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RESEARCH ARTICLE

Influence of additives on melt viscosity, surface tension, and film formation of dry powder coatings

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Abstract

Background: Limited information on thermally cured dry-powder coatings used for solid dosage forms has been available in the literature. *Aim*: The aim of this study was to characterize the film formation process of Eudragit® L 100-55 dry-powder coatings and to investigate the influence of film additives on melt viscosity and surface tension. *Methods*: The coating process employed no liquids and the plasticizer was combined with the polymer using hot melt extrusion. Thermoanalytical methods including differential scanning calorimetry and thermogravimetric analysis (TGA) were used to investigate the thermal properties of the dry-coating formulations. The rheological behavior of the coating formulations were characterized with the extrusion torque, and the surface energy parameters were determined from contact angle measurements. The influence of the level of triethyl citrate (TEC) as plasticizer and polyethylene glycol (PEG) 3350 in the polymer film on film formation was investigated using a digital force tester. *Results*: TGA confirmed thermal stability of all coating excipients at the investigated curing conditions. Increasing TEC levels and the addition of PEG 3350 as a low melting excipient in the coating reduced the viscosity of the polymer. Plasticization of the polymer with TEC increased the surface free energy, whereas the admixture of 10% PEG 3350 did not affect the surface free energy of Eudragit® L 100-55. The spreading coefficient of the polymers over two sample tablet formulations was reduced with increasing surface free energy. During the curing process, puncture strength, and elongation of powder-cast films increased. The effect of curing time on the mechanical properties was dependent on the plasticizer content. *Conclusions*: The incorporation of TEC and PEG 3350 into the Eudragit® L 100-55 powder coating formulation improved film formation. Mechanical testing of powder-cast films showed an increase of both elongation and puncture strength over the curing process as criterion for polymer particle fusion, where film formation progressed faster at high plasticizer levels.

Key words: *Eudragit® L 100-55; dry powder coating; film formation; melt viscosity; surface free energy*

Introduction

The mechanism of film formation occurring in dry coating processes has been described in the literature[1,2]. However, there is little information available on the characteristics of thermally cured dry powder coatings used for pharmaceutical solid oral dosage forms. The properties that have been used to evaluate film formation in pharmaceutical coatings included glass transition temperature and minimum film formation temperature of the polymers, dissolution data, and scanning electron micrographs[3–5]. The main parameters that influence film formation of such dry powder coatings, including melt viscosity and surface tension of the polymer, have not been discussed in the pharmaceutical literature.

Huang and coworkers[1] divided the film formation process for dry coating into four stages. Initially, powders are deposited on the surface and packed together. Second, sintering and coalescence of the polymer particles occur. Film leveling mainly takes place during the curing process, and lastly, cooling of the film completes the process[1]. A high initial packing density of the coating powder is essential for polymer particle fusion. Johnson, Kendall, and Roberts[6] introduced a model to determine the contact area between two spheres that were pressed into contact. According to this theory, the diameter of the contact spot was dependent

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on three main parameters: external force, surface attractions, and elastic properties of the deformed particles[7]. The film-forming process of powder coatings is dependent on coalescence of the polymer particles and wetting of the tablet surface[2]. The main driving force for coalescence and leveling is the surface tension of the polymer, with a low surface tension resulting in wavy surfaces and a high surface tension causing crater defects due to poor wetting properties[8]. The main resistance to fusion of polymer particles is the melt viscosity of the polymer. According to Nix and Dodge[9], the time needed to fuse two polymer particles increases with decreasing surface tension, as expressed in the following equation:

$$t = f\,(\eta R_c/\sigma), \tag{1}$$

where t is the flow time, η is the melt viscosity, R_c is the average radius of curvature, and σ is the surface tension of the polymer.

Orchard[10] developed a model for the surface leveling in viscous liquids and gels that also describes the flow of powder coatings[2]. According to this model, the rate of leveling is increased for polymers with high surface tension, low melt viscosity, and small particle size, and for polymeric films with high film thickness. Additives including plasticizers can affect melt viscosity as well as the surface tension of polymers. The incorporation of plasticizers was shown to significantly reduce the melt viscosity of polymers[9,11]. The effect of additives on the surface free energy was shown to be dependent on the amount and type of additive, although small amounts of dibutyl sebacate and dibutyl phthalate to ethyl cellulose films did not influence the surface free energy of cast polymer films[12]. In contrast, the inclusion of different grades of PEG increased the surface free energy of Eudragit® RS films[13].

The objective of this study was to characterize the curing process of dry powder Eudragit® L 100-55 films and to investigate the influence of the plasticizer triethyl citrate (TEC) and the coating excipient polyethylene glycol 3350 (PEG 3350) on melt viscosity, surface tension, and film formation.

Materials and methods

Materials

Eudragit® L 100-55 was donated by Evonik Industries AG (Piscataway, NJ, USA). TEC was supplied by Vertellus Materials Inc. (Greensboro, NC, USA). PEG 3350 NF was purchased from the DOW Chemical Company (Midland, MI, USA). Lactose monohydrate NF, magnesium stearate, and the model drugs chlorpheniramine maleate (CPM) and sodium valproate (SoVa) were purchased from Spectrum Chemical Mfg. Corp. (Gardena, CA, USA). Microcrystalline cellulose (Avicel® PH-101 and PH-200) was supplied by FMC Corp. (Newark, DE, USA). Kollidon® K 30 was donated by BASF Corp. (Mount Olive, NJ, USA). Cab-O-Sil M-5P was supplied by Cabot Corp. (Tuscola, IL, USA).

Hot-melt extrusion

Eudragit® L 100-55 was preplasticized with up to 40% TEC by melt extrusion using a Randcastle Model RC 0750 with a 6-mm die that was connected to a Randcastle Pelletizer RCP-2.0 (Randcastle Extrusion Systems, Inc., Cedar Grove, NJ, USA). The temperature zones of the extruder were kept at 80°C (zone 1), 110°C (zone 2), 115°C (zone 3), and 120°C (die). The screw speed was set to 20 rpm and resulted in drive amps between 0.3 and 0.5 for the 20% TEC level and between 0.1 and 0.2 for the TEC concentration of 40%. The extruded pellets were subsequently ground into a fine coating powder using a cryogenic mill (Model CF, Micron Powder systems, Summit, NJ, USA) and screened using mechanical shaking. The particle size fraction between 200 and 100 mesh (75–150 μm) was then used in this study for dry powder coating as recommended in a previous study[5].

Thermal analysis

The thermal stability of the coating excipients and a powder-cast film was investigated using thermogravimetric analysis (TGA). A sample of approximately 10 mg was equilibrated to 50°C and then heated at a rate of 10°C/min to 800°C. At isothermal conditions, the equilibration of the sample to 50°C was followed by heating to 60°C and the temperature was then kept constant for 6 hours.

Relative melt viscosity

The mixing torque necessary to extrude Eudragit® L 100-55 containing various amounts of TEC and PEG 3350 was determined using a Haake MiniLab-Compounder (Thermo-Fisher Scientific Inc., Waltham, MA, USA) in the cycle mode. The screw speed was set to 10 rpm. The temperature range was adjusted for each formulation. The maximum temperature did not exceed 125°C to avoid side chain degradation of the polymer[14]. The torque cutoff value occurred at 550 Ncm and restricted measurements at low temperature values.

Contact angle measurements

A Carver Laboratory Press (Model M, ISI Inc., Round Rock, TX, USA) was used to manufacture compacts from preplasticized Eudragit® L 100-55, PEG 3350, and

Table 1. Tablet formulations.

	Formulation 1	Formulation 2	Formulation 3
	CPM (%)	CPM (%)	Sodium valproate (%)
Model Drug	15	15	15
Avicel® PH-101	46.25		
Avicel® PH-200		81.25	81.25
Lactose monohydrate	35		
Kollidon® 30	3	3	3
Magnesium stearate	0.5	0.5	0.5
Cab-O-Sil	0.25	0.25	0.25

three tablet formulations at a 1000-kg compression force (Table 1). 3 μL of either water, ethylene glycol, or diiodomethane was placed on to the surface of the compacts using a microsyringe with Teflon tip. The contact angle was determined by measuring the tangent to the curve of the sessile droplet using a Goniometer (Model No. 100-00-115; Ramé-Hart Inc., Mountain Lakes, NJ, USA) within 5 sec after drop deposition. The measurements were performed in triplicate at 25°C. The apolar and the acid–base components of the surface free energy were calculated according to an approach by van Oss and coworkers using the following equation[12,15]

$$\gamma_L(1+\cos\theta)=2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}}+\sqrt{\gamma_S^{+}\gamma_L^{-}}+\sqrt{\gamma_S^{-}\gamma_L^{+}}\right), \quad (2)$$

where γ is the surface free energy, θ is the measured contact angle, γ^{LW} is the apolar component associated with the Lifshitz–van der Waals (LW) interactions, γ^{+} is the electron acceptor parameter (Lewis acid) of the acid–base contributions, and γ^{-} is the electron donor parameter (Lewis base) of the acid–base contributions. The subscripts 'S' and 'L' distinguish between the solid and the liquid used in the experiment. The surface free energy parameters of the liquids were taken from the literature[12,16].

Preparation and characterization of free films

Free films were prepared from the preplasticized Eudragit® L 100-55 that contained 20%, 30%, or 40% of TEC based on the polymer weight. The polymer was blended with 10% PEG 3350 based on the weight of the extrudate ground using mortar and pestle. Before curing in a static oven at 60°C, the coating powder was pressed into films using a compression force of 10 kN on a surface area of 22 cm^2 for 3 minutes to ensure a dense powder packing (Carver Laboratory Press, Model M; ISI Inc., Round Rock, TX, USA). The compression force was reduced during the curing process to 10 N. The mechanical properties of powder-cast Eudragit® L 100-55 films were investigated using a puncture test previously described by Bodmeier and Paeratakul[17,18]. A Chatillon Universal Tension/Compression Tester Model TCD-200 (Ametek, Largo, FL, USA) with a DFGS 50 digital force gauge was used to study puncture strength and elongation of powder-cast polymer films after up to 12 hours of curing at 60°C. The puncture probe (length, 31 mm; diameter, 6 mm; dome shaped end) was lowered toward the center of the film specimen that was clamped into a film holder at a crosshead speed of 10 mm/min. The film holder consisted of an open-mouth aluminum cup with an inner diameter of 15 mm and an upper mounting plate. The load (N) and deflection (mm) at maximum was used to determine the maximum puncture strength (MPa) and % elongation at maximum (puncture strength = F/A_{cs}, where F is the load and A_{cs} is the cross-sectional area in the path of the cylindrical opening; % elongation = $[\{(R^2 + D^2)^{1/2} - R\}/R] \times 100$, where R is the radius of the film and D is the deflection of the probe). Statistical analysis of the data was performed using SPSS Version 15.0.

Results and discussion

Thermal stability

The raw materials Eudragit® L 100-55, TEC, and PEG 3350 as well as a powder-cast film were subject to TGA to evaluate the thermal stability during the curing process. Two different TGA methods were evaluated. Incremental heating of the samples, as shown in Figure 1, demonstrated thermal stability with no signs of degradation occurring at the curing temperature 60°C. TEC decomposed above 200°C, whereas the polymers Eudragit® L 100-55 and PEG 3350 showed signs of degradation above 300°C. Petereit and Weisbrod[14] employed TGA combined with mass spectroscopy to characterize the thermal degradation process of acrylic

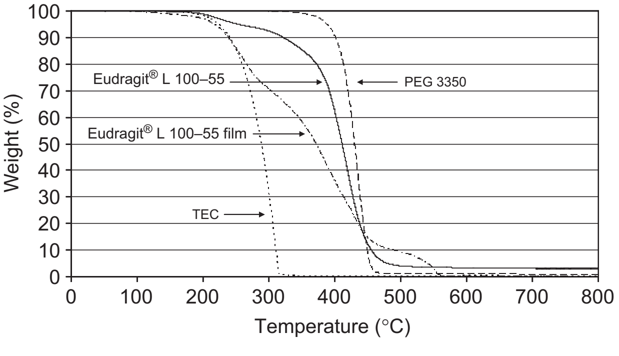

Figure 1. Thermal stability of Eudragit® L 100-55, PEG 3350, and TEC.

Table 2. Cumulative percent weight loss of Eudragit® L 100-55, PEG 3350, and TEC after isothermal TGA analysis at 60°C for 6 hours.

Material	Eudragit® L 100-55	TEC	PEG 3350
Weight loss after 6 hours at 60°C	0.13%	2.19%	0.07%

polymers. It was demonstrated that Eudragit® polymers showed a loss of functional groups above approximately 130°C. Reactions of the main chain such as depolymerization or cross-linking were noted at processing temperatures above approximately 300°C. The TGA profile of a powder-cast film exhibited weight loss in the same temperature ranges and at ratios expected based on the raw materials. The polymer film contained 30% TEC based on the polymer weight and 10% PEG 3350 based on the weight of the ground extrudate and was cured for 24 hours in a static oven at 60°C before analysis.

Isothermal TGA analysis at 60°C over 6 hours revealed stability of the coating excipients, with minimal weight loss occurring over the time frame investigated (Table 2). The 6-hour time frame corresponded to the curing time investigated in this study. The weight loss of Eudragit® L 100-55 and PEG 3350 was negligible, less than 0.2%. The highest weight loss with a value of approximately 2% was noted for TEC. In a powder-cast film as described in the previous paragraph the loss of TEC would result in a combined weight loss of less than 0.5%.

Relative melt viscosity

Melt viscosity is considered the main resistance for polymer flow and polymer–particle fusion[9]. The temperature dependence can be expressed by the Arrhenius–Frenkel–Eyring equation[19]:

$$\eta = B \exp\left(\frac{E_\mathrm{a}}{RT}\right), \tag{3}$$

where B is a polymer-specific constant, E_a is the activation energy of the viscous flow, R is the gas constant, and T is the absolute temperature. The logarithm of the melt viscosity plotted against the reciprocal value of temperature in an Arrhenius diagram results in a straight line at a constant shear rate when the activation energy is independent of temperature[20]. The surface tension is linearly temperature dependent, decreasing with increasing temperatures[8]. However, this effect is less pronounced compared with the temperature effect on melt viscosity.

Torque data have been widely used to characterize the rheological behavior of polymers under processing conditions[21–23] and to determine the relative melt viscosity of materials[24]. At constant rotor speed, the equilibrium torque was shown to be directly proportional to the apparent shear viscosity[25,26]. Torque data for the circulation of each formulation in a twin-screw extruder were graphed in a direct plot and in an Arrhenius diagram (Figure 2). The plasticizer content had a strong effect on shear viscosity, with decreased viscosity being noted with increasing plasticizer levels. It has been proposed that a decrease reduces the time needed for polymer–particle fusion and leveling of a polymer film[9,10]. The incorporation of PEG 3350 into Eudragit® L 100-55-based powder coating formulations as a low melting coating excipient was previously recommended to assist with coating powder adhesion[5]. PEG 3350 is a known plasticizer for Eudragit® L 100-55, and it additionally reduced the viscosity of Eudragit® L 100-55. Therefore, the inclusion of PEG 3350 was expected to have a positive effect on film formation.

All investigated formulations followed a linear relation when the natural logarithm of the torque was plotted against the reciprocal absolute temperature in the investigated temperature range. The square of the correlation coefficient (R^2) from regression analysis for Eudragit® L 100-55 containing 20%, 30%, or 40% TEC based on the polymer weight was 0.943, 0.995, and 0.988, respectively. The addition of 10% PEG 3350 based on the weight of the ground extrudate to the preplasticized polymer resulted in R^2 values of 0.997, 0.997, and 0.977. This linear relationship can be used to predict the viscosity outside of the investigated temperature range[27]. Extrapolation to the curing temperature of 60°C continued the trend of torque reduction with increasing plasticizer levels (data not shown).

The flow activation energy at constant shear rate can be obtained from the slope that was determined using regression analysis as described earlier[28]. Since only torque data were available to describe the rheological behavior of the dry powder coating formulations, the slopes were compared relative to each other and no flow activation energy values were calculated. Figure 2B does not show a clear trend on the slope for increasing TEC amounts in the coating formulation. The slope slightly declined for the TEC content of 30% compared with the 20% TEC ratio and increased again for the 40% TEC level. In contrast, a small decline of the slopes was observed for all TEC concentration after the addition of PEG 3350 as coating excipient and thus resulted in a small decrease of the flow activation energy.

Surface free energy parameters

One simple method to determine the surface free energy parameters in terms of the LW and acid–base contribution of multicomponent systems is the analysis of contact angles with both hydrophilic and hydrophobic liquids[15]. This method has been used in pharmaceutical research to characterize adhesion between

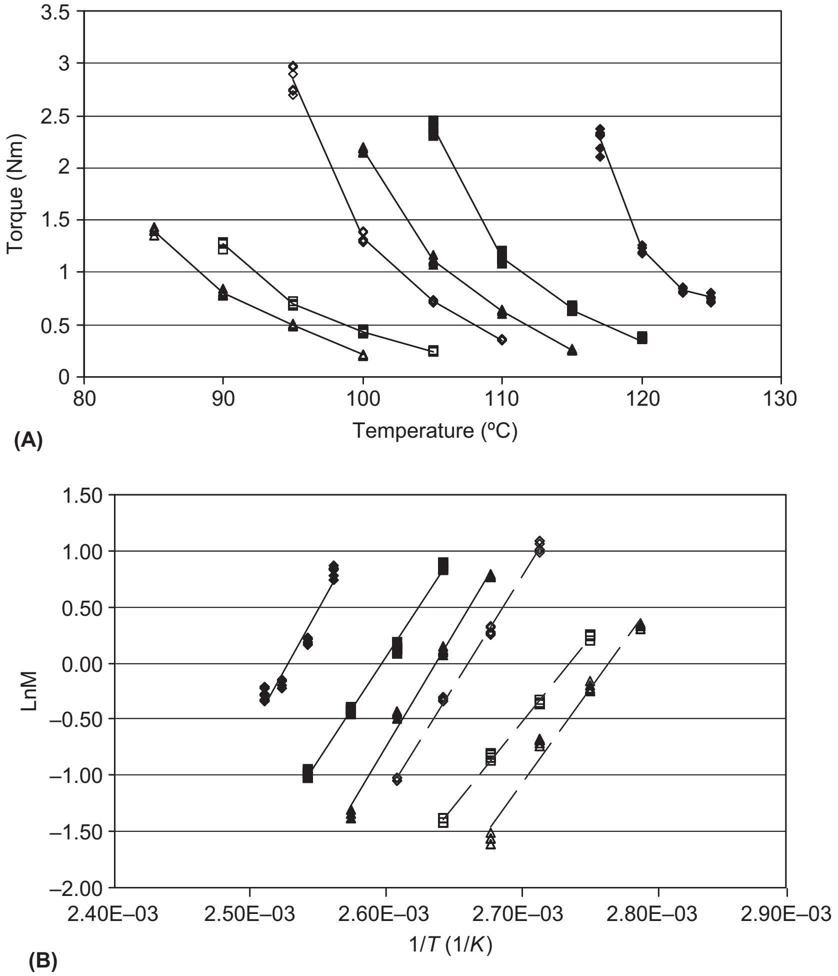

Figure 2. Influence of plasticizer content and the addition of 10% PEG 3350 based on the weight of the ground extrudate on the shear viscosity of Eudragit$^{®}$ L 100-55. ♦ Eudragity$^{®}$ L 100-55 containing 20% TEC. ■ Eudragit$^{®}$ L 100-55 containing 30% TEC. ▲ Eudragit$^{®}$ L 100-55 containing 40% TEC. ✧ Eudragit$^{®}$ L 100-55 containing 20% TEC and PEG. ◇ Eudragit$^{®}$ L 100-55 containing 30% TEC and PEG. Δ Eudragit$^{®}$ L 100-55 containing 40% TEC and PEG. The TEC content was based on the polymer weight. A: Direct plot. B: Arrhenius plot.

polymer film and substrate surfaces[12,29,30] and wetting phenomena in a wet-granulation process[31]. Young's equation requires a smooth and homogeneous surface with no interactions or adsorption occurring to calculate the interfacial energy between two materials.

$$\gamma_{\mathrm{sv}} = \gamma_{\mathrm{sl}} + \gamma_{\mathrm{lv}} \cos\theta, \tag{4}$$

where γ is the surface tension (or surface free energy) and θ is the contact angle. The subscripts sv, sl, and lv refer to the interfaces between solid and vapor, solid and liquid, and liquid and solid, respectively. Although these assumptions are often difficult to meet in practice, contact angle studies are acknowledged for the comparative determination of surface properties of materials[12,30]. In this study, the contact angles decreased over time, a phenomenon that has previously been described for the sessile drop method[12,30]. Previous workers have reported that the advantage of the sessile drop method, compared to advancing contact angles, is the low prevalence of salvation, hydration, or swelling of the analyzed material, provided that the contact angle is immediately measured after deposition of the drop on the surface[30]. Oss et al.[15] recommended the use of three different liquids of which two must be polar to determine the surface free energy parameters of surfaces.

The nonpolar (dispersion) and polar components of the surface energy of compacts of preplasticized Eudragit$^{®}$ L 100-55, PEG 3350, and the two model drug tablet formulations are presented in Table 4. In a preliminary study with diiodomethane, ethylene glycol, and water, all materials listed in Tables 3 and 4 were determined to be Lewis bases and strongly monopolar with a

Table 3. Influence of plasticizer content and the addition of PEG 3350 on the surface-free energy parameters of Eudragit® L 100-55 that were determined using contact angle measurements, $n = 3$.

	Contact angles for liquids (°)		Surface free energy parameters (mJ/m^2)		
	Water	Diiodomethane	γ^+	γ^-	γ^{LW}
PEG 3350	22.0 ± 2.6	24.3 ± 2.1	0	58	46
Eudragit® L 100-55					
0 TEC (bulk)	63.0 ± 3.6	50.0 ± 1.0	0	26	34
20 TEC	58.7 ± 1.2	31.0 ± 1.0	0	23	44
30 TEC	58.7 ± 2.1	26.0 ± 2.0	0	22	46
0 TEC/10PEG	60.3 ± 1.2	48.7 ± 1.5	0	28	35
20 TEC/10PEG	49.0 ± 1.5	29.0 ± 1.0	0	33	45
30 TEC/10PEG	21.3 ± 1.5	16.7 ± 1.5	0	56	49

Table 4. Interfacial energies (γ) between PEG 3350 and Eudragit® L 100-55 containing various amounts of TEC and PEG 3350 as well as between PEG 3350, Eudragit® L 100-55 and two model tablet formulations.

	PEG 3350	CPM tablets (formulation 1)	CPM tablets (formulation 2)	SoVa tablets (formulation 3)
Polymer (P)	$\gamma_{\text{P-PEG}}$ (mJ/m^2)	$\gamma_{\text{P-CPM}}$ (mJ/m^2)	$\gamma_{\text{P-CPM}}$ (mJ/m^2)	$\gamma_{\text{P-SoVa}}$ (mJ/m^2)
PEG 3350	0	1	2	4
Eudragit® L 100-55				
0 TEC (bulk)	1	0	0	1
20 TEC	0	1	2	3
30 TEC	0	1	2	4
0 TEC/10PEG	1	0	0	1
20 TEC/10PEG	0	1	2	4
30 TEC/10PEG	0	1	3	5

Lewis acid component of surface interaction (γ^+) of approximately zero. The results correspond to literature values for the acrylic polymer and PEG[32,33]. Further studies were performed solely with diiodomethane and water with the assumption that γ^+ equals zero to avoid negative square roots in the calculations as already described for materials with improved adhesion behavior, such as corona or flame-treated polyolefins[32]. The equation for the calculation of the Lewis base component then simplifies to[32]

$$-2\sqrt{\gamma_L^+\gamma_S^-} = \gamma_L(1+\cos\theta_{L/S}) + 2\sqrt{\gamma_L^{LW}\gamma_S^{LW}}, \qquad (5)$$

where γ is the surface free energy, θ is the measured contact angle, γ^{LW} is the apolar component associated with LW interactions, γ^+ is the electron acceptor parameter, and γ^- is the electron donor parameter of the acid-base contributions. The subscripts 'S' and 'L' distinguish between the solid and the liquid used in the experiment. The surface free energy parameters of the liquids were taken from the literature[12,16]. Contact angles of materials were shown to decrease with temperature, though not markedly[34,35]. As the temperature coefficient for PEG and acrylic polymers is less than 0.1 mJ/m^2/K[33], the interfacial energies were determined at 25°C as approximation although the coating temperature and curing temperature were 70–75°C and 60°C, respectively. No contact angle data could be obtained for compacts made from Eudragit® L 100-55 with a TEC content of 40%. At this high plasticizer concentration, the contact angles decreased rapidly both for diiodomethane and water.

The surface free energy can be calculated from the surface free energy parameters using the following equation[15]:

$$\gamma_{TOT} = \gamma^{LW} + 2\left(\sqrt{\gamma^+\gamma^-}\right), \qquad (6)$$

where γ^{LW} is the apolar LW parameter. γ^+ and γ^- are the Lewis acid and Lewis base components of the surface free energy, respectively, which describe electron donor/acceptor interactions. Since all materials from Table 3 were determined to be monopolar Lewis bases, the surface free energy equaled the LW parameter. The surface free energy of Eudragit® L 100-55 increased with increasing TEC content. In contrast, the addition of PEG 3350 to the coating formulation did not show any influence on the surface free energy of the polymer, although

PEG 3350 resulted in an increase of the Lewis base component of the surface free energy.

The spreading coefficient of material A over material B can be determined using the following equation[12,36]:

$$S = \gamma_B - \gamma_A - \gamma_{AB} > 0, \tag{7}$$

where γ is the surface free energy. The interfacial energy γ_{AB} between two materials was calculated according to the following equation[15]:

$$\gamma_{AB} = \left(\sqrt{\gamma_A^{LW}} - \sqrt{\gamma_B^{LW}}\right)^2 + 2\left(\sqrt{\gamma_A^{+}\gamma_A^{-}} + \sqrt{\gamma_B^{+}\gamma_B^{-}} - \sqrt{\gamma_A^{+}\gamma_B^{-}} - \sqrt{\gamma_A^{-}\gamma_B^{+}}\right), \tag{8}$$

where γ^{LW} is the apolar component, γ^{+} is the electron acceptor, and γ^{-} is the electron donor parameter. Since γ^{+} was set to zero, the interfacial energies were based on the LW interactions. The interfacial energy is the free energy change in expanding the interfacial area between two materials[36]. The interfacial energies between PEG 3350, three tablet formulations, and various Eudragit® L 100-55 powder coating formulations are presented in Table 4. Since PEG 3350 had a low interfacial energy with preplasticized Eudragit® L 100-55, which decreased with increasing TEC levels, PEG 3350 was an effective priming material and has been used as low melting coating excipient for the powder coating with preplasticized Eudragit® L 100-55.

The CPM and sodium valproate formulations were chosen because they have been used previously in dry coating studies with Eudragit® L 100-55[5]. The contact angles for water and diiodomethane were 21.3 ± 1.5° and 48.7 ± 1.2° for CPM tablets (formulation 1), 40.0 ± 3.6° and 60.3 ± 1.2° for CPM tablets (formulation 2), and 41.3 ± 2.1° and 69.3 ± 1.5° for sodium valproate tablets (formulation 3). These contact angles resulted in γ^{LW} and γ^{-} values of 35 and 71 mJ/m^2 for CPM tablets (formulation 1), 28 and 61 mJ/m^2 for CPM tablets (formulation 2), and 23 and 67 mJ/m^2 for sodium valproate tablets (formulation 3). The interfacial energy between the tablet formulations and preplasticized Eudragit® L 100-55 increased with increasing TEC levels and thus affected spreading over the investigated tablet formulations, whereas PEG 3350 did not have a strong impact (Table 4). Using the interfacial energies, the spreading coefficients of PEG 3350 and preplasticized Eudragit® L 100-55 over the tablet cores were determined, and the results are presented in Figure 3. The spreading coefficients of PEG 3350 over tablet formulation 1 through 3 were –12, –20, and –27 mJ/m^2, respectively. Positive spreading coefficients result in spreading of one material over the other. Most spreading coefficients are negative but it should be noted that only LW interactions were considered in the model. The calculated spreading coefficients for the sodium valproate tablets are highly negative and therefore more difficult to compensate with other aspects of adhesion compared to the CPM tablets. Tablet formulations 1 and 2 differ in the filler composition. Tablets with higher microcrystalline cellulose content were characterized by a lower spreading coefficient compared to tablets containing lactose monohydrate in the formulation.

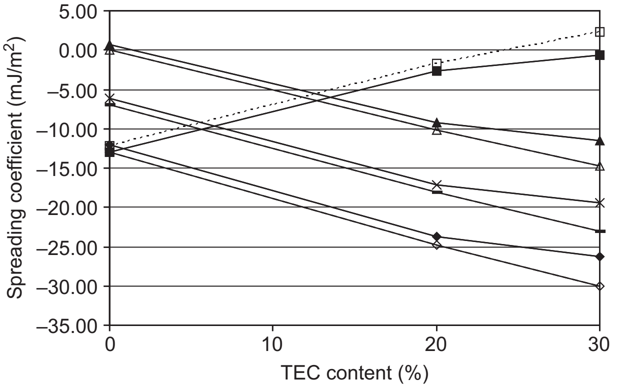

Figure 3. Spreading coefficients. ■: PEG 3350 over Eudragit® L 100-55. ◇ PEG 3350 over Eudragit® L 100-55 containing 10% PEG 3350. ▲ Eudragit® L 100-55 over CPM tablets (Formulation 1). Δ Eudragit® L 100-55 containing 10% PEG 3350 over CPM tablets (Formulation 1). × Eudragit® L 100-55 over CPM tablets (Formulation 2).-Eudragit® L 100-55 containing 10% PEG 3350 over CPM tablets (Formulation 2). ♦ Eudragit® L 100-55 over sodium valproate tablets (Formulation 3). ◇Eudragit® L 100-55 containing 10% PEG 3350 over sodium valproate tablets Formulation 3).

Mechanical properties

After powder deposition and packing, sintering, coalescence, and film leveling occur during the curing process of dry powder coatings[1]. In this study, the progress of film formation and extent of polymer particle fusion were studied using a puncture test on free films and the results are shown in Figure 4. The data were then analyzed using a one-way ANOVA followed by Tukey's HSD ($P < 0.05$) of all possible paired comparisons, and the results are presented in Table 5. The glass transition temperature of Eudragit® L 100-55 preplasticized with 20%–40% TEC has been previously shown to be below the curing temperature of 60°C and thus in a rubbery state for all TEC levels after admixture of PEG 3350[5]. The powder-cast films were characterized by an initial maximum load of less than 0.6 N, which corresponded to a puncture strength of less than 0.1 MPa for all investigated plasticizer levels (data not shown). Eudragit® L 100-55 films containing TEC concentrations of 30% and 40% based on the polymer weight were characterized by

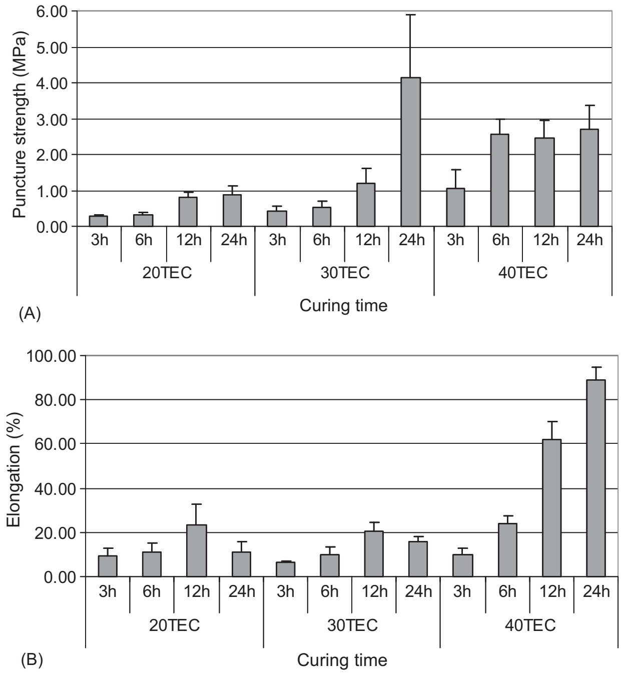

Figure 4. Influence of curing time at 60°C on the puncture strength and elongation of powder-cast films from preplasticized Eudragit® L 100-55, $n = 3$.

an increase of puncture strength over time, whereas it did not change for films containing 20% TEC concentrations, as shown in Figure 4A. The puncture strength plateaued after 6 hours of curing while the elongation continuously increased over 24 hours. Elongation increased for all TEC levels. Plasticizer molecules that are embedded in a polymer matrix generally reduce interactions between polymer chains and number of entanglements, and hence increase the flexibility and decrease the mechanical strength of polymer films. It has been demonstrated that increasing plasticizer levels result in an increase in elongation of polymer films but a decrease in tensile strength and elastic modulus[37,38]. Interestingly, the puncture strength of films containing higher plasticizer levels was increased compared with films containing lower TEC concentrations after 12 hours of curing, although elevated plasticizer levels generally decrease the mechanical strength of polymer films. The increase in puncture strength for powder-cast films with rising TEC levels over 12 hours hence demonstrated that polymer particle fusion and film formation progressed faster at high plasticizer content, as proposed by Nix and Dodge[9].

Conclusions

The incorporation of TEC into the Eudragit® L 100-55 powder coating formulation improved film formation because of a reduction of the polymer viscosity and an increase of the surface free energy of the polymer. Both viscosity and surface free energy of Eudragit® L 100-55 coating formulations were shown to be a function of the TEC content. However, high-TEC concentrations affect spreading of the film coating over the core tablet. The addition of PEG 3350 as low melting coating excipient can improve film formation because of an additional reduction of viscosity. PEG 3350 did not affect the surface free energy of Eudragit® L 100-55. Mechanical testing of powder-cast films showed an increase of both

Table 5. Results of Tukey's HSD post hoc test ($P < 0.05$) for mechanical properties of Eudragit® L 100-55 powder-cast films with 20%, 30%, or 40% TEC after 3, 6, 12, and 24 hours of curing at 60°C.

	20TEC				30TEC				40TEC			
	3 hours	6 hours	12 hours	24 hours	3 hours	6 hours	12 hours	24 hours	3 hours	6 hours	12 hours	24 hours
20TEC												
3 hours	—							*		*	*	*
6 hours	**	—						*		*	*	*
12 hours	**	**	—					*		*	*	*
24 hours			**	—				*		*	*	*
30TEC												
3 hours			**		—			*		*	*	*
6 hours			**			—		*		*	*	*
12 hours					**		—	*				*
24 hours								—	*	*	*	
40TEC												
3 hours			**						—			*
6 hours	**	**		**	**	**			**	—		
12 hours	**	**	**	**	**	**	**	**	**	**	—	
24 hours	**	**	**	**	**	**	**	**	**	**	**	—

*Significant difference puncture strength (MPa). **Significant difference elongation (%).

elongation and puncture strength over the curing process as criterion for polymer particle fusion, where film formation progressed faster at high plasticizer levels.

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