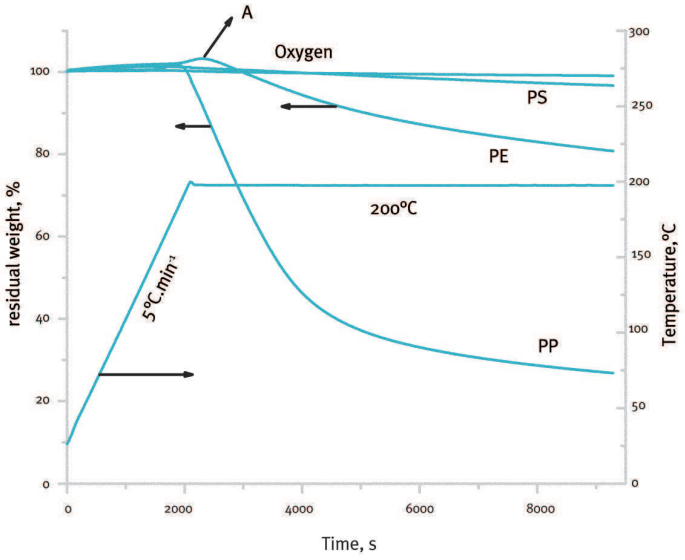


Figure 36 (left). Non-isothermal thermogravimetry runs of pure PE, PP, PS and PMMA plastics films in nitrogen and in oxygen, with a heating rate of 5°C.min^{-1}

Figure 37 (right). Thermogravimetry of polypropylene (PP), polyethylene (PE), polystyrene (PS) and polymethyl methacrylate (PMMA) in oxygen. The samples were heated by the rate 5°C.min^{-1} to 200°C then the temperature was kept constant for 2 hours. The arrow A shows on the weight increase due to reaction of the polymer with oxygen

Instrument

Mettler-Toledo TGA/SDTA 851e.

Sampling size

0.2-10 mg, films of maximum diameter 2 mm, powders, liquids.

Examples and results

The example of output from non-isothermal thermogravimetry for four typical polymers may be seen on the Figure 36. The effect of oxygen depends on the original polymer structure and thus it may be very significant or the effect is almost negligible. The advantage of the nonisothermal method in nitrogen is the weak influence of stabilisers (antioxidants) on the observed curve. The less popular in thermogravimetry assessment are isothermal degradation experiments (Figure 37) which may bring another kind of information about the sample as, e.g. to indicate on the presence of stabilisers if the experiments are carried out in oxygen or more precise way of determination of the integral amount of VOCs released at lower temperatures.

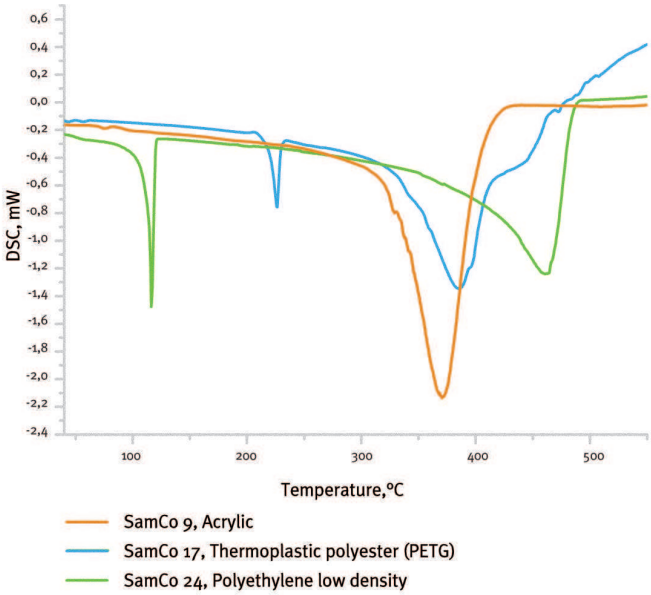


Figure 38. DSC course of oxidation of polypropylene powder, oxygen. Numbers denote the rate of heating in $^{o}C.min^{-1}$

1.5.3. Differential scanning calorimetry (DSC)

Introduction

Differential scanning calorimetry is the thermoanalytical procedure where two insulated pans, one containing the sample and the other some reference substance, are heated together so that their temperature remains either constant or increases according to some pre-set program. Provided that in measuring pan some temperature difference is generated due to the physical or chemical process, the corresponding amount of heat is immediately compensated by changing power of the heater. The method measures the amount of heat absorbed or released by a sample while temperatures in both pans are kept constant. Thus, heat capacities, melting enthalpies, phase transitions temperatures, the extent of crystallinity and other exothermic or endothermic process occurring in the plastics up to the total destruction may be monitored.

Instrument

Mettler-Toledo DSC 821e.

Sampling size

0.5-10 mg, films of maximum diameter 4 mm, powders, liquids.

Examples and results

The method may be exemplified by Figure 38 where SamCo 9, 17 and 24 DSC records in nitrogen are compared. Semi crystalline polymers like polyethylene and thermoplastic polyester give the distinct melting endotherm while amorphous poly(methyl methacrylate) performs only glass transition temperature Tg. At higher temperatures (above 300°C all polymers examined show the endotherm of active decomposition into volatiles which coincide with maximum rate of volatile release determined by nonisothermal thermogravimetry.

1.5.4. Heat of combustion

Introduction

Macromolecules of plastics give the combustion heat in dependence on the composition of the material. Thus hydrocarbon polymers containing only C-C and C-H bonds give the combustion heats above 40 kJ/g while those containing other atoms such as O, N, halogens, etc. have the combustion heats lower.

Instrument

IKA bomb calorimeter.

Sampling size

30 mg-several grams, any form.

Summary

Determination of the combustion heat and of other parameters from CL, TG and DSC may help in identification of unknown polymers as it was e.g. done with the series of unknown polymers provided from Smileplastic Company (Figure 39).

Polymers were supplied originally as a set of unknown polymers which were successfully identified by infrared spectroscopy technique and other methods. In the Figure 39 there may be found not only combustion heats but some additional parameters such as a residue remaining on thermogravimetry pan at 550°C (nitrogen, the rate of heating 5°C/min) indicating particularly the presence of fillers, temperature of the maximum rate of release of volatiles, maximum rate of the volatiles release, combustion heats, temperature of DSC melting endotherm, maximum and temperature of maximum chemiluminescence intensity at 250°C, etc. These parameters follow from the non-isothermal thermogravimetry, chemiluminescence and differential scanning calorimetry.

Jozef Rychlý and Lyda Rychlá

Sample No.	Residue at 550 ° C, nitrogen, %	Temperature of maximum release of volatiles, °C, nitrogen	Maximum rate of release of volatiles, nitrogen, rel.u./s	Heat of combustion, J/g	Temperature of DSC melting endotherm, °C	I_{max} of CL, counts/s/1mg	Temperature of I_{max}, °C
1 PE	0.4	464.3	0.00251	47 426	132.2 133.6	135 783	› 250
2 HIPS	4.3	414.9	0.00251	41 325		1 075	› 250
3 PMMA	0.7	246.7 356.1	1.2e-4 0.00151	27 767		8 240	› 250
4 PC	26.9	508.3	0.00174	32 085		708	› 250
5 PBT	4.4	386.9	0.00226	26 425	224.4	122 404	› 250
6 CA	36.9	231.9	7.8e-4	-		10 177	231.5
7 PP	1.5	421.5	0.0016	49 160	164.2	1 043 728	› 250
8 PET	10.6	420.1	0.00164	24 891	249.8	1 934	› 250
9 PBT	5.3	388.1	0.00227	26 951	225.5	2 902	248.5
10 PA 6,6	3.8	421.5	0.00128	32 432	263.7	1 383 507	232.8
11 PVC flexible	12.5	266.7 448.4	0.00215 2.9e-4	26 003		11 276	216.4
12 NR	44.8	364.1	7.3e-4	39 284		1 736	› 250
13 CN	12.1	193.3	0.00239	19 463		22 125	226.1
14 PS*	5.2	405.5	0.00245	49 575*		72 735	› 250
15 POM	0.04	369.5	0.00375	17 472		335 511	246.0
16 PA 6,6	4.0	421.5	0.00132	32 196 32 013	264.2	616 811	› 250
17 POM homopolymer	0.7	376.1	0.00332	18 437	177.9	74 462	241.6
18 PUR ether	7.6	143.9 274.7 376.1	4.9e-5 3.4e-4 9.1e-4	38 343*		158 397	› 250
19 PUR ester	2.0	273.3 377.5	6.1e-4 0.00134	30 229*		9 773	› 250
20 UF	22.8	181.3 246.7 278.7 332.1	1.2e-4 4.9e-4 5.8e-4 3.8e-4	16 197		741 318	› 250
21 MF	36.4	249.3 326.7	1.7e-4 0.001197	16 179		59 959	› 250
22 PF	43.2	336.1	6.1e-4	26 455		40 499	250
23 PVC rigid	23.8	272.1 449.5	0.0017 5.2e-4	20 629		4 035	› 250
24 PS	1.1	404.1	0.00264	43 092		28 821	› 250
25 SBS	37.8	297.2 430.9	3.4e-4 4.9e-4	28 609		8 613	› 250
26 UP	28.6	362.6	6.2e-4	21 237		9 895 38 665	152.1 › 250
27 Vulcanite	12.8	260.1 336.1 380.1	2.8e-4 4.1e-4 6.3e-4	29 927		25 165	242.3
28 CS resin	27.4	312.1	4.9e-4	20 488		966 898	› 250
29 SI	68.4	456.3 545.7	1.2e-4 2.7e-4	11 936		9 954	› 250
31 Thermoplastic PUR ether	5.3	329.5 394.4	8.0e-4 0.00106	28 180		34 439	› 250

32 Thermoplastic PUR ester	5.5	346.7 394.9	9.6e-4 7.4e-4	32 199	57 439	› 250
33 Hoof	24.0	302.7	4.5e-4	21 347	380 865	› 250
34 CA	9.1	114.5 354.7	1.1e-4 0.00161	21 387	114 878	246.6
35 Shellac	72.3-	388.1 442.9 533.7	1.7e-4 1.0e-4 1.9e-5	11 577	1 151 1 667	167.2 › 250
36 PHB	1.1	278.7 354.7	0.00207 0.00103	25 000	29 925	› 250

Figure 39. Table with additional parameters which may help in identification of the set of unknown polymers

1.5.5. Mechanical properties of polymers

Introduction

The physical properties of polymeric materials are dependent on both the underlying chemical, and physical, structures. Their properties are essentially governed by the length of the long chain backbone, the functional group linkages, polymer processing methods, and the degree of homogeneity. These factors govern their response to external stresses and, as a consequence, their choice of application.

Both thermal and mechanical properties are intimately linked. Since the primary and secondary thermal transitions, such as temperature of melt and the glass transition temperature, relate to molecular motion, it becomes apparent that the larger scale physical properties will also be related to the underlying structure, and will be influenced by temperature. Although thermosetting plastics are often found within museum and heritage collections, particular focus will be given to the mechanical properties of thermoplastics, since it is these materials that exhibit the greatest variation in properties.

Viscoelastic behavior

For an ideal elastic solid, the strain applied to a material has a linear relationship with the applied stress

$$\sigma = E\varepsilon$$

where E is the Young's modulus of elasticity. This behavior is known as Hooke's law, which states that the applied stress is proportional

to the resultant strain, but independent of the strain rate (Cowie 1991).

However, in the case of organic polymers the response is not entirely elastic, as they will exhibit characteristics that are intermediate between an elastic solid and a liquid capable of viscous flow.

This liquid component is described by Newton's law, where the stress is independent of strain, but proportional to the strain rate. Therefore the response of a polymer to an external load is dependent on both magnitude and time. This characteristic duel component affords organic polymers the term viscoelastic. The viscoelastic nature of polymers means that the mechanical properties are time (or frequency) dependent and temperature dependent.

1.5.5.1. Tensile stress-strain analysis

Stress-Strain analysis provides information on the bulk physical properties of a sample, such as the resistance to deform, and the extensibility of a material. It is also helpful to monitor changes in properties during the ageing and degradation processes. In the most common tensile experiments the sample is clamped at each end and subjected to a constant extension and the force required to maintain this extension rate is measured.

Although there are many modes of mechanical deformation, the behavior of thermoplastics under tension is the primary focus here. Tension refers to the application of an equal force at either end of a sample.

For simple tension, if the length of a rod, X_o, is subjected to a tensile force, F, there will be a change in length of dx. The elongation of the sample is known as the strain, and is defined as the extension per unit length.

$$\varepsilon = \frac{dx}{X_o}$$

The corresponding force is proportional to the cross-sectional area (A) of the sample, calculated as F/A. This is termed the stress, σ. An extension of (dx) will cause a corresponding contraction in the perpendicular coordinates of the sample (Cowie 1991). However, in simple uniaxial experiments it is often assumed that the cross sectional area of the sample will remain constant; this measure of stress is known as engineering stress.

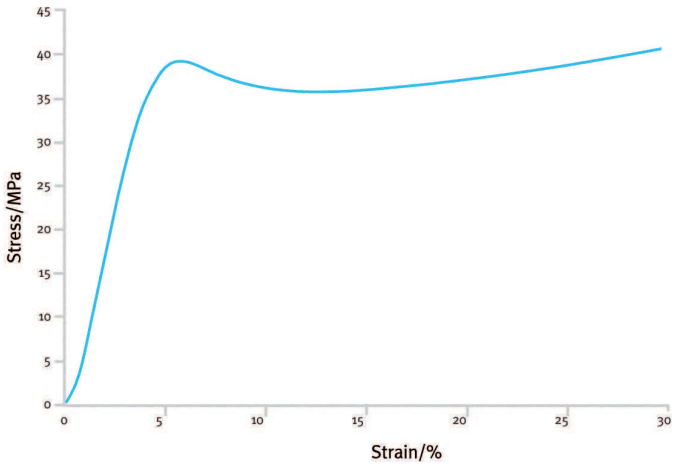


Figure 40. Example of a stress strain curve of a cellulose acetate sample at room temperature, subjected to a strain rate of 5 $mm.min^{-1}$

Instrument

An Instron 5885H tensile tester fitted with a 500 N load cell, a capacity where the sample breaks within the linear range of the cell. Fitted with rubber faced grips, using a crosshead speed of 5 $mm.min^{-1}$.

Sample size

Test strips of uniform width and thickness, with the nominal width not less than 5 mm. Where possible the gauge length of the specimen should be between 100-250 mm, unless it can be experimentally shown that there is no appreciable effect on the results ASTM D882-09.

Examples and results

When a sample is subject to an axial force of such as that described above, a stress-strain curve can be constructed (Figure 40), from which a number of key features can be derived.

The initial slope of the curve is referred to the Young's modulus (E) and is defined as $E = d\sigma/d\varepsilon$. This corresponds to the rate of change of stress as a function of stress and can be used as a measure of the materials response to the applied stress.

The yield stress, σY, refers to the region of the stress-strain curve where a maximum is reached. This is the point at which the material begins to plastically deform i.e. irreversible deformation of the sample. Prior to this point the material is in its region of elasticity, and is capable of returning to its original conformation on removal of the applied force. The elongation at yield is the corresponding strain, εY.

The ultimate tensile strength, σS, is the final stress at the point of break. For thermoplastics, the point of rupture usually follows a process known as cold-drawing. After the yield point the sample forms a neck, which propagates along the length of the sample. The load remains stable as the amorphous regions become oriented in the direction of drawing, until ultimately the neck reaches the tensile clamps, the load increases, and the neck fracture.

1.5.5.2. Dynamic mechanical analysis (DMA)

DMA applies a sinusoidal force or displacement to the sample and measures the samples response to that frequency in the form of amplitude and phase difference, also known as the phase lag, δ. For

a completely elastic material no time lag would be seen between the applied sinusoidal force, or displacement, and the samples response. The phase lag is equal to zero.

For a viscous material, a phase lag is experienced between the applied force and the displacement amplitude. The difference is found to be 1/4 cycle behind that of the force; the phase lag is equal to 90 degrees (Gabbott 2008). Thermoplastics have characteristics intermediate to both viscous and elastic materials.

As such, the displacement is separated into two parts: in-phase and out-of-phase. These correspond to the portion of the deformation that is elastic, stored energy (E'), and viscous, dissipative energy (E''), respectively. The two phases are calculated by taking into account the angular shift of the response:

$$E' = \cos \delta \left|\frac{F}{y}\right| \frac{1}{k} \qquad E'' = \sin \delta \left|\frac{F}{y}\right| \frac{1}{k}$$

The energy lost per cycle can be determined from the relationship between the in and out-of-phase components and is often referred to as the damping factor, tan δ.

$$\tan \delta = \frac{E''}{E'}$$

The complex Young's modulus (E*) is calculated using the maximum force, F (N), the maximum displacement, y (m) and a geometry constant, K (m-3) (Gabbott 2008).

$$E^* = \left|\frac{F}{y}\right| \frac{1}{k}$$

Since a polymer's properties are time, temperature and strain rate dependent, the above variables can be exploited to monitor alterations in relaxation behaviour, which are dependent on molecular structure.

Instrument

Dynamic mechanical analyser with a choice of geometric arrangements, being single cantilever bend, dual cantilever bend, tension, compression, shear and three-point bend.

Sampling size

Sample size is dependent on the geometry of the clamping system, the modulus of the sample and the experimental parameters.

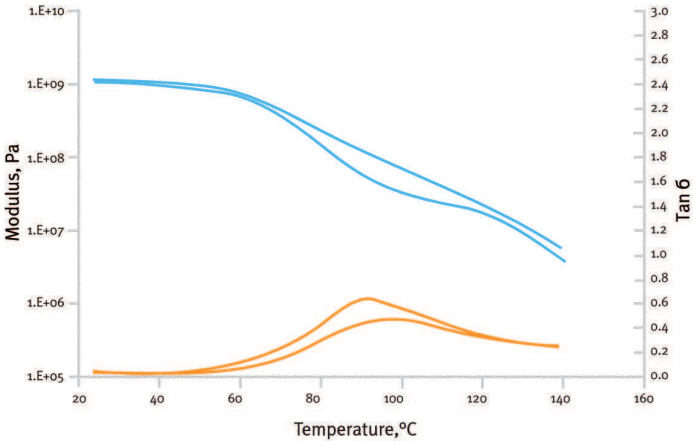


Figure 41. Dynamic mechanical analysis in tension mode of a cellulose acetate propionate sample subjected to a frequency of 1 and 10 Hz, a displacement of 0.01 mm and a temperature rate of 2˚C per minute. Tensile modulus (blue) and damping factor (orange) shown at two frequencies

Examples and results

The most common experimental setup for dynamic mechanical analysis is to apply a constant time/frequency over a temperature range with a constant temperature rate. Focus here is given to the tension clamp. Similar to the stress-strain analysis described in the previous section, DMA tension experiments use a clamp at either end of a sample with a drive shaft that applies a uniaxial extension to the sample. The material response is recorded as a function of time, temperature, frequency, displacement or load. Figure 41 shows an example of a DMA experiment performed on a cellulose acetate propionate sample in tension mode. As the temperature is increased there is a drop in the tensile modulus, seen here as a change in the gradient of the slope (blue curve). The orange curve illustrates the relationship between the elastic and inelastic phase as a function of temperature.

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