## Characterization of Microgels By Brookfield Viscometry With Cylindrical, T-Bar, and Flags Impeller Spindles

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ABSTRACT: Neutralized 0.5% microgels of the crosslinked copolymer of methyl vinyl ether and maleic anhydride were characterized by the penetrating ball test and by Brookfield viscometry with the # 7 cylindrical, T-E, and flag-impeller spindles. Apparent wall slip between the microgel and the #7 cylindrical spindle is a surface phenomenon that is more pronounced for "hard" microgels than for "soft" microgels and depends strongly on the interaction between the surface of the spindle and the microgel. Apparent wall slip can be enhanced by coating the #7 spindle with hydrophobic polymers and polymers with carboxyl groups and suppressed by coating the spindle with vinylpyrrolidone-based polymers. Similar apparent wall slip was also noticed for the cross-linked polyacrylic acid microgel. Apparent wall slip was not noticed when the T-E spindle and the flag-impeller spindle were used in viscosity measurement. The viscosity of microgels measured with a #7 spindle coated with polyvinylpyrrolidone, a T-E spindle, and a flag-impeller spindle correlate well with each other, indicating that the apparent wall slip is suppressed equally well by these three spindles. A simple penetrating ball test was used to differentiate hard microgels from soft microgels. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 67-74, 1999

**Key words:** viscosity; wall slip; microgel; crosslinked copolymer of methyl vinyl ether and maleic anhydride; crosslinked polyacrylic acid

## INTRODUCTION

Lightly crosslinked polymers with pendant carboxylic acid groups are widely used as thickeners, suspending agents, and emulsion stabilizers for many personal care and pharmaceutical products. They include alternating copolymers of methyl vinyl ether and maleic anhydride (PMVE/ MA) cross-linked with 1,9-decadiene (Stabileze<sup>®</sup> resins) and polyacrylic acid (PAA) crosslinked with allyl ethers of pentaerythritol or sucrose (Carbomer resins). These lightly crosslinked polymers are produced by precipitation polymerization as very fine particles. On neutralization of

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the carboxyl groups, the particles can swell up to a few hundred times their original size to form a microgel with superstructure. The swollen gel particles become closely packed at or above the overlap concentration and are sterically confined by their neighbors.<sup>1</sup> The rheological property of the closely packed microgel superstructure is very complex and different from that of true polymer solutions. Microgels also display solid-like behavior, such as the dominant elastic nature, the relative small change of storage modulus with frequency, creep, and yield stress.<sup>1,2,3</sup>

During the viscosity measurement, wall slip can occur in gels, cements, dispersions, and emulsions.<sup>4</sup> This apparent wall slip is caused by a region of higher-velocity gradient adjacent to the wall.<sup>4</sup> The wall reduces the local concentration of suspended particles.<sup>4</sup> When a shear stress is ap-

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plied to the material, large velocity gradients are produced in this low-viscosity layer, resulting in apparent wall slip.<sup>4</sup> Wall slip has been studied by making measurements with two gap sizes for parallel-plate geometry.<sup>4</sup>

Solid-like behaviors, such as yield stress and creep compliance, have been observed in Carbomer microgels.<sup>1,3</sup> However, no wall slip was reported for Carbopol<sup>®</sup> 941, a low-viscosity grade of the Carbomer resins, even at concentration as high as 3.9 wt % using cone and plate and parallel plate fixtures.<sup>1</sup> Wall slip was not mentioned in the two earlier papers on the rheological properties of Carbopol<sup>®</sup> 940, a high-viscosity grade of the Carbomer resins using cone and plate or parallel plate fixtures.<sup>2,3</sup>

Slip, "being a surface phenomenon, is sensitive to the roughness and wetting characteristics of the solids surface".<sup>4</sup> Affixing sand paper or porous flat glass frit to the tool surfaces has been used in literature to suppress wall slip.<sup>4</sup> Wall slip is also eliminated using the vane device, because yield stress is measured along a cylindrical surface defined by the outer tips of the vane blades, not along a wall.<sup>4</sup>

A Brookfield viscometer with the #3, 5, and 7 spindles has been specified in the United States Pharmacopeia (USP) for many years for measuring the viscosity of different grades of Carbomer resins.<sup>5</sup> However, no precaution is noted in these USP methods about the potential apparent wall slip in the viscosity measurement of the Carbomer microgels. According to Brookfield Engineering Laboratories, Inc., rotational viscometers, such as disks (#3 and 5) and cylinder (#7), are not suitable for viscosity measurement of nonflowing or slow-flowing materials such as gels, because "rotating spindles tend to channel (push the sample materials aside) to exert a negligible and meaningless torque on any sensing device.<sup>6</sup> Brookfield Engineering Laboratories recommends using the T-bar spindles for this type of material.<sup>6</sup>

In this article, apparent wall slip was studied by measuring the Brookfield viscosity of neutralized 0.5% Stabileze<sup>®</sup> (PMVE/MA) and Carbopol<sup>®</sup> (PAA) microgels with a Brookfield Model RVDVII viscometer and the #7 spindle. The effects of coating the #7 spindle with different polymers on viscosity and apparent wall slip were studied. Viscosities were also measured with a Brookfield Model HB DVII+ viscometer with a flag-impeller spindle and a Brookfield Model RVDVII viscometer with the T-E spindle. Based on these results, the most suitable spindle for the measurement of Brookfield viscosity of microgels is recommended.

## **EXPERIMENTAL**

## Apparatus

A Brookfield Model RVDVII viscometer with the #7 spindle (a cylindrical spindle with diameter 0.125 in. and length 1.983 in.) at 20 rpm and the T-E spindle (a T-shaped spindle with a crossbar length 0.604 in. and a crossbar diameter 0.028 in.) at 10 rpm and a Brookfield Model HBDVII+ viscometer with the flag-impeller spindle (MVS-1Y) at 30 rpm were used in this study. The impeller spindle has two flags of length 0.591 in. and width 0.191 in., which are mounted on opposite sides of the shaft with a diameter of 0.21 inch. Viscosity was measured at ambient temperatures (23  $\pm$  2°C) in an 8 oz wide-mouth jar with an inner diameter about 2.15 inches, which is more than 10 times larger than the diameter of the #7 spindle and the width of the flag-impeller spindle. Shear rate at the surface of the #7 spindle is 4.18  $sec^{-1}$  at 20 rpm. Shear rate cannot be calculated for the flag-impeller spindle and the T-E spindle.<sup>6</sup> No spindle guard was used. Viscosity of the microgels studied in this article is not very sensitive to small changes in temperature.<sup>1</sup> The viscosity readings stabilized quickly (within 30 s) for most of the samples in this study. If the readings did not stabilize (e.g., in the presence of severe apparent wall slip), then the range of viscosity within a 1-min period was reported. The HBDVII+ viscometer with the flag-impeller spindle was calibrated with a silicone oil viscosity standard (54,900 cp) from Brookfield Engineering Laboratory. In the penetrating ball test, a metal ball 0.6000 in. in diameter and weighing 15.115 g from Haake was rolled slowly off the edge of a platform at a height of 4 inches from the level of microgel into an 8 oz wide-mouth jar used for Brookfield viscosity measurement. The depth of penetration was measured with a ruler from the gel level to the bottom of the ball.

## Materials

A Stabileze<sup>®</sup> 06 resin (PMVE/MA) from International Specialty Products (Wayne, NJ) and a Carbopol<sup>®</sup> Ultrez 10 resin (PAA) from BF Goodrich (Brecksville, OH) were used in this study. The Carbopol<sup>®</sup> Ultrez 10 is a new grade of Carbopol<sup>®</sup> resins that is similar to the Carbopol<sup>®</sup> 940 in viscosity. The silicone oil viscosity standard (54,900 cp) was from Brookfield Engineering Laboratory. The 20% aqueous solution of Gafquat<sup>®</sup> 755N, a neutralized and quaternized random copolymer of vinylpyrrolidone (VP) and dimethylaminoethylmethacrylate, was from International Specialty Products (Wayne, NJ).

## Preparation of the Microgels for Viscosity Measurement

## 0.5% PAA Microgel

Here, 1 g of the sample was mixed with 196 g of water at 47°C in an 8-oz jar with vigorous shaking, then 3 g of 10% aqueous sodium hydroxide was added to neutralize the gel. The sample jar was tapped against a cork ring to remove air bubbles larger than  $\frac{1}{8}$  in. before viscosity was measured. Alternatively, the sample jar could be centrifuged at 2500 rpm for 15 min to remove air bubbles. The pH of the PAA microgel was determined to be 6.6.

## 0.5% PMVE/MA microgel

Exactly 1.25 g of the sample was weighed and transferred in a 500-mL glass kettle. Deionized water was added to make the total weight 232.5 g. A heating mantle and an anchor stirrer were attached to the reaction vessel. Agitation was started at a low speed (100-200 rpm). The temperature was set to 80°C, and heat was turned on with continuing agitation. The speed was increased to 500 rpm when all of the powders had been wetted and immersed in water. Temperature was maintained at 80°C until no undissolved particles were visible. This typically took 40-60min. The heating mantle was removed to verify that the solution was completely hydrolyzed (i.e., when the solution became translucent). After the solution was completely hydrolyzed, the heating mantle was removed and the solution was cooled to room temperature with continuous stirring. Then 17.50 g, or 17.2 mL, of 0.5N NaOH was added to neutralize the sample to form a thick and clear gel. Stirring was continued with reduced speed ( $\sim 300$  rpm) for 5 min to ensure that the gel was thoroughly mixed. The gel was transferred to an 8 oz jar using a clean spatula. The sample jar was tapped against a cork ring at least 100 times to remove air bubbles larger than  $\frac{1}{2}$  in. before measuring viscosity. Alternatively, the sample jar can be centrifuged at 2500 rpm for 15

min to remove air bubbles. The pH of the PMVE/MA gels prepared by the foregoing method normally was 6.5–7.5.

## **Coating of the #7 Spindles**

To alter the surface of the #7 spindles, a thin layer of polymer was coated onto the spindles. After the spindles were dipped into the polymer solutions, they were dried under ambient conditions for at least 1 h by placing them vertically with the screw head down to allow excess solution to drain by gravity. Further drying of the spindles under vacuum and at 60°C would have no effect on the results. The spindles were coated once with the 2% solutions and twice with the 1% solution. The same viscosity can be obtained with spindles coated with one or two layers of the 2% polymer solutions. The first layer was allowed to dry for at least 1 h before the second layer was applied. The following polymers were used to coat the #7 spindles:

- from International Specialty Products, PVP K-90 (high-molecular-weight polyvinylpyrrolidone), PVP K-30 (low-molecular-weight polyvinylpyrrolidone), PVP/VA E-335 (30/70) random copolymer of VP and vinyl acetate), PVP/VA E-535 ((50/50 random copolymer of VP and vinyl acetate), PVP/VA E-735 (70/30 random copolymer of VP and vinyl acetate), Gantrez® ES-225 (half acid and half ethyl ester of the PMVE/MA, referred to as ES-225 in later discussions), Gantrez® ES-425 (half acid and half butylester of the alternating PMVE/MA, referred to as ES-425 in later discussions), ACV-4026 and 4037 (hydrolyzed PMVE/MA), and Gafquat® 734 (quaternized copolymer of VP and dimethylaminoethylmethacrylate, referred to as 734 in later discussions)
- from Scientific Polymer Products, PS (polystyrene), PMS (polymethyl styrene), SBR (block copolymer of styrene/butadiene), SIR (block copolymer of styrene/isoprene), PMMA (polymethylmethacrylate), PIBMA (polyisobutylmethacrylate), PBMA (polybutylmethacrylate), and PAA (polyacrylic acid).

The solvents and the concentrations of the polymers used to coat the #7 spindles were as follows:

- 2% in ethanol: Gantrez<sup>®</sup> ES-225 and ES-425; PVP/VA E-335, E-535, and E-735; Gafquat 734; PVP K-30 and K-90
- 2% in toluene: SBR and SIR
- 2% in methyl ethyl ketone: PS, PMS, PMMA, PBMA, and PIBMA
- 1% in water/methanol (50/50): polyacrylic acid
- 2% in water: ACV-4026 and 4027.

## **RESULTS AND DISCUSSION**

Determination of the Viscosity of Microgels With the Brookfield Model RVDVII Viscometer and the #7 Spindle

## Brookfield Viscometry With the Uncoated #7 Spindle

According to ASTM D-2196<sup>7</sup> for non-Newtonian materials, two Brookfield viscosity results obtained by the same operator at different times should be considered suspect if they differ by more than 7%. However, it was found in this laboratory that in the determination of Brookfield viscosity of neutralized 0.5% microgels via the Brookfield RVDVII viscometer with the #7 spindle, the difference in viscosity from two operators sometimes can be as high as 100%.

A comprehensive investigation of the problem showed that following a well-defined spindlecleaning procedure can significantly reduce the difference between two operators, indicating that the characteristics of the #7 spindle surface are critical to viscosity measurement. This is rather surprising, because only the geometry and dimension of the spindle, not the surface or material of construction of the spindle, are expected to be critical in viscosity measurement. In this study the #7 spindles were first cleaned with soap and water, then scrubbed thoroughly with paper towels under running tap water. From 12 independent measurements with meticulously cleaned and dried #7 spindles, with a 95% confidence level, the precision of the viscosity of a PMVE/MA microgel can be expressed as  $73,000 \pm 6400$  cp, with a coefficient of variation of 4.1%.

To study this surface problem more thoroughly and systematically, the viscosity of the 0.5% microgels were determined with the #7 spindles coated with various polymers to modify the surface characteristics of the spindles in a controlled manner.

## Certification of the #7 Spindles

Because the characteristics of the #7 spindles are critical to the viscosity measurement of microgels, the uncoated #7 spindles used in this study must be certified with standards before use. A silicone oil with a certified viscosity of 54,900 cp from Brookfield Engineering Laboratory and a Gafquat<sup>®</sup> 755N solution were used to certify that the nine #7 spindles used in this study can provide consistent viscosity data for homogeneous solutions. Using the nine #7 spindles, the Brookfield viscosity of the silicone oil standards and Gafquat<sup>®</sup> 755N were found to be very consistent, varying from 52,800 to 54,000 cp and from 43,300 to 46,200 cp, respectively. These results showed that the nine uncoated #7 spindles are very consistent in dimension (length and diameter), yielding reproducible viscosity for the silicone oil standard and the Gafquat<sup>®</sup> 755N.

## **Certification of the Coated Spindles**

To ensure that coating the spindle did not change the dimension of the spindle and generate false data, Brookfield viscosities of the silicone oil standard and the Gafquat<sup>®</sup> 755N solution were measured again with the #7 spindles coated with the polymers described earlier. These were found to vary from 52,500 to 55,000 cp and 43,200 to 46,600 cp, respectively—the same as the nine #7 spindles without the polymer coatings. Coating the spindles with the different polymers changes only the spindles surface characteristics, not the dimensions. In other words, the gap size and shear rate are held as constants in the study with the #7 spindles.

# Brookfield Viscosity of the PMVE/MA Microgel Using Coated Spindles

As a control, the viscosities of the PMVE/MA microgel measured with the nine #7 spindles without coatings vary from 61,500 to 66,000 cp. The viscosity of the PMVE/MA microgel was also measured with a Brookfield Model RVDVII viscometer and the T-E spindle at 10 rpm and found to be 98,000 cp. The results in Figure 1 indicate that coating the #7 spindles with polymers with carboxyl groups (ES-225, ES-425, ACV-4026 and 4037) drastically reduces viscosity, whereas coating the spindles with VP-based polymers (PVP, PVP/VA, and 734) increases the viscosity measured for the PMVE/MA microgel. The results in Figure 2 show that coating the spindles with the



**Figure 1** The effect of coating the #7 spindle with polar polymer on the viscosity of PMVE/MA microgel. Coating on the #7 spindle: (1) none (control), (2) ES-225, (3) ACV-4037, (4) ES-425, (5) PVP/VA E-735, (6) PVP K-30, (7) PVP/VA E-335, (8) PVP/VA E-535, (9) 734.

hydrophobic polymers significantly reduces the viscosity measured for the PMVE/MA microgel. It should be pointed here that this is very different from Gafquat<sup>®</sup> 755*N*, a 20% aqueous solution of a cationic copolymer, where coating the #7 spindle with hydrophobic polymers, polymers with carboxyl groups, a cationic polymer (Gafquat<sup>®</sup> 734), and VP-based polymers has no effect on the measured viscosity.

#### Brookfield Viscosity of the PAA Microgel

To determine whether similar phenomena would also occur with other microgels, the Brookfield



**Figure 2** The effect of coating the #7 spindle with hydrophobic polymer on the viscosity of PMVE/MA microgel. Coating on the #7 spindle: (1) none (control), (2) PS, (3) PMS, (4) SBR, (5) SIR, (6) PMMA, (7) PEMA, (8) PBMA, (9) PIBMA.



**Figure 3** The effect of coating the #7 spindle on the viscosity of the PAA microgel. Coating on the #7 spindle: (1) none (control), (2) ACV-4037, (3) ACV-4026, (4) PVP K-30, (5) 734, (6) PVP/VA 335, (7) SBR, (8) PMS, (9) PMMA, (10) PA.

viscosity of a PAA microgel was determined with the #7 spindles with and without coating. Without the coating, the Brookfield viscosity varied from 50,000 to 56,000 cp for the PAA microgel. The results in Figure 3 indicate that for the PAA microgel, a drastic decrease in viscosity also occurs when the spindles are coated with polymers with carboxyl groups (ACV-4037, ACV-4026, and polyacrylic acid), decreased viscosity is noticed when the spindles are coated with hydrophobic polymers, and increased viscosity is noticed when the spindles are coated with VP-based polymer and copolymers.

The results in Figure 1, 2, and 3 demonstrate that the viscosity of the PMVE/MA microgel and the PAA microgel measured with the #7 spindle depends strongly on the interaction between the surface of the spindle and the microgel. Apparent wall slip, as a surface phenomenon, can occur between the surface of the #7 spindle and the microgel and can be enhanced or reduced by coating the spindle with the appropriate polymers.

For the PMVE/MA microgel and the PAA microgel, which are anionic microgels at neutral pH, coating the spindle with anionic polymers enhances apparent wall slip due to the electrostatic repulsion between the spindle surface and microgel surface. Coating the spindle with VP-based polymers suppresses apparent wall slip, because these polymers are known to form strong bonding complex with polyacrylic acid and copolymer of methyl vinyl ether and maleic anhydride.<sup>8–10</sup> Coating the spindle with hydrophobic polymers

Sample	Viscosity (cp)				
	#7 spindle	#7 spindle with PVP K-90	T-E spindle	Flag- impeller spindle	Depth of Penetration (inch)
Hard microgels					
A	71,800	113,000	135,000	99,600	$\frac{7}{8}$
В	46,200	102,000	139,000	105,000	$\frac{1}{2}$
С	45,600	110,000	NA	115,000	$\frac{\tilde{7}}{8}$
D	54,500	114,000	163,000	108,000	$\frac{3}{4}$
E	51,000	NA	151,000	111,000	ŇĂ
F	59,500	117,000	158,000	129,000	$\frac{7}{8}$
G	44,600	124,000	144,000	108,000	ŇÅ
Н	66,500	120,000	150,000	107,000	NA
Soft microgels					
A	51,000	61,000	79,000	55,000	$1\frac{3}{8}$
В	46,400	53,000	69,000	47,100	$1\frac{3}{4}$
С	44,500	49,000	64,000	46,900	$1\frac{5}{8}$
D	55,000	71,000	87,000	62,900	$1\frac{3}{2}$
Е	54,000	65,000	76,000	57,500	$1\frac{3}{2}$
F	43,000	48,000	61,500	40,300	$\overset{\circ}{2}$
G	37,600	40,000	51,000	38,200	$2\frac{3}{8}$

Table I Depth of Penetration and Brookfield Viscosity of the Hard and Soft PMVE/MA Microgels

enhances apparent wall slip due to the reduction in the affinity of the spindle surface to the hydrophilic microgels.

It is interesting to note that in Figure 1, apparent wall slip is much more severe if the #7 spindle is coated with Gantrez<sup>®</sup> ES-225 (a half-acid and half-ethyl ester copolymer) than with Gantrez<sup>®</sup> ES-425 (a half-acid and half-butyl ester copolymer). This indicates that the half-butyl ester groups provide much more steric hindrance than the half-ethyl ester groups to reduce the electrostatic repulsion between the carboxyl groups from the microgels and the half-acid groups of Gantrez<sup>®</sup> ES polymer coatings on the spindles.

Carbopol<sup>®</sup> resins can contain up to 20% soluble uncrosslinked polyacrylic acid molecules.<sup>2</sup> If the spindle is not meticulously cleaned and retains some polyacrylic acid residue, then the viscosity measured could be erroneously low, due to the enhanced apparent wall slip. This precaution is not specified in the current USP method.<sup>5</sup>

## Characterization of the Hard and Soft PMVE/MA Microgels by the Penetrating Ball Test

While studying the properties of the microgels, it was noticed that some microgels are harder to

mix manually and are very uneven and rough on the surface and others are softer to mix and are even and smooth on the surface. However, in many cases Brookfield viscosity measured with the uncoated #7 spindle showed no significant differences between the hard and soft microgels. The penetrating ball test was developed to find a simple and rugged method not based on rotational viscometry to differentiate the hard microgels from the soft microgels. The results in Table I indicate that in general, the depth of penetration is less than 1 in. for the hard microgels and more than 1 in. for the soft microgels.

## Determination of the Viscosity of Hard and Soft PMVE/MA Microgels With the Brookfield Model RV Viscometer With the T-E Spindle and the Brookfield Model HBDVII+ Viscometer With the Flag-Impeller Spindle

To further explore the apparent wall slip problem, the viscosities of several hard and soft PMVE/MA microgels were measured with the Brookfield RV viscometer with the #7 spindle with and without PVP K-90 coating, the Brookfield RV viscometer with the T-E spindle, and the Brookfield HV DVII+ viscometer with the flag-impeller spindle. The results in Table I indicate that Brookfield viscosities for the hard and soft microgels measured with the uncoated #7 spindles overlap significantly. In other words, due to apparent wall slip, Brookfield viscosity measured with the uncoated #7 spindle cannot be used with confidence to differentiate the hard microgel from the soft microgel. The results in Table I also indicate that coating the #7 spindle with PVP K-90 to greatly suppress apparent wall slip increases the viscosity of the hard microgels much more than the soft microgels. In other words, apparent wall slip noted for the #7 uncoated spindle depends on the nature of the microgel and apparent wall slip is more severe for the hard microgel than for the soft microgel. The viscosities measured with the PVP K-90 coated #7 spindle, the T-E spindle, and the flag-impeller spindle correlate well with each other. This indicates that apparent wall slip is suppressed equally well by these three spindles.

The flowability of the swollen, overlapping, and closely packed microgel particles is severely limited.<sup>1</sup> This is evidenced by the small air bubbles in the microgel remaining stationary throughout the viscosity measurement. The #7 spindle is localized and is surrounded by microgel particles that are restricted to flow or rotate. Depending on the surface characteristics or the coating on the #7 spindle, different degrees of detachment can occur between the surface of the spindle and the microgel particles. Apparent wall slip can occur easily, and the Brookfield viscosity measured by the #7 spindle is not representative of the bulk viscosity of the microgels. Coating the #7 spindle with the VP-based polymers introduced a strong bonding complex between the surface of the #7 spindle and the microgel particles to prevent detachment of the surface #7 spindle from the microgel particles; therefore, the Brookfield viscosity measured is more representative of the bulk viscosity of the microgel.

Apparent wall slip is greatly suppressed for the T-E spindle and the flag-impeller spindle, because these spindles are not localized inside the microgels. As soon as the fine crossbar of the T-E spindle and the opposing flags of the flag-impeller spindle sweep through one location inside the closely packed, swollen microgel particles, the swollen particles quickly repack and regenerate the superstructure of the microgel before the next revolution begins. In essence, the fine crossbar of the T-E spindle and the opposing flags of the flag-impeller spindle sweep through the continuous superstructure of the microgels in different locations in the sample jar as the shaft rotates. This is similar to the suppression of wall slip by the vane-type device.<sup>4</sup> Thus, Brookfield viscosity measured by the T-E spindle and the flag-impeller spindle is more representative of the bulk viscosity of the microgels.

The reduction of apparent wall slip with the flag-impeller spindle also significantly reduces the variation in microgel viscosity. For example, the coefficient of variations of four lots of the PMVE/MA microgel range from 0.2 to 0.8%, which are about an order of magnitude less than the coefficient of variation of the viscosity determined with a #7 spindle. Even though the T-E spindle can measure viscosity without apparent wall slip, the fine crossbar on the tip of the T-E spindle is easy to deform to generate erroneous results. Therefore, it is not a rugged method for quality assurance laboratories. The flag-impeller spindle, which is relatively sturdy and capable of measuring the rheological properties of microgels with high precision and without apparent wall slip, is a more suitable spindle than the #7 spindle specified in the USP for the characterization of microgels.

#### CONCLUSIONS

Apparent wall slip between the microgel and the #7 cylindrical spindle depends strongly on the nature of the microgel and the interaction between the surface of the spindle and the microgel. Apparent wall slip leads to large variations in viscosity measurement.

For the PMVE/MA microgel and the PAA microgel, which are anionic microgels at neutral pH, coating the spindle with anionic polymers can enhance apparent wall slip due to the electrostatic repulsion between the spindle surface and the microgel surface. Coating the spindle with VP-based polymers can greatly suppress apparent wall slip, because the VP-based polymers can form a strong bonding complex with polymers that have carboxyl groups. Coating the spindle with hydrophobic polymers can enhance apparent wall slip due to a reduced affinity of the spindle surface to the hydrophilic microgels.

Apparent wall slip is more pronounced for hard microgels than for soft microgels. The uncoated #7 spindle can not differentiate the hard microgels from the soft microgels due to apparent wall slip.

The T-E spindle and the flag-impeller spindle, which sweep through the superstructure of the microgels continuously, can greatly suppress apparent wall slip. There is good correlation among the viscosity measured with the #7 spindle coated with polyvinylpyrollidone, the T-E spindle, and the flag-impeller spindle for the hard and soft microgels.

The flag-impeller spindle, which is relatively sturdy and is capable of measuring the rheological properties of microgels with high precision and without apparent wall slip, is a more suitable spindle than the #7 spindle specified in the USP for the characterization of microgels.

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