International Journal of Pharmaceutics, 20 (1984) 295–305
Elsevier

IJP 00697

Evaluation of film coating compositions by thermomechanical analysis. I. Penetration mode

F.C. Masilungan [1] and N.G. Lordi [2]

[1] *Pharmaceutics Department, F-70, Smith Kline & French Laboratories, Philadelphia, PA 19101 and*
[2] *College of Pharmacy, Rutgers University, Piscataway, NJ 08854 (U.S.A.)*

(Received November 14th, 1983)
(Modified version received February 27th, 1984)
(Accepted March 15th, 1984)

Summary

The effects of plasticizers, solvents, moisture and additives on various polymer film coating compositions of tablets were studied by thermomechanical analysis (TMA) in the penetration mode. Plasticizers lowered the softening point of a film former and the degree of lowering depended on the type and level of plasticizer used. Some additives affected the thermomechanical behavior of ethyl cellulose but not hydroxypropyl methylcellulose. Entrapped solvents and moisture plasticized film coating compositions. Plasticization reduced the hygroscopicity of a film and the degree of reduction depended on the amount and type of plasticizer used. Findings agree with those of earlier investigations. Thus, it appears that TMA can be used in developing film coating formulations and processes.

Introduction

A simple and rapid method of characterizing the coating of a film-coated tablet is needed when developing and optimizing a film coating formulation or process to avoid a time-consuming and expensive trial and error approach. A test used to examine paints and industrial coatings directly on their substrates for product development and quality control is thermomechanical analysis (TMA). Some of the applications of TMA include predicting the distortion resistance of automotive

---

Correspondence: F.C. Masilungan, Pharmaceutics Department, F-70, Smith, Kline and French Laboratories, Philadelphia, PA 19101, U.S.A.

lacquers (DuPont App. Brief no. 10), monitoring the physical changes of exterior coatings on aging (Holsworth et al., 1974) and determining or monitoring the degree of cure of thermoset primers (Bender and Thayer, 1970; DuPont, App. Brief no. 27; Miranda, 1971).

Because film coatings of tablets are polymeric in nature, as are paints and industrial coatings, they could exhibit characteristic thermorheological behavior under thermal stress which can be assessed by TMA. To confirm that TMA can evaluate film coating compositions of tablets, the technique has to demonstrate how critical factors, such as process variables affect film coating compositions. This paper presents preliminary studies of the effects of plasticizers, solvent entrapment or retention, moisture absorption, casting solvents and additives on tablet film coating compositions using thermomechanical analysis in the penetration mode.

Thermomechanical analysis

Thermomechanical analysis measures and records the change of physical dimension of a material under compression or tension as a function of temperature (Daniels, 1966; Turi, 1981). In compressive measurements, the depth of penetration of a loaded probe into a sample is recorded as a function of temperature or time while for tension tests, the extension under isothermal or non-isothermal conditions of a sample is recorded. Such properties as glass transition temperature (T_g), softening temperature (T_s), tensile modulus, compression modulus, expansion coefficient, shrink temperature and creep properties can be defined by TMA.

In the penetration test below the T_g or T_s, the polymer exhibits resistance to penetration. Because there is no thermal energy to allow the segments of the chain to move as a whole, the movements of individual atoms are limited. As the temperature increases, immobilized chain segments are freed, becoming more flexible. Approaching the transition temperature, there is a corresponding increase in void volume in the polymer, allowing the polymer to become penetrable. In the tension test, the material slowly elongates because of creep and thermal expansion. At the transition temperature, the material begins to stretch at a rapid rate over a narrow temperature interval by the same principle involved in the penetration test.

In this study, the transition temperature refers to the softening temperature which corresponds to the intersection of the extrapolations of the baseline and the penetration line.

Materials and Methods

Materials

The film formers studied were hydroxypropyl methylcellulose (HPMC) [1], polyvinylpyrrolidone (PVP) [2], hydroxypropyl methylcellulose phthalate (HPMCP) [3], cel-

---

[1] Methocel E-15, Dow Chemicals, Midland, MI.

[2] K-30, Ruger Chemicals, Irvington, NJ.

[3] HP-55 (Shin-etsu Chemicals), Biddle Sawyer, New York, NY.

TABLE 1

FILM COMPOSITIONS (% w/w) AND CONDITIONING TIMES AND TEMPERATURES

Film no.	Polymer	Additive (% w/w)	Solvent	Cond. time/temp. (h/ °C)
E1-E4	Ethyl cellulose	Diethyl phthalate (0, 5, 20, 30)	Ethyl acetate	2/60
E5-E7	Ethyl cellulose	Castor oil (5, 20, 40)	Ethyl acetate	2/60
E8-E10	Ethyl cellulose	PEG 400 (5, 20, 40)	Ethyl acetate	2/60
E11-E13	Ethyl cellulose	Glyceryl triacetate (10, 20, 35)	Ethyl acetate	2/60
E14	Ethyl cellulose	Talc (20)	Ethyl acetate	2/60
E15	Ethyl cellulose	Titanium dioxide (2)	Ethyl acetate	2/60
E16	Ethyl cellulose	Titanium dioxide + Castor oil (2 + 20)	Ethyl acetate	2/60
E17-E20	Ethyl cellulose	Propylene glycol (0, 9, 17, 33)	MeCl–MeOH–IPA (4:3:3)	2/60
E21-E23	Ethyl cellulose	Propylene glycol (0, 33, 50)	Isopropyl alcohol	2/60
E24-E27	Ethyl cellulose	Propylene glycol (0, 17, 33, 50)	Methylene choloride	2/60
E29-E32	Ethyl cellulose	Propylene glycol (0, 17, 33, 50)	MeCl–IPA (6:4)	not cond.
H33-H35	Hydroxypropyl methylcellulose	Diethyl phthalate (0, 10, 20)	MeCl–MeOH–IPA (4:3:3)	2/25 + 24/40
H36-H37	Hydroxypropyl methylcellulose	PEG 4000 (10, 20)	MeCl–MeOH–IPA (4:3:3)	2/25 + 24/40
H38-H39	Hydroxypropyl methylcellulose	Propylene glycol (10, 20)	MeCl–MeOH–IPA (4:3:3)	2/25 ± 24/40
H40-H41	Hydroxypropyl methylcellulose	Glyceryl triacetate (10, 20)	MeCl–MeOH–IPA (4:3:3)	2/25 + 24/40
H42	Hydroxypropyl methylcellulose	Opaspray (56)	MeCl–MeOH (7:3)	2/25 + 24/40
H43	Hydroxypropyl methylcellulose	(0)	Water	48-60/25
H44	HPMC : EC (4:1)	(0)	MeCl–MeOH–IPA (4:3:3)	2/25 + 24/40
HP45-HP47	Hydroxypropyl methylcellulose phthalate	Diethyl phthalate (0, 5, 20)	MeCl–EtOH (1:1)	2/25 + 24/40
HP48-HP49	Hydroxypropyl methylcellulose phthalate	Diethyl phthalate (0, 20)	MeCl–MeOH (1:1)	2/25 + 24/40
HP50-HP51	Hydroxypropyl methylcellulose phthalate	PEG 400 (5, 20)	MeCl–EtOH (1:1)	2/25 + 24/40
HP52	Hydroxypropyl methylcellulose phthalate	PEG 400 (20)	MeCl–MeOH (1:1)	2/25 + 24/40
HP53-HP54	Hydroxypropyl methylcellulose phthalate	Glyceryl triacetate (5, 20)	MeCl–EtOH (1:1)	2/25 + 24/40
HP55	Hydroxypropyl methylcellulose phthalate	Glyceryl triacetate (20)	MeCl–MeOH (1:1)	2/25 + 24/40
C56-C57	Cellulose acetate phthalate	Diethyl pthalate (0, 20)	Acetone	7 days silica gel desiccator
C59	Cellulose acetate	Glyceryl triacetate (20)	Acetone	7 days silica

lulose acetate phthalate (CAP) [4], and ethyl cellulose (EC) [5].

The plasticizers included polyethylene glycol (PEG) 400, PEG 4000, propylene glycol (PG), diethyl phthalate (DEP), glyceryl triacetate (TA) and castor oil (CO).

The solvents used were ethyl acetate (EA), methylene chloride (MeCl), isopropyl alcohol (IPA), methyl alcohol (MeOH), acetone (DMK), absolute alcohol (EtOH) and water.

The additives incorporated were titanium dioxide, talc and opaspray. [6]

Preparation of films

Films were prepared by evaporating off the solvents of 5% w/v polymer solutions or dispersions, contained in carefully levelled teflon-coated steel pans, for 10–14 h at room temperature (22–25 °C) for organic solvent systems and 48–60 h at the same temperature for aqueous systems. The films formed were stripped from the pans and conditioned before testing. The compositions, conditioning times and temperatures are shown in Table 1.

The thickness of the film test samples ranged from 0.0053 to 0.0069 cm, but the thickness of a large number of the samples tested was 0.0061 cm.

Apparatus and testing procedure

TMA measurements of film samples were taken with a DuPont Thermomechanical Analyzer Model 942/Thermal Analyzer Model 900 in the penetration mode using a 50 g load for EC, HPMCP, CAP and PVP and a 100 g load for HPMC at a heating rate of 10°/min and at a sensitivity of 0.02 mV/in. Tests were run in duplicate.

Moisture absorption test

The films were conditioned at room temperature (25 °C) in a desiccator, containing a saturated solution of NH_4Cl, which gave a relative humidity of 79%. Before testing, the weight change of the sample which represents moisture absorbed or loss was determined and expressed on a weight basis.

Solvent retention test

The films used in this test were prematurely stripped from the pans so that they contained considerable amounts of solvents. The solvents were driven off by blowing heated air (50 °C) on the sample in several steps. Following each drying step, the sample was weighed and then analyzed. The percent volatile loss was calculated on a weight basis.

Results and Discussion

Effect of plasticizers

The introduction of a plasticizer to a film former lowered its softening point and

---

[4] Eastman Organic Chemicals, Rochester, NY.

[5] N-50, Hercules Powder, Wilmington, DE.

[6] Red, K-1-1838, Colorcon, West Point, PA.

the degree of lowering depended on the quantity and type of plasticizer used. The more efficient the plasticizer, the greater was the lowering of the softening temperature.

Moelter and Schweizer showed that the softening temperatures of cellulose acetate films was a function of the fractional mole plasticizer content of the film, expressed by the following equation:

$$T_s = T_0 e^{-kn} \tag{1}$$

where T_s is the softening temperature in °C of a plasticized film, T_0 denotes the softening temperature in °C of an unplasticized film, n is the mole fraction of the plasticizer and k is the softening point depression coefficient (Moelter and Schweizer, 1949). The coefficient k which is the slope of the linear plots of $\ln T_s$ versus mole fraction of the plasticizer in the film is a measure of plasticizer efficiency. High values of k indicate high plasticizer efficiency and low k values mean low plasticizer efficiency.

Figs. 1, 2 and 3 show the general influence of plasticizers on the thermomechanical behavior of EC, HPMC and HPMCP films, respectively, using Eqn. 1. Practically all the films examined show that the natural log of their softening temperatures vary linearly with plasticizer content, as predicted by Eqn. 1. The k values of the linear plots are listed in increasing order of efficiency in Table 2, together with their respective correlation coefficients.

Fig. 1 shows that the best plasticizer for ethyl cellulose is DEP and the poorest is PG, with a k value of 2.34 for DEP and 0.97 for PG (Table 2). PG brought about insignificant changes in the thermomechanical characteristics of EC which indicate ineffective plasticization.

The deviation of the EC + PEG 400 curve from linearity (Fig. 1) was believed to be due to loss of plasticizer during testing because the film showed slight blushing. Since the plasticizer could have been loosely bound to the polymer, it could have

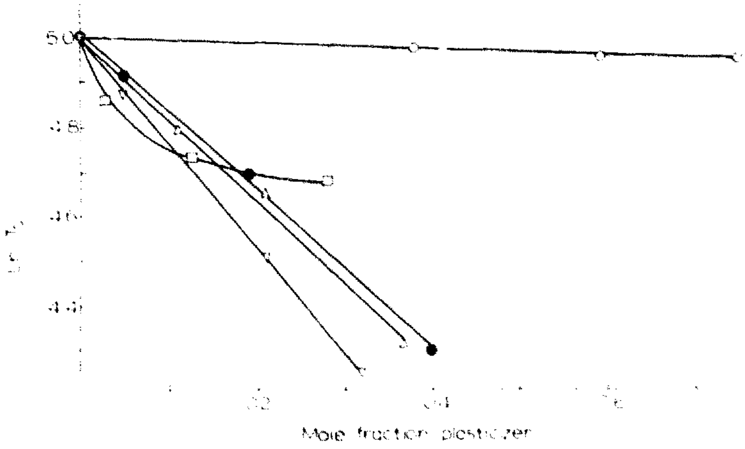

Fig. 1. Effect of plasticizers on the softening temperature of ethyl cellulose. ○, propylene glycol; △, glyceryl acetate; ▽, diethyl phthalate; □, PEG 400; ●, castor oil.

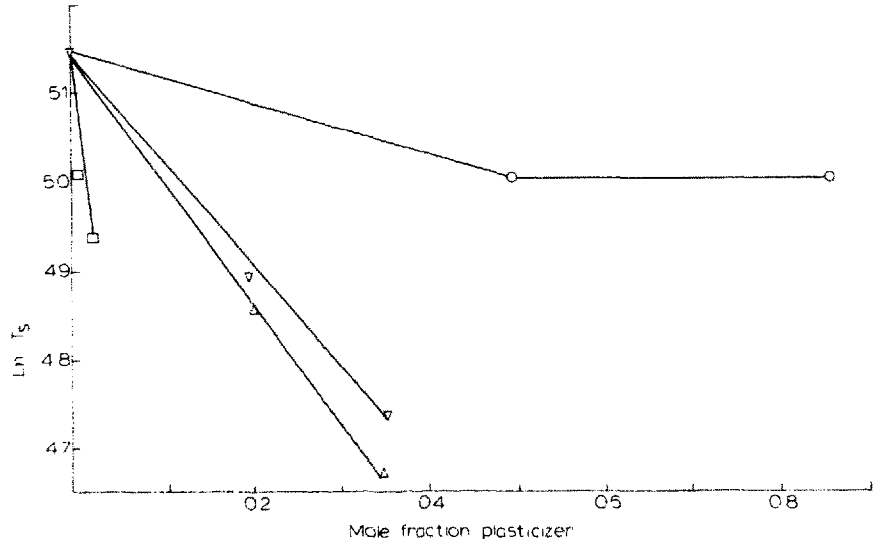

Fig. 2. Effect of plasticizers on the softening temperature of hydroxypropyl methylcellulose. ○, propylene glycol; △, glyceryl triacetate; ▽, diethyl phthalate; □, PEG 4000.

migrated from the plasticized film when the film was heated, which would result in a higher softening temperature.

Fig. 2 demonstrates the effect of the various plasticizers on HPMC. The best plasticizer for the film former was PEG 4000. Surprisingly, propylene glycol, a

TABLE 2

SOFTENING POINT DEPRESSION COEFFICIENTS (k) OF PLASTICIZERS FOR EC, HPMC AND HPMCP FILMS

Plasticizer for film	k	Correlation coefficient
EC		
DEP	2.34	1.00
TA	2.34	0.98
PEG 400	1.00	0.88
PG	0.07	0.97
CO	1.77	1.00
HPMC		
DEP	2.30	1.00
TA	2.4	0.98
PEG 4000	8.86	0.98
PG	0.35	0.89
HPMCP		
DEP	1.59	1.00
TA	1.63	0.98
PEG 400	2.96	1.00

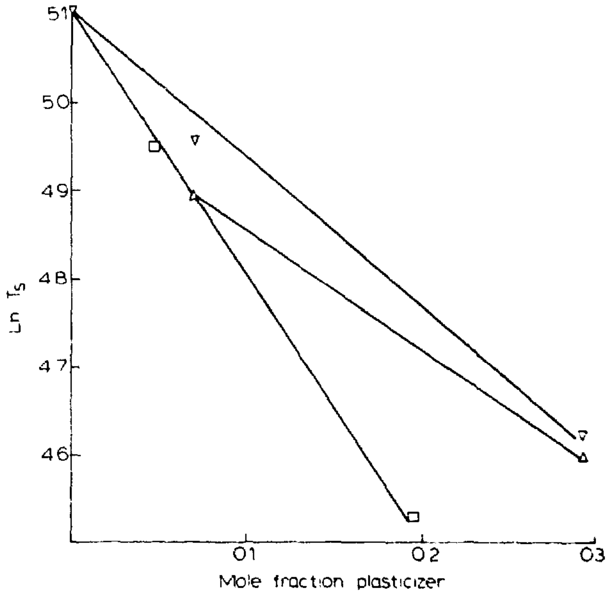

Fig. 3. Effect of plasticizers on the softening temperature of hydroxypropyl methylcellulose phthalate. △, glyceryl triacetate; ▽, diethyl phthalate; □, PEG 400.

generally recommended plasticizer for HPMC did not exhibit any appreciable activity on the film former, as substantiated by its low k value. DEP and TA were more efficient plasticizers than PG at all levels. Poor plasticization by PG on HPMC may be due to hydrogen bonding which would reduce the movement of the chain molecule. Also, because PG is a relatively small molecule, when interspersed in the large polymer structure, it may not adequately reduce the rigidity of the polymer.

In HPMCP films, PEG 400 appeared to be the best plasticizer (Fig. 3), followed by TA then DEP. The deviation of TA curve from a straight line is attributed to the low retentivity of the plasticizer in the film at high concentrations.

Effect of additives

The effect on Ts by the addition of opaquant-extenders are shown in Table 3. The

TABLE 3

EFFECT OF ADDITIVES ON THE SOFTENING TEMPERATURES (°C) OF EC AND HPMC FILMS

No additive		With additive	
Film	T_s	Film	T_s
EC	149	EC + 20%TALC	146
		EC + 2%TiO_2	146
EC + 20%CO	109	EC + 20%CO + 2%TiO_2	118
HPMC	175	HPMC + OPASPRAY	173

softening temperature of EC dropped slightly from 149 °C to 146 °C with the addition of talc or titanium dioxide. On the other hand, 2% titanium dioxide increased the softening characteristics of a plasticized film, EC + 20%CO from 109 °C to 118 °C. No significant change in thermomechanical behavior of HPMC due to opaspray was observed.

Effect of solvents

The effect of solvents on the thermomechanical deformation of the film is shown in Table 4. The similarity between the softening temperatures of unplasticized EC films prepared from EA, MeCl, MeCl–IPA, MeCl–MeOH–IPA or IPA suggests that the thermomechanical properties of EC is independent of casting solvents. The findings agree with those reported (Haas et al., 1952) which showed that solvents such as benzene, carbon tetrachloride and nitropropane have no effect on the softening point of EC.

By contrast, HPMC films may not be independent of the casting solvents as the T_s of HPMC films cast from water and from MeCl–MeOH–IPA were significantly different.

Casting solvents also affected the penetration characteristics of unplasticized HPMCP films. There was a significant difference between the softening temperatures of the film-former cast from MeCl–EtOH and MeCl–MeOH. By contrast, casting solvents had no effect on the thermomechanical behavior of HPMCP plasticized with DEP or PEG 400. There was no significant difference between their softening characteristics.

Effect of solvent retention

The effect of solvent retained or entrapped on the mechanical behavior of

TABLE 4

SOFTENING TEMPERATURES (°C) OF EC, HPMC AND HPMCP FILMS CAST FROM VARIOUS SOLVENT SYSTEMS

EC		HPMC		HPMCP	
Casting solvent	T_s	Casting solvent	T_s	Casting solvent	T_s
EA	149	Water	175	MeCl–EtOH	153
MeCl	147	MeCl–MeOH–IPA	172	MeCl–MeOH	165
				HPMCP + 20%DEP	
MeCl–IPA	149				
MeCl–MeOH–IPA	148			MeCl–EtOH	103
IPA	147			MeCl–MeOH	103
				HPMCP + 20%PEG400	
				MeCl–EtOH	93
				MeCl–MeOH	92

EC + 17%PG, EC + 33%PG and EC + 50%PG films is illustrated in Fig. 4.

It shows that: (a) solvent entrapped or retained in the film lowers the softening temperature of the material which suggests that the residual solvent is acting as a plasticizer for the film; (b) the steeper slopes of the curves at low levels of entrapped or retained solvents indicate that the rate of change of the softening behavior of the films is higher with lower contens of solvents; and (c) the amount of solvent retained is influenced by the concentration of the plasticizer in the film, i.e. after evaporating the solvent for 4 h, the films which contained 17%, 33% and 50% PG, retained 13.5%, 36% and 54% volatiles, respectively.

The above findings are consistent with those of published reports (Doolittle, 1954, Haas et al., 1952).

Effect of moisture absorption

The influence of moisture absorption on the softening characteristics of film coating compositions is shown in Fig. 5.

The testing of CAP and HPMC films was discontinued after 8 weeks of storage at 79% R.H. The films exhibited excessive blushing; they turned waxy and opaque white. Also, some films lost instead of gained weight on storage, an observation that could be attributed to the volatilization of the breakdown products of the plasticizer when hydrolyzed, i.e. for film containing triacetin, loss of acetic acid, a volatile breakdown product of the plasticizer (Crawford and Esmerian, 1971). Another reason for weight loss could be due to the residual solvents that might have originally been present in the film before storing at 79% R.H., which could have volatilized on storage. Nevertheless, the magnitude and mode of moisture absorption found in this study agree with findings of relevant literature (Crawford and Esmerian, 1971; Malm et al., 1951).

The softening temperatures of the films gradually dropped on storage at 79% R.H. showing that moisture affects the thermomechanical characteristics of the films. Since the presence of moisture increases the softening characteristics of film coating compositions, it plasticizes films.

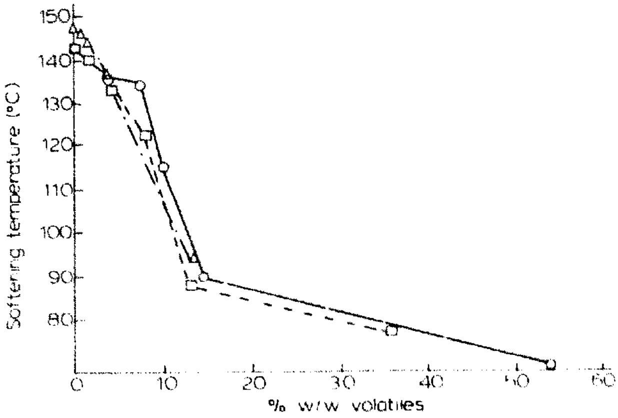

Fig. 4. Effect of solvent retention on softening temperature. △, EC + 17% PG; □, EC + 33% PG; ○, EC + 50% PG.

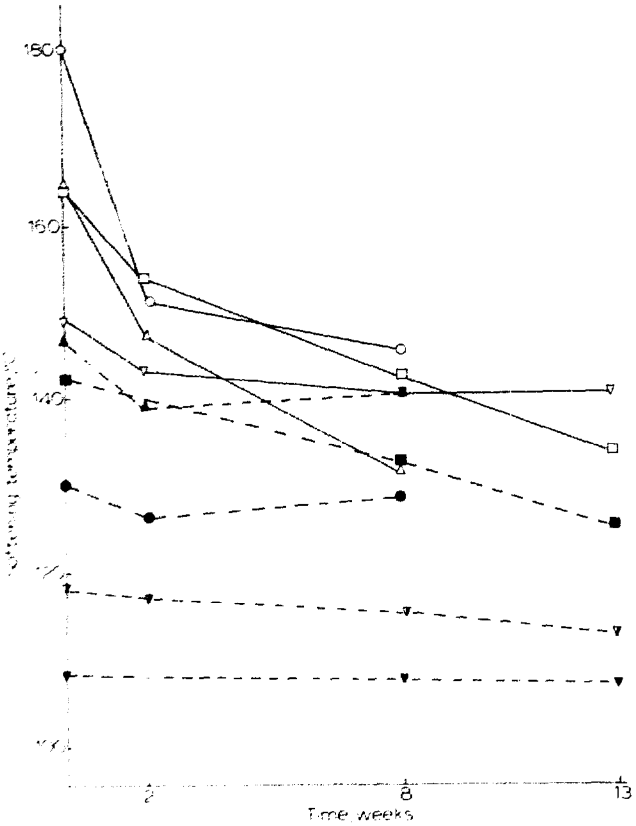

Fig. 5. Softening temperature profiles of CAP, HPMC, HPMCP and EC films stored at 79% R.H. ○, CAP; △, HPMC; □, HPMCP; ▽, EC; ●, CAP+20% DEP; ▲, HPMC+10% PG; ■, HPMCP+5% DEP; ▽, EC+10% TA; ▼, EC+20% TA.

The slopes of the T_s-time curves (0–8 weeks) of unplasticized films being steeper than those of the plasticized films show that the change of softening behavior due to moisture is greater for unplasticized films. This suggests that the presence of plasticizers lowers the moisture uptake capacities of film coating composition and thereby reducing the thermomechanical deformation of films brought about by moisture absorption. The study thus shows that certain plasticizers could be effective protective agents for film coatings against moisture.

A quantitative relationship between the T_s change and absorbed moisture could not however be derived because the gravimetric method used for determining the moisture absorbed by the film included the weight of loosely bound surface moisture and did not reflect the actual moisture content within the film.

Conclusion

The results of these preliminary studies show that the general effects of process variables (plasticizers, additives, solvents or moisture) on film coating compositions can be evaluated from the thermomechanical behavior of films using TMA. Because TMA can show the relative efficiencies of plasticizers, it could be used to select the most suitable plasticizer for a film coating formulation. Furthermore, because it can monitor, even at low levels, the moisture or solvent in a film during its drying process, TMA could help establish drying conditions (temperature and length of drying time) of a coating process. Since it can detect changes in the thermomechanical deformation of films brought about by the nature of their casting solvents and the presence of additives, the test could also be used to select the spraying solvent or type and level of additives appropriate for a film coating formulation. Consequently, TMA provides a valuable tool that can be used in developing, screening and optimizing coating formulations or processes.

Although the results of these studies were obtained from free films, they may be similar to those of film coatings tested directly on the tablets. Results of preliminary work on selected film coated tablets showed that there was no significant difference between the thermomechanical behavior of the free or unsupported film coating and the film coating while attached to the tablet, as measured by T_g values. However, further evaluation to confirm these findings is necessary.

References

Bender, H.S. and Thayer, D.W., Rapid method for determination of cure of thermoset primers. J. Paint Technol., 42 (1970) 746–750.

Crawford, R.R. and Esmerian, O.K., Effect of plasticizers on some physical properties of cellulose acetate phthalate films. J. Pharm. Sci., 60 (1971) 312–314.

Daniels, T., Thermal Analysis, Wiley, New York, 1966, pp. 150–162.

Doolittle, A.K., Technology of Solvents and Plasticizers, Wiley, New York, 1954, pp. 240–265.

DuPont Application Brief no. 10, Paint properties from TMA data, (1968) 1–4.

DuPont Application Brief no. 27, Cure of elastomers, pp. 1–2.

Haas, H.C., Farney, L. and Valle, C., Some properties of ethyl cellulose films. J. Colloid. Sci., (1952) 584–599.

Holsworth, R.M., Provder, T. and Ramig, A., Physical characterization of coatings upon aging. J. Paint Technol., 46 (1974) 76–95.

Malm, C.J., Emerson, J. and Hiatt, G.D., Cellulose acetate phthalate as an enteric coating material. J. Pharm. Ass., 40 (1951) 520–525.

Miranda, T.J., Comparison of evaporative rate analysis with thermomechanical analysis for thermosetting acrylic coatings. J. Paint Technol., 43 (1971) 51–54.

Moelter, G.M. and Schweizer, E., Heat softening of celllose acetate. Ind. Eng. Chem., 41 (1949) 684–689.

Turi, E.A., Thermal Characterization of Polymeric Materials, Academic Press, 1981.