



## Characterization of physical and viscoelastic properties of polymer films for coating applications under different temperature of drying and storage

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### ABSTRACT

The increasing tendency to enhance consumer products with added functionality is leading to ever more complex products. Nowadays more and more particulate products are coated to give the product specific functionalities. An appropriate approach is needed to be able to satisfy customer's requirements. In this work, three reference well-known coating agents, namely two grades of hydroxypropyl methylcellulose (HPMC) and one polyvinyl alcohol (PVA) were selected and investigated. Aqueous solutions of such polymers were obtained and viscosity and shear stress were measured function of shear rate, temperature and polymer concentration. The viscosities of the solutions appear to be mainly shear rate independent, they clearly show Newtonian behaviour. Drying and storage conditions influence on morphology and structure of the cast films were evaluated using scanning electron microscope (SEM). Dynamic mechanical thermal analysis (DMTA) experiments were carried out on HPMC and PVA cast films to assess the viscoelastic properties over wide temperature–frequency range. The time–temperature superposition principle was used to determine the shift factor,  $a_T$ , and to compose a master curve. Magnitudes and profiles of storage modulus,  $E'$ , loss modulus,  $E''$ , and  $\tan \delta$  master curves are discussed with relation to drying and storage conditions. No impact of drying temperature on the polymer properties was observed whereas the effect of storage temperature resulted to be relevant in terms of shifts in glass transition temperature and, only partially, changes in the magnitudes of  $E'$  and  $E''$ .

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### 1. Introduction

Failure of coating layer mostly results from thermo-mechanical loadings. Temperature and humidity gradients occurring during storage may result in mechanical stresses and worsening of the strength of the coating shell. Moreover, shrinkage of the coating material during storage and usage may introduce additional internal stresses especially at the interface core-coating layer. These stresses are generally considered to have a negative influence on the reliability of the product. This is expected to become an even greater problem as a result of ongoing production sites and market globalization which is accompanied with higher repetitive and drastic temperature and humidity gradients.

The problem, in fact, is that both during the drying and the storage stage temperature and humidity can vary drastically and residual stresses (thermal and mechanical) are generated which may lead to failure during subsequent usage. Undesired coating fail-

ure can in principle be avoided by knowing the conditions which the particles are subjected to and optimizing the coating design such that the coating's strength is high enough to resist. The issue is, however, that for reliable predictions highly accurate material data is needed. In fact, smart product design and reliable processes are only possible if one understands the relevant material properties.

The majority of coatings applied to tablets are polymers and their performance is based on the intrinsic characteristics of the bulk polymer, the solvent system from which they are applied and the process conditions, under which they are applied, dried and successively stored before use. Drying and storage temperature might be place by place extremely different giving as much as different performances. In order to prevent un-expected worsening of the coating quality due to wrong conditions and predict the just-before-use characteristics the effect of drying and storage temperature has to be assessed.

The common approach for designing (thermo-mechanically) reliable coating shell is by means of physical testing of solid films casted out of aqueous solutions of the selected coating agents as model of coating shell. Aqueous solutions of chosen coating agent are cast, dried and stored according to the typical coating processes

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and successively tested by subjecting them to thermal, mechanical, or combined thermo-mechanical loads. Based on the results of these tests, the design can be adjusted and the final quality of the product enhanced.

In the case of the polymer coatings, film formation mainly depends on the dispersed polymer fusing to form a continuous uniform film. Thus 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. Dynamic mechanical thermal analysis results to be a powerful tool for the evaluation of the viscoelastic properties of the polymeric material. Viscoelastic properties such as storage modulus,  $E'$ , loss modulus,  $E''$ , and glass transition temperature,  $T_g$ , are evaluated to gauge the performance of the polymer film coating.

Finally, in coating technology the rheological properties of the material used as coating agent are critical to the formation of the film-coating shell and are themselves function of their intrinsic characteristics, namely molecular weight or concentration as well as of process variables, namely shear rate or temperature. Once the polymer has been sprayed onto the surface of the core particles, the spreading of the droplets occurs over the compact surface in order to produce a dried coating film. Thus, knowing how the coating solution behaves in terms of spray-ability, spreading and dry-ability results to be essential in an attempt of coating process optimization.

Among various materials, film formers and synthetic water-soluble polymers such as hydroxypropyl methylcellulose (HPMC) and polyvinyl alcohol (PVA) are now used extensively in the coating of tablets as well as many other different applications. They include excipient in extended release tablet formulations, in formulation of sustained release dosage forms as a swell-able and hydrophilic polymer and tablet, pellet or granule (Ford et al., 1985; Ebube et al., 1997). Moreover they are used primarily for pharmaceutical coating and as binders for solid dosage forms. These materials are available in a wide range of degree of substitution, molecular weight, viscosity, and particle size influencing the properties of the subsequent film coatings (Rowe, 1986; Alderman, 1984; Capan, 1989; Hogan, 1989) and they basically due to their importance to good film-forming properties that enable the production of a tough and protective coating, their nontoxic property, ease of handling, and relatively simple manufacturing technology (Freely and Davis, 1988; Shah et al., 1996).

This work is part of a larger project focussing on the characterization and modeling of coating material properties in a quality by design optic. In this part of the project we review the use of thermal-mechanical analytical methods in characterizing the performances of HPMC and PVA cast films and examines the relationship of casting temperature, drying and storage temperature with strength of such films. In this paper we will first discuss the rheological properties of the reference coating solutions. In the second part we focus on the morphological and viscoelastic characterization of the cast films obtained from the reference coating solutions. Predicting viscoelastic behaviour of certain type of polymers from the knowledge of the intrinsic properties of the material itself cannot be generally valid of course. Nevertheless it will be

applicable to describe the effect of the parameters mentioned above for a set of closely related materials. Moreover a better understanding of these relationships makes the end-user aware of the importance of the end-process handling of the products and thus to tailor the material to meet the desired properties (i.e. viscoelasticity).

## 2. Experimental

### 2.1. Materials

The materials used are two commercially available hydroxypropyl methylcellulose, Pharmacoat<sup>®</sup> 603 and Pharmacoat<sup>®</sup> 615 (Syntapharm, Mülheim an der Ruhr, Germany) and one polyvinyl alcohol, Mowiol<sup>®</sup> 4-98 (Sigma-Aldrich, UK). We will refer to the coating agent as HPMC 603, HPMC 615 and PVA 4-98 respectively throughout this paper. Both well-known coating compounds largely used for food and pharmaceutical encapsulation, in the present study are used as reference materials for their wide availability in the market as well as the abundant literature. Table 1 depicts the details on the used polymers. The bulk materials are reported to have glass transitions ranging from 154 to 170 °C (Kararli et al., 1990; Joshi and Wilson, 1993; Hancock and Zografi, 1994), from 155 to 188 °C (Kararli et al., 1990) and from 47 to 73 °C (Aoi et al., 1998; Lai et al., 1999) for HPMC 603, HPMC 615 and PVA 4-98 respectively (exact values depend on the definition used, the water content as well as on the equipment). They have apparent bulk density of 1.28 to 1.39 g/cm<sup>3</sup> for HPMC's (Gustafsson et al., 1999) and from 1.05 to 1.211 g/cm<sup>3</sup> (Nies and Messing, 2006). They present a melting point of 280–320 °C (Sakellariou and Rowe, 1995) for HPMC's and PVA 4-98 (Mbhele et al., 2003) respectively.

### 2.2. Preparation of solutions

Both HPMC and PVA aqueous solutions were prepared at 3% (w/w). HPMC was dispersed and dissolved in 1/3 of the required amount of demi-water and heated to >80 °C with a heated magnetic stirrer. The polymer gradually disperses to form uniform slurry. The remaining water was added as ice water after complete dissolution of the polymer in order to get rapid hydration. The solution was then cooled in an ice bath while vigorously stirring with an overhead stirrer at 500 rpm for 30 min. The clear aqueous solutions obtained were then allowed to hydrate overnight at 5 °C and allowed to de-foam and equilibrate at room temperature for several hours before use.

PVA was dispersed into cold water with continuous stirring. The mixture was heated to 90–95 °C in a water bath. After dissolution of the polymer the solution was cooled down to room temperature with continuous stirring. The dissolution speed increased with increasing temperature and decreasing molecule size. Foam formation was minimized by making use of an overhead stirrer at low speed. Prior to use the PVA solutions were set to room temperature. It is important to note that the viscosity of PVA solutions can increase with storage time.

**Table 1**  
Physico-chemical characteristics of the polymers used in the present work.

Polymer	Grade	Degrees of substitution (% w/w)		$M_w$	Viscosity <sup>a</sup> (mPa s)	Mol% hydrolysis	Polymerization
		Methoxy	Hydroxypropoxyl				
Pharmacoat	603	28.7	8.9	13,000	2.85		
Pharmacoat	615	28.9	8.8	65,000	15.40		
Mowiol	4-98			27,000	4-5	98-98.8	~600

<sup>a</sup> 4% solution in water (20 °C).

**Table 2**  
Description of the drying-storage history of the tested samples.

Analysed effect	Cast films manipulation					
	Drying conditions			Storage conditions		
	Temperature (°C)	RH (%)	Time (days)	Temperature (°C)	RH (%)	Time (days)
Influence of drying temperature	–18	50–55	2			
	RT	50–55	2			
	40	50–55	2		none	
	55	50–55	2			
	70	50–55	2			
Influence of storage temperature	RT	50–55	2	–18	50–55	60
	RT	50–55	2	RT	50–55	60
	RT	50–55	2	40	50–55	60
	RT	50–55	2	55	50–55	60
	RT	50–55	2	70	50–55	60

### 2.3. Viscosity of solutions

For designing and optimizing of spray coating industrial processes, viscosity, and its relationship with shear rate, polymer concentration in the solution and temperature, is an essential parameter. Low viscous solutions and high solid content in the coating solution would lead to less water to remove and minimization of the contact between the core and the water which give shorter coating time and maxim production efficiency. On the other hand, low viscosity solution gives reduced physical properties of the film coating.

Viscosities of HPMC 603, HPMC 615 and PVA 4-98 aqueous solutions were measured using a rotational viscometer AR-G2 Rheometer using Standard-Size DIN aluminium concentric cylinders (TA Instruments, Delaware, USA) coupled with a Peltier/Plate Temperature controlled Heating System. The shear stress and the viscosity were obtained as a function of shear rate, which was gradually increased from 1 to 1000 s<sup>-1</sup> in 32 min. The experiments were performed at 40, 55 and 70 °C in order to determine the impact of temperature on viscosity. Fresh samples (approximately 20 mL solution) were used in the measurements at each temperature, in duplicate. Data obtained were analyzed using TA Orchestrator 7.2 (TA Instruments, Delaware, USA) and viscosity values obtained at 1000 rad s<sup>-1</sup> were used for comparison.

### 2.4. Film casting and sample preparation

Free films were cast from aqueous solutions containing 3% (w/w) HPMC 603, HPMC 615 and PVA 4-98. Neither additives nor plasticizers were added to the solutions. The films were cast on glass surface (300 mm × 200 mm × 5 mm) using a films applicator (casting area = 175 mm × 115 mm) which amount was selected to produce dry films with a thickness of approximately 100 ± 5 μm. The glass surface was leveled prior to application of the film by means of a level indicator. Film casting, drying and storage were carried out within a controlled environmental cabinet which was capable of simulating the temperature/RH conditions of a fluid bed during typical film coating process. Based on fluid bed temperatures (used in parallel works belonging to this project) during top-spray fluid bed coating process, three conditions were selected, 40 °C/50% RH, 55 °C/50% RH and 70 °C/50% RH. Room temperature, 25 °C/55% RH and –18 °C/3% RH were also consider in the study.

In order to assess the influence of drying temperatures, once pored on the glassy surfaces, the wet films have been let to dry for 1 day at different temperatures ranging from –18 to 70 °C. The relative humidity in all the case was kept constant at 50–55. After 1-day drying time the dried films were straight forward tested. For the evaluation of storage temperature's influence, the wet films were first cast, then dried at room conditions, 25 °C and 50% RH, for

2 days and later on stored for 2 months at different temperatures, namely –18, 25, 40, 55, 70 °C. Also in this case the relative humidity was kept constant at 50–55%. A summary of casting–drying-storage conditions is listed in Table 2. 1-Day drying and 2 months storage time frames were selected being them used in parallel coating processes experiments and thus representative of the latter.

Once the films were dried – still under simulated coating conditions – they were first peeled off the glass surface using two scalpels, then the average thickness was determined in at least five measurements using a digital micrometer (Digimicro, Nikon MU-501, Japan). The measurements were done random over the entire film. Only films with a uniform thickness between 95 and 105 μm were kept for subsequent tests: all the others were discarded. Dried films were collected, marked and sealed in polyethylene bags, in order to prevent curling during storage. The humidity of both the controlled-temperature cabinets and ambient conditions was kept constant.

Prior to testing the surface homogeneity, morphology and structure of the films were measured with scanning electron microscopy (SEM).

### 2.5. Scanning electron microscopy (SEM)

Scanning electron microscopy is an effective method for qualitative analysis of the surface structure and morphological homogeneity of the coating shell. All the images were produced with secondary electrons using a Philips XL 20 scanning electron microscope (electron source from conventional tungsten's filament) operated at acceleration voltage of 15 kV. Samples were prepared by attaching approximately 15 particles to a metallic support with araldite adhesive and a thin layer of gold was applied using an Edwards Sputter Coater (pulse mode, 6 min plasma coating) to improve the conductivity and reduce charging. The only way to obtain cross-sections which do not alter the structure was to freeze a strip of film in liquid nitrogen and break it while frozen.

### 2.6. Thermo gravimetric analysis (TGA)

Thermo gravimetric analyses using a TGA 7 (PerkinElmer Massachusetts, USA) with a dry nitrogen purge were performed to determine the water content of HPMC 603, HPMC 615 and PVA 4-98 dried films. Alumel (152.17 °C) and Perkalloxy (594.47 °C) were used to calibrate the temperature reading and the weight measurement was calibrated using reference materials according to the manufacturer's instructions. Approximately 5–20 mg of HPMC 603, HPMC 615 and PVA 4-98 coated Purox were placed in alumina crucibles for TGA and the weight loss was measured during heating from 25 to 150 °C at a heating rate of 10 °C/min followed by a constant temperature of 150 °C for 10 min. The difference between the initial and

the final sample weight was used as a measure for the water content of the samples. All the experiments were performed in duplicate at least and the results averaged.

### 2.7. Viscoelastic characterization: dynamic mechanical thermal analysis DMTA

The viscoelastic properties of the dried-stored films were investigated using a Q800 DMA from TA Instruments (New Castle, Delaware, USA) equipped with a hermetically closed controlled-temperature and humidity oven. Tensile setup was used for all the experiments applying a continuous frequency sweeps with frequencies from 0.5 to 60 Hz. The tests were performed at a strain of 0.05% with rising temperature, from 25 to 225 °C at a heating rate of 1 °C/min. Sample's dimensions were approximately 8 mm × 40 mm × 0.1 mm. The samples were kept thin (100 ± 10 μm thickness) to minimize frame stiffness effects and avoid thickness-effect. Amplitude of 5 μm, a preload force of 0.05 N, a minimum dynamic force of 0.002 N and a force track at 125% were used. A duplicate was performed for each measurement. For the DMTA tests, the testing environment was equilibrated to ambient conditions, 25 °C and 50% RH in order to perform the tests on films which had been dried and stored under conditions mentioned above. Particular care was taken in order to minimize the time for mounting of the sample in the clamps. The storage modulus,  $E'$ , loss modulus,  $E''$ , the  $\tan \delta$  and the glass transition temperature,  $T_g$ , were calculated (Jones, 1999) and carefully analysed. Storage modulus,  $E'$ , reflects the stiffness and the strength of the polymer and is a measure of the maximum energy the polymer can store in one oscillation's cycle while loss modulus,  $E''$ , represents the total energy dissipated by the polymer (Ferry, 1980). They represent, basically, the most important parameters when choosing the proper polymer coating agent.  $\tan \delta$  (which is the ratio of  $E''/E'$ ) is a measure of how close the sample is to the ideal elastic behaviour. Higher the  $\tan \delta$ , higher the viscoelasticity of the polymer and thus better the ability to survive the cycling stresses. When this kind of measurements is performed through a range of temperatures, the changes in such properties as a function of temperature can be monitored, and this allows the identification of  $T_g$  (Ferry, 1980; Herzog et al., 2005). It is observed macroscopically by a sudden change in the physical and mechanical properties of the polymer. In both pharmaceutical and food industry  $T_g$  plays an important role in several processes such as for example film formation during coating (Okhamafe and York, 1988), drying and storage (Her and Nail, 1994; Ferrero et al., 1999). Moreover  $T_g$  is important for establishing a maximal temperature for use, that is, a material operational limit. When  $T_g$  of a polymer is exceeded, certain mechanical properties may be compromised severely. The polymer coating layer, for instance, may not survive mechanical stresses or became sticky and agglomerate-merge to other particles forming big useless lumps.

The changes in viscoelastic properties of polymer coating as function of temperature and time have significant effect on the functional properties of the coating shell. Predicting changes in viscoelastic properties and designing coating polymer shell with well-defined, reproducible properties can be related to the behaviour and acceptability of the coated pellets. The most widely used empirical equation, which can be used to describe the temperature dependence of viscoelastic properties of polymers in the rubbery state is the Williams–Landel–Ferry (WLF) equation (Williams et al., 1955). The time temperature superposition enable the prediction of mechanical behaviour of polymers as function of time, over time scales which are not experimentally accessible. Being based on the observations that temperature and frequency effect on  $E'$  and  $E''$  are interrelated, the resulting individual curves – log modulus plotted versus temperature for different frequency – obtained from DMTA may be so re-expressed that such individual

**Table 3**

Arrhenius parameters for HPMC 603, HPMC 615 and PVA 4-98 at a shear rate of 298 s<sup>-1</sup>.

Material	$E_a$ (kJ mol <sup>-1</sup> )	$\eta$ (Pa s)	$r^2$
HPMC 603	5.591	0.194	0.9957
HPMC 615	8.890	0.124	0.9679
PVA 4-98	6.251	0.145	0.9697

curves may be shifted along the log frequency scale and superimposed to give a single master curve which describe the  $E'$  and  $E''$  at any arbitrarily chosen temperature over a wide range of frequency. We then characterize the shape changes of the  $E'$ ,  $E''$  and  $\tan \delta$  master curves. This brings a set of parameters such as glassy and rubbery modulus, the position and the shape of glass transition region. The obtained parameters are then related to the drying and storage temperature of cast films. Before performing DMTA experiments, the water content of each sample was measured by TGA (Section 2.6).

## 3. Results and discussion

### 3.1. Rheological characterization of solutions

The aqueous solutions of HPMC 603, HPMC 615 and PVA 4-98 obtained as described in Section 2.2, and kept at 23 °C and 50–55% RH, were extensively characterized. Viscosity and shear stress were measured as function of temperature, shear rate and concentration and the values fitted with general well-known equations in order to validate the results and provide us with the tools to better trigger the spraying coating process.

Viscosities and shear stress of aqueous solutions of HPMC 603, HPMC 615 and PVA 4-98 (3% polymer content) were measured function of shear rate which was ranging from 1 to 1000 s<sup>-1</sup>. All rheological measurements were conducted in triplicate. The average viscosities and shear stresses are shown in Fig. 1.

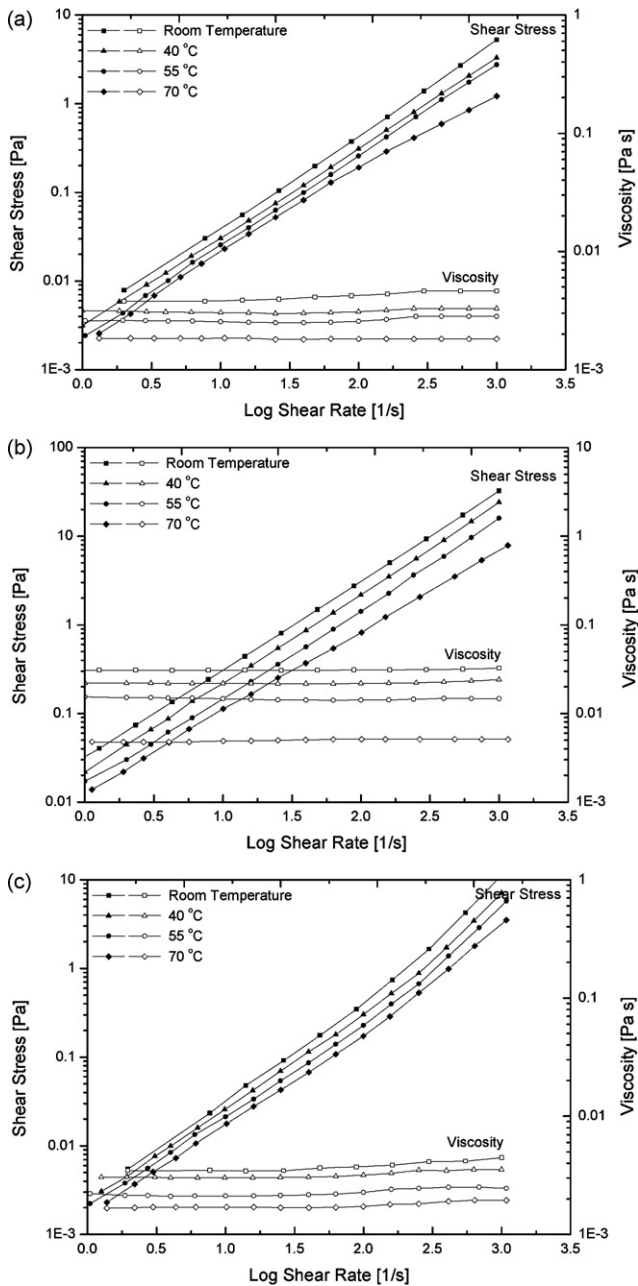
The viscosities of HPMC 603, HPMC 615 and PVA 4-98 measured at different temperatures appear to be shear rate independent, typical of Newtonian materials. As expected, the viscosity decreases, with increasing temperature, from  $5 \times 10^{-3}$  to  $2 \times 10^{-3}$ , from 0.03 to  $5 \times 10^{-3}$  and from  $4.5 \times 10^{-3}$  to  $2 \times 10^{-3}$  for HPMC 603, HPMC 615 and PVA 4-98 respectively. However, slight deviation from Newtonian behaviour, were observed for the experiments carried out at 70 °C mainly due to extremely low viscosities involved and some errors associated with cone inertia and torque spring compliance.

It is well established that for Newtonian liquids, viscosity is related to the temperature by the well-known Arrhenius relationships:

$$\log \eta = \log \eta_0 + \frac{E_a}{RT} \quad (1)$$

where  $\eta_0$  is a constant depending on the nature of the solution called pre-exponential factor (is assumed to be independent of temperature),  $E_a$  is the activation energy for viscous flow (J mol<sup>-1</sup>),  $R$  is the universal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>) and  $T$  is the absolute temperature (K). Fig. 2 shows the Arrhenius behaviour of the three solutions at a shear rate of 298 s<sup>-1</sup>. The values for the activation energies are given in Table 3 together with the correlation coefficients of the squares linear regression.

The experimental determined values of the viscosity,  $\eta$ , were used to calculate (Eq. (2)) the relative  $\eta_{rel}$ , specific,  $\eta_{sp}$  and reduced,  $\eta_{red}$  polymer viscosities. The relationship between the latter and the polymer concentration in the solutions has been determined



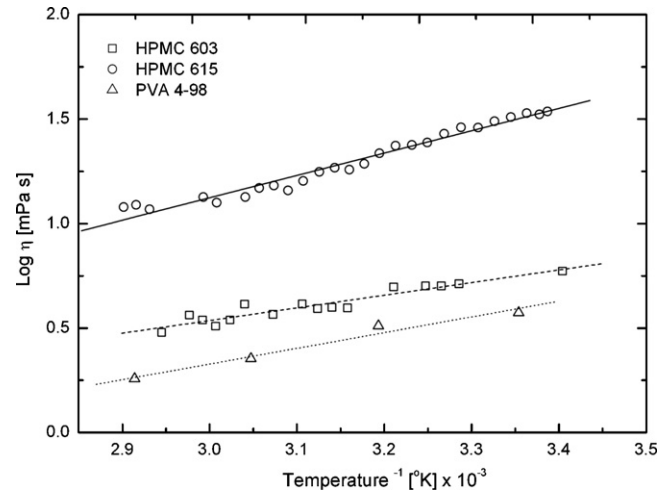
**Fig. 1.** Shear stress (full symbols) and viscosity (empty symbols) of 3% HPMC 603 (a) and HPMC 615 (b) and PVA 4-98 (c), solutions at varying shear rate measured at room temperature (RT) ( $\square$ ), 40 °C ( $\Delta$ ), 55 °C ( $\circ$ ) and 70 °C ( $\diamond$ ).

and plotted in Fig. 3:

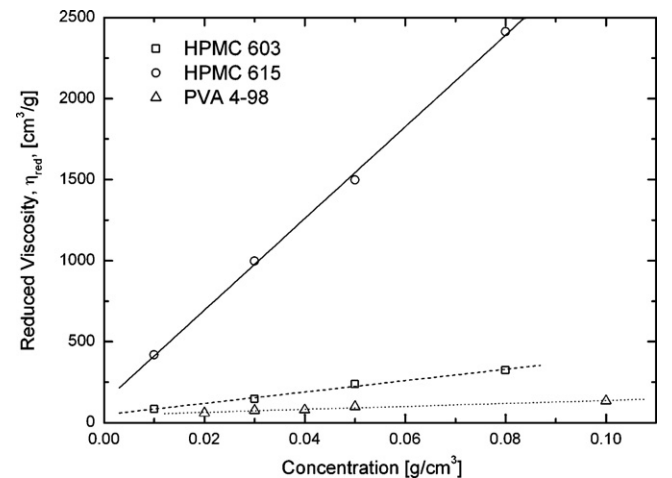
$$\eta_{\text{rel}} = \frac{\eta}{\eta_{\text{sol}}} \quad \eta_{\text{sp}} = \eta_{\text{rel}} - 1 \quad \eta_{\text{red}} = \frac{\eta_{\text{sp}}}{C} \quad (2)$$

where  $\eta_{\text{sol}}$  is the viscosity of the solvent used and  $C$  is the polymer concentration ( $\text{g}/\text{cm}^3$ ).

The values for reduced viscosity,  $\eta_{\text{red}}$ , at zero concentration were obtained by extrapolation of the reduced viscosity/concentration relationship using a linear fitting and the results compared with the value already present in literature. The values for the reduced viscosities at zero concentration are given in Table 4 together with the correlation coefficients of the squares linear regression. The data fitting results rather good, being the  $r^2$  within the 0.95 range. The reduced viscosities at zero concentration agree pretty well with the values in literature with the observed differences probably being



**Fig. 2.** Temperature dependence of the viscosity of 3% (w/w) aqueous solutions of HPMC 603, HPMC 615 and PVA 4-98 solutions at a shear rate of 298  $\text{s}^{-1}$ .



**Fig. 3.** Reduced viscosity,  $\eta_{\text{red}}$ , function of concentration for aqueous solution for HPMC 603 ( $\square$ ), HPMC 615 ( $\circ$ ) and PVA 4-98 ( $\Delta$ ). Linear fitted lines: HPMC 603 dashed line, HPMC 615 solid line, PVA 4-98 dotted line.

due to experimental errors and small inaccuracies of the tests. Thus we considered that the behaviour of HPMC 603, HPMC 615 and PVA 4-98 solutions were satisfactorily described by the general equations listed above.

### 3.2. Cast films

#### 3.2.1. Effect of drying temperature

**3.2.1.1. Morphological characterization.** Because of the functionality of the tablet coatings, it is deliverable to have an exhaustive means of evaluating coating morphology, prior to extensive

**Table 4**

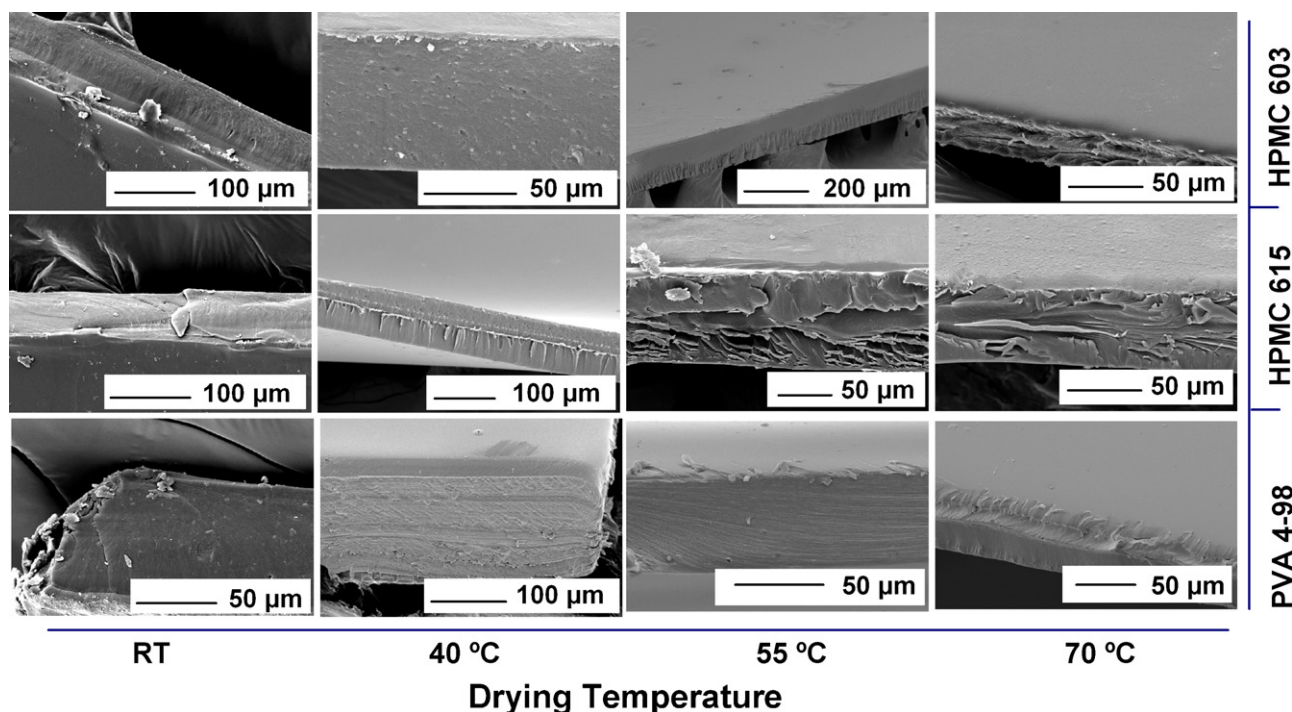
Intrinsic viscosity, ( $\eta$ ), derived from reduced viscosity  $\eta_{\text{red}}$  for aqueous solutions of HPMC 603, HPMC 615 and PVA 4-98 at 25 °C.

Solution	$\eta$ ( $\text{cm}^3 \text{g}^{-1}$ )		$r^2$
	Calculated	Literature	
HPMC 603	49.539	48.3 <sup>a</sup>	0.9514
HPMC 615	129.21	155.4 <sup>a</sup>	0.9987
PVA 4-98	46.223	41 <sup>b</sup> , 42 <sup>c</sup>	0.9681

<sup>a</sup> Law and Kayes (1983).

<sup>b</sup> Lewandowska (2005).

<sup>c</sup> Nagy (1993).



**Fig. 4.** Scanning electron microscope cross-sections of HPMC 603 (1st row), HPMC 615 (2nd row) and PVA 4-98 (3rd row) cast films dried at room temperature (RT), 40 °C, 55 and 70 °C.

mechanical characterization. The wet films obtained by aqueous solutions of HPMC 603, HPMC 615 and PVA 4-98 were let to dry and stored according to methods described in Section 2.4 (Table 2). The dried films were then analysed by scanning electron microscope, SEM, and the morphological-structural characteristics analysed in terms of drying temperature's effect. Fig. 4 shows SEM images of HPMC 603, HPMC 615 and PVA 4-98 films dried at different temperature.

Generally looking at the cross-sections of the pictures the structures show a kind of short-range orientation due to the casting process. In general their thickness varied with the viscosity grades, with the viscosity grades, with the more viscous solutions producing thicker and stiffer films.

HPMC 603 and HPMC 615 were smooth, clear and colourless (Kwok et al., 2004). However HPMC 615 was harder and stiffer owing to its higher viscosity grade (higher molecular weight). When cast and dried at room temperature, HPMC 603 and HPMC 615 were not strongly adhering and could be easily detached from the surface of the casting plate. They were extremely soft, flexible and easy to handle. Some portions, particularly at the edges were self-detaching once the rest of the film was being peeled off. Neither spots-patches nor separated air bubbles could be noticed meaning equal drying rate all over the structure. Raising the drying temperature the pictures show that the films have some pores, which are probably the result of non-homogeneous drying of the films. The surface of the film, in fact, probably dried faster than the rest of the polymer film. The water trapped in the structure evaporated during the drying process causing the formation of small "holes" in the already dry coating surface. HPMC 603 at 70 °C and HPMC 615 at 55 and 70 °C present a lamellar-like structure in the horizontal direction. High drying temperature (70 °C) made the cast films very adhesive and to stick strongly to glass surface, although still peelable. Similar behaviour for PVA 4-98 cast films. In general they were not very clear, slightly hazy throughout or in some sections of the film. These films were quite brittle and extremely hard. The ones dried at low temperature were pretty use to peel off. In this case a drying temperature of 55–70 °C lead to extremely adhesive

not-peelable films impossible to handle. Several cracks and air bubbles could be detected in many areas of the films including bumps and holes. Sufficient part of PVA 4-98 dried at 55 °C could be collected and used for morphological and mechanical characterization though. Before performing viscoelastic characterization the water content of the dried films was measured by TGA (see Section 2.6) and the results are listed in Table 5.

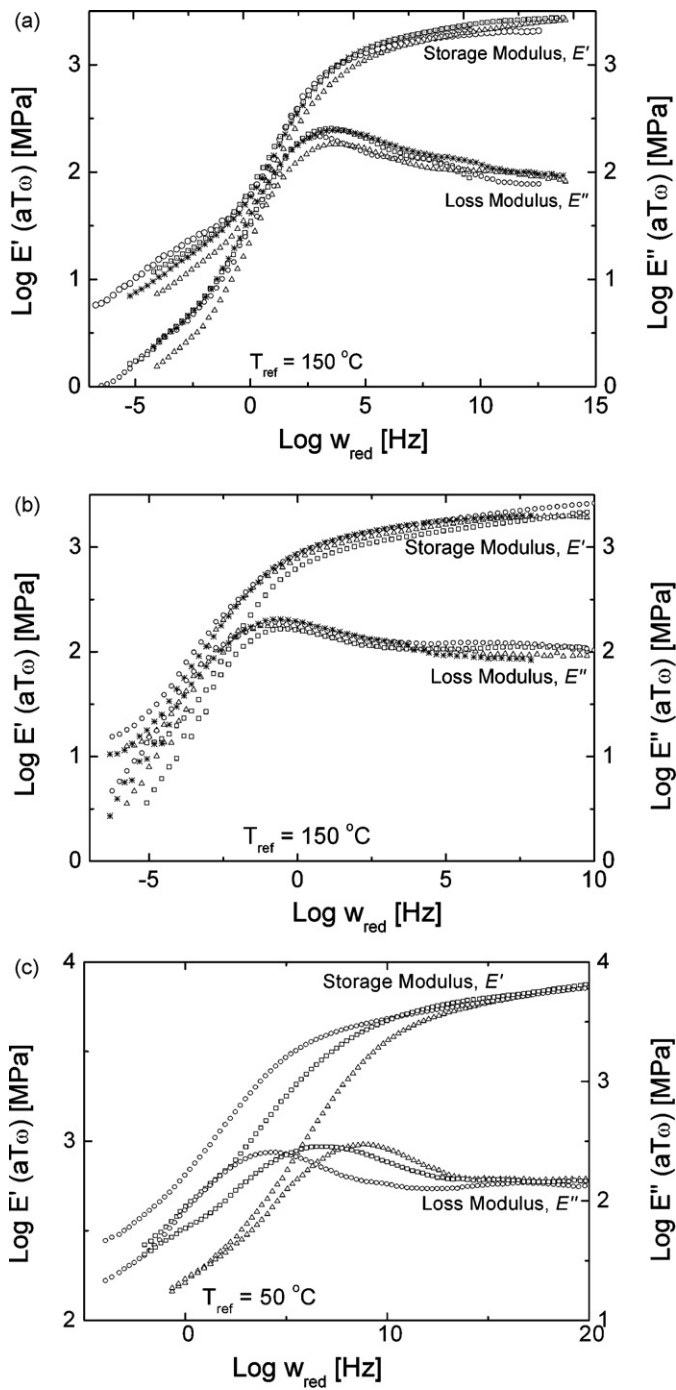
**3.2.1.2. Viscoelastic-mechanical characterization.** It is well known that polymers show strong temperature and time dependent behaviour, i.e. viscoelastic behaviour. Typically at temperatures well below the glass transition temperature  $T_g$ , polymers exhibit a relatively high modulus, called the glassy modulus, representing the elastic component. As the temperature is increased through  $T_g$ , the material goes through the transition region and the stiffness drops dramatically, with a small temperature, increase to a value called rubbery modulus or equilibrium modulus. For uncrosslinked polymers (thermo plastics), such as HPMC 603, HPMC 615 and PVA 4-98, the stiffness exhibits only a very short plateau and then decrease to zero and the material behaves like a viscous liquid. The loss modulus first increases and then peaks to a maximum around glass transition temperature and finally it decreases again with a further increase of the temperature. This phenomenon is also reflected by  $\tan \delta$ . This factor is associated with small chain segment movement caused by partial loosening of the polymer structure.

Cast films (3% aqueous solutions) from HPMC 603, HPMC 615 and PVA 4-98 dried at different temperatures (see Table 2) were

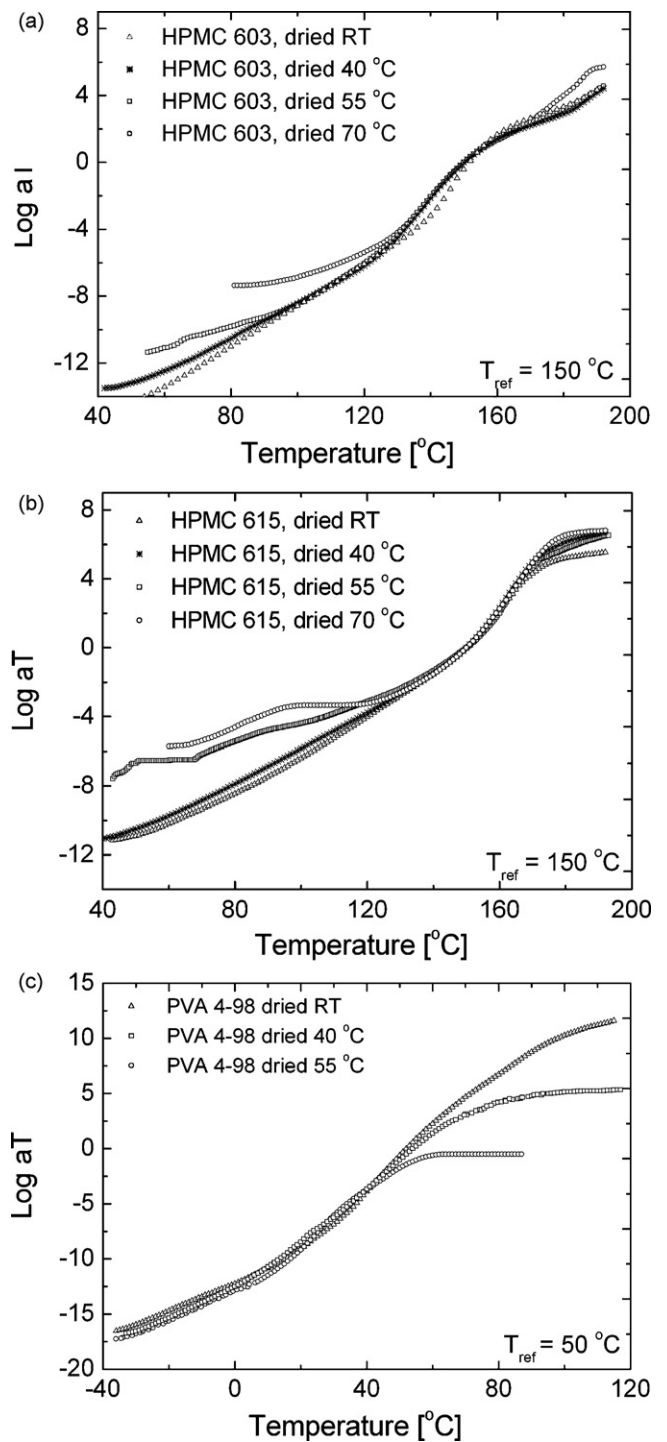
**Table 5**

Water content,  $W_c$ , for HPMC 603, HPMC 615 and PVA 4-98 cast films dried at room temperature, 40, 55, and 70 °C measured by TGA.

	RT	40 °C	55 °C	70 °C
HPMC 603	2.99	2.19	2.48	1.79
HPMC 615	1.84	1.55	1.69	1.32
PVA 4-98	7.98	4.95	4.51	3.99



**Fig. 5.** Plot of  $E'$  and  $E''$  master curves with respect to reduced frequency ( $w_{\text{red}}$ ) for HPMC 603 (a), HPMC 615 (b) and PVA 4-98 cast films dried at room temperature ( $\Delta$ ),  $40^\circ\text{C}$  (\*),  $55^\circ\text{C}$  ( $\square$ ) and  $70^\circ\text{C}$  ( $\circ$ ). Note that no test-able sample for PVA 4-98 dried at  $70^\circ\text{C}$  could be obtained.



**Fig. 6.** Shift factor ( $a_T$ ) function of temperature for HPMC 603 (a), HPMC 615 (b) and PVA 4-98 (c) cast films dried at room temperature, 40, 55 and  $70^\circ\text{C}$ . For HPMC 603 and HPMC 615 the  $T_{\text{ref}} = 150^\circ\text{C}$  while  $T_{\text{ref}} = 50^\circ\text{C}$  for PVA 4-98.

**Table 6**

Effect of drying temperatures on  $T_g$  (both as max of  $\tan \delta$  and inset of  $E'$ ) for HPMC 603, HPMC 615 and PVA 4-98 cast films dried at room temperature, 40, 55, and  $70^\circ\text{C}$  measured by DMTA.

	RT		40 °C		55 °C		70 °C	
	$T_{g-E'}$	$T_{g-\tan \delta}$	$T_{g-E'}$	$T_{g-\tan \delta}$	$T_{g-E'}$	$T_{g-\tan \delta}$	$T_{g-E'}$	$T_{g-\tan \delta}$
HPMC 603	138.7	151.3	139.2	152.2	138.9	149.9	140.8	152.8
HPMC 615	152.9	165.5	154	170.1	154.1	170	155.7	173.6
PVA 4-98	16.1	33	24.3	41.5	27.8	42.5	40.1	49.9

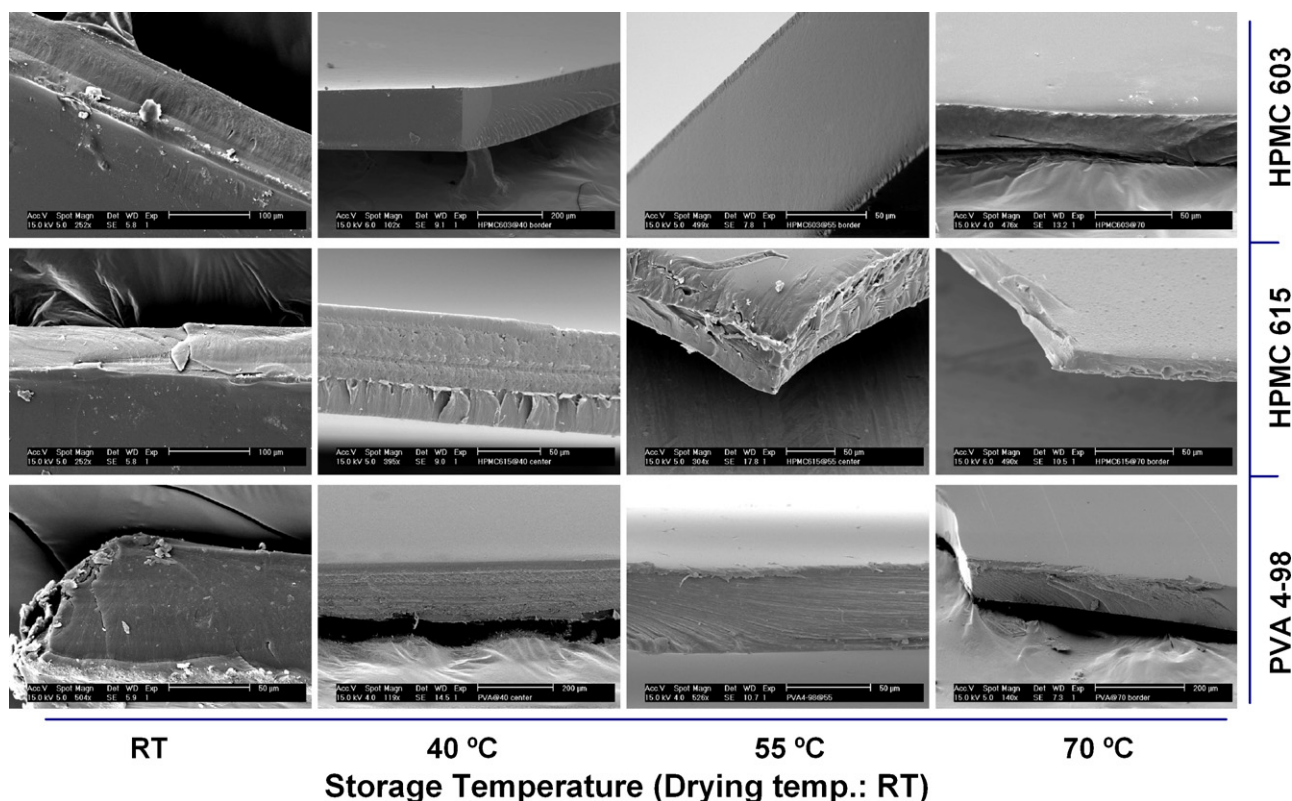


Fig. 7. Scanning electron microscope cross-sections of HPMC 603 (1st row), HPMC 615 (2nd row) and PVA 4-98 (3rd row) cast films dried at room temperature and then stored at 40, 55 and 70 °C.

tested by means of DMTA, in order to assess the effect of such drying conditions on the viscoelastic properties.

According to the time–temperature superposition principle the obtained  $E'$ ,  $E''$  and  $\tan \delta$  calculated from DMTA experiments are shifted along frequency axis to a reference temperature,  $T_{ref}$ , to generate the master curves. The master curves are used to predict viscoelastic behaviour and polymer transition kinetics the chosen coating agents. Fig. 5 shows the master curves for the  $E'$  and  $E''$  obtained after shifting the data on frequency to the  $T_{ref} = 150$  °C, for HPMC 603 (Fig. 5a) and HPMC 615 (Fig. 5b) and to  $T_{ref} = 150$  °C for PVA 4-98 cast films dried at room temperature, 40, 55 and 70 °C and then immediately tested. It can be seen that this resulted in a good superposition of all the data. The absolute values measured for both moduli are in the order of magnitude which is typical for these types of polymers. Similar results can be found in literature (Kararli et al., 1990; Mutalik et al., 2006; Okhamafe and York, 1984; Gomez-Carracedo et al., 2003; Aoi et al., 1998) for HPMC and PVA films. Concerning  $E'$ , Fig. 5a shows that the glassy modulus plateau is not much affected by the drying temperature in anyone of the three cases. Same consideration can be done for magnitude of  $E''$ , being drying temperature independent before glass transition temperature. The small changes in magnitude have to be addressed to clamping effects, which are more present in HPMC's samples. No shift to lower/higher frequency scales has been detected for HPMC 603 and HPMC 615 whereas consistent shift towards lower reduced frequencies can be seen in PVA 4-98. In this case the transition region, reflected from both drastic decrease of  $E'$  and positive peak of  $E''$ , is moving from 10 Hz to approximately 4 Hz. Such changes in  $T_g$  are also evident looking at Table 6 which lists the glass transition temperature of cast films function of the drying temperature measured by DMTA.  $T_g$  as both maximum of the  $\tan \delta$  and inset of  $E'$  has been calculated. The  $T_g$  values are used to represent the end of the transition period and is included in this work to give

an indication of the size of the transition range and also because it represents the maximal end-use temperature of coated particles. Moreover, it is well known that  $T_g$  (together with values of viscosity) can be used to estimate sticky point of amorphous particles and avoid agglomeration and collapse of a fluid bed in coating process. The  $T_g$ , as inset- $E'$ , of two different grades of HPMC was determined to range between 139 and 140.8 °C and between 152.9 and 155.7 °C respectively. The  $T_g$  of PVA 4-98 was determined to be in the range 16.1–40.1 °C while the drying temperature is increased. These values are about 20 °C lower than ones found in literature (Kararli et al., 1990; Mutalik et al., 2006; Aoi et al., 1998) but for different type of manipulation and measurement methods.

The  $T_g$  on the basis of max- $\tan \delta$  is always about 7–15 °C higher than the  $T_g$  based on inset- $E'$ . In fact, the latter is preferable if one use  $T_g$  as temperature at which the mechanical properties began to be compromised. Note that the glass transition is a transition region which makes it dependent on the time scale of measurement and the measurement equipment.

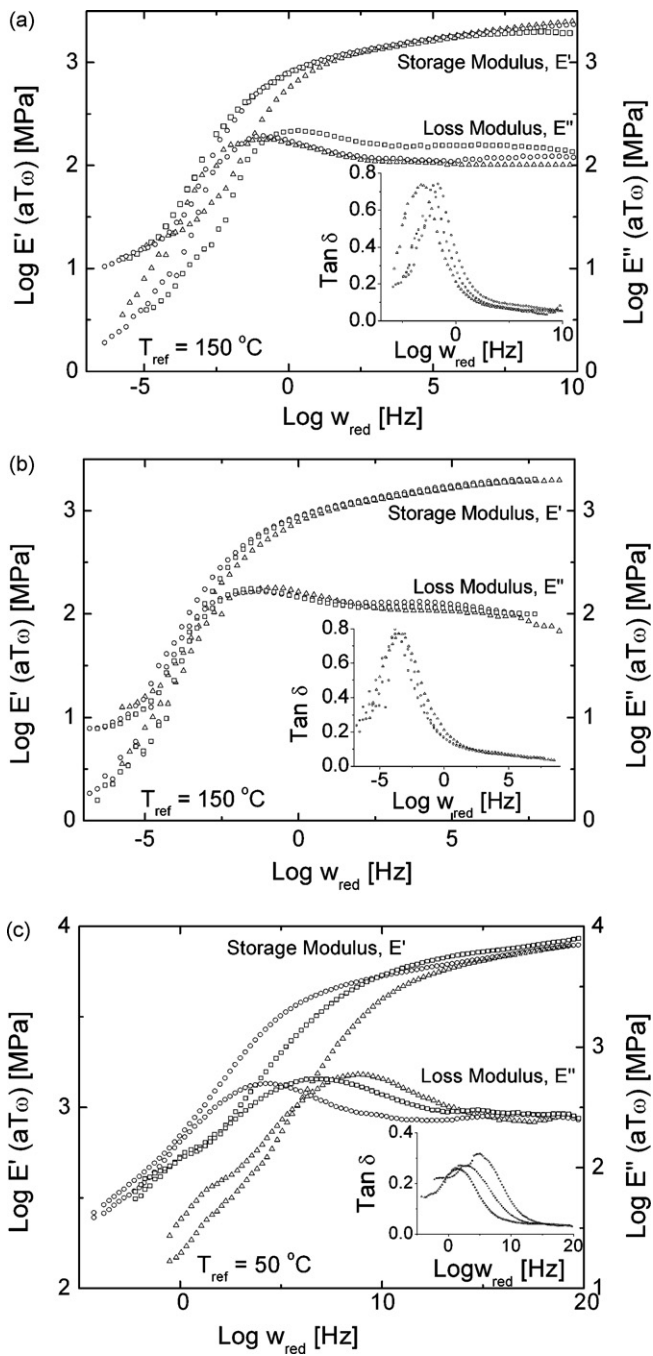
Fig. 6 reports the calculated shift factors,  $a_T$ , for HPMC 603 (a), HPMC 615 (b) and PVA 4-98 (c).

### 3.2.2. Effect of storage temperature

**3.2.2.1. Morphological characterization.** The wet films obtained by aqueous solutions of HPMC 603, HPMC 615 and PVA 4-98 were let to dry at room temperature (23 °C, 50–55% RH) and then stored according to temperatures described in Section 2.4 (Table 2). The dried films were then analysed by scanning electron microscope, SEM, and the morphological–structural characteristics analysed in terms of storage temperature's effect. Fig. 7 shows cross-section SEM images of HPMC 603, HPMC 615 and PVA 4-98 films stored at different temperature.

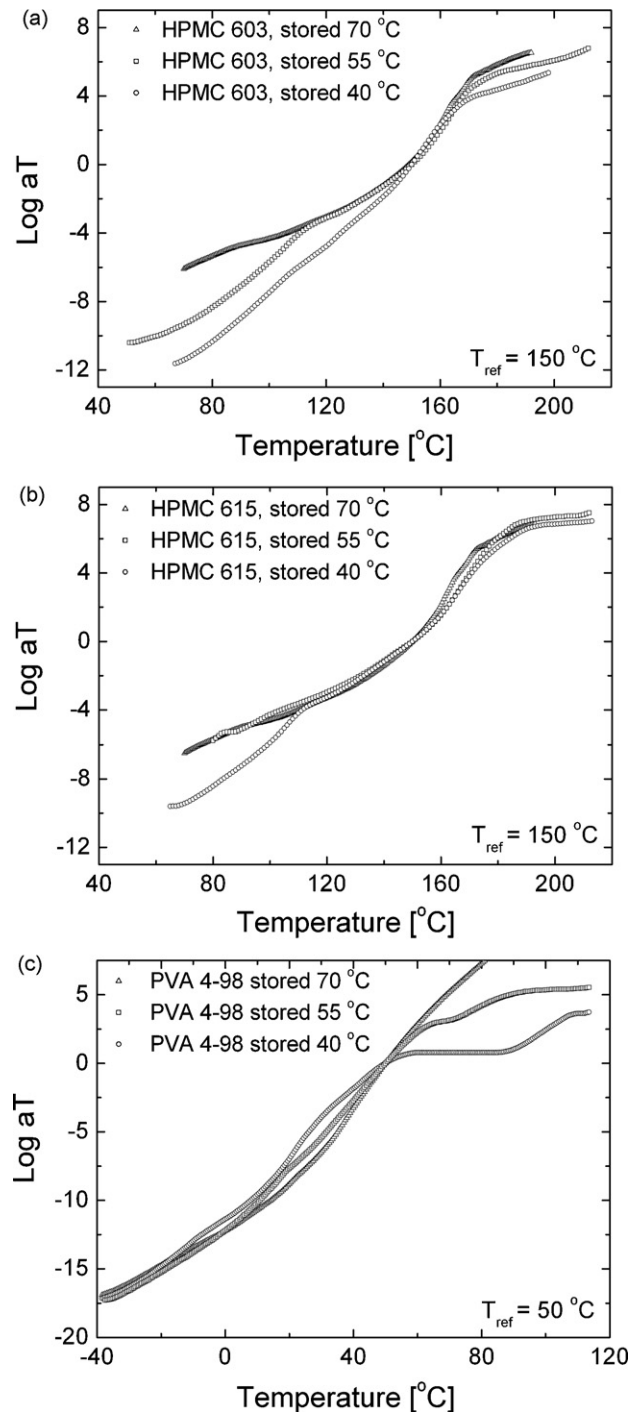
As we can see from the pictures, in this case the morphology, at macroscopic level at least, does not seem to be affected by





**Fig. 8.** Plot of  $E'$  and  $E''$  master curves with respect to reduced frequency,  $w_{red}$  for HPMC 603 (a), HPMC 615 (b) and PVA 4-98 (c) cast films dried at room temperature and then stored at 40 °C ( $\Delta$ ), 55 °C ( $\square$ ), and 70 °C ( $\circ$ ). A plot of  $\tan \delta$  master curve is presented as inset.

the storage temperature in all three cases. They are all presenting homogeneous, dense and well-blended structure. In fact, once the polymer is dried, we do not have changes and/or rearrangement of the polymer chains as long as the material is stored at temperature below glass transition. Nevertheless also in the case of PVA 4-98 which glass transition is the same range of storage temperature used in this analysis no major differences in structure could be detected. Before performing viscoelastic characterization the water content of the dried films was measured by TGA (see Section 2.6) and the results are listed in Table 7.



**Fig. 9.** Shift factor,  $a_T$ , function of temperature for HPMC 603 (a), HPMC 615 (b) and PVA 4-98 (c) cast films dried at room temperature and then stored at 40 °C ( $\Delta$ ), 55 °C ( $\square$ ), and 70 °C ( $\circ$ ). The reference temperature,  $T_{ref}$  is 150 °C for HPMC samples and 50 °C for PVA 4-98.

**3.2.2.2. Viscoelastic-mechanical characterization.**  $E'$ ,  $E''$  and  $\tan \delta$  were calculated and data analyzed making use of the time-temperature superposition principle. As reference temperature,  $T_{ref}$ , 150 °C was chosen for HPMC603 and HPMC 615, and 50 °C for PVA respectively.

Fig. 8 shows the master curves of  $E'$ ,  $E''$  and  $\tan \delta$  (as inset) as function of reduced frequency,  $w_{red}$ , for HPMC 603 (a), HPMC 615 (b) and PVA 4-98 (c) films dried at room temperature and then straightforward stored in oven for 2 months at various temperatures ranging from room temperature to 70 °C. In Fig. 8 we can

**Table 7**

Water content,  $W_c$ , for HPMC 603, HPMC 615 and PVA 4-98 cast films dried at room temperature, 40, 55, and 70 °C measured by TGA.

	RT	40 °C	55 °C	70 °C
HPMC 603	2.01	1.5	1.32	1.02
HPMC 615	1.8	1.31	1.28	1.19
PVA 4-98	7.05	3.9	2.78	2.15

**Table 8**

Effect of storage temperatures on  $T_g$  (both as max of  $\tan \delta$  and inset of  $E'$ ) for HPMC 603, HPMC 615 and PVA 4-98 cast films dried at room temperature and then store (2 months) at 40, 55, and 70 °C measured by DMTA.

	40 °C		55 °C		70 °C	
	$T_g$ - $E'$	$T_g$ - $\tan \delta$	$T_g$ - $E'$	$T_g$ - $\tan \delta$	$T_g$ - $E'$	$T_g$ - $\tan \delta$
HPMC 603	137.3	153.1	139.6	152.3	140.9	155.8
HPMC 615	152.3	170.7	157.1	170.1	157	174.9
PVA 4-98	27.9	42.6	54.3	61.9	61.8	67.2

see that with the exception of HPMC 615 the storage temperature seems to influence the polymer properties, especially the glass transition. Also in this case no significant impact of storage temperature on the glassy and rubbery plateau can be observed, while the shift in  $T_g$  with storage temperature is clearly visible especially in the case of PVA 4-98 and HPMC 603. Almost no shift in glass transition region for HPMC 615 has been detected. For PVA 4-98,  $w_{red}$ , shifts from about  $10^9$  to  $10^3$  from drying temperature = 70 °C to drying temperature = 40 °C whereas for HPMC 603, for the same temperature range, we have a shift from about 10 to  $10^{-2}$ . The same shift can be observed in  $\tan \delta$  master curves (see insets of Fig. 8a and c).

In Fig. 9 the shift factors,  $a_T$ , calculated to get the master curves are shown as function of temperature.

Table 8 shows the glass transition temperature of cast films function of the storage temperature. Also in this case  $T_g$  as both maximum of the  $\tan \delta$  and inset of  $E'$  has been calculated and compared. The  $T_g$ , as inset- $E'$ , of HPMC 603, HPMC 615 and PVA 4-98 was determined to range between 137.3 and 140.9 °C, between 152.3 and 157 °C and between 27.9 and 61.8 °C respectively.

#### 4. Conclusion

In this paper a complete mechanical characterization of polymeric cast films, as model of sprayed coating film onto core pellets, is performed in order to relate the effect of drying and storage temperature on the viscoelastic properties of the final products. Three grades of HPMC and three grades of PVA are taken as reference materials and dissolved in to form aqueous solutions and then cast on glassy substrate. They were straightforward dried and stored using different conditions (temperature) and then tested in DMTA for their viscoelastic behaviour, namely storage modulus,  $E'$ , loss modulus,  $E''$ , damping factor,  $\tan \delta$  and glass transition temperature  $T_g$ . The viscosity and the shear stress of the starting solutions were measured as well as the morphology of the final cast films by scanning electron microscope. Viscosity of the polymer solutions was measured as function of temperature and shear rate. The solutions were found to have Newtonian behaviour having viscosities independent from shear rate and shear stresses directly proportional to shear rate. The viscosity of HPMC 615 solution was found to be much higher than one from HPMC 603 which has practically the same viscosity as PVA 4-98 solution. Good agreement of the data was found with the model and literature data. In the second part of this work drying and storage temperature effect have been taken into account. In this part the data obtained from DMTA experiments were processed using time-temperature superposition principle and  $E'$ ,  $E''$  and  $\tan \delta$  master curves were obtained. The

drying temperature was found to affect quite deeply the morphology of the cast films while almost no effect at all was found in terms of viscoelastic behaviour. Cast films stored at room temperature and then stored at different temperatures present similar macroscopic morphology. Nevertheless a shift of glass transition region towards lower reduced frequencies while raising the storage temperature has been found. This shift is particularly important in the case of PVA 4-98 and HPMC 603. The glassy and the rubbery plateau also in this case do not seem to be affected by the (storage) temperature. Concluding, the determination of the viscoelastic behaviour of polymeric films function of intrinsic physico-chemical properties and/or post-casting handling is extremely important in obtaining certain quality in the final product.

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