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# Rheological Properties of the Cosmetic Gel Including Carboxymethyl Chitosan

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**Abstract:**

The growing interest in the modification of chitosan with improved solubility has been introduced new applications to enhance chitosan biological properties. The aim of the current study was to obtain carboxymethyl chitosan (CMC) and to apply it as stabilizer for preparation of cosmetic gels. For this purpose, initially, chitosan was reacted with monochloroacetic acid under alkaline conditions and the structure of carboxymethyl chitosan was characterized by FTIR, ATR-IR and NMR studies. Spectroscopic data confirmed that the synthesis of CMC was successful. CMC was incorporated in cosmetic gel and the rheological properties of the products were evaluated. The results obtained indicated that CMC has an excellent potential for application in cosmetic formulations.

**Key words:** ATR-IR spectrum, carboxymethyl chitosan, cosmetic gels, $^{13}$C NMR spectra, rheological properties, shear rate

## INTRODUCTION

Over the past decades polymers have changed our everyday live. Natural polymers are usually biodegradable and they offer excellent biocompatibility [1]. Chitin is among the most abundant polysaccharides [2], that is found in the exoskeleton of crustaceans, the cell walls of fungi, and other biological materials [3, 4]. This polysaccharide can be used mostly for the production of chitosan [5]. Chitosan is a linear cationic biopolymer composed of randomly distributed β-(1–4)-linked D-glucosamine and N-acetyl-D-glucosamine, obtained after partial deacetylation of chitin [6].

Chitosan is associated with various important biological effects such as anticancer, wound healing, antimicrobial, antioxidant, as excipients in various formulations including control release, drug delivery products etc [7]. Chitosan have a wide range of applications in adsorption, biomedicine, cosmetics, food preservatives, biosensors, and emulsion stabilization, mainly due their desirable properties such as non-toxicity, biodegradability and renewability [8, 9, 10].

However, chitosan is unsoluble in water and other common solvents. The problem of solubility may be resolved to some extent by the use of different synthesized derivatives of chitosan. Further, the enormous application of chitosan and its derivatives has challenged the researchers to find more new and improved derivatives possessing newer applications in the various fields of science [7].

Carboxymethyl chitosan (CMC) is water-soluble chitosan derivative and present an attractive biocompatible, non-toxic and biodegradable polymer. It is prepared by the reaction of chitosan with monochloroacetic acid in alkaline condition and finds applications in different fields as pharmacy, foods and cosmetics [11-19].

Cosmetic and cosmeceutical products include, besides active ingredients, excipients and additives such as thickening agents, stabilizers, preservatives, colorants and perfumes [20]. While the active ingredients, such as photo-protective or bioactive compounds, are the main compounds that determine the function of the products, excipients have the purpose of dissolving the active compound in other ingredients. They regulate the delivery of the active ingredients as well as the aesthetical presentation of the product. Stabilizers maintain the stability of the cosmetic product during its lifetime and thickeners increase the viscosity of the product maintaining a proper texture of the cosmeceutical product, which is needed to distribute the active ingredients.

Traditional gel forming components mostly used in cosmetics are Acrylates/C10-30 Alkyl Acrylate Crosspolymer and Hydroxyethylcellulose (HEC). Acrylates/C10-30 Alkyl Acrylate Crosspolymer designed to efficiently impart thickening, stabilizing and suspending properties to a variety of personal care products. In most situations, this polymer should be added to the water at the start of the batch cycle. This will allow it time to thoroughly wet out and disperse. At this point, the pH is about 3 with a very low viscosity and the system requires neutralization. Upon neutralization in the pH range from 5 to 11 the polymer instantly thickens. A major disadvantage of the polymer is its sensitivity to electrolytes and UV. HEC is a modified, nonionic cellulose polymer, used as a gelling and thickening agent for aqueous cosmetic and personal care formulations. It produces crystal clear gel products and thickens the aqueous phase of cosmetic emulsions. It can also be used to efficiently thicken shampoos, body washes and shower gels. The typical use rate in the products is about 0.1 - 3 %.

The use of chitosan derivatives based on their water solubility holds great promise in the field of cosmetics. The potential applications of carboxymethyl chitosan derivatives in the production of cosmetics include moisture absorption–retention, antimicrobials and emulsion stabilizing agents [21, 22]. Carboxymethyl chitosan is has anionic functionality, high viscosity, large hydrodynamic

volumes, cation-binding characteristics, large osmotic pressures and gel-forming capabilities [23].

A 0.25% CMC dispersion showed moisture retention that is comparable to that of a 20 % aqueous solution of propylene glycol, and its viscosity is almost equal to that of hyaluronic acid (HA) [24]. Studies by Chen et al., [25] showed that moisture retention is dependent on the structural properties of polymers (e.g., the site of substitution, molecular weight and degree of deacetylation). Moisture absorption and retention by carboxymetyl derivatives of chitosan at different substitution sites (6-O-CMCS, 3,6-O-CMCS, or N-CMCS) and different molecular weights showed moisture absorption abilities in the following descending order: 6-O-CMCS > 3,6-O-CMCS > HA > N-CMCS [25]. In contrast, the higher molecular weight and the intermolecular hydrogen bonds of the molecular chains might be a factor in regulating the moisture absorption and retention abilities of these derivatives [26]. Muzzarelli et al. [27] proposed the use of N-CMCS in cosmetic products for buccal applications such as toothpastes, mouthwashes, gingival gels, or artificial saliva formulations. The use of this polymer in buccal products has been explored because of its mucoadhesive properties [28, 29]. 0.3 – 0.5 % CMC with 50 % degree of substitution was successfully incorporated in emulsion systems and the reported results indicate that CMC can successfully replace the stabilizer Carbomer that has traditionally been used in pharmaceutical and cosmetic oil/water emulsions.

Due to all these characteristics, chitosan and chitosan derivatives are very attractive candidates for applications as absorption promoters and hydrating agents, delivery system and stabilizers [30]. Therefore, the aim of the current research is to evaluate the rheological properties of the cosmetic gels including carboxymethyl chitosan as stabilizer, compared to traditional stabilizers used in cosmetics.

## MATERIALS AND METHODS

Chitosan with a molecular weight of 100 – 300 kDa was purchased from Acros Organics (Belgium). Other chemicals were of analytical grade and were used without further purification.

**Synthesis of CMC**

The synthesis of CMC was prepared according to the previously described procedure [31-33]. The structure of CMC was characterized by FTIR-ATR and $^{13}C$ NMR spectroscopy.

**Preparation of the cosmetic gel**

The preparation included the dispersion of the hydrogels of phase A in water with constant stirring at ambient temperature to complete dissolution and then an addition of glycerin to obtain a clear solution. Phase B, dissolved in a minimum quantity of water, was added to sample № 1. Then, the rest of the components C (solubilizer), D (perfume and active ingredient), E (preservative) were added to each sample (№ 1, 2 and 3). The composition of the prepared cosmetic gels was summarized in Table 1.

Some physical parameters (appearance, colour, odour, pH) of all tested gels were determined.

**Rheological behavior**

The rheological behavior of the prepared cosmetic gels was studied by rotary viscometer „Reotest 2" (Germany), equipped with a measuring cylinder system and shear rate ranging from 0.17 to 72.9 $s^{-1}$, based on the preliminary experiments.

## RESULTS AND DISCISSION

The spectra of the FTIR-ATR and $^{13}C$ NMR spectroscopy were presented in Fig. 1 and 2, respectively. In addition the main assignments from chitosan and CMC FTIR spectra were summarized (Table 2).

$^{13}C$ NMR spectrum of CMC (Fig. 2) shows typical chemical shifts for successful incorporation of new functional group to chitosan chains: δ 178.04 (-$CH_2$**C**OOH), 177.78 (-**C**$OCH_3$), 175.94 (C=O substituted on –OH), 171.35 (C=O substituted on –NH), 101.51 (C-1), 78.40 (C-4), 77.98 (C-5), 73.89 (C-3), 70.29 (-$CH_2$COOH substituted on O-6), 69.48 (-$CH_2$COOH substituted on O-3), 61.19 (C-6), 60.02 (C-2), 57.41 (O**C**$H_2$COOH).

The results of the spectral analysis (Fig. 1 and 2) of CMC confirm that the modification of chitosan with monochloracetic acid was successfully conducted.

Table 1. Composition of cosmetic gels

| Phase | Ingredients INCI, (% w/w) | Samples | | |
|---|---|---|---|---|
| | | № 1 | № 2 | № 3 |
| A | Aqua | q.b. 100 | q.b. 100 | q.b. 100 |
| | Glycerine | 5.00 | 5.00 | 5.00 |
| | Acrylates/C10-30 Alkyl Acrylate Crosspolymer | 0.30 | – | – |
| | Hydroxyethylcellulose | – | 2.00 | 2.00 |
| | Carboxymethyl chitosan | – | 0.50 | – |
| B | Triethanolamine | 0.30 | – | – |
| C | PEG-40 Hydrogenated Castor Oil | 2.10 | 2.10 | 2.10 |
| D | Rosa damascena Absolute | 0.30 | 0.30 | 0.30 |
| E | 2-Bromo-2-Nitropropane-1,3-Diol | 0.05 | 0.05 | 0.05 |

Table 2. FTIR and ATR-IR characteristic bands of chitosan and CMC.

| Band frequency ($cm^{-1}$) | | Assignments |
|---|---|---|
| ATR-IR | FTIR | |
| | 3419 | Axial stretching of O-H and N-H bonds |
| | 2880 – 2926 | Axial stretching of C-H bonds |
| | 1659 | Axial stretching of C=O bonds |
| 1591 | 1589 – 1650 | Angular deformation of the N-H bonds of the amino groups, carboxy groups (which overlaps with N-H bend) |
| 1411 | 1413 | Carboxymethyl group |
| 1321 | 1321 – 1381 | Axial stretching of C-O-C, coupling of C-N stretching and N-H angular deformation |
| 1061 | 1028 – 1157 | Glycosidic bonds, C-O-C and C-O stretchings |
| | 897 | Vibration of ring |

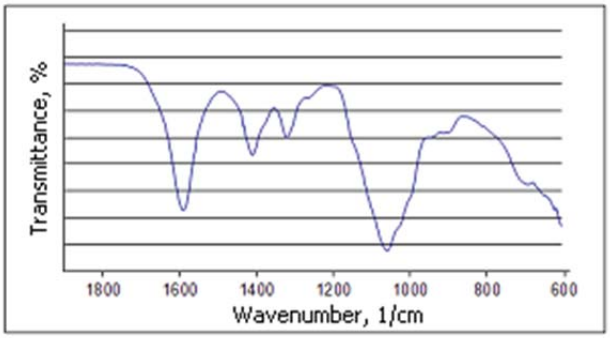


Fig. 1. ATR-IR spectrum of CMC.

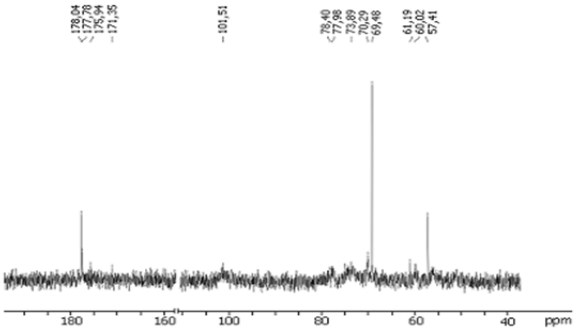


Fig. 2. $^{13}C$ NMR spectrum CMC (126 MHz, $D_2O$)

Table 3. Characteristics of gels.

| Parameters | sample № 1 | sample № 2 | sample № 3 |
|---|---|---|---|
| Appearance | Viscous clear gel | | |
| Colour | Pale-yellow | | |
| Odour | Typical rose | | |
| pH | 6.88 | 7.71 | 6.55 |

Table 4. Values of the coefficients K and the determination coefficient $R^2$ of model gels.

| Sample | K | n | $R^2$ |
|---|---|---|---|
| Sample № 1 | 56.106 | 0.218 | 0.9996 |
| Sample № 2 | 19.513 | 0.499 | 0.9947 |
| Sample № 3 | 9.617 | 0.561 | 0.9964 |

In this study CMC was used for preparation of cosmetic gel. When intended for skin, gel formulations impart a feeling of smoothness to the skin and protect it from adverse environmental conditions and dehydration. Some physical parameters of all tested gels are shown in Table 3.

The different pH values of the samples can be probably explained by the differences in the nature of the used gel-forming component.

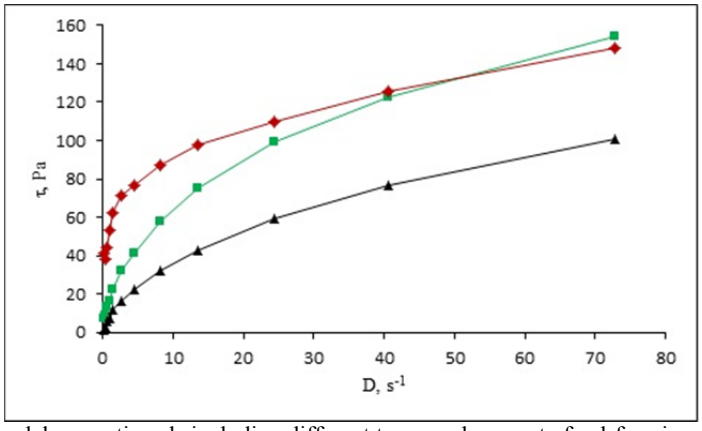


Fig. 3. Rheograms of model cosmetic gels including different types and amount of gel-forming component: ◆ – sample № 1; ■ – sample № 2; ▲ – sample № 3

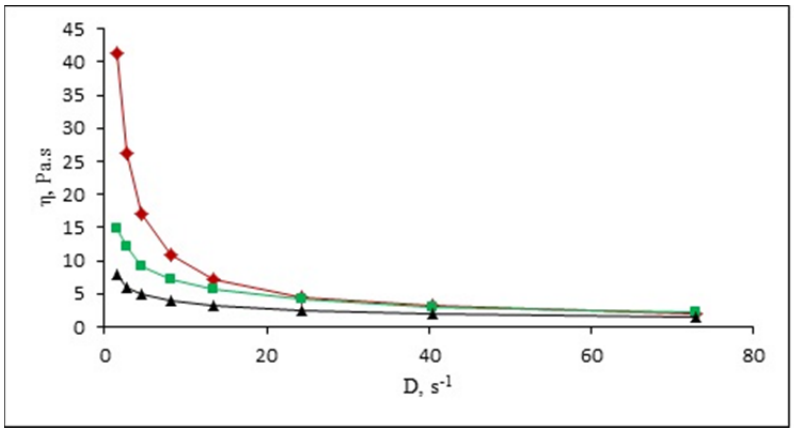


Fig. 4. Viscosity of model cosmetic gels including different types and amount of gel-forming component as a function of the shear rate:
◆ – sample № 1; ■ – sample № 2; ▲ – sample № 3

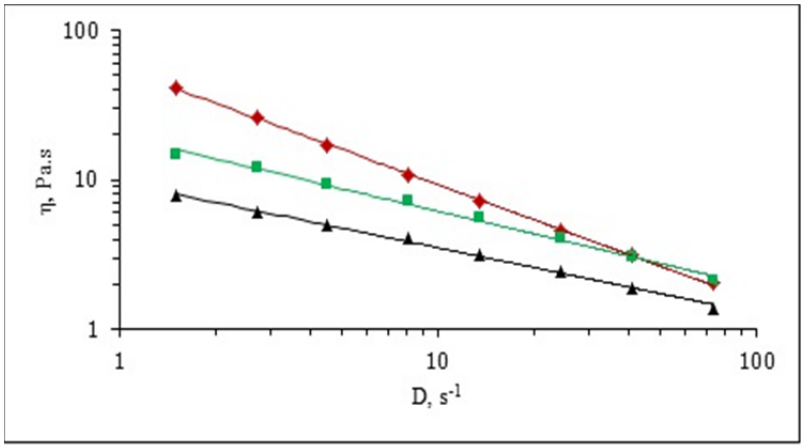


Fig. 5. Viscosity of model cosmetic gels including different types and amount of gel-forming component as a function of the shear rate, presented in logarithmic coordinates: ◆ – sample № 1; ■ – sample № 2; ▲ – sample № 3

The rheological properties of gels depend on various technological factors including the type of gel-forming component used for the preparation. Therefore, its influence on the rheological properties of gels has been studied. For this purpose, samples obtained with different gel-forming components were used – 0.3 % Carbomer (sample № 1) ; 2 % HEC and 0.5 % CMC (sample № 2); 2 % HEC (sample № 3).

The rheological characteristics were determined by a rheoviscosimeter, shear rate (D) in the range of 0.17 - 72.9 $s^{-1}$ and a temperature of 25 °C.

The rheograms of the analyzed samples are shown in Fig. 3. It was obvious that the sample including 0.3 % Carbomer characterized as a non-nuotonic fluid. A similar type of rheological behavior also showed the gels with 2 % HEC + 0.5 % CMC and 2 % HEC.

Viscosity is also defined as the main rheological property of gels. The viscosity values of the samples as a function of the shear rate (D) in an interval of variation of 1.5 to 72.9 $s^{-1}$ were shown in Fig. 4

It was seen that the viscosity of the samples decrease with increasing the value of D (Fig. 4). That confirmed the non-Newton type of rheological behavior. For example, in a D-variation in the range of 2.7 to 13.5 $s^{-1}$, the relative reduction in the viscosity of the gel, containing 0.3 % Carbomer is 72.5 %. In a sample with 2 % HEC and 0.5 % CMC the decrease was 54 % and in the gel with 2 % HEC – 47 %, respectively.

It was obvious that in the indicated variation interval of D, sample № 1 was destroyed to the highest degree, followed by sample № 2 and sample № 3. It is evident from Fig. 4 that up to D = 13.5 $s^{-1}$ gel № 1 has the highest viscosity and sample № 3 - the lowest one. At higher values of D more than 13.5 $s^{-1}$ the samples had close viscosity values. For example, at D = 40.5 $s^{-1}$ the absolute difference between the viscosities of sample № 1 and sample № 2 is 0.1 Pa.s and between № 1 and sample № 3 - 1.2 Pa.s, respectively.

The viscosity dependence as a function of the shear rate in logarithmic coordinates is shown in Fig. 5.
According to the graphic in logarithmic coordinates the dependence was linear (Figure 6) and the variance of the viscosity of D can be described by an equation of Ostwald-de Waele [34]:

$$\eta = K.D^{n-1} \quad (1)$$

where η – sample viscosity (Pa.s); D – shear rate, ($s^{-1}$); K – consistency index; n – flow index.

The values of the coefficients in equation (1) for the three model gels were presented in Table 4.

The relatively high values of $R^2$ indicate that equation 1 is suitable for calculating the viscosities of the gel samples analyzed, depending on the D values in the range of 1.5 to 72.9 $s^{-1}$.

## CONCLUSION

In this study samples obtained with different gel-forming components were used and the rheological behavior of the products was investigated. It has become increasingly important factor for today's formulators in optimizing the performance and sensory attributes of final products. The used stabilizers can be the key to the gels' rheological behavior. The results obtained in this research indicated that water soluble carboxymethyl chitosan which could be successfully find applications in pharmaceutical and cosmetics.

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