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Characterisation of the mechanical properties of polymer films formed from aqueous polymer dispersions by creep testing

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Abstract

The mechanical properties of films formed from an aqueous dispersion of polymethlymethacrylate (Eudragit NE30D) and as mixture with an aqueous dispersion of ethylcellulose (Aquacoat ECD30), have been assessed by applying creep tests at different temperatures, using a dynamic mechanical analyser. In the region of linear creep, the film prepared from 100% Eudragit was far less elastic than when 60% Aquacoat was present. In this region, when the applied stress was doubled, the strain response was doubled. In the non-linear region of behaviour, there is clear evidence that the mixed film is more elastic than the film containing only Eudragit. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aquacoat ECD30; Creep test; Dynamic mechanical analysis; Eudragit NE30D

1. Introduction

The majority of coatings applied to tablets are polymers and their performance is based on the characteristics of the polymer, the solvent system from which they are applied and the conditions under which they are applied. Successful coating requires that the polymer solution or dispersion is applied to the surface and the fluid carrier is removed by the application of heat. In the case of the polymer dispersions, film formation depends on the dispersed polymer fusing to form a continuous film. The mechanical properties of the films as a function of temperature would be a useful property to evaluate in assessing the performance of a film forming formulation. Generally, the evaluation of the tensile strength and the Young's modulus are the standard approach to such characterisation. These measurements however, do not fully characterise polymers, especially when there are transitions of phase involved. An alternative approach is to apply creep tests.

Creep tests measure the time-dependent change in the observed strain under defined stress. A typical creep-time curve for polymer films can be divided into three parts (Hertzberg, 1996). Materi-

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als, after an instantaneous initial strain has developed, often undergo a period of transient response to the stress applied. The strain rate decreases with time and reaches a minimum steady-state value. In the third stage, the creep rate increases again leading to final rupture of the film. In classical creep experiments, however, experiments are performed such that the recovery phase is initiated while the strain-rate value is still in the steady-state region. The decrease in the strain-rate during the transient stage is related to the change in the substructure of the film, resulting in an overall increase in the resistance to dislocation motion. The constant strain-rate during the steady-state creep stage, however, indicates that the film substructures have stabilised and that there is a dynamic balance between strain hardening and softening processes. In more general terms, creep curves might not possess a transient or a steady-state stage. In the first case, the creep curve is linear throughout, whereas in the second case, the transient part of the curve ends in a linear part parallel to the time axis. If the creep-time curve is fully linear, steady flow will result in permanent deformation, whereas the occurrence of only a transient stage should result in complete recovery.

Static creep tests of films, i.e. the application of a static load (stress) for a defined time, can be undertaken by tensile or compressive test arrangements. Tensile tests involve the gripping of the test specimen and pulling. Such tests produce a more or less uniform extension of the sample unless ‘necking’ occurs (Crissman and Zapas, 1989). However, the clamping process can prove difficult and there are ‘ end effects’, which can have a marked influence on the longitudinal strain. A compression test, i.e. uniaxial compression of a thin cylindrical sample between two plates are often preferred if soft materials are to be tested or where the samples loose their integrity during clamping or tensile testing (Whorlow, 1992).

One major influence factor on the creep response of polymer films is the temperature at which the measurements are made. Time-temperature superposition is given if the particular change of temperature changes the rate of retardation or relaxation processes by the same factor. The creep compliance at T_1 has then a value equal to the original compliance at T_0 at an earlier or later time. On a logarithmic time scale, the change in temperature is hence seen as a shift sideways and the distance of the shift is called the ‘shift factor’ (Ferry, 1980). However, superposition is often not observed because the structure of the film will vary with the temperature, resulting in different creep responses. This has to be considered when calculating activation energies, as the Arrhenius equation assumes similar behaviour of the materials at each temperature tested.

Initial experiments with films using a mechanical strength testing instrument fitted with pneumatic grips to perform static tensile creep studies, proved unsatisfactory due to lack of sensitivity of the system. To overcome this problem, creep tests have been performed with a dynamic mechanical analyser in compression mode.

2. Materials and methods

Two aqueous film-coating preparations were studied. The first was Eudragit NE30D marketed by Röhm Pharma (Darmstadt, Germany) and the second was Aquacoat ECD30 marketed by FMC (Philadelphia). The number average molecular mass M_n, weight average mass M_w and the average weight average molecular mass M_z were determined by size exclusion chromatography. Two columns of mixed polystyrene (Polymer Laboratories, Loughborough, UK), a Perkin Elmer (High Wycombe, UK) interface with a Waters Associates (Oslo, Norway) chromatographic pump (run at 1 ml $\min^{-1}$) and injection systems were used. The detector was a Perkin-Elmer LL25 refractive index detector. The samples were dissolved in filtered stabilised tetrahydrofuran, with 0.5% w/w as an internal marker. Samples were injected into a 100 μl closed loop. The data were collected and analysed by a PC with software written by the Bradford University Polymer Science Group. Eudragit NE30D samples were compared to a series of polymethylmethacrylate (PMMA) standards (Polymer Laboratories, Loughborough, UK).

The results for these determinations are presented in Table 1. There were two peaks for the Eudragit NE30D, a major broad peak and a smaller narrow peak.

2.1. Preparation of free films

Cast films were prepared from the Eudragit NE30D and a mixture of 60% Eudragit NE30D and 40% Aquacoat ECD30. For both systems, the dispersions were diluted with an equal amount of purified water before pouring onto 10 cm diameter PTFE containers. The films were left to dry at ambient temperature in a class 2 clean environment. The films were ≈1 mm thick, exact thickness ±0.001 mm being determined with a micrometer (Mercer, Leicester, UK).

2.2. Creep analysis

2.2.1. Initial determination of linearity

The measurements were performed with a Dynamic Mechanical Analyzer (Perkin Elmer, High Wycombe) in the compression mode. A sample of polymer 6 mm in diameter was cut from the cast films and placed between a pair of 5 mm stainless steel parallel plates. Strain is determined as the difference in the spacing between the upper and lower plate supporting the sample. A linearly increasing stress was applied at a rate of 176 $\mathrm{Pa\,s^{-1}}$ to a maximum stress of 1.27×10^5 Pa. The sample was allowed to recover over a 12-min period. Tests were carried out at 0, 30, 60 and 90 °C.

Table 1
The number average M_n, weight average M_w and average weight M_z and the ratio M_w/M_n for the samples of Eudragit NE30D and Aquacoat ECD30

	Eudragit NE30D		Aquacoat ECD30
	Peak 1	Peak 2	
M_n	29,000	1200	4500
M_w	135,000	1200	65,000
M_z	480,000	1500	167,000
M_w/M_n	4–5	4–5	3–4

The values are the average of seven replicates.

2.2.2. Linear creep studies

Experiments were undertaken at 30 °C using parallel plate compression mode. The stress was applied for 30 min and the strain recovery was followed for a further 30 min. Samples were then subjected to double the initial stress for 30 min and the recovery region monitored.

2.2.3. Non-linear creep

To simulate non-standard conditions, which are much more likely to occur during tablet coating, non-linear creep studies were performed. These consisted of stressing a sample in the same mode as previously at 1.27×10^5 Pa for 30 min, followed by relaxation for 30 min both at a temperature of 0 °C. The temperature was then increased to 30, 60 and 90 °C and the standard test procedure followed.

3. Results and discussion

3.1. Initial investigation of linearity

The results for the application of a linear stress are illustrated for the two types of film in Fig. 1(A, B). For the 0 °C experiments with Eudragit, the stress/strain response is linear throughout the test. The response of the same polymer at 90 °C is also linear, but only after an initial lag time, i.e. there is no transient stage. At 30 and 60 °C, the response shows a transient stage followed by a steady-state creep stage. All samples showed some degree of both plasticity and elasticity. The amount of elastic recovery ranged from 45 to 60% and was not related to the temperature of the test (see Table 2). The addition of Aquacoat to the Eudragit results in films which provide very limited linear stress–strain responses and show widely differing elastic recovery (see Table 2). The 0 °C sample recovers 90% of its original dimensions, while the 90 °C sample recovers by 10%. The mixed films tend to show a higher degree of resistance to stress and a much greater change in type of behaviour with temperature. Hence, the film substructures formed by the alignment of the molecules of the different polymers are not stabilising and the mixed film therefore moves and

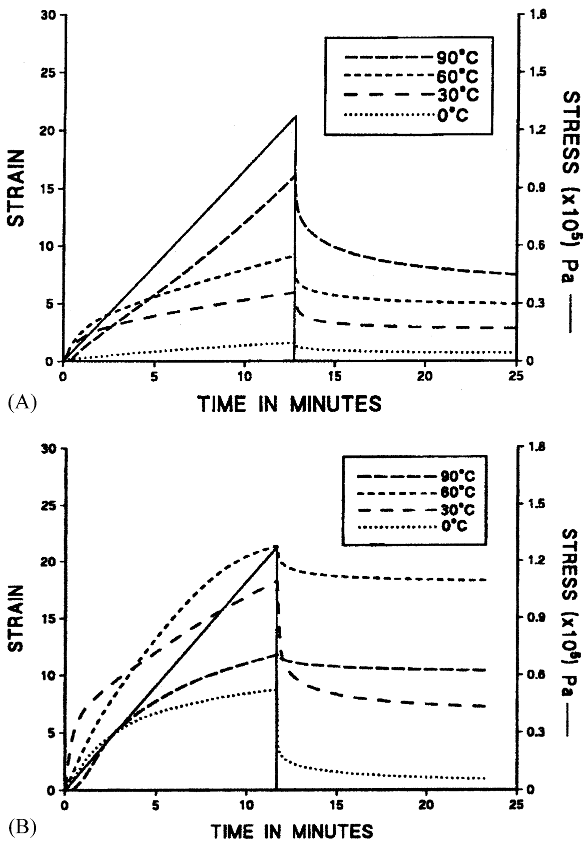

Fig. 1. Strain behaviour at a constant stress rate (depicted as a solid line) at 0, 30, 60 and 90 °C for films prepare from (A) Eudragit NE30D and (B) a mixture of Eudragit NE30D and Aquacoat ECD30 (60%).

deforms to a larger extent than the film formed from Eudragit alone.

3.2. Linear creep

The Boltzmann supposition principle implies that the response of a sample, e.g. strain at any time, is proportional to the value of the initialising signal, i.e. stress. It is assumed that the strains are small and each increment of stress creates an independent contribution. The total creep in a system is the sum of the individual increments and is therefore a function of the entire loading history. To test the behaviour of the samples, they were subjected to two stresses. The results for the single Eudragit and the mixed Eudragit/Aquacoat films are shown in Fig. 2. The maximum applied stress and its associated strain and the percent of elastic recovery are presented in Table 3. For the application of approximately the same stress, the mixed film develops far greater deformation, but in both cases doubling this stress approximately

Table 2
The elastic recovery after the application of a non-linear stress to films prepared from Eudragit NE30D and a mixture of Eudragit NE30D and Aquacoat ECD30 (60%)

Temperature °C	Recovery %	
	Eudragit	Eudragit/Aquacoat
0	10	2
30	>100	60
60	20	30
90	20	30

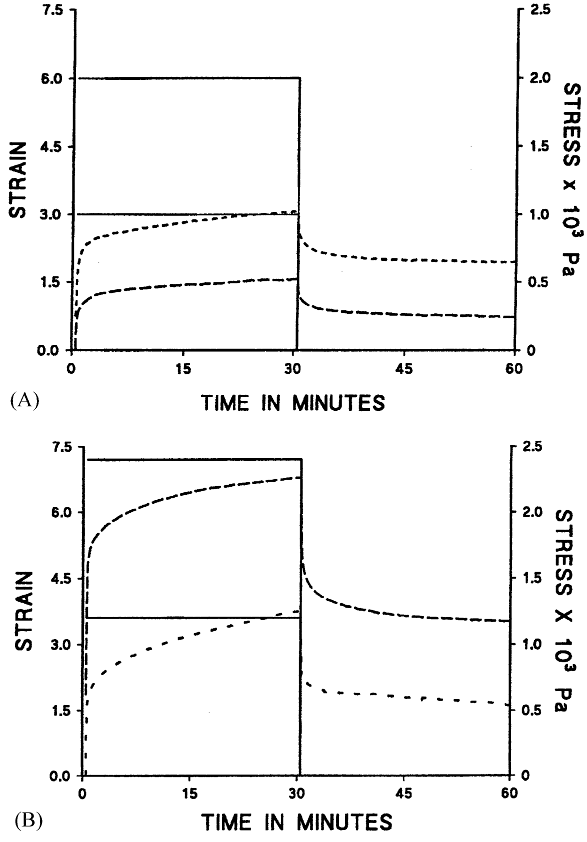

Fig. 2. The creep recovery of films prepared from (A) Eudragit NE30D and (B) a mixture of Eudragit NE30D and Aquacoat ECD30 (60%). The solid line represents the applied stresses.

Table 3
The strain response and the elastic recovery of films prepared from Eudragit NE30D and a mixture of Eudragit NE30D and Aquacoat ECD30 (60%) on removal of the stress

Material	Applied stress (Pa) × 10^3	Maximum strain (corrected)	% Elastic recovery
Eudragit	1.0	1.5	50
Eudragit	2.0	3.0	50
Eudragit/Aquacoat	1.2	2.5	55
Eudragit/Aquacoat	2.4	5.4	60

doubles the strain, supporting the Boltzmann supposition principle for these materials. At 30 °C both films show approximately the same percentage of elastic recovery, although that for the mixed film is far greater.

3.3. Non-linear creep

The results of stressing and relaxing the sample repeatedly as the temperature is increased are shown for the two types of film in Fig. 3. The repeated stressing of the same sample shows a different response in the two types of sample. The single component film has a lower deformation and lower recovery than the mixed film at 0 °C. As the temperature is increased however, the single component film shows less resistance to deformation than the mixed film. The recovery for the two systems shows similarities and differences: the single component film shows only a slight recovery at low temperature indicating a high component of plasticity in the sample, whereas the mixed film shows a larger degree of recovery. This indicates physical interactions between the two polymers, adding flexibility to the system. As the temperature increases, the percentage recovery increases and then becomes constant at 60 and 90 °C. This type of change in response also occurs with the mixed film, although the values are not identical.

4. Conclusions

The results clearly indicate that it is possible to measure the visco-elastic behaviour of films, which are used in film coating and quantitative values can be assigned to the mechanical aspects of these films.

The increased flexibility of the mixed films could be of advantage for the functionality of these films. They could be less prone to mechanical damage during processing and could be effective at a lower thickness as controlled release films.

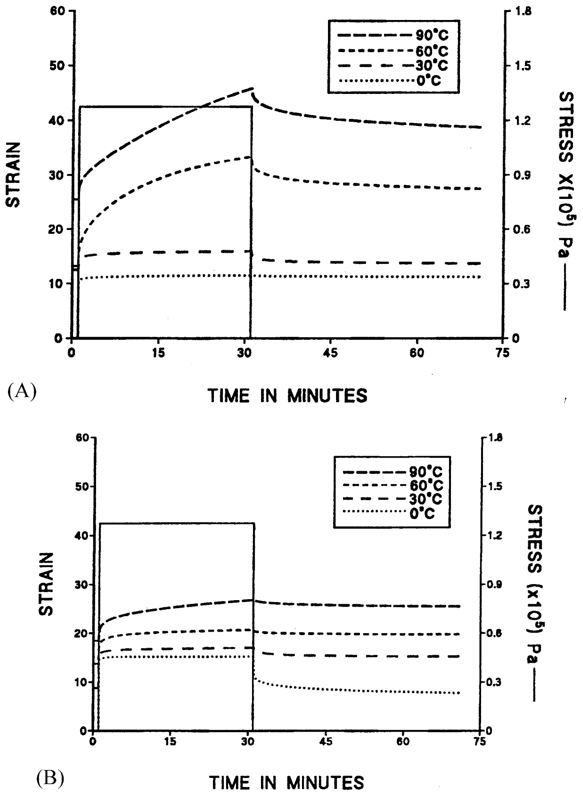

Fig. 3. The creep recovery of films stressed at 1.27 × 10^5 Pa for 30 min then allowed to relax for a further 30 min for films prepared from (A) Eudragit NE30D and (B) Aquacoat ECD30 (60%). The solid line represents the applied stress.

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