RHEOLOGICAL CHARACTERIZATION
OF EASY-TO-DISPERSE (ETD) CARBOPOL HYDROGELS

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ABSTRACT

Experimental determinations of apparent viscosity were used to investigate
the rheological behaviour of easy-to-disperse (ETD) Carbopol 2001, 2020 and
2050 hydrogels, involving different polymer concentrations, degrees of
neutralization, agitation times and shear rates. Mathematical expressions were
obtained, based on the power law, to allow calculation of the viscosity of each
system, for the different variables studied. These equations proved valid within the
5.5-7.5 pH range, i.e., the pH interval of greatest interest in pharmaceutics and
cosmetics. The rheological behaviours of the three types of ETD hydrogels were
investigated comparatively and with respect to Carbopol 940, i.e., one of the most
widely utilized hydrogels.

INTRODUCTION

Carbopols are polymers of polyacrylic acid cross-linked to allyl sucrose (1). Their
molecular weights are relatively high (between 2×10^6 and 30×10^6 Dalton),
depending on the type of Carbopol (2). The dispersions of these polymers in water
are acid and highly fluid, with near-Newtonian rheological behaviour at low
polymer concentrations. It is well established (3) that the addition of a neutralizing
agent such as sodium hydroxide, triethanolamide, etc., decrease the turbidity of the dispersion and considerably increases its consistency. This is because of an elongation of the polymer chains under the influence of electrostatic repulsion forces. The chains interlink to produce a water-retaining three-dimensional network, the result of which is the formation of a high-viscosity transparent gel (4). The physical and sensory characteristics of these gels make them very useful in pharmaceutics and cosmetics, and they are commonly employed as bases in topically applied anti-inflammatory drugs, in the controlled release of drugs, in the production of solar filters, and so on (5-8).

One of the problems encountered in the industrial utilization of these polymers is the considerable time required to secure a correct formulation. In effect, Carbopol in powder form requires about 24 hours in contact with water to achieve full hydration. However, easy-to-disperse (ETD) Carbopols 2001, 2020 and 2050 have recently been commercialized. These are more easily hydrated and thus require less water exposure times. Posteriorly, and following neutralization, they yield perfectly homogeneous and transparent hydrogels.

The purpose of the present study was to investigate the rheological properties of ETD Carbopol hydrogels by characterizing their pseudoplastic behaviour and determining their consistency by means of a mathematical model based on the power law. This study allowed us to determine the hydrogel viscosity of each Carbopol type as a function of shear rate and polymer concentration. The model was found to be valid for totally structured hydrogels, i.e., those within the approximate 5.5-7.5 pH range. Finally, the rheological behaviour of these hydrogels was contrasted with that of Carbopol 940, which we had investigated in earlier studies (3,4).

**MATERIAL AND METHODS**

The different hydrogels corresponding to the three types of ETD Carbopols, i.e., 2001, 2020 and 2050 (B.F. Goodrich Chem. Co., Avon Lake, OH, USA) were prepared as described below.

The amount of Carbopol required for each concentration was weighed, along with the water needed to obtain a total of 150 g. The Carbopol was gradually added
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through a sieve onto the vortex of water formed by a magnetic stirrer spinning at about 300 rpm. Agitation was maintained for 30 min. The resulting dispersion was stored at rest and in darkness for 24 hours, followed by a further 1-minute agitation period prior to neutralization. Although ETD Carbopols require less time for hydration, they were prepared as described above to allow comparison with Carbopol 940 (B.F. Goodrich Chem. Co., Avon Lake, OH, USA). The concentrations investigated were 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35% (w/w), in each case.

Neutralization was carried out by adding NaOH 5N to reach the desired pH. The latter was measured with a digital pHmeter (Crison Instruments, micropH 2002) at 6 different points within the hydrogel, to detect possible differences. As such differences were not very significant, the average of the 6 measurements was taken to represent the mean pH value of the gel. The hydrogels were prepared for pH values in the 4-9 range and at 0.5 intervals, approximately.

Following preparation and neutralization, the hydrogels were again stored at rest and in darkness for a further 24 hours. The corresponding viscosity measurements were then made using a Brookfield Digital DV-II viscometer. Five cylindrical spindles of different sizes and with 8 angular velocities (ω) in the range 0.3-60 rpm were used. Taking into account the geometric characteristics of the cylinders and receptacle, these angular velocities yielded shear rates (γ) of 0.063, 0.126, 0.314, 0.628, 1.26, 2.51, 6.28 and 12.57 s⁻¹.

In order to determine the possible thixotropic character of the hydrogels, we obtained the up curve (corresponding to agitation time, t = 0) for increasing shear rates, along with the different down curves (decreasing γ) after agitation times of 1, 2, 3, 4, 5 and 6 min. Agitation was carried out with the same viscometer cylinder at 60 rpm. All viscosity measurements were made at 25 °C.

RESULTS AND CONCLUSIONS

With the aim of characterizing the rheological behavior of the hydrogels investigated, we determined the apparent viscosity (η) of each of them as a function of the different shear rates applied and of the different concentrations, degrees of neutralization and agitation times indicated. The viscosity was found to remain
practically constant in all cases, for the different agitation times involved, i.e., the hydrogels exhibited no noticeable thixotropic behaviour. Hence, the measurements obtained after a 1-minute agitation time were considered, in all cases.

Firstly, and to analyze the influence of the degree of neutralization on the rheologic properties of the gels, we plotted a log-scale graphic representation of the values of \( \eta = f(\dot{\gamma}) \) for each of the three types of Carbopol and each concentration employed, for all the pH values studied. As an example, Figure 1 shows the graphs \( \eta = f(\dot{\gamma}) \) corresponding to the ETD Carbopol 2050 0.3% (w/w) dispersion, for the pH values indicated. For all concentrations, the points exhibit a linear distribution which also applies to the rest of the gels investigated. In addition, at pH \( \geq 5.5 \) and \(< 7.5\), approximately, the straight lines \( \eta = f(\dot{\gamma}) \) practically overlap. This shows that rheological behaviour in this interval does not depend upon the degree of neutralization. However, at pH values of under 5.5, the gel is not totally structured, while at pH > 7.5 its three-dimensional structure begins to break down. Hence, in

![Graph showing apparent viscosity (η) as a function of shear rate (\dot{γ})](image)

**FIG.1.-** Apparent viscosity \((\eta)\) as a function of shear rate \((\dot{\gamma})\) for the ETD Carbopol 2050 0.3 % (w/w) hydrogels, and corresponding to the indicated values of pH.
FIG. 2 - Apparent viscosity ($\eta$) as a function of shear rate ($\dot{\gamma}$) for the ETD Carbopols 2050 and 2001 hydrogels for the same pH values (in the order of 6.5) and for concentrations of 0.20 and 0.35 %.

Both cases consistency is clearly less than in the 5.5-7.5 pH range. This observation also applies to the rest of the hydrogels, which led us to consider only those pH values within the above mentioned 5.5-7.5 interval, i.e. precisely the range of greatest interest in pharmaceutics and cosmetics.

On the other hand, in order to evaluate the influence of concentration of gel on the viscosity, we plotted a log-scale graphic representation of $\eta = f(\dot{\gamma})$ for each concentration of the different Carbopol types and for each pH. Figure 2 shows the values corresponding to Carbopols 2050 and 2001 for the same pH, and for concentrations of 0.20 and 0.35 % in both cases. The values obtained for the ETD Carbopol 2020 gels fell between those corresponding to the two previously mentioned gels; they were therefore not represented, to improve the clarity of the Figure. As may be observed, the hydrogels of greatest viscosity correspond to ETD Carbopol 2001 formulations, while the ETD Carbopol 2050 hydrogels possess the lowest viscosities.
The same Figure also shows viscosity to increase with concentration, what logically occurs in all Carbopol gels. This increase is better reflected in Figure 3, where the values of $\eta = f(\dot{\gamma})$ are graphically represented on a log-scale for the ETD Carbopol 2020 hydrogels at pH values about 6.5 and at all concentrations studied. In addition, a slight variation in the slopes of the resulting straight lines is observed.

The log-scale linear distribution of the experimental points of $\eta = f(\dot{\gamma})$ observed in all cases allows us to describe the hydrogels by means of the power law (Ostwald-de Waele model), which is mathematically expressed as follows (9, 10):

$$\eta = K \dot{\gamma}^{n-1}$$  \hspace{1cm} (1)

where consistency, $K$, and the power law index, $n$, have values that may be determined by minimum squares fitting of $\eta$ as a function of $\dot{\gamma}$. Since in all cases...
FIG. 4.- Mean consistency index ($\bar{K}$) as a function of concentration for each of the different hydrogels indicated.

The correlation coefficient obtained was greater than 0.995, we consider this model to be adequate. On the other hand, it has been found that for each of the different Carbopol types at a given concentration, and in the pH interval 5.5-7.5, both the consistencies and power law indices are independent of the degree of neutralization, for the differences encountered were random and in no case exceeded 5%. Thus, a mean consistency and mean power index ($\bar{K}$ and $\bar{n}$, respectively) have been assigned to each of the hydrogels investigated - the consideration of the variable pH being unnecessary in this case. However, differences were observed between the $\bar{K}$ and $\bar{n}$ values corresponding to the different Carbopol types and for the different polymer concentrations in the hydrogel formulations.

The graphic representations of $\bar{K} = f (c)$ for the three types of hydrogel investigated are shown in Figure 4. The distribution of the points allows minimum squares fitting using linear functions in the cases of ETD Carbopols 2020 and 2050, and a second-degree polynomial function in the case of ETD Carbopol 2001.
TABLE 1
Mean Consistency and Mean Power Law Index as a function of concentration for the three ETD Carbopol studied (and the corresponding correlation coefficients).

<table>
<thead>
<tr>
<th>ETD Carbopol</th>
<th>$\bar{K}$ (Pa.s$^n$)</th>
<th>$\bar{n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>$-70.3 + 840.7c - 1130c^2$ ($r = 0.996$)</td>
<td>$0.84c - 0.045 + 0.057/c$ ($r = 0.999$)</td>
</tr>
<tr>
<td>2020</td>
<td>$4.63 + 107.9c$ ($r = 0.999$)</td>
<td>$0.42 - 0.337c$ ($r = 0.995$)</td>
</tr>
<tr>
<td>2050</td>
<td>$-0.36 + 44.5c$ ($r = 0.974$)</td>
<td>$0.385 - 0.07c$ ($r = 0.564$)</td>
</tr>
</tbody>
</table>

The equations obtained, with the corresponding correlation coefficients, $r$, are reflected in Table 1. These expressions allow us to calculate the mean consistency, $\bar{K}$, of any of the hydrogels within the concentration range 0.1%-0.35% (w/w), and for degrees of neutralization between 5.5 and 7.5.

As for each Carbopol type and concentration the power law index values are independent of the degree of neutralization within the above mentioned interval 5.5 $\leq$ pH $\leq$ 7.5, we also calculated the corresponding mean power index values, $\bar{n}$, in each case. The graphic representation of $\bar{n}$ as a function of concentration for each of the three hydrogel types is shown in Figure 5. It stands out that, with the exception of ETD Carbopol 2001 at a concentration of 0.1%, the remaining $\bar{n}$ values all fall within the interval 0.30-0.45, approximately, thus indicating that the rheological behaviour of these gels is pseudoplastic ($\bar{n} < 1$), and does not undergo important changes upon varying concentration. In fact, a slight decrease in $\bar{n}$ may be seen on increasing concentration - what means a slight increase in pseudoplasticity - in the case of ETD Carbopol 2001 and 2020, while $\bar{n}$ remains practically constant in the case of ETD Carbopol 2050.

Also shown in Figure 5 is the fact that the $\bar{n}$ values corresponding to ETD Carbopol 2050 are lower than for the other two Carbopol types at all concentrations. This shows that ETD Carbopol 2050 possesses the most pseudoplastic character of all three Carbopol types investigated, though the differences with respect to ETD Carbopol 2050 are minimal within the
FIG. 5.- Mean power index ($\bar{n}$) as a function of concentration for each of the different hydrogels indicated.

Concentration range $0.10\% \leq c \leq 0.20\%$. The least pseudoplastic gels were those formulated with ETD Carbopol 2001, particularly at the lower end of the concentration range.

The lines shown in Figure 5 were obtained by minimum squares fitting of $\bar{n}$ as a function of concentration, employing the more simpler functions providing sufficiently acceptable correlation coefficients, r. The equations obtained, with the corresponding r values, are reflected in Table 1. The correlation coefficients of the first two equations for $\bar{n}$ are seen to be satisfactory. In relation to ETD Carbopol 2050, the small magnitude of r is explained by the fact that the straight line slope is practically negligible - thus showing that concentration exerts only a minimal effect upon the pseudoplastic behaviour of these gels. As a result, in this case, we considered $\bar{n}$ to be independent of concentration and assigned it the mean value for the different concentrations employed. The result obtained was $\bar{n} = 0.38$, with a standard error of $\pm 0.02$, approximately. In addition, these were precisely the gels of lowest consistency of all three Carbopol gels investigated (see Fig. 4).
On replacing in equation 1 the expressions obtained for the consistencies and power law indices provided in Table 1, we derived the following expressions:

\[ \eta_{2001} = (-70.3 + 840.7c - 1130c^2) \gamma^{(0.84c \cdot 1.045 + 0.057 / c)} \]  
(2)

\[ \eta_{2020} = (4.63 + 107.9c) \gamma^{(-0.38 \cdot 0.337c)} \]  
(3)

\[ \eta_{2050} = (-0.36 + 44.5c) \gamma^{(-0.62)} \]  
(4)

which are the mathematical models representing the rheological behavior of each of the ETD Carbopols studied, and where the apparent viscosity, \( \eta \), is expressed in Pa.s, concentration, \( c \), as % (w/w), and shear rate, \( \gamma \), in s\(^{-1}\).

The agreement between theoretical and experimental values has been shown by graphically representing the theoretical values, \( \eta_{\text{theor}} \), provided by the equation corresponding to each Carbopol type, as a function of the experimental values, \( \eta_{\text{exp}} \), corresponding to the same conditions of concentration and shear rate. Figure 6 shows the points \( (\eta_{\text{exp}}, \eta_{\text{theor}}) \) corresponding to ETD Carbopol 2020. In each case over 200 points were plotted and subjected to minimum squares linear fitting as \( \eta_{\text{theor}} = f(\eta_{\text{exp}}) \). The three linear fits yielded excellent correlation coefficients \( r > 0.98 \), thus demonstrating the adequacy of the rheological model obtained to reproduce the experimentally derived values.

Finally, we compared the rheological behaviour of the ETD Carbopols with that of Carbopol 940, the simplified model of which (in the pH range 5.5-7.5, with agitation time = 1 min.) corresponds to a power law equation of the form (11):

\[ \eta = (304c \cdot 30.2) \gamma^{(0.46c \cdot 0.78)} \]  
(5)

On graphically representing the consistency and power law index values provided by equation (5) as a function of concentration, we obtained the lines shown in Figures 4 and 5, respectively. From Figure 4 we deduce that the variation in Carbopol 940 consistency is analogous to that observed in ETD Carbopol 2001, with a greater rate of increase than in the case of the other ETD Carbopols. However, over the entire concentration interval studied, the consistency was somewhat less than for those gels formulated with ETD Carbopol 2001.
FIG. 6.- Apparent viscosity derived from the formulas proposed in Table 1 ($\eta_{\text{theor}}$), as a function of the experimental measurements obtained by viscometer ($\eta_{\text{exp}}$) for the different hydrogels of ETD Carbopols 2020 obtained for all variables introduced in the study.

On the other hand, the power law index exhibits slight differences with respect to the values corresponding to the ETD Carbopol 2020 and 2050 hydrogels in the 0.10%-0.20% concentration range. However, it increases with concentration (i.e., pseudoplasticity decreases), with an increase similar yet less accentuated to that observed for the ETD Carbopol 2001 preparations in the 0.25%-0.35% concentration range.

To summarize, Carbopol 940 hydrogel consistency rises on increasing the concentration, as in the case of the ETD Carbopols. In this sense, Carbopol 940 behavior is intermediate between ETD Carbopol 2001 on one hand, and ETD Carbopols 2020 and 2050 on the other. However, the increase in power law index with concentration, fundamentally observed in Carbopol 940 formulations, may be due to the fact that the three-dimensional matrices that they develop are more...
difficult to deform, i.e., their physical structure is stronger than in the case of the ETD Carbopol preparations - particularly at polymer concentrations in excess of 0.25%.

REFERENCES


