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RESEARCH PAPER

# The Effect of Different Plasticizer Molecular Weights and Concentrations on Mechanical and Thermomechanical Properties of Free Films

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## ABSTRACT

*Plasticizers are usually added to improve the mechanical and conditional (thermomechanical) quality of film coatings. Different molecular weights and concentrations of polyethylene glycol were incorporated as plasticizers in hydroxypropylmethylcellulose (HPMC) films. Thermomechanical and mechanical properties of cast films were tested using tensile and dynamic mechanical thermal analysis (DMTA) testing, respectively.*

*The results, as expected, showed that addition of plasticizer caused a decrease in both mechanical and thermomechanical properties, but lower grades had more effect than higher molecular weights and concentrations.*

*The conclusion could be drawn that combining different grades of plasticizers to optimize mechanical and thermomechanical properties is more efficient than using different concentrations of plasticizers.*

***Key Words:*** *Hydroxypropylmethylcellulose; Plasticizer; Glass transition; Dynamic mechanical thermal analysis; Aqueous film coating; Mechanical properties*

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## INTRODUCTION

Aqueous film-coating techniques are of current interest in the pharmaceutical industry. Tablets are film-coated for many reasons. The coating provides protection for the tablet core and as such must remain intact, have suitable mechanical properties, and be durable to prevent chipping and cracking during handling. The composition of coating formulations usually contains many additives in addition to the polymer, and in most formulations plasticizers are included to enhance the flexibility of the films. Most of the water content that acts as a plasticizer is already lost by evaporation (1). Polyethylene glycol 6000 inclusion is related to controlled release dosage forms (2). The effect of plasticizer type and concentration on the incidence of bridging on film-coated tablets was studied by Rowe and Forse (3). Incorporation of plasticizer in film formulations mainly alters their mechanical properties, e.g., elongation, modulus, and stress (4). The thermomechanical properties of hydroxypropylmethylcellulose (HPMC) free films were reported by Johnson et al. (5) using dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) methods. Polydextrose and titanium additives resulted in increasing both mechanical and adhesion properties of films (6). The objective of this work was to study the role of plasticizer molecular weights and concentrations in the two main conditional properties, e.g., maximum tensile strength and glass transition temperature of HPMC free films.

## MATERIALS AND METHODS

### Materials

Methocel E5, hydroxypropylmethylcellulose (HPMC) was purchased from Colorcon, Ltd., UK. Polyethylene glycol (PEG) 300, 600, 1500, and 4000 were purchased from Merck & Co., Inc.; PEG 400 was purchased from Sigma Chemical Co.

### Methods

#### Preparation of HPMC Solutions and Films

The desired amount of HPMC, with and without various molecular weights of PEG, was weighed and mixed with approximately half the desired hot distilled water. The remaining water was then added as cold water, mixed thoroughly, and the solutions left overnight. The concentration of PEG was kept constant at 10%, 20%, and 30% w/w of HPMC. The solutions were cast onto a clean glass plate by a thin layer chromatography applicator and left overnight to evaporate the solvent at room temperature. The films were then peeled off and used for different tests.

#### Tensile Testing

The polymeric films were cut after casting and drying using a scalpel (test section $15 \times 5\,cm^2$). The thickness of each sample was measured by a micrometer in five different places. The mean of these recordings was used in the calculations of maximum tensile strength. The films were stored at 50% relative humidity for 3 days before testing. Three specimens of each formulation were tested using a tensile tester, Dy 26 Adamel, France.

#### Dynamic Mechanical Thermal Analysis

By this method, changes in internal molecular mobility, secondary relaxation in the glassy state, and glass transition temperature ($T_g$) can be detected as a function of temperature and impressed frequency.

For a viscoelastic material, the storage modulus $E'$ is the elastic response (recoverable energy) and the loss modulus $E''$ is the viscous response (lost energy). The tangent of the loss angle, $\tan\delta$, is equal to the ratio of lost energy to stored energy per cycle:

$$\tan\delta = \text{loss modulus/storage modulus} = E''/E' \quad (1)$$

Equation (1) shows the response of the material changes with temperature at fixed frequency. At the glass transition temperature a sharp drop in modulus and a peak for $\tan\delta$ are observed.

The films were stored at 50% relative humidity for 3 days at room temperature, then tested by DMTA at Polymer Laboratories (Amherst, MA) to determine the glass transition temperature ($T_g$).

The sample size was 5 mm long × 10 mm wide. The film thickness was variable between 0.05 and 0.09 mm. Experiments were performed in tensile mode at ×1 strain (16 m nominal peak-to-peak displacement in the sinusoidal strain wave generated by the DMTA equipment) and 1 Hz from 80 to 200°C at 3°C/min in the reducing mode.

## RESULTS AND DISCUSSION

### Plasticizer Compatibility

The samples were chosen by visual observation for detection of incompatibility. Any sample that showed any sign of incompatibility such as spotting was discarded at this stage. Only 16 samples were suitable for subsequent testing (Tables 1 and 2). The samples containing polyethylene glycol 1500, 4000 in concentration greater than 20% showed spotting.

### Tensile Results

The results showed that PEGs have a marked effect on decreasing maximum tensile strength at breaking point. The maximum tensile strength at breaking point was increased as the molecular weight of PEG was decreased and the concentration of plasticizer was increased (Table 2). These effects could be explained by gel theory. In this theory it is assumed that active center forces attract polymer molecules in solution to each other. These bonds are in a dynamic equilibrium in solution form (making and breaking). As they break water molecules are in competition for the sites. Plasticizers will also be in competition for the same sites and will thus reduce the number of active centers and the number of polymer–polymer contacts, so they could decrease the rigidity of the three-dimensional structure formed on drying. Table 2 and Fig. 1 show that low molecular weights of PEGs are more effective as plasticizers. This can be explained by the fact that there will be more molecules, and therefore presumably more chances of competition for an active site, per gram of added PEG.

*Table 1*

*The Effect of Different Plasticizer Molecular Weights and Concentrations on Glass Transition Temperature (°C)*

| HPMC(A) 153.8 | 10% | 20% | 30% |
|---|---|---|---|
| A + PEG300 | 109.40 | 87.18 | 76.98 |
| A + PEG400 | 119.22 | 117.76 | 92.70 |
| A + PEG600 | 122.72 | 121.96 | 119.42 |
| A + PEG1500 | 127.12 | 123.96 | |
| A + PEG4000 | 148.66 | 61.98 | |
| | | 144 | |

*Table 2*

*The Effect of Different Plasticizer Molecular Weights and Concentrations on Maximum Tensile Strength at Breaking Point (MPa)*

| HPMC(A) 36.92 | 10% | 20% | 30% |
|---|---|---|---|
| A + PEG300 | 14.93 | 11.20 | 6.16 |
| A + PEG400 | 18.14 | 12.65 | 7.77 |
| A + PEG600 | 21.93 | 18.22 | |
| A + PEG1500 | 25.30 | | |
| A + PEG4000 | 26.67 | | |

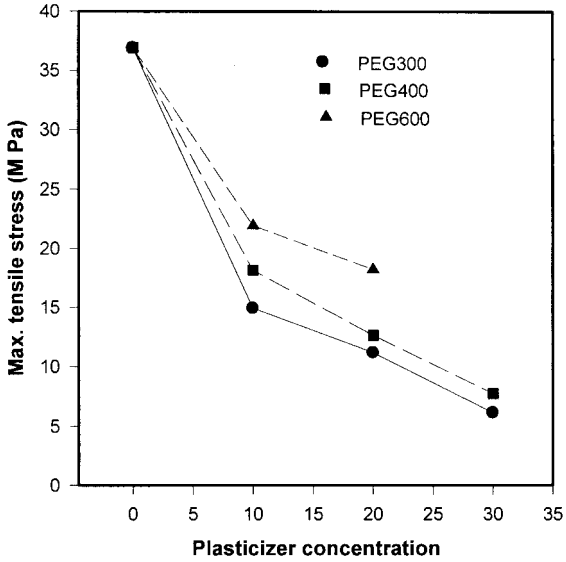


**Figure 1.** The effect of plasticizer addition on maximum tensile strength at breaking point (MPa).

### DMTA Results

A sample DMTA spectrum for HPMC film is presented in Fig. 2 where the elastic component of the tensile modulus ($E'$) and the mechanical loss ($\tan\delta$) are plotted as a function of temperature for unplasticized HPMC E5 films. Tan $\delta$ peaks at 153.8°C, which correlates with the glass transition temperature. The data from DMTA experiments or HPMC films without and with different plasticizer molecular weights and concentrations are presented in Fig. 3.

The results also show that the $T_g$ decreased as the molecular weight of PEG decreased and this

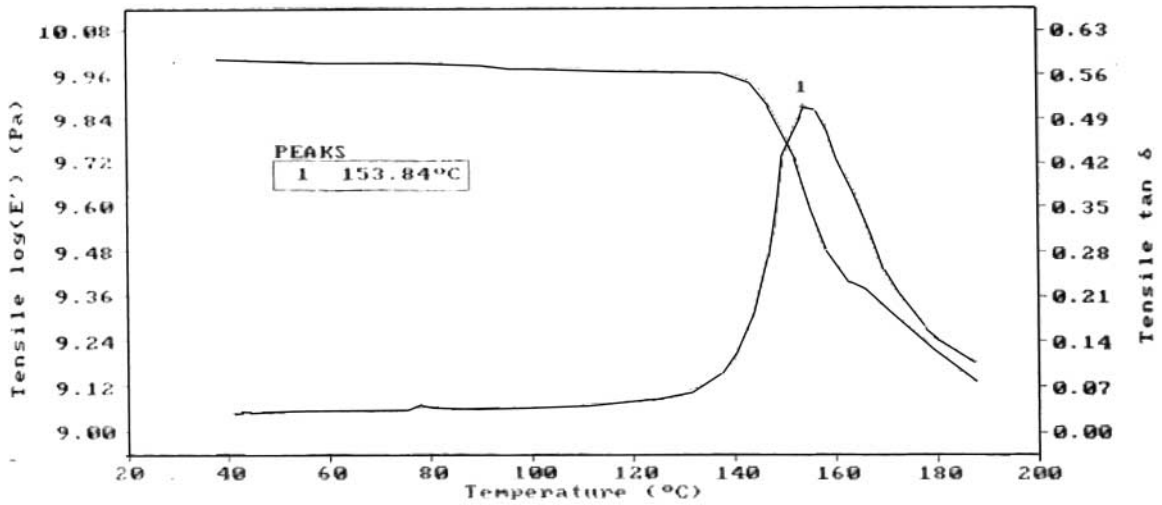


**Figure 2.** Determination of glass transition temperature for HPMC E5 free films from a DMTA thermogram.

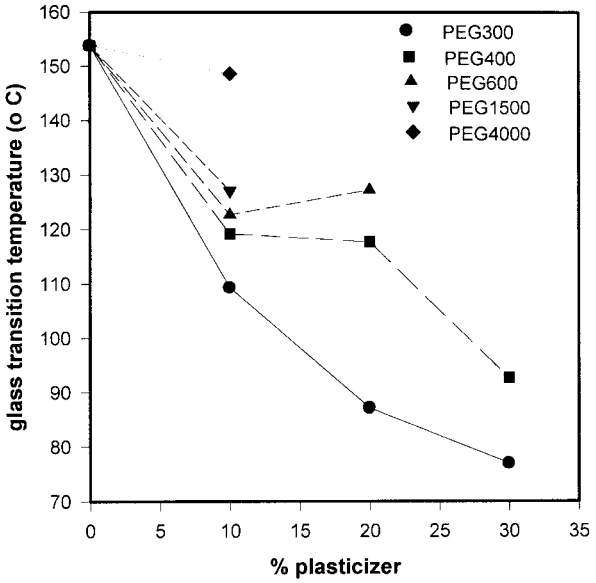


**Figure 3.** The effect of plasticizer addition on glass transition temperature of HPMC E5 films.

effect was more pronounced for lower molecular weights than higher molecular weights ($p < .05$). The effect of molecular weight of PEGs was much higher than the effect of their concentration, but with the same trend. All thermograms (Table 2) show only one peak for $\tan\delta$ but at different temperatures, except Fig. 4, which shows a DMTA thermogram for a film made from HPMC E5 + PEG 4000, 20% w/w. In this thermogram $\tan\delta$ shows two peaks at 61.98 and 144°C. This phenomenon occurred by separation effect of PEG 4000 from HPMC during the film forming, leading to the formation of two separate phases in the film, which appeared as weak spots. These weak spots could not be detected by visual observation on the film surface, but this incompatibility could be detected by $T_g$ measurement.

Plotting glass transition temperature ($T_g$) against maximum tensile force data for HPMC films with 10% w/w concentration of different molecular weights of PEGs (Fig. 5) showed that a lower molecular weight of PEGs (300, 400) decreased both the glass transition temperature and the maximum tensile strength at breaking point. Increasing the molecular weight of plasticizers would increase these items. According to the scheme of Lever and Phys (7), the tendency is towards a soft, tough film. The decrease in glass transition temperature and maximum tensile strength at breaking point, could make these films satisfactory, although the low strength and $T_g$ may adversely affect the film physical resistance to marking, scratching, etc. This problem will be seen to be critical when we notice the role of other excipients in decreasing the glass transition temperature, causing a marked reduction in film strength.

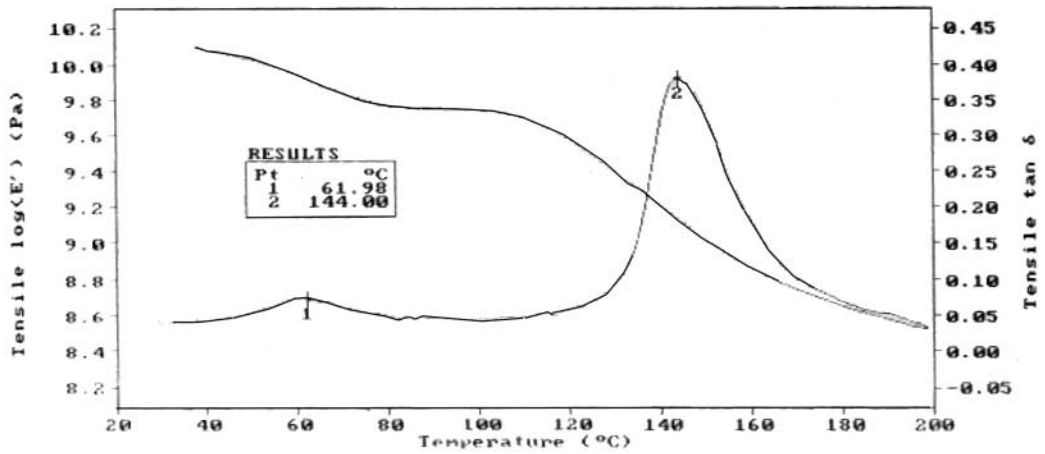


**Figure 4.** Determination of glass transition temperature for HPMC E5 + 20% PEG4000 free films from a DMTA thermogram.

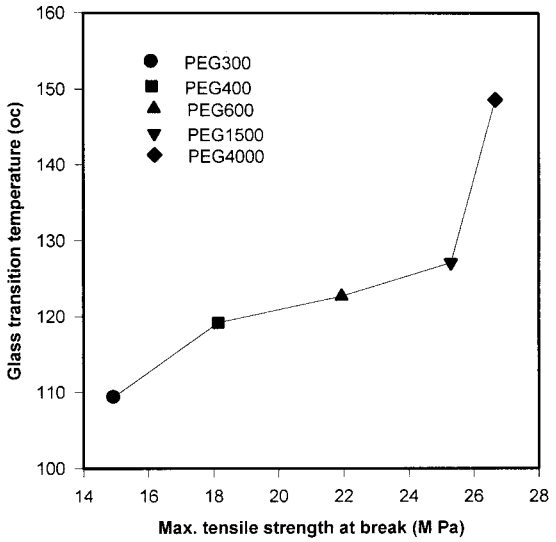


**Figure 5.** The relationship between $T_g$ and maximum tensile strength at breaking point for HPMC E5 free films with 10% of different plasticizers.

## CONCLUSION

This study has shown that incorporation of PEG as plasticizer into the HPMC films made from aqueous solutions resulted in decreasing maximum tensile strength and $T_g$ at breaking point. These effects would be decreased more with the inclusion of low molecular weights (300–400) than higher molecular weights of PEGs. These results could help us to choose the best plasticizer with suitable concentration in film-coating processes.

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