

Effect of Molecular Weight Distribution on the Sprayability of Poly(Methyl Methacrylate)

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Synopsis

Factors which influence the sprayability of poly(methyl methacrylate) lacquers are discussed. A method of predicting this property based on considerations of the molecular weight distribution of the polymer is presented.

Introduction

The use of poly(methyl methacrylate) in the surface coating industry offers a number of advantages over some of the older types of vehicle. For example, in systems which dry by solvent evaporation, nitrocellulose has been virtually replaced by poly(methyl methacrylate) because of the greatly improved gloss retention on exposure.¹

Initially, attempts to use polymers of methyl methacrylate were only partially successful because of the difficulties encountered in spray application. The systems had pronounced tendencies to form long filaments before adhering to the surface being coated and this resulted in a rough and uneven surface texture. This phenomena is referred to as cobwebbing or simply webbing.

One method of overcoming cobwebbing is to reduce the application solids by the addition of suitable solvents, but this approach is limited by commercial considerations which require dry film builds of at least 1.5 mils from three-coat applications.

A major step towards the control of webbing resulted from the realization that this property was related to the viscosity-average molecular weight:² the lower the molecular weight, the less the tendency to web. However, it was also known that gloss retention on exposure decreased with decreasing molecular weight, and hence a compromise between the tendency to web (solids at application viscosity) and durability was reached, and a viscosity-average molecular weight within the range of 55,000-105,000 was chosen as suitable for poly(methyl methacrylate)-based lacquers.²

However, experience in our laboratories has shown that a knowledge of the viscosity-average molecular weight is not sufficient to predict the properties of a poly(methyl methacrylate)-based lacquer, and this was clearly

illustrated when two polymers of approximately the same average molecular weight showed quite distinct spraying properties.

It is now generally accepted that molecular weight distribution is related to polymer properties,³ and in this paper work is described which is aimed at relating molecular weight distribution to sprayability of poly(methyl methacrylate)-based lacquers.

Experimental

The molecular weight values were calculated from the equation

$$M = 1.47 \times 10^6 (N_r - 1 - \ln N_r)^{0.65}$$

where M = viscosity-average molecular weight, and

$$N_r = \frac{\text{Efflux time of polymer solution}}{\text{Efflux time of solvent used in polymer solution}}$$

The efflux times were measured in accordance with the procedure of ASTM-D-445-46T Method B, a solution of 0.5 g. of the polymer being tested in 100 cc. of ethylene dichloride being used to determine the efflux time of the polymer solution. The determinations were run at 30°C. in a modified Ostwald viscometer tube No. 1, BSS standard.

The molecular weight distributions were measured by a modification of the method described by Desreux and Spiegels.⁴

A glass column was packed with glass beads (80% less than 30 mesh) to a height of 85 cm. and maintained at a temperature of $30 \pm 0.01^\circ\text{C}$. by means of a constant temperature jacket. A solution of the polymer under test (7.5 g.) in ethylene dichloride (200 cc.) was allowed to evaporate, with constant stirring, in contact with other glass beads (200 g.). The glass beads containing the polymer coating were then placed on top of the column beads and the column filled with water in such a manner that all air bubbles were excluded.

Acetone was run into a constant dilution tank containing originally 100% water, and the solvent from this tank used to elute the column. Samples were collected at 50 cc. intervals and each sample evaporated, the residue

TABLE I
White Lacquer

	Amt., %
Titanium dioxide	14.8
Poly(methyl methacrylate)	23.5
Benzyl butyl phthalate	7.35
Linseed oil monoglyceride	0.51
Toluene	40.4
Acetone	8.1
Butyl acetate	5.34
	100.00

weighed, and then the viscosity-average molecular weight determined. This procedure was continued until all polymer was eluted from the column.

Large quantities of polymer fractions with narrow molecular weight ranges were prepared by fractionation using toluene/40–60° petroleum ether as a solvent/nonsolvent mixture. This procedure was repeated until a satisfactory narrow distribution was obtained when measured by the method above.

Polymer A was produced by adding 50 parts of freshly distilled methyl methacrylate monomer containing 0.2 parts of benzoyl peroxide to toluene maintained at its reflux temperature, the addition taking place at a constant rate over a period of 6 hr. Heating was continued for a further 2 hr., and the resulting solution was employed in the production of the spraying lacquer.

TABLE II
Solvent Mixture

	Amt., wt.-%
Acetone	40
Petroleum distillate (b.p. 92–118°C.)	10
Toluene	10
Xylene	10
Cellosolve acetate	30
	<u>100</u>

TABLE III
Molecular Weight Distribution of Polymer A and Calculation of Webbing Characteristics*

Fraction	% Present	Webbing resist- ance constant	Effective webbing resist- ance	Webbing tendency constant	Effective webbing tendency
0–15,000	9.0	110	990		
15,000–25,000	3.9	100	390		
25,000–35,000	6.4	91	582		
35,000–45,000	6.9	83	573		
45,000–55,000	7.2	75	540		
55,000–65,000	21.2	67	1420		
65,000–75,000	7.2	58	418		
155,000–165,000	34.0			45	1530
165,000–175,000	4.2			65	273
			<u>4913</u>		<u>1803</u>

* The ratio of overall webbing tendency (1803) to overall webbing resistance (4913) is less than unity, and this polymer was predicted to provide commercial sprayable non-webbing coating compositions. The effective webbing resistance and effective webbing tendency are obtained by multiplying the concentration of a given polymer fraction by its corresponding constant.

Polymer B was prepared by standing inhibitor-free methyl methacrylate, 50 parts, at room temperature for 40 days, then adding 0.4 parts of benzoyl peroxide and proceeding in a similar manner to polymer A.

All polymer fractions and polymers A and B were evaluated for sprayability in the formula shown in Table I.

These were thinned before spraying with an equal volume of solvent having the composition shown in Table II.

Polymer A gave a smooth film when sprayed under these conditions while polymer B formed a rough cobweb-type structure.

The molecular weight distribution and calculations for webbing of polymer A and polymer B are shown in Tables III and IV, respectively.

TABLE IV
Molecular Weight Distribution of Polymer B and Calculation of Webbing Characteristics*

Fraction	% Present	Webbing re-sistant constant	Effective webbing resistance	Webbing tendency constant	Effective webbing tendency
0-15,000	40.1	110	4400		
15,000-25,000	4.2	100	420		
25,000-35,000	3.8	91	346		
35,000-45,000	1.0	83	83		
45,000-55,000	1.0	75	75		
55,000-65,000	29.0	67	1943		
65,000-75,000	8.9	58	516		
75,000-85,000	2.0	50	100		
85,000-95,000	0.5	42	21		
95,000-105,000	0.5	33	17		
105,000-115,000	0.5	25	13		
115,000-125,000	0.5	16	8		
125,000-135,000	—	9			
145,000-155,000	0.5			25	13
155,000-165,000	2.4			45	108
165,000-175,000	1.1			65	72
500,000-600,000	0.2			920	184
600,000-750,000	0.4			1200	480
750,000-1,000,000	1.1			1640	1804
1,000,000-1,500,000	1.5			2480	3720
1,500,000-2,000,000	0.8			3600	2880
	100.0		7942		9261

* The ratio of overall webbing tendency (9261) to overall webbing resistance (7942) is greater than unity, and this polymer was predicted to web when sprayed after incorporation in commercial coating compositions.

Discussion

Following an initial observation that methyl methacrylate polymers of approximately the same viscosity-average molecular weight had different spraying characteristics, two polymers were prepared in which the distribu-

tion was deliberately varied by changing the processing conditions but the average molecular weights were kept as comparable as possible. Measurement of the molecular weight distribution of these polymers by a method similar to that described by Desreux and Spiegels⁴ showed that one polymer (polymer A) had a relatively narrow molecular weight range comparable with commercial polymers of this type whereas the other polymer (polymer B) possessed a broader distribution. Polymer A gave sprayable lacquers when pigmented and plasticized whereas polymer B showed cobwebbing under the same conditions.

In order to derive a quantitative method for predicting sprayability, a number of polymer fractions with narrow molecular weight range (approximately ± 5000) were prepared on a large scale with toluene/petroleum ether as a solvent/nonsolvent composition. These were evaluated in a pigmented and plasticized lacquer formula at a controlled solids content. It was found that no webbing occurred unless the polymer fraction had a molecular weight greater than 140,000 (± 5000), and on this basis the frac-

TABLE V
Webbing Tendency Constants

Viscosity-average molecular weight	Webbing tendency constant (WT)
135,000-145,000	0
145,000-155,000	25
155,000-165,000	45
165,000-175,000	65
175,000-185,000	90
185,000-195,000	115
195,000-205,000	138
205,000-215,000	160
215,000-225,000	180
225,000-235,000	200
235,000-245,000	230
245,000-255,000	250
255,000-265,000	270
265,000-275,000	295
275,000-285,000	315
285,000-295,000	340
295,000-305,000	360
305,000-325,000	395
325,000-345,000	440
345,000-365,000	483
365,000-385,000	528
385,000-405,000	575
405,000-450,000	640
450,000-500,000	745
500,000-600,000	920
600,000-750,000	1200
750,000-1,000,000	1640
1,000,000-1,500,000	2480
1,500,000-2,000,000	3600

TABLE VI
Webbing Resistance Constants

Viscosity-average molecular weight	Webbing resistance constant (WR)
0-15,000	110
15,000-25,000	100
25,000-35,000	91
35,000-45,000	83
45,000-55,000	75
55,000-65,000	67
65,000-75,000	58
75,000-85,000	50
85,000-95,000	42
95,000-105,000	33
105,000-115,000	25
115,000-125,000	16
125,000-135,000	9
135,000-145,000	0

tions could be divided into webbing and nonwebbing types. It was also discovered that the tendency of webbing fractions to induce webbing in low molecular weight fractions was proportional to the concentration and to a constant related to molecular weight. This constant we have called the webbing tendency (WT). Similarly, the tendency of the nonwebbing fractions to reduce webbing tendencies, has been called the webbing resistance (WR). The values of these constants for a range of webbing and nonwebbing fractions have been determined experimentally by preparing mixtures of high and low molecular weight fractions which just cobweb and then arranging that the product $C_a WT_a / C_n WR_n = 1$ or $C_a / C_n = WR_n / WT_a$ where C_a is the concentration of webbing fraction a, C_n is the concentration of nonwebbing fraction n, WT_a is the webbing tendency of fraction a, and WR_n is the webbing resistance of fraction n.

This ratio was then normalized by multiplying both numerator and denominator by a factor which would yield whole numbers for WT. These are recorded in Table V. In a similar manner the WR constants for the lower molecular weight fractions were determined and are recorded in Table VI.

Therefore in a polymer mixture the overall webbing tendency may be represented by the sum of the products of the webbing tendency and concentration of each narrow molecular weight fraction. The overall webbing resistance is defined in a similar manner. Where the ratio of overall webbing tendency to overall webbing resistance is less than 1, the polymer mixture is sprayable without cobwebbing at a solids content of approximately 24%. Conversely, where this ratio is greater than 1, the polymer mixture will cobweb under these conditions.

As an illustration of the use of these calculations the polymers A and B have been assessed, and the predicted webbing properties are in agree-

ment with the practical sprayability of the lacquer solutions based on these polymers.

The use of these constants, therefore, results in a more accurate method of predicting the spraying properties of poly(methyl methacrylate) lacquers than simple measurement of average molecular weight values.

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References

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Résumé

On discute les facteurs qui influencent la possibilité de vaporisation de laques de polyméthacrylate de méthyle. On présente une méthode qui permet de prévoir cette propriété, se basant sur la distribution des poids moléculaires dans ces polymères.

Zusammenfassung

Es wird der Einfluss verschiedener Faktoren auf die Versprühbarkeit von Polymethylmethacrylat-Lacken diskutiert und eine Methode angegeben, die es gestattet, Voraussagen über diese Eigenschaft auf Grund einer Betrachtung der Molekulargewichtsverteilung des Polymeren zu treffen.

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