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Dynamic mechanical thermal analysis studies of polymer films prepared from aqueous dispersion

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Abstract

Dynamic Mechanical Thermal Analysis of cast and sprayed films of an aqueous dispersion of polymethyl methacrylate (Eudragit NE30D) and mixtures with an aqueous dispersion of ethylcellulose (Aquacoat ECD-30) has been undertaken. Such analysis allows the identification of glass transition temperatures and the degree of miscibility of the polymers. It was found that the two polymers formed as cast or sprayed films were not miscible but had an optimal composition of 30% of the ethylcellulose dispersion in the polymethyl methacrylate dispersion. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Dynamical mechanical thermal analysis (DMTA); Ethylcellulose dispersion (Aquacoat); Glass transition; Temperature; Miscibility; Polymethyl methacrylate dispersion (Eudragit NE30D)

1. Introduction

In a previous study, the application of creep test to the characterisation of the properties of polymer films at a range of temperatures, has been described by Lafferty et al. (2002). Here the strain response equal to a constant stress and its removal as a function of time were recorded. Such measurements were able to show that by mixing two types of polymer dispersions, the visco-elastic properties of the films could be changed. A further approach to mechanical testing of polymer films is the technique of thermal mechanical analysis (TMA). Here a probe is pressed into a preformed film at a known force and the depth of penetration is measured as the temperature is increased. The material softens as it passes through the glass transition region, allowing probe penetration. This technique was employed by Fukumori et al. (1988) to study the properties of the Eudragits L30D, RS30D and NE30D. Goodhart et al. (1984) studied Aquacoat ECD 30 plasticised with triethyl citrate or dibutyl subacetate. Okhamafe and York (1988, 1989) examined free films of hydoxypropylmethyl cellulose and polyvinyl alcohol by differential scanning calorimetry (DSC) and TMA. They found that some but not all transitions could be related by

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the two methods. Subjecting a material to a dynamic mechanical force provides a further alternative to the detection of small changes in the state of the material. The application of a sinusoidal mechanical force induces a sinusoidal strain, which is then measured. The response is resolved into that part which is in phase with the applied stress (the elastic component) and that, which is out of phase with the applied stress (the viscous component). The technique can be used to study molecular structure and phase morphology. Such an approach is the torsional braid pendulum, which was used in a series of studies by Sakellariou et al. (1984, 1985, 1986b, 1994), Sakellariou and Rowe (1995) to examine the glass transition and miscibility of a series of blends of polymers and plasticisers in solution. In this experimental technique clean glass braids, which have been impregnated with polymer solutions and dried are subjected to a sinusoidal strain at constant frequency as a function of temperature. This approach does not allow the study of the films themselves nor is the equipment universally available. There are no reports in the pharmaceutical literature of there use for aqueous dispersions of polymers, which form films by a completely different mechanism than those formed from solution and their properties are very dependent on the conditions of formation. Hence studies of such systems need to be able to study the films themselves. There are several types of commercial Dynamic Mechanical Thermal Analysis (DMTA) systems available, which allow films to be studied. A stress can be applied to various configurations to prepared samples. Such systems, which usually have good temperature control, can identify how the storage (elastic) and loss (viscosity) modulii and tan δ (ratio of the loss and the storage modulii) changes with temperature and in particular can identify the value of the glass transition temperature. Data can be collected either at constant frequency, by scanning temperature or at constant temperature by scanning at a range of frequencies. Frequency scans at constant temperature are open to more precise interpretation (Ferry, 1980) but the experimental range available is usually only sufficient to cover one relaxation region. In the current work a dynamic mechanical thermal analysis approach was applied to polymer films produced from the aqueous dispersion Eudragit NE30D and its mixtures with Aquacoat ECD-30.

2. Materials and methods

Cast films were prepared from an aqueous dispersion of polymethyl methacrylate (Eudragit NE30D), (Rohm Pharma, Darmstadt, Germany) and a mixture with an aqueous dispersion of ethylcellulose (Aquacoat ECD-30, FMC Corp., Philadelphia, USA) as described by Lafferty et al. (2002). Spray films were produced by spraying on to a sheet of PTFE placed inside a perforated pan coater and applying the coating solution with a pneumatic nozzle positioned 8 cm from the sheet. The inlet air temperature was between 48 and 56 °C and the spray was applied intermittently with a spraying time of 5 s followed by a drying time of 12 s. Films were allowed to dry in the coating pan until they felt dry to the touch and then removed from the PTFE sheet. Both sprayed and cast films were stored over silica gel until required for testing. Rectangular samples 20×10 mm with a thickness of 5 mm were cut from these films and heated at 85 °C for 1 h prior to testing. These samples were clamped at one end and the central drive shaft to provide a single cantilever action. The samples are subjected to a constant stress, at a frequency of 1 Hz, at temperature ranging from -50 to 150 °C (heating rate of 3 °C/min) in a DMTA (Polymer Laboratories, Loughborough, UK). The stress applied was chosen to ensure that strains of less than 10% of sample thickness were achieved. The results are the mean of five replicate determinations.

3. Results and discussion

Attempts to produce sprayed films for the single component dispersions proved to be unsuccessful as the formation of free films of the dimensions required with sufficient uniformity in thickness was not possible. Spraying films onto surfaces and attempting to measure the change caused by the presence of the film was also unsuccessful. The best approximation was achieved by spraying the mixed dispersions onto steel shims 0.25 mm thick covered with a film of 0.1 mm. This provided the best results at temperatures up to 60 °C, but above 100 °C the data were not very smooth and the transitions were not well defined. Cast films were therefore used throughout the tests except for mixed component films, where spraying could also produce films.

When examining the results, it is important to identify the various components of the curves produced. The typical response of an amorphous polymer subjected to a constant sinusoidal mechanical stress of constant frequency as a function of temperature is illustrated in Fig. 1. The values of the storage modulii are illustrated as the solid line and fall as the temperature increases. The value of tan δ, however, shows peaks when the average molecular relaxation time t equals 1/2 π, where v is the frequency. The transition occurring at the highest temperature is called the α transition relaxation or dispersion, and is usually the most intense response. The α transition is commonly thought to arise due to movement of the polymer backbone (Ward, 1985) which is also the movement attributed to the glass transition. The transition occurring at the second highest temperature is called the β transition and is thought to arise due to motions of the side chains. The third transition is called the γ transition and occurs due to the rotation of the side chains, commonly methyl groups.

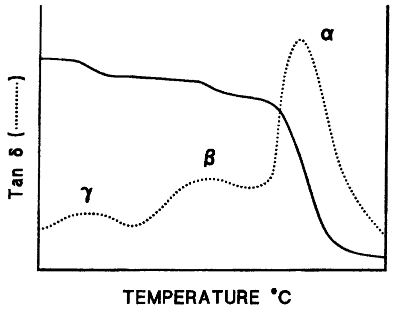

Fig. 1. Typical tan δ and storage modulus (E') response of an amorphous polymer to a dynamic stress analysed at a constant frequency scanning temperature.

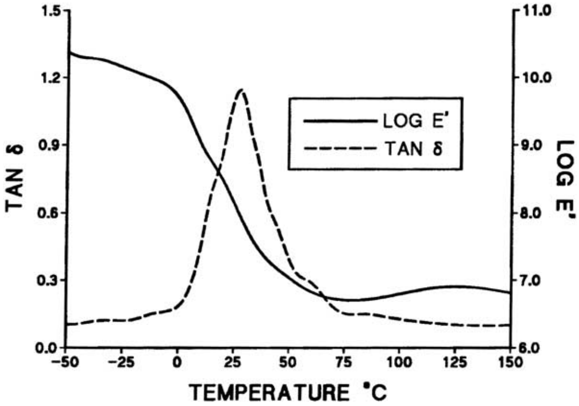

Fig. 2. A typical response of a Eudragit NE30D 100% cast film to a sinusoidal mechanical strain at 1 Hz. The peak in tan δ occurs at 28 °C.

The results for films of Eudragit NE30D (Fig. 2) and its 70% (Fig. 3) and 50% mixtures with Aquacoat ECD-30 (Fig. 4) illustrate the results obtained. The Eudragit NE30D provides one major peak in the tan δ curve, which occurs at 28 °C, which is probably due to the glass transition arising due to the motion of the polymer backbone. The film consisting of 70% Eudragit NE30D and 30% Aquacoat ECD 30 exhibits two peaks in the tan δ curve. The peak at 36 °C could be attributed to the glass transition of the Eudragit component. The broader peak at around 115 °C could be due to the Aquacoat component,

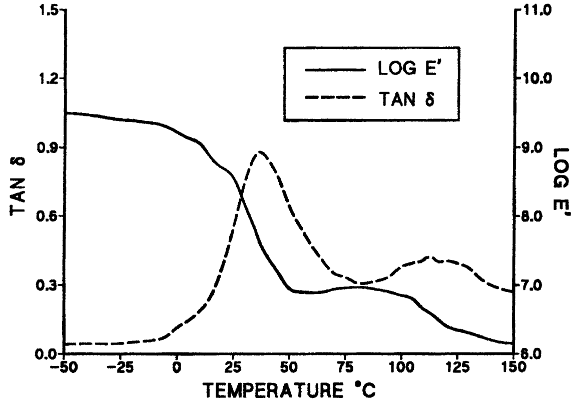

Fig. 3. A typical response of Eudragit NE30D/Aquacoat ECD-30 70% cast film to a mechanical strain at 1 Hz. The peak at 36 °C is attributed to the Eudragit component and the broad at 115 °C to the Aquacoat component.

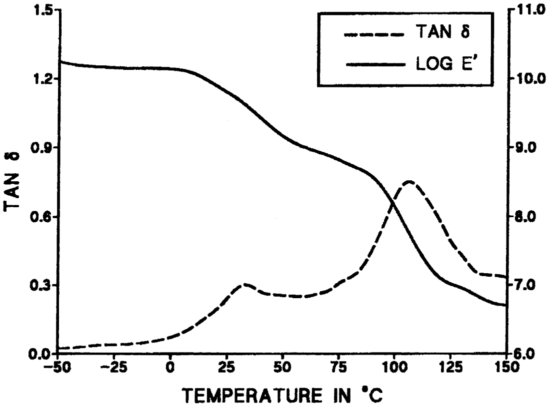

Fig. 4. A typical response of Eudragit NE30D/Aquacoat ECD-30 50% cast film to a mechanical strain at 1 Hz. The peak at 33 °C is attributed to the Eudragit component and the peak at 105 °C to the Aquacoat component.

but as films could not be cast from this material in the absence of plasticisers, it is difficult to be totally sure as no reference results could be obtained. The film composed of equal proportions of Eudragit and Aquacoat also exhibits two peaks in the tan δ curve. The most prominent around 105 °C is probably attributable to the Aquacoat component, while the smaller peak at about 33 °C could be due to the Eudragit. It is noticeable that the size of this peak diminishes as the proportion of this component decreases. The storage modulus E has a value at about 10^9–10^{10} Pa at −50 °C for each of the three samples. By the time the temperature has reached 150 °C, the value has dropped to approximately 10^{-3} Pa. These constant frequency experiments provided indications of glass temperature of the films, which had not been possible by DSC. The question arises as to whether when the mixed polymers were used were they homogeneous? The systems being studied here are complex stabilised aqueous dispersions. Hence it is not possible to use the solubility parameter approach described by Sakellariou et al. (1986a) for the prediction of miscibility as the polymers are not in solution and the films are formed by fusion of the polymer particles, which are surrounded by protective, stabilising layers. Miscibility in the field of thermodynamics indicates the existence of a single phase down to the molecular level. However, the term is often used to imply that the system appears to be homogeneous in terms of the tests applied. DSC techniques can detect ‘miscibility’ to a level of approximately 15 nm. A single Tg value assessed with such a technique only signifies that the domain is below 15 nm. It is generally thought that the cooperative segmental motion that leads to the value of Tg involves the movement of 50–100 backbone carbon atoms, which have a domain size of 2.3 nm. The use of the Tg value and dynamic mechanical thermal analysis to examine miscibility of these polymers seems reasonable as long as it is remembered that in pure thermodynamics, the results only represent the state of dispersion.

For a completely miscible system, a single combined loss peak will be observed. The tan δ loss peak, maximum $T_{\max}$ for the blend can be predicted to move monotonically in line with the Gordan and Taylor (1952) equation

$$T_{\max} = V_1 T_{\max 1} + V_2 T_{\max 2},$$

where V_1 and V_2 are the volume fraction components of materials 1 and 2 and $T_{\max}$ values are the tan δ loss peak maxima for each of the components. Where complete phase separation occurs, each phase exhibits its characteristic relaxation and the position of the α transition is not composition dependent (Wetton et al., 1986). The results for a series of compositions of mixtures of Eudragit and Aquacoat between 50 and 100% Eudragit were measured. It was not possible to form films consisting solely of Aquacoat and mixtures containing less than 25% exhibited a very broad shallow transition for which it was not possible to identify the Aquacoat component curve. The relative peak tan δ height for the two components is shown in Fig. 5, which illustrates that the height of the tan δ peak is proportional to the film component composition. The relationship between the film composition and the maximum temperature at which the peak tan δ occurs is illustrated in Fig. 6. The results indicate a maximum value at a composition of about 70% Eudragit. This may represent the composition with the maximum miscibility, but in general, it can be concluded that, while composite films are formed, the two polymers are not miscible.

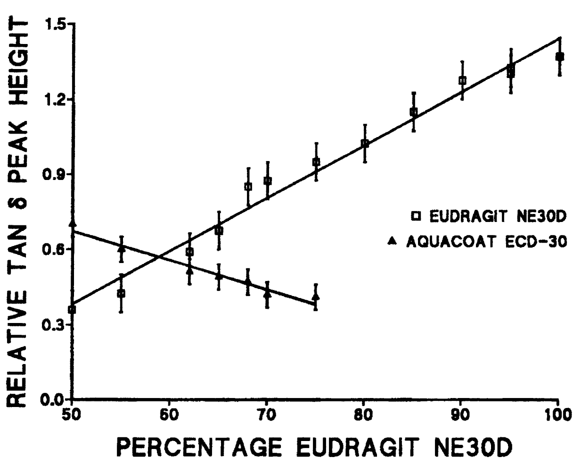

Fig. 5. The relationship between the peak tan δ height and the composition of Eudragit NE30D/Aquacoat ECD-30 cast films.

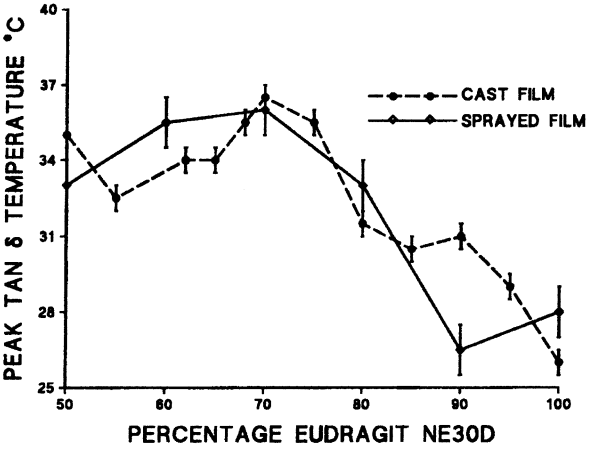

Fig. 6. Peak tan δ temperature at 1 Hz as a function of Eudragit NE30D/Aquacoat ECD-30 film composition for sprayed and cast films.

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