Egypt. J. Chem. **58**, No. 4, pp. 403-414 (2015)

Synthesis and Characterization of Fenugreek Gum Carbamate

A.A. Ragheb, A.A. Abd EL- Rahman, M.A. Ibrahim[*], I. Abd EL- Thalouth and A.R. Abd Al- Moaty[**]

National Research Center, Dokki, Giza, [*]Faculty of Applied Arts, Helwan University and [**]High Institute of Applied Arts and Design Academy, Cairo, Egypt.

GALACTOMANNAN gum was isolated from fenugreek seeds and subjected to react with urea at high temperature in the solid state. The obtained carbamate derivatives were purified via dissolution in water, filtration followed by extraction in Soxlet using 75% ethylalcohol. The purified products were evaluated via measuring the solubility, nitrogen content and rheological properties. The nitrogen content increases from 1.45 to 4.13 by increasing the amount of urea from 20 to 100g / 100g of the dry gum. The solubility of the carbamate derivatives in water was found to be depending on the extent of reaction expressed as % N. Samples acquire 1.45% N or less is soluble in water, while those contain higher % N are insoluble in water but soluble in 1% sodium hydroxide solution. All of the samples are characterized by non-Newtonian pseudoplastic behaviour regardless of the % N , the storing time or the solvent used and their apparent viscosity at any specific rate of shear was found to be depending on its nitrogen content. Evaluation of these derivatives as thickening agents in textile printing will be published in another article.

Fenugreek is an annual legume, it is one of the few legumes that retains its endosperm. The endosperm of fenugreek is a gum that surrounds the seed (the embryo and cotyledons). The endosperm contains high amounts of galactomannan, which is used as thickening agent in the food and textile industry [(1)].

The galactomannan in fenugreek consists of one molecule of galactose and one molecule of mannose, giving it somewhat different chemical and functional properties than guar gum [(2,3)].

Recently in our laboratory galactomannan gum was isolated from several plant seeds and subjected to chemical modification [(4-8)]. To our knowledge no systematic study has been carried out, so far, on carbamation of fenugreek gum. Modification of fenugreek gum by reacting it with urea would yield essentially fenugreek gum carbamate derivative which may find several applications in textile chemical teclnology.

Hence, the current work presents a thorough investigation into synthesis and characterization of fenugreek gum carbamate derivatives. Implementation of such derivatives in printing cotton fabries will be published in another paper.

Experimental

Materials

Plant seeds

Clean, dry fenugreek seeds cultivated in Egypt, purchased from the local market was used as a raw material in the present work.

Extraction of the gum

For the separation of the galactomannan gum from fenugreek seeds; the endosperm was thoroughly separated from the hull and germ. This was carried out mechanically; where the three components of the seeds, namely hull, endosperm and germ differ in their hardness properties like the guar seeds; the procedure adopted was carried out as follows:

The clean, dry fenugreek seeds were grounded under mild conditions using a laboratory mixer. The grounded seeds were then sieved to remove the germ which possesses the lowest hardness. The remaining part was soaked over night in water, to allow the gum to swell. The swelled gum was separated from the other components of the seeds via filtration through a muslin cloth.

The separated gum was either used as it is, *i.e.* in the viscous form or precipitated using comercial ethyl alcohol, dired and finally grinded to fine powder.

Carbamation

The extracted dry fenugreek gum was allowed to react using the solid state technique [9] as follows:

Fenugreek gum and urea (5:1), (5:2), (5:3), (5:4) and (5:5) were mixed well in the solid state in a laboratory mortar. The mixture was transferred to porcelain crucible then subjected to high temperature (165^{o}C) for 60 min.

Furthermore, another 3 samples were prepared at the ratio (5:1) dry gum urea: for 20,40 and 60 min. At this end the thermally treated mixtures were dissolved in distilled water at room temperature precipitated with ethyl- alcohol, filtered on a sintered glass funnel and washed several times with 85% ethyl alcohol to ensure complete removal of unreacted urea. Finally the treated gum precipiteated was dried in a desiccators containing calcium chloride, and analyzed for nitrogen.

Analysis and measurements

Determination of nitrogen content

Nitrogen content of the prepared fenugreek carbamate gum derivatives (expressed as N%) was determined using the microkjedahl method [10].

Measurement of the the rheological properties of the pastes

The rheological properties of prepared derivatives pastes were mearured using a rotary viscometer (Rheomat -15 zurich Switzerland [11].

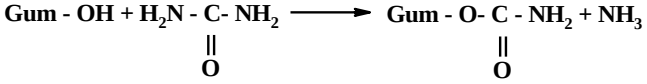
The corresponding apparent viscosity was calculated according to the following equation:

$$\eta = T/D$$

where: η is the apparent viscosity in poise
T is the shearing stress (dyne – cm^{-2})
D is the rate of shear (S^{-1})

Results and Discussion

As previously mentianed the min aim of the present work is to senthesis, characterize and utilize fenugreek carbamate derivatives to be used as thickeners in direct and discharge printing styles. To achieve this goal galactomannan gum was isolated from fenugreek seeds. The isolated gum was precipitated using commercial ethyl alcohol, dried and finally grinded to a fine powder. After that the gum was subjected to react with urea using different amount (20, 40, 60, 80 and 100g/100g of the dry gum) at high temperature (165°C) for 60 minutes. The reaction can be represented as follows [12,13].



After the necessary purification, the modified fenugreek gum samples were analyzed for nitrogen, (which is an indication of the degree of carbamate substitution in the gum molecules), and its influence on solubility was investigated – the results obtained are given in Table 1.

TABLE 1. Effect of urea concentration on percent nitrogen content and on the solubility of the obtained carbamate derivatives.

Amount of urea g/100g of dry gum	N%	Solubility in	
		Water	1% NaOH Solution
0	0	Soluble	Soluble
20	1.453	Insoluble	Soluble
40	2.062	Insoluble	Soluble
60	2.307	Insoluble	Soluble
80	3.160	Insoluble	Insoluble
100	4.126	Insoluble	Insoluble

The reaction was conducted at 165°C for 60 min.

The data in Table 1 indicate that, the amount of urea plays a dominate role in the extent of reaction between fenugreek gum and urea, where the reaction increases regularly by increasing the amount of urea from 20 to 100g/100g gum (the nitrogen content expressed as N% increased from 1.45 to 4.13%).

It is also clear from the data that, the treatment with urea under the previous conditions converted the gum to the insoluble state in water.

But in state of using 1% NaOH, the fenugreek gum carbamate became soluble on using urea up to 60g/100g gum (Table 1).

Further increase in the amount of urea more than 60g; *i.e.* 80 and 100g converted the product to be insoluble in water, due to increase in the carbamoyl groups which can be hydrolyzed by sodium hydroxide to convert the carbamoyl group to carboxyl group and increase the solubility of the prepared gum.

Based on the previous investigation and to obtain water soluble derivatives, the effect of reaction time (20, 40 and 60 min) with urea at the smallest concentration (20g) was studied. The results obtained are given in Table 2.

TABLE 2. Effect of reaction time of fenugreek gum/ urea reaction product* on N% and on solubility of the products.

Reaction time (at 165°C)	N%	Solubility in	
		Water	1% NaOH Solution
0 min	0	Swelled	Soluble
20 min	0.592	Soluble	Soluble
40 min	0.740	Soluble	Soluble
60 min	1.453	Insoluble	Soluble

• The amount of urea was 20 /100g.

It is clear from the data of Table 2 that all the products obtained on using 20g urea /100g dry gum are water soluble except the sample prepared at 60 min.

But in state of using 1% NaOH, the fenugreek gum carbamate became solubled on using urea up to 60g /100g gum (Table 1).

Further increase, in the amount of urea more than 60g; *i.e.* 80 and 100 gm converted the product to be insoluble in water.

Rheolgoical properties

To investigate the effect of the presence of carbamate groups in fenugreek gum molecules on the rheological properties of the products, pastes at a concentration of 6% were prepared either in water or 1 % sodium hydroxide solution and the rheological properties of the obtained pastes were measured using Rheomat – 15. The results obtained for the freshly prepared pastes and after storing for 24 hr are represented in Fig. 1-5.

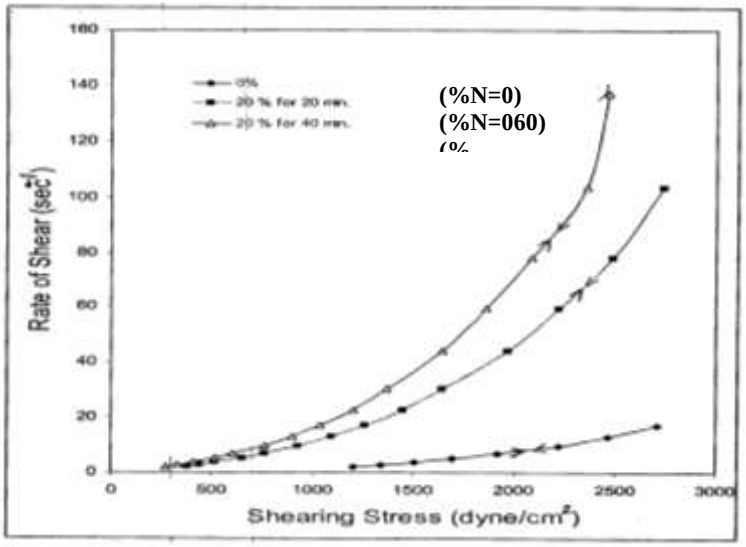


Fig. 1. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek glactomannan gum (6%) at different rates of shear (freshly prepared).

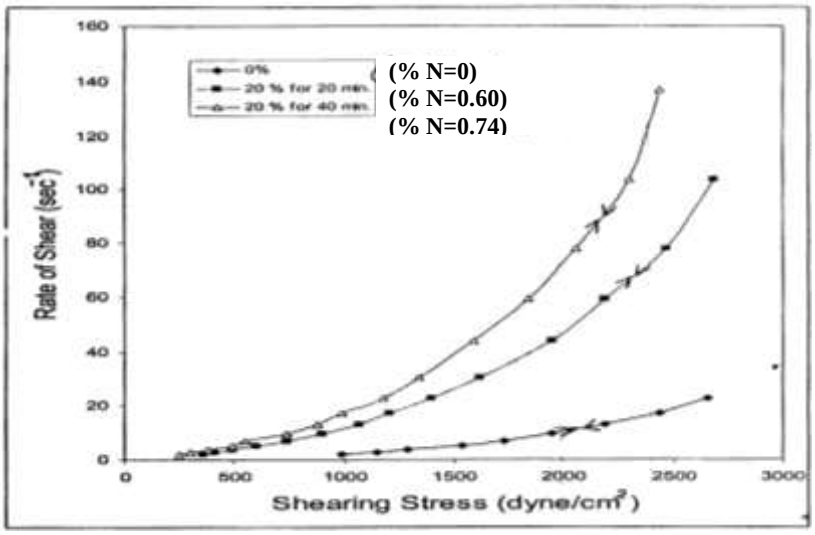


Fig. 2. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek glactomannan gum (6%) at different rates of shear (after 24 hr storing).

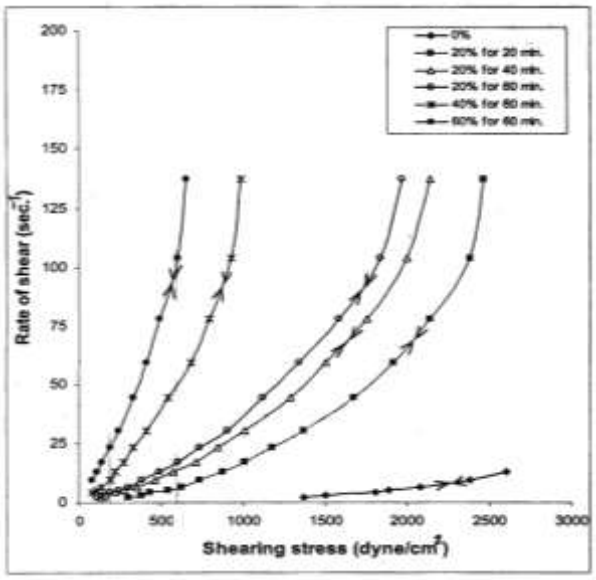


Fig. 3. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) at different rates of shear (freshly prepared).

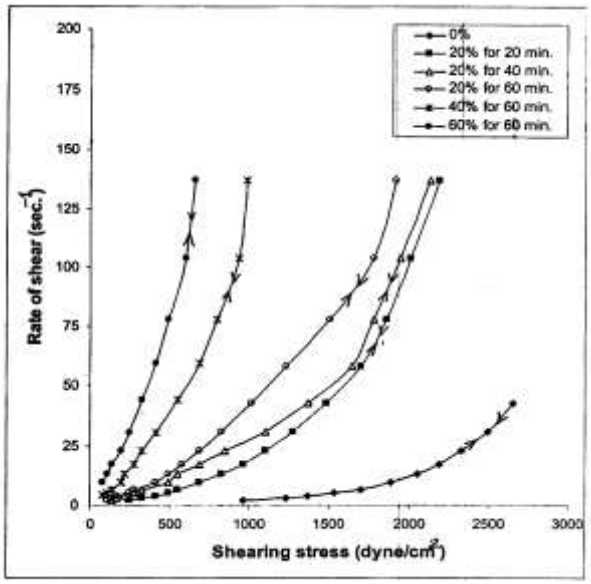


Fig. 4. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) treated with NaOH (1%) at different rates of shear (after 24 hr storing).

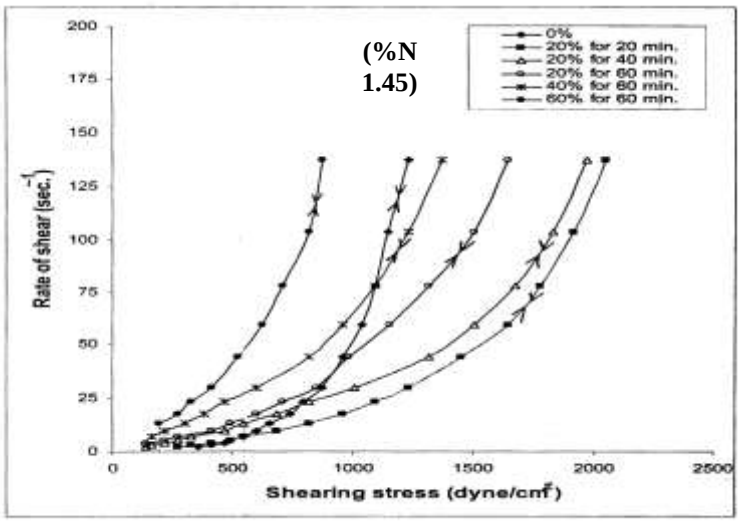


Fig. 5. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) treated with NaOH (1%) at different rates of shear (after 3 days. storing).

Figures 1 and 2 represent the rheological properties of the untreated and carbamate gum derivatives which acquire %N of 0.592 and 0.74 dissolved in water. The results signify that all the pastes before and after modification for the freshly prepared or after storing the pastes for 24 hr are characterized by non Newtonian pseudoplastic behaviour since the rheogams are not linear and the up and down flow curves are concident. However, the location of the theograms with respect to the rate of shear axis depends on the degree of modification. As the %N increases the rheogram is shifted far from the rate of shear axis indicating an increase in the apparent viscosity as it is clear from Table 2. Storing of the pastes for 24 hr has practically no influence on the rheological characterestic of these pastes.

It is also clear from Fig. 4-5 that, pastes prepared from fenugreek gum carbamate samples of different N% dissolved in 1% sodium hydroxide solution also still characterised by non- Newtonian pseudoplastic behaviour as the original pure fenugreek gum pastes. It is also observed that, the values of the shearing stress decrease regularly as the degree of substitution, expressed as N% increases. And in all cases of fenugreek gum carbamate samples the shearing stress values decrease by increasing storing time. This means that the presence of carbamate groups has a remarkable effect on the apparent viscosity of their pastes as it is clear from the tables of viscosity.

Apparent viscosity

The apparent viscosity of the aforementioned pastes was calculated from the values of shearing stress and rate of shear. The obtained data are given in Tables 3-7.

Generally speaking, it is clear from the data that, upon increasing the applied rate of shear on the thickener pastes, their apparent viscosity decreases. Furthermore; it is clear from the data that, at a given rate of shear the apparent viscosity of fenugreek gum carbamate depends on the concentration of urea used in the preparation of the carbamate derivative, where it decreases as the concentration of urea increases.

For example from Table 5 at rate of shear 6.779 (sec^{-1}) the apparent viscosity decrease from 44.428 to 24.233 poise as the urea concentration increase from 20 to 40%. The decrease in the apparent viscosity of fenugreek gum carbamate samples by increasing urea concentration may be due to the thermal hydrolytic cleavage of fenugreek gum molecules by increasing urea concentration at 165^{o}C. The hydrolytic cleavage of fenugreek gum molecules causes the formation of lower molecular weight products which acquire relatively lower apparent viscosity.

On comparing Tables 5, 6 and 7. It is clear that storing of these pastes in accompanied by a decrease in their apparent viscosity. However the presence of carbamate groups on fenugreek galactomannan gum increases the stability of these pastes for storing. Since the % decrease in the apparent viscosity of the original gum is relatively higher than the modified gum.

TABLE 3. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) at different rates of shear (freshly prepared).

Rate shear ($sec.^{-1}$)	Apparent viscosity in poise on using Urea concentration at:		
	Untreated sample	20% Urea Treated for 20min	20% Urea Treated for 40min
2.180	552.623	175.834	125.596
2.927	458.360	149.668	112.251
3.851	391.041	135.086	106.647
5.139	330.328	127.869	101.229
6.779	282.726	113.090	88.856
9.771	226.975	95.273	78.480
13.12	187.820	83.475	68.867
17.26	157.046	72.971	60.280
23.03	-	63.010	52.130
30.380	-	54.075	45.062
44.100	-	44.702	37.251
59.220	-	37.449	31.439
77.920	-	31.976	26.705
103.90	-	26.352	22.662
137.10	-	-	17.973

TABLE 4. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) at different rates of shear (after 24hr storing).

Rate shear ($sec.^{-1}$)	Apparent viscosity in poise on using Urea concentration at:		
	Untreated sample	20% Urea Treated for 20min	20% Urea Treated for 40min
2.180	452.146	163.275	113.036
2.927	392.880	140.314	102.897
3.851	334.162	127.977	99.537
5.139	298.361	117.213	95.901
6.779	254.453	109.051	80.778
9.771	198.954	92.471	75.658
13.12	166.951	81.376	66.780
17.26	141.183	69.798	57.107
23.03	115.321	60.663	51.122
30.380	-	53.173	44.161
44.100	-	44.081	36.009
59.220	-	36.987	31.129
77.92	-	31.624	26.353
103.90	-	25.825	22.135
137.10	-	-	17.774

TABLE 5. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) treated with NaOH (1%) at different rates of shear (Fresh).

Rate shear ($sec.^{-1}$)	Apparent viscosity in poise via using carbamation concentration at:					
	0%	20% for 20min	20% for 40 min	20% for 60 min	40% for 60 min	60% for 60 min
2.180	627.981	138.155	62.798	50.238	-	-
2.927	514.485	130.960	56.125	47.950	-	-
3.851	469.249	113.757	56.878	49.768	-	28.439
5.139	367.624	106.557	53.278	46.771	-	26.639
6.779	306.959	92.895	52.506	44.428	24.233	24.233
9.771	243.788	75.658	47.636	39.230	22.416	21.399
13.12	198.254	66.780	43.824	37.564	22.955	22.208
17.26	-	58.694	41.244	34.899	22.208	20.868
23.03	-	51.122	36.855	32.099	20.211	19.615
30.380	-	45.062	33.346	29.741	19.827	18.025
44.100	-	37.872	29.180	25.455	18.625	15.521
59.220	-	32.364	25.428	22.654	16.182	13.870
77.920	-	27.408	22.488	20.380	14.055	12.298
103.90	-	22.926	19.237	17.656	11.858	10.540
137.10	-	17.973	15577	14.378	9.985	8.188

TABLE 6. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) treated with NaOH (1%) at different rates of shear (after 24 hr storing).

Rate shear ($sec.^{-1}$)	Apparent viscosity in poise via using carbamation concentration at:					
	0%	20% for 20min	20% for 40 min	20% for 60 min	40% for 60 min	60% for 60 min
2.180	439.587	125.596	62.798	50.238	-	-
2.927	420.942	112.251	56.878	47.950	46.771	-
3.851	355.492	106.647	56.125	46.771	35.549	-
5.139	298.361	95.901	53.278	42.659	26.639	-
6.779	250.414	80.778	50.439	42.032	20.194	-
9.771	193.349	70.054	48.467	40.389	19.615	-
13.12	156.516	62.606	41.737	378.564	18.782	14.608
17.26	126.906	55.521	39.658	33.312	17.449	15.86
23.03	101.055	47.555	36.855	29.772	16.644	14.226
30.380	82.013	40.556	36.050	27.037	15.321	13.518
44.100	60.223	31.043	31.043	22.971	12.416	10.554
59.220	-	25.981	27.740	20.805	11.096	10.171
77.920	-	21.785	22.840	19.362	10.190	9.136
103.90	-	18.446	18.710	17.128	9.223	7.905
137.10	-	15.976	15.577	13.979	7.189	6.390

TABLE 7. Effect of urea concentration & reaction time on the apparent viscosity of carbamated fenugreek galactomannan gum (6%) treated with NaOH (1%) at different rates of shear (after 3 hr storing).

Rate shear ($sec.^{-1}$)	Apparent viscosity in poise via using carbamation concentration at:					
	0%	20% for 20 min	20% for 40 min	20% for 60 min	40% for 60 min	60% for 60 min
2.180	163.275	125.596	62.798	-	-	-
2.927	140.314	112.251	56.878	46.771	-	-
3.851	120.867	106.647	56.125	42.623	21.329	-
5.139	95.901	95.901	53.278	42.032	21.311	-
6.779	80.778	80.778	48.468	40.389	20.218	-
9.771	61.647	70.545	47.636	37.564	19.615	8.406
13.12	50.085	62.606	41.737	35.549	16.695	8.347
17.26	42.830	55.521	39.658	34.889	15.863	8.322
23.03	34.477	47.555	35.666	30.910	14.266	8.111
30.380	28.840	40.556	32.445	27.938	13.518	7.931
44.100	21.730	32.905	29.801	22.351	12.417	7.450
59.220	17.106	27.740	25.428	19.418	11.558	6.935
77.920	14.055	22.840	21.428	16.866	10.190	6.324
103.90	11.067	18.446	17.656	14.493	8.959	5.797
137.10	8.986	14.979	14.378	11.982	7.189	4.92

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(*Received* 26/12/2012;
accepted 11 / 8/2015)

تصنيع و صفات كربامات صمغ الحلبة

أميرة عبد المعطي راغب - أمال عبد العاطي عبد الرحمن ، محمد عوض ابراهيم*، ابراهيم عبد الثالوث*وعادل رشدي ابو المعاطي**
المركز القومي للبحوث ، الجيزة ، * كلية الفنون التطبيقية - جامعة حلوان و**المعهد العالي للفنون التطبيقية و التصميم الأكاديمي- القاهرة - مصر.

تم فصل صمغ الجالاكتومانان من البذور وتعريضها للتفاعل مع اليوريا في درجة حرارة عالية في الحالة الصلبة. هذا وقد تم تنقية المشتقات الكرباماتية التي تم الحصول عليها عن طريق ذوبانها في الماء، ثم الترشيح، تليها الاستخلاص في سوكسليت باستخدام الكحول الاثيلي (75%). تم تقييم المنتجات المنقاة عن طريق قياس الذوبان، محتوى النيتروجين والخصائص الريولوجية. وقد اوضحت النتائج التي تم الحصول عليها ان هناك زيادة في المحتوى النيتروجيني بنسبة تتراوح من 1.45 الي 4.13 وذلك عن طريق زيادة كمية االيوريا من 20 إلى 100 جم/100 جم في الصمغ الجاف. وقد وجد ان معدل الذوبان للمشتقات الكرباماتية في الماء يعتمد علي مدي رد فعل التفاعل الناتج عن نسبة للنيتروجين. هذا وقد اوضحت النتائج ان العينات التي تحتوي علي 1.45% نيتروجين أو أقل قابلة للذوبان في الماء، بينما التي تحتوى علي نسبة مئوية أعلي للنيتروجين تكون غير قابلة للذوبان في محلول هيدوكسيد الصوديوم بتركيز 1%. و تتميز كل من العينات من سلوك بسيدوبلاستيك غير النيوتونية بغض النظر عن النسبة المئوية للنيتروجين . وقد وجد ان كلا من وقت التخزين، المذيبات المستخدمة واللزوجة الظاهرية في اى معدل معين من القص يعتمد علي محتوى النيتروجين. وسيتم نشر التقييم لهذه المشتقات في طباعة المنسوجات في مقالات اخري.