The Effects of Shear on Neutralized Carbomers in Aqueous Conditions

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With thanks to Ensign Laboratories

Abstract

‘Carbomer’ is the generic name for a class of high molecular weight cross linked polymers of acrylic acid. Carbomers play an important role in many commercial products such as gels, creams and lotions, providing viscosity, stabilization and suspension properties. Understanding how the preparation of the carbomer can affect the final product is vital in developing new products without issue and maintaining quality in existing ones. One such factor that can affect the behavior of the carbomer is the method of dispersing the carbomer into an aqueous medium.

This report looks at the changes in viscosity between neutralized and un-neutralized carbomers in aqueous conditions that have been subjected to either high shear or low shear mixing. Carbomers deemed to be affected by shear were then further investigated by incorporating into a finished product, e.g. a cream. This was to determine if the magnitude of change due to shearing during the carbomer preparation had any effect on the final product. The carbomers considered in this research were from Lubrizol’s Carbopol and Pemulen range of products.

From the investigation conducted, it was found that a number of carbomers were affected by shear as a result of the method of dispersion used. Use of the ‘shear sensitive’ carbomers in commercial production could require the use of low shear mixing which would result in a longer dispersion times and increased production costs.

Contents

Background

'Carbomer' is the generic name for a commercially important class of water absorbing molecules. Carbomers are high molecular weight cross linked polymers of acrylic acid, which when neutralized have the ability to absorb and retain water, resulting in a viscous gel or liquid. The dried carbomer comes in the form of a light weight white powder. A general monomer of an acrylic acid polymer can be seen below in Figure 1.

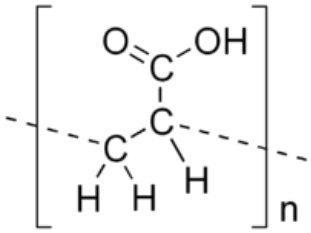

Figure 1: Acrylic Acid Monomer

The resulting product of neutralization has a number of applications in cosmetic and therapeutic production, with different carbomers being suited to different products. These products include shampoos, moisturizers, body washes, oral medication and sunscreens. Figure 2 shows the increase in size of the carbomer as it is hydrated and then neutralized. It is this property of the carbomer that allows it to act as a rheology modifier in many products.

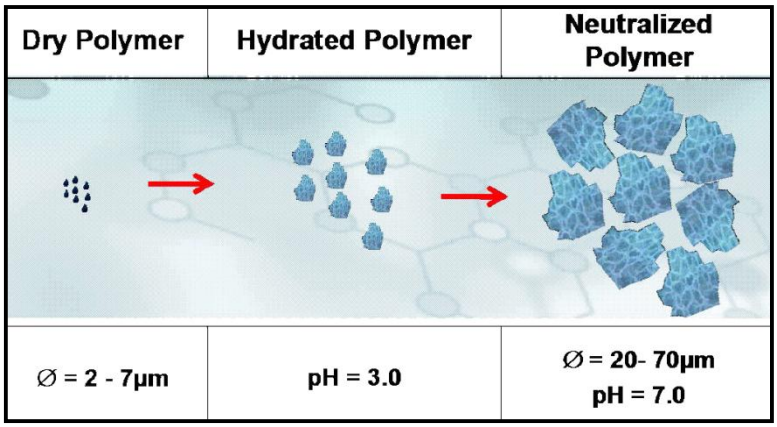

Figure 2: relative size of carbomer [2]

Most carbomers are classified as having a long or short rheology to indicate the nature of the polymer and amount of cross linking present. A short rheology corresponds to a highly cross linked polymer, whereas a long rheology corresponds to a lightly cross linked polymer. The physical appearance of each of these types of carbomer can be seen in Figure 3 below.

The carbomers considered in this report use either benzene, ethyl acetate or ethyl acetate/cyclohexane cosolvents as the polymerization solvent during synthesis. More information on this can be found in Appendix Two.

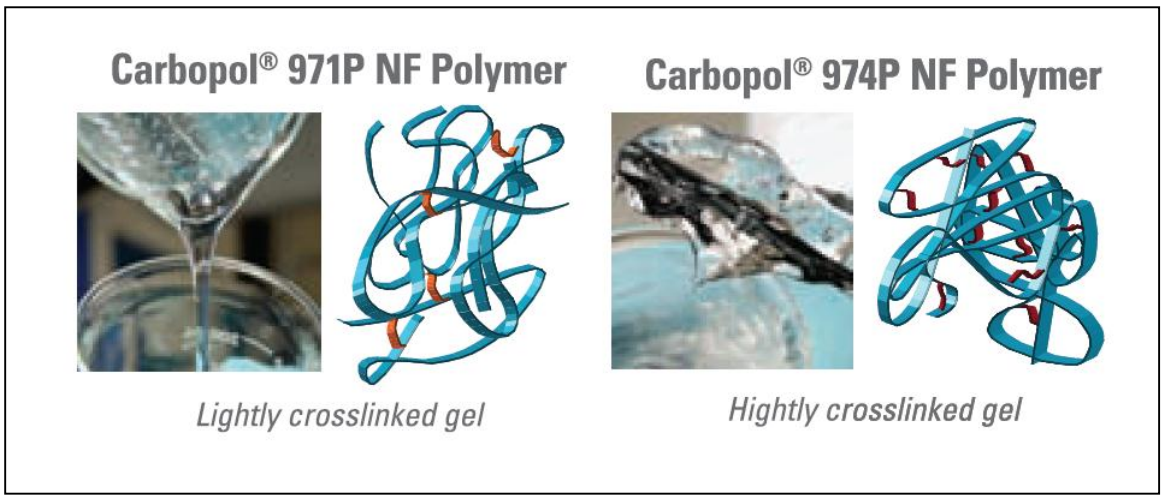

Figure 3: cross linking and viscosities in Carbomers

Sourced from Lubrizol website [3]

Carbomers in this report

-Recommended applications for carbomers investigated

Carbopol 934

- Medium to high viscosity gels/emulsions
- Short rheology (highly cross linked)

Carbopol 940

- Thickener for clear aqueous/hydroalcoholic gels

Carbopol 971P

- oral and mucosal contact applications such as oral liquids
- Low viscosity lotion/gels.
- Long rheology (lightly cross linked)

Carbopol 974P

- oral and mucosal contact applications such as oral liquids
- Short rheology (highly cross linked), produces highly viscous gels

Carbopol 980

- Efficient thickener for formulating clear aqueous and hydroalcoholic gels
- Short rheology (highly cross linked)

Carbomer U 10

- Bath gels, Hand, body and face lotions, Sunscreen lotions
- Provides high viscosity, stabilization and suspension properties
- Short rheology (highly cross linked)

Carbopol ETD 2020

- Easy to disperse
- Oral care products, clear gels, and hydroalcoholic gels

Carbopol ULTREZ 20

- Lotions, Body washes, Hair and skin gels, Bath gels
- Rheology modifier and stabilizer

Carbopol ULTREZ 21

- Personal care products (moisturizer, hand sanitizer, hair gel, sunscreen)
- Retains clarity and properties at high concentrations

Carbopol 981

- Clear low-viscosity lotions and gels (Topical Applications)
- Long flow rheology (lightly cross linked)

PEMULEN TR-1

- Polymeric emulsifier
- Used with other Carbomers where higher viscosity emulsions are required

PEMULEN TR-2

- Used for low-viscosity emulsions. (Application via spray mechanism)
- Can emulsify high levels of oil (up to 50% by weight) within a pH range of 4-5

Method

Each of twelve carbomers were tested for a change in final viscosity of the prepared dispersions by employing two methods of preparations, 'high shear' using a homogenizer and 'low shear' using a 3 prop stirrer. The carbomer, a white powder, was in all cases slowly added to water in 1.0%w/v, 0.5%w/v or 0.2%w/v amounts based on recommended levels stated in individual carbomer technical datasheets. For high shear preparations, the dispersion was milled at 5000rpm for five minutes. For low shear preparations involved mixing using a 3 prop impeller at 300 to 500rpm until the powder was uniformly dispersed. This method of dispersion varied from 30 to 90 minutes depending on the carbomer used. A 10% w/v solution of Sodium Hydroxide was used to adjust the pH to the range in which each carbomer shows maximum viscosity. Viscosity was measured using a RV viscometer before and after neutralization.

From the evaluation of methods of dispersion, two carbomers were then used to formulate a basic cream to determine how the change in viscosity due to shearing, affects a final product. The two carbomers, Carbopol 981 and Carbopol 971P, were chosen as they showed significant changes in viscosity indicating they are both 'shear sensitive' carbomers. Furthermore, these two carbomers were identified as being used in many company products and as such further investigation was warranted. The cream consisted of a main phase containing water, glycerol and preservatives with an oil phase containing emulsifiers and emollients. The Carbopol represented 0.1-0.2% of the batch by weight. The Carbopol dispersion was subjected to either high or low shear mixing before addition to the main phase. Once the Carbopol dispersion was added to the main aqueous phase, the main mix was then neutralized with Sodium Hydroxide prior to combining with the oil phase to form an emulsion. No homogenization was used to form an emulsion, either during the combining of the phases or the cooling process. Finished product viscosity was measured at 25^{o}C initially and then repeated on the following day in order to determine if the viscosity built with time.

Results

Table 1 shows the viscosities for each Carbopol both before and after neutralization and for high shear and low shear mixing.

Table 1: Carbomer Viscosities

Carbomer	Viscosity(High Shear) cP		Viscosity(Low Shear) cP		Final % Difference (Neutralized)
Neutralization	Before	After	Before	After	
Carbopol 934	34.8	25850	33.2	27800	1
Carbopol 940	255	43800	520	44400	2
Carbopol 971P	114	2100	992	6200	99
Carbopol 974P	55.2	24950	66.0	33500	29
Carbopol 980	57.2	41600	63.2	50600	20
Carbopol ETD 2020	32.8	66600	26.0	76800	14
Carbopol Ultrez-20	26.0	72200	37.6	77200	7
Carbopol Ultrez-21	22.0	59200	14.0	46600	24
Carbopol 981	160	2450	442	6700	93
Carbomer U-10	12.0	55400	12.4	53800	2
Pemulen TR-1	30.0	4960	28.8	8760	55
Pemulen TR-2	41.6	470	61.2	2330	133

Table 2 and Table 3 show the viscosities of each cream manufactured, where the added carbomer is dispersed using either high or low shear mixing.

Table 2: viscosities measured after settling for Carbopol 971P in cream Formula One

Carbomer	Viscosity(High Shear) cP	Viscosity(Low Shear) cP	Final % Difference
Control	3700		
Carbopol 971P	12800	17700	40

Table 3: viscosities measured after settling for Carbopol 981 in cream Formula Two

Carbomer	Viscosity(High Shear) cP	Viscosity(Low Shear) cP	Final % Difference
Carbopol 981	20900	31500	32

Discussion

Three Carbopols (Carbopol 971P, Carbopol 981 and Pemulen TR-2) were seen to be significantly affected in their final viscosities by the type of shearing they were subjected to. The percentage changes between the high and low shear dispersions were above 90% (Table 2) and thus these carbomers can be classed as 'shear sensitive'. Several other Carbomers, such as Carbopol 974P, Pemulen TR-1 and Carbopol Ultrez-21, showed a measurable change indicating they are affected by shear to some degree. However, other carbomers such Carbopol 934 and Carbopol 940 show little to no change in viscosity.

As a general observation, the carbomers with a lower range of theoretical viscosities seem to correspond to those most affected by high shear.

From Table 2 the viscosity of the control cream for formula one can be seen to be 3700cP. The data collected shows a measurable change between the two different Carbopol dispersion viscosities of 32%. This result is quite similar to the percentage difference of 29% obtained when testing the viscosity of the carbomer in an aqueous system. Though the sheared carbomer results in a noticeably lower viscosity, there is still a significant effect when compared to the control cream.

Table 3 shows a 40% difference between the final viscosities obtained using different dispersions. While still high, this value is nowhere near as extreme as the 93% difference obtained when measuring the carbomer in an aqueous system. The effect of shearing is reduced when in product form as other components in a formulation can add to the viscosity of a product (e.g. waxes, emulsifiers). However, even a 40% difference due to the method of dispersing the carbomer can be the difference between a product being within specification or not.

While the formulas used for the creams cannot be fully disclosed due to commercial sensitivity, they contained a mixture of water, glycerol, waxes acting as emulsifiers and emollients, preservatives and sodium hydroxide to neutralize the carbomer.

The two methods of preparation of the Carbopol in both the aqueous system and the cream are directly related to processes used in the production of therapeutic and personal care products. Both the low shear impeller and the high shear homogenizer are laboratory sized versions of the equipment used when preparing commercial quantities. This correlation allows for greater reliability of the data collected when transferred to an industrial scale. A key point in the production process is the time taken to prepare a product. To homogenize the small laboratory sized batches of carbomer took approximately five minutes, whereas completely dispersing the carbomer using the impeller, took up to 90 minutes. Scaled up to large batches (2000-10000kg), a process which may take 30 minutes in the laboratory using a high shear Rotosolver, can be extended to 2 hours or more if low shear mixing is required, thus increasing production costs due to extra energy and labour required.

A third and more efficient way of dispersing carbomers exists in the form of a venturi aspirator. In a venturi aspirator there is no mechanical work or shear exerted onto the fluid. Instead a vacuum is generated by the working fluid, drawing the carbomer in and mixing it through without use of a mechanical mixing process. While use of a venturi aspirator to disperse the carbomer is likely the optimum option, the company does not have these facilities and as such it was not investigated in this report. However, if future issues with shear sensitive carbomers arise, this could be a viable option.

This research project is not standalone or complete in itself. Instead it works as a guide when selecting an appropriate method of carbomer dispersion.

Conclusion

The following table summarizes the carbomers investigated and indicates the optimum method for preparing dispersion.

Shear Sensitive	Subject to some shear sensitivity	Not affected by shear
• Carbopol 971P • Carbopol 981 • Pemulen TR-2	• Carbopol 974P • Carbopol 980 • Carbopol ETD 2020 • Carbopol Ultrez-21 • Pemulen TR-1	• Carbopol 934 • Carbopol 940 • Carbopol Ultrez-20 • Carbomer U-10
Low shear impeller or venturi aspirator recommended.	Either impeller or milling accepted.	Unaffected by milling

Appendices

Appendix One: Raw Data

HS-High Shear

LS-Low Shear

Table 4: % in solution, viscosity and pH data

Carbopol	% w/v in solution	pH range	Final pH (HS)	Final pH (LS)	NaOH to neutralize (mL)	Spindle/rpm
934	0.5	7.0-7.2	6.99	7.01	7.2	6 @ 20
940	0.5	7.0-7.2	7.10	7.13	8.50	7 @ 20
971P	0.5	7.3-7.8	7.43	7.53	9.04	6 @ 20
974P	0.5	7.3-7.8	7.44	7.50	9.22	6 @ 20
980	0.5	7.0-7.2	7.16	6.98	8.21	7 @ 20
ETD 2020	1.0	5.8-6.3	5.84	5.89	9.50	7 @ 20
Ultrez-20	1.0	5.8-6.3	6.01	5.98	11.10	7 @ 20
Ultrez-21	0.5	5.8-6.3	6.25	6.30	5.90	7 @ 20
981	0.5	7.0-7.2	7.10	7.02	8.38	6 @ 20
U-10	0.5	7.3-7.8	7.80	7.40	9.11	7 @ 20
Pemulen TR-1	0.2	7.0-7.2	7.22	7.16	2.89	5 @ 20
Pemulen TR-2	0.2	7.0-7.2	7.12	7.20	2.72	4 @ 20

Appendix Two: Polymer selection guide for semi-solid formulations

		Application Type				
Product Trade Name	Residual Solvent	Lotions	Creams	Gels	Bioadhesives	Oral Liquids/Semisolids
Carbopol® Polymers						
971P NF	Ethyl Acetate	●		●	●	●
974P NF	Ethyl Acetate	●	●	●	●	●
980 NF	Cosolvent		●	●	●	
981 NF	Cosolvent	●		●	●	
ETD 2020 NF	Cosolvent	●	●	●	●	
Ultrez 10 NF	Cosolvent	●	●	●	●	
934 NF	Benzene	●	●	●	●	
934P NF	Benzene	●	●	●	●	●
940 NF	Benzene		●	●	●	
941 NF	Benzene	●		●	●	
Pemulen™ Polymers						
TR-1 NF	Cosolvent	●	●	●	●	
TR-2 NF	Cosolvent	●	●	●	●	

Figure 5: Applications for Carbopol [4]

References

[1] The Lubrizol Corporation, online database, viewed July 2014, https://www.lubrizol.com

[2] Pharmaceutical Polymers for Controlled Release Tablets and Capsules, The Lubrizol Corporation, May 2011

[3] Carbopol Polymers for controlled release matrix tablets, The Lubrizol Corporation,

[4] Formulating Semi-solid Products, The Lubrizol Corporation, May 2011