Hydrogel Membranes Based on Gum Tragacanth with Tunable Structure and Properties. I. Preparation Method Using Taguchi Experimental Design

A. Kiani, M. Shahbazi, H. Asempour

Polymer Engineering Department, Amirkabir University of Technology, Tehran 1591634311, Iran

ABSTRACT: Gum tragacanth (GT) was exploited to create a series of novel hydrogel membranes with diverse swelling properties. The films of this biopolymer were crosslinked with applying heat only, as well as application of four types of chemical crosslinking reagents, including glycerin, ethylene glycol, triethylene glycol, and glutaraldehyde. The effects of the crosslinking agent concentration, crosslinking reaction temperature (57–97°C) and reaction time (2–24 h) on the equilibrium swelling of each series of the synthesized hydrogels were investigated by the aid of Taguchi method of experimental design. This approach facilitated the study of interaction of a large number of variables spanned by factors and their levels with a small number of experimental runs. In all cases, it was found that by increasing the concentration of each type of the crosslinking reagent and extension of the crosslinking reaction time, the swelling capacity of the prepared hydrogel films decreased. However, by increasing the crosslinking temperature, the equilibrium swelling capacity changed by passing through a minimum. As a whole, the equilibrium swelling values of the hydrogels proved that a broad range of hydrogel membranes having the crosslinking densities of $0.83–23.87 \times 10^{-6}$ mol/cm^3 and swelling capacities of 120–1580 g/g was achieved successfully from GT. Thus, GT was assigned as a promising biopolymer for preparing membranes with diverse structural and swelling characteristics. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 99–108, 2012

Key words: gum tragacanth; hydrogel membrane; equilibrium swelling; crosslinking density; Taguchi experimental design

INTRODUCTION

In the past two decades, there has been a growing interest in developing hydrogels (insoluble but swellable polymeric networks in water[1,2]) from polymers with natural sources.[3–6] Such materials with high capacity of imbibing large amounts of water or biological fluids[7] have found applications in several fields, mainly in formulation of controlled release systems for delivering active agents (biomedicals, agriculturals, and cosmetics) to a site,[8–12] membranes for separating solutes,[13] wound dressing,[14] tissue engineering[15,16] etc. In this context, several routes have been utilized for preparation of hydrogel systems from polysaccharides,[2,17,18] the materials which are available from both plant and animal sources.[19]

Among different sorts of hydrogel materials, those based on polysaccharides such as cellulose, starch,[3,20] and natural gums[9,10,21–23] have attracted great attention, mainly due to their appropriate water absorbency, and outstanding biocompatibility and biodegradability.[1,18]

In this study, we have undertaken a research project focused on preparation of a series of new polymeric hydrogel membranes based on gum tragacanth (GT) as a starting material utilizing Taguchi method of experimental design.

GT is the most viscous of natural plant gum known, with outstanding structural stability to heat,[24,25] acidity,[26] and aging.[24] The gum is produced as a dried exudation from the stems and branches of *Astragalus gummifer* and other Asiatic species of *Astragalus* such as *Astragalus gossypinus* or *Astragalus microcephalus*.[26,27] The gum is obtained in two different forms of ribbon and flake.[26]

GT is composed of a complex mixture and highly branched, heterogeneous polysaccharides, occurring as a slightly acidic calcium, magnesium, and potassium salt.[27,28] This biopolymer consists of two major fractions: a water-soluble fraction called tragacanthin and an insoluble but swellable fraction called bassorin.[26,29,30] The chemical structures of these fractions have been extensively studied by several research workers,[31–36] but due to the complexity and diversity of the gum structure, its exact microstructure is not comprehensively understood yet. However, it is well known that the gum molecules are built up of the sugar residues of α-D-galacturonic acid, β-D-xylose, α-L-fucose, L-arabinose, α-D-

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Correspondence to: H. Asempour (asempour@aut.ac.ir).

galacturonic acid methylester, and β-D-galactose.[37] The physical, rheological, and solution properties of GT with unknown and known botanical sources have also been the subject of a number of studies.[24–26,28–30,38–41]

The primary and secondary hydroxyl and carboxylic acid groups present in GT molecules provide positions for reacting with crosslinking reagents bearing hydroxyl, carboxylic acid, amine, and aldehyde groups, or with multivalence metal ions and also for internal esterification reaction upon heating.

This work was aimed at producing five series of GT derivatives with the aid of crosslinking reagents of glycerin (Gl), ethylene glycol (EG), triethylene glycol (TEG), and glutaraldehyde (Glt), and also inducing internal esterification reaction by heat alone. It was hoped that the swelling and rheological characteristics of the produced hydrogels would provide enough information for expanding the applications of the crosslinked gum, mainly as membranes. The conditions used for the crosslinking reactions were organized using Taguchi method of design of experiments (DOE).

Alternative to conventional optimization procedures, DOE and statistical tools help to gain more information about the optimization conditions in a few trials.[42] Among various statistical experimental designs, Taguchi experimental design offers distinct advantages by which many factors can be examined simultaneously and much quantitative information can be extracted with a few experimental trials.[43] Taguchi method of DOE involves establishment of large number of experimental situation described as orthogonal arrays (OA) to reduce experimental errors and to enhance their efficiency and reproducibility of the laboratory experiments.[42]

MATERIALS AND METHODS

The GT used in this study was a high quality ribbon type, collected from the stems of gossypinus species of Astragalus bushes, growing in central areas of Iran. The raw gum was ground into fine powder for subsequent experiments. Gl 87% ($d = 1.23$ g/cm^3), EG ($d = 1.11$ g/cm^3), and TEG ($d = 1.12$ g/cm^3) as crosslinking reagents, the analytical grades of H$_2$SO$_4$, NaOH, HCl, KOH, and the other chemicals used in this study were obtained from Merck Co. (Germany). A 25% aqueous solution of Glt ($d = 1.06$ g/cm^3) was obtained from Merck-Schuchardt Co. (Germany). All of these chemicals were used as received.

Characterization of the GT powder

The fine powder of the whole gum was subjected to the following analysis before any modification:

The ash content of the gum was determined in a muffle furnace by slowly heating 1–2 g of GT up to 600°C for 8 h. The amount of the ash was then reported as the mean of three separate measurements of the remnants in the crucible.

The moisture content of the gum powder was measured using the standard method of AOAC.[44]

To determine carboxylic acid content of the gum, 1% (w/v) aqueous solution of the gum was titrated against 0.01 N aqueous solution of NaOH using phenolphthalein as indicator.

The pH values of 0.5 and 1% (w/v) aqueous solution of GT were evaluated by the aid of a calibrated digital pH-meter (PTR79, ZAG Chemie).

The viscosity of 1% (w/v) aqueous solution of the gum was determined using a Brookfield Synchro-Lectric Viscometer, RVT-E Model (USA) at ambient temperature.

The mineral content of the gum was evaluated using X-ray fluorescence technique using Phillips, X'Unique II (Netherland) apparatus.

The chemical structure of the gum was evaluated by obtaining its FTIR spectrum, using Bomem FTIR Spectrophotometer (Canada).

Thermal behavior of the gum was evaluated with the aid of a differential scanning calorimeter (Dupont DSC920 instrument) and a gravimetric analyzer (Dupont TGA instrument) using a heating rate of 10°C/min in normal atmosphere. Also, DSC curve of the sample was obtained under isothermal condition at 120°C.

Crosslinking of the gum

In this study, five series of hydrogel membranes based on GT were prepared by applying heat alone (denoted as H-C series), and reacting the gum with Gl (denoted as Gl-C series), EG (denoted as EG-C series), TEG (denoted as TEG-C series), and Glt (denoted as Glt-C series).

To prepare the above-mentioned GT crosslinked derivatives, aqueous solutions containing exact amounts of GT and crosslinking reagent were prepared in deionized water. The solutions were stored at 4°C for 24 h to reach the required homogeneity. The exact amount of each solution was transferred into a PE Petri dish (with radius of 13.5 cm and depth of 10 mm). The dish was then left in a vacuum oven (200 mbar, at ambient temperature) for slow evaporation of the solvent. When the water content of the samples reached to about 20% w, the vacuum pressure was reduced to 100 mbar. Then, the oven temperature was adjusted at a certain value and the sample left for a certain time under this condition to undergo crosslinking reaction.

The evaluation of the effects of the variables on the properties of GT crosslinked samples was

TABLE I
Variables and Their Levels Employed in the Taguchi's Experimental
Design for Equilibrium Swelling of H-C, Gl-C, EG-C, and TEG-C Series
of Hydrogel Membranes

Sample series	Factor	Symbol	Level 1	Level 2	Level 3
H-C	A	[GT] (% w/v)	0.5	0.75	1
	B	T (°C)	57	77	97
	C	t (hr)	2	6	24
Gl-C	A	$[OH]_{Gl}/[COOH]_{GT}$	0.33	0.5	1.0
	B	T (°C)	57	77	97
	C	t (hr)	2	6	24
EG-C	A	$[OH]_{EG}/[COOH]_{GT}$	0.25	0.5	1.0
	B	T (°C)	57	77	97
	C	t (hr)	2	6	24
TEG-C	A	$[OH]_{TEG}/[COOH]_{GT}$	0.5	1.0	-
	B	T (°C)	77	97	-
	C	t (hr)	6	24	-

executed by utilizing the OA of Taguchi method of experimental design (DOE)[45] for H-C, Gl-C, EG-C, and TEG-C series. In the case of Glt-C series, a full factorial design was applied. The initial concentration of GT solution denoted by [GT], the mole ratio of the functional groups of the crosslinking reagents to that of GT denoted by $[X]_Y/[X']_{GT}$, and the crosslinking reaction temperature and time denoted by T and t, respectively, were taken as variables in this study.

In H-C, Gl-C, and EG-C series, a standard L9 OA was adopted while for TEG-C series L4 OA was the basis for the formulation of different hydrogel samples. The levels of the variables studied for each series of hydrogel membranes and the general layouts of L4 and L9 Taguchi's experimental design are shown in Tables I to III, respectively.

Swelling measurements

The equilibrium swelling value (Q_∞) for each of the crosslinked GT films was determined using teabag method.[37] Accordingly, a specimen of the film with precise weight ($\sim$ 0.2 g), previously dried in a vacuum oven at 37°C, was transferred into a pre-weighed polypropylene screen as teabag. The bag was then immersed in distilled water (500 mL) and allowed to reach equilibrium swelling state at ambient temperature. To make sure that the equilibrium swelling is achieved, the bag containing the speci-

men was removed from water at different time intervals, allowed to drain and finally weighed. The equilibrium swelling value (g/g) was then reported as the weight of the water absorbed by the specimen in equilibrium state per gram of the initial specimen.

Rheological characteristics

The crosslinking density of the GT crosslinked films were determined by carrying out frequency sweep experiments on disks of the equilibrated swollen samples in shear mode at 25°C and in the linear viscoelastic region (1% strain amplitude). A cone and plate geometry of a Paar Physica US200 rheometer Rheo-Mechanical Spectrometer (RMS) with a cone angle of 1° and a diameter of 75 mm was used for performing the experiments. The following equation was employed to calculate the crosslinking density (n_x) of each sample using the value of shear modulus (G) obtained from RMS experiments:[21]

$$n_x = \frac{G}{RT v_{2s}^{1/3} v_{2r}^{2/3}} \qquad (1)$$

where R is the gas constant, T is absolute temperature, and v_{2s} and v_{2r} are polymer volume fractions

TABLE II
Layout of Experiments and Arrangement of the Factors
and Their Levels in an L4 Orthogonal Array

Experiment	Factor A	Factor B	Factor C
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

TABLE III
Layout of Experiments and Arrangement of the Factors
and Their Levels in an L9 Orthogonal Array

Experiment	Factor A	Factor B	Factor C	Factor D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	3	3
5	2	2	1	1
6	2	3	2	2
7	3	1	2	2
8	3	2	3	3
9	3	3	1	1

TABLE IV
Physical and Chemical Characteristics of GT Powder
Used in this Study

Property	Value
Moisture content (wt %), 105°C	10.5
pH (0.5 and 1% w/v solution)	5–5.5
Ash content (wt %), 600°C	3.45
Carboxylic acid conc. [—COOH] (mol/100 g TG)	1.47×10^{-2}
Brookfield viscosity (cp) (1% w/v, Spindle LV5, 18°C, 10 rpm)	12,240
Some mineral amounts (ppm)	
Ca	11,847
Mg	1057
K	711
Mn	72
Fe	27
Zn	20

in the swollen state [$v_{2s} = 1/(1 + Q_\infty)$] and in the relaxed state, respectively.

To determine the crosslinking densities of the films that were not experimented by RMS technique, the polymer–solvent interaction parameter (χ_1) for each series of the prepared films was calculated using the Flory-Rehner[22] correlation [eq. (2)] for the samples with known n_x values from RMS results:

$$- [Ln(1 - v_{2s}) + v_{2s} + \chi_1 v_{2s}^2] = V_1 n_x \left[v_{2s}^{1/3} - \frac{v_{2s}}{2} \right] \quad (2)$$

where V_1 is the molar volume of the solvent. Knowing χ_1 and v_{2s} values, the crosslinking density for each sample film was determined using Flory-Rehner equation [eq. (2)].

The average molecular weight between crosslinking points ($\overline{M_c}$) in each sample film was calculated using the following equation[46]:

$$\overline{M_o} = \frac{2\rho_p}{\varphi \cdot n_x} \quad (3)$$

where φ is the functionality of crosslinking reagent and ρ_p is the polymer density.

RESULTS AND DISCUSSION

The physical and chemical characteristics of the gum are presented in Table IV.

In Table IV, the rather high value of ash content (3.45%) is indicative of GT salt content of Ca^{2+}, Mg^{2+}, K^+, and other metal ions. As it was expected, the gum also contains significant amounts of free carboxylic acid groups (COOH).

The aqueous solutions of GT over concentration of 1% (w/v) are highly viscous. So, in this study, the concentrations of the gum aqueous solutions were kept within the range of 0.5–1% (w/v) to avoid difficulty in preparation of homogeneous solutions.

The FTIR spectrum obtained for GT powder [Fig. 1(a)] was almost the same as reported by previous workers,[37,47] and showed a strong absorption band in 3100–3700 cm^{-1} due to alcoholic and carboxylic acid O—H stretching vibration, and the absorption bands at 2933 cm^{-1}, 1758 cm^{-1}, and 1624 cm^{-1} due to the stretching vibrations of C—H, acidic C=O, and carboxylate C=O groups, respectively. The absorption band at 1233 cm^{-1} in the finger-print region could be attributed to the stretching vibration of acidic C—O groups.
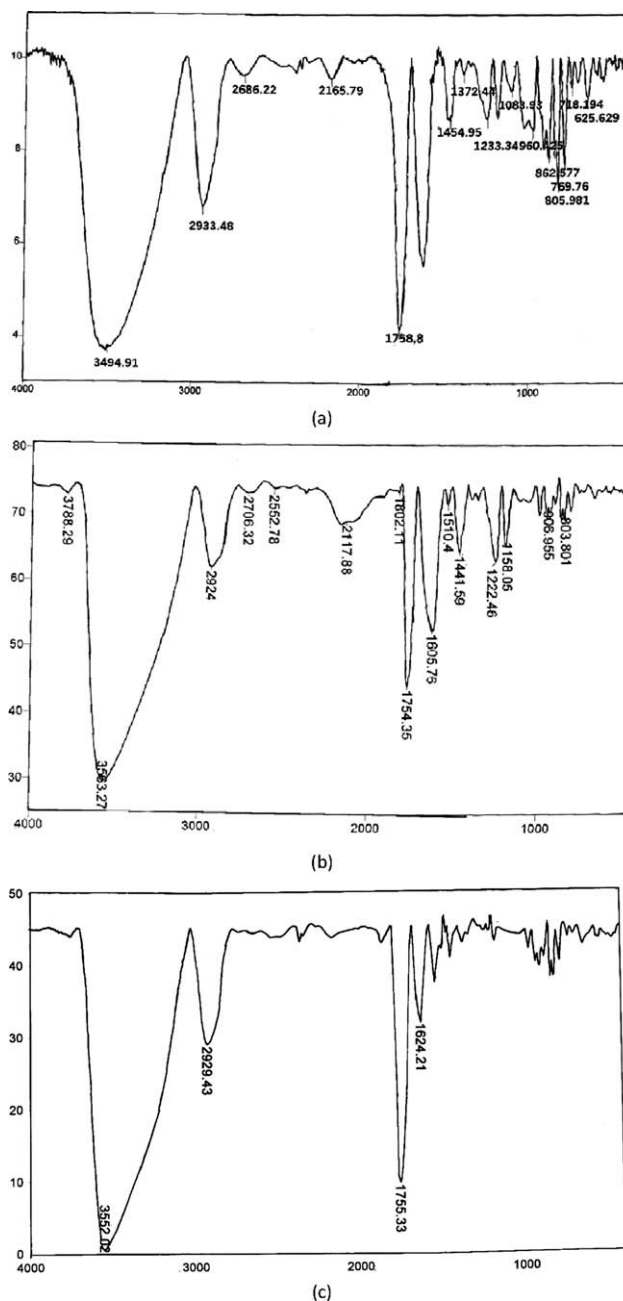

Figure 1 FTIR spectra of (a) raw GT, (b) H-C2 sample, and (c) Glt-C17 sample.
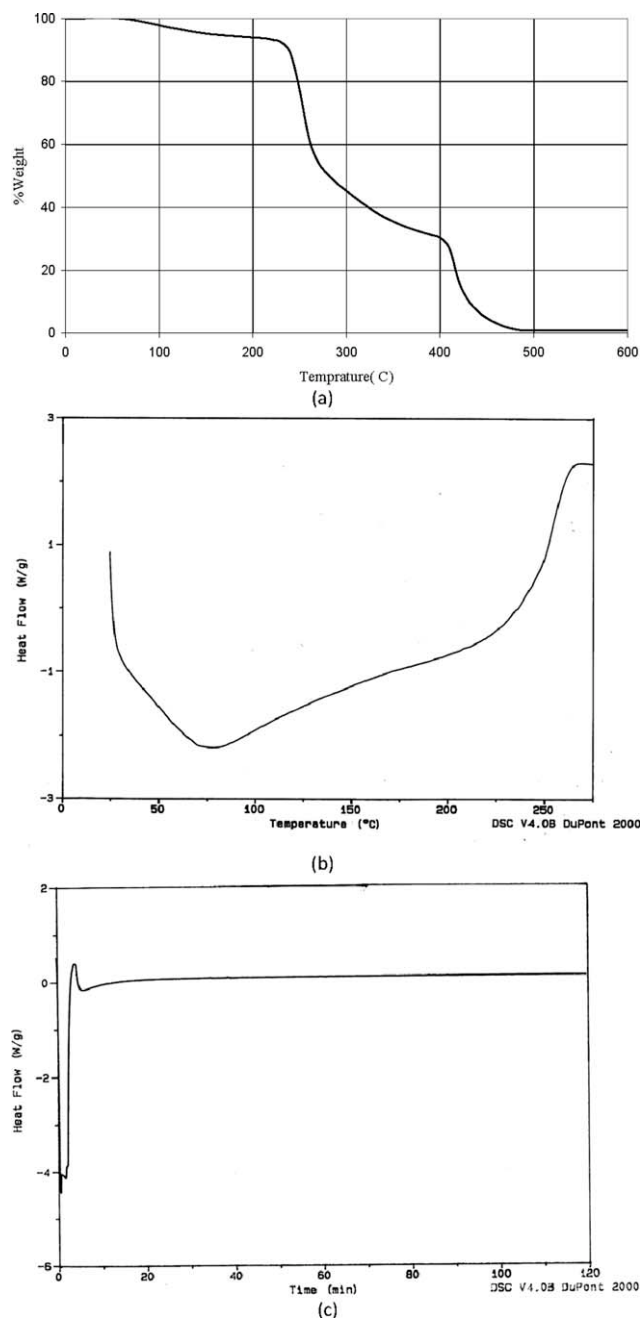
Figure 2 (a) TGA thermogram, (b) DSC thermogram, and (c) isothermal DSC thermogram at 120°C for GT powder.

Figure 2(a–c) represents the thermogravimetric analysis (TGA), DSC, and isothermal DSC curves of the gum powder, respectively. Based on TGA thermogram [Fig. 2(a)], the initial weight loss of about 10 wt % is due to the release of absorbed humidity by the gum followed by a two-step weight loss at 230°C and 405°C that is believed to be due to the heterogeneous nature of the gum. The thermal stability of the gum up to 230°C could be inferred from both TGA and DSC thermograms [Fig. 2(a,b)]. The char yield of about 0.8 wt % proved the presence of carboxylate groups in the GT structure which were

accompanied by metal cations. Isothermal DSC thermogram of GT at 120°C [Fig. 2(c)] revealed that the gum resists thermal degradation for over 2 h.

On the basis of the results obtained from viscosity measurements, as well as DSC studies [Fig. 2(c)], it was found that the dried GT powder does not undergo crosslinking reactions on heating at 100–120°C. However, in presence of adequate amount of water ($\sim$ 20 wt %), the gum undergoes crosslinking reactions beyond $\sim$ 60°C either in presence or absence of the crosslinking reagents. This was proved by testing the solubility of the sample films prepared under the conditions noted in Tables V and VI as they remained insoluble in distilled water after 2 weeks. The values of equilibrium swelling (Q_∞), crosslinking density (n_x), and average molecular weight between crosslinking points ($\overline{M_c}$) for all of the crosslinked films, prepared based on GT, are given in Tables V and VI.

Table V indicates the conditions selected for crosslinking of the wet films of GT (having $\sim$ 20 wt % water) through heating. The experiments were designed based on L9 OA of Taguchi method (Table III). FTIR spectrum of H-C2 sample, as shown in Figure 1(b), did not provide strong evidence on the occurrence of crosslinking in GT film through heating. This was due to the formation of ester functionality through reaction of carboxylic acid and hydroxyl groups of the gum, wherein an overlap of absorption bands of acidic and esteric groups would mask their contribution. However, considerable decrease in intensity of bands at wave numbers lower than 960 cm^{-1} as well as a shift in 1233 cm^{-1} absorption band to 1222 cm^{-1}, which was attributed to the stretching vibration of esteric C—O groups, could be a sign of the crosslinking occurrence in GT through heating only.

The individual effects of each variable on equilibrium swelling of the H-C series presented in Table V are depicted in Figure 3(a–c). As it was seen, by increasing the initial concentration of the gum solution (in fact, increasing the thickness of the gum film) from 0.5% (w/v) to 0.75% (w/v), the absorption capacity of the crosslinked film is decreased slightly, most probably due to the decreasing of the surface/volume ratio of the films. However, by increasing the [GT] to 1% (w/v), an abrupt increase in equilibrium swelling was observed. This result could be interpreted in terms of the lower crosslinking reactions occurred in the central layers of the thick film of GT, possibly due to the trapped water (either as the initial moisture or some water produced through condensation reactions) which prevented progress of the esterification reactions. Therefore, more hydrophil, free hydroxyl and carboxylic acid groups existed in the central layers of the thick film, hence its more absorption capacity.

TABLE V
Taguchi Method of Experimental Design Applied to Evaluate the Effects of Different Variables on the Properties of GT Hydrogels Belonging to H-C, Gl-C, EG-C, and TEG-C Series

H-C samples	[GT] (% w/v)	T (°C)	t (hr)	Q_∞	n_x (mol/cm^3)	$\overline{M_c}$ (g/mol)
H-C1	0.5	57	2	606.9	4.1	–
H-C2	0.5	77	6	403.8	8.09	–
H-C3	0.5	97	24	368.2	9.45	–
H-C4	0.75	57	24	321.5	11.85	–
H-C5	0.75	77	2	544.7	4.91	–
H-C6	0.75	97	6	441.8	6.97	–
H-C7	1	57	6	1582.1	0.83	–
H-C8	1	77	24	1054.8	1.63	–
H-C9	1	97	2	1390.4	1.03	–
Gl-C samples	[OH]$_{Gl}$/[COOH]$_{GT}$					
Gl-C1	0.33	57	2	967.6	3.01	21,114
Gl-C2	0.33	77	6	528.2	8.27	10,984
Gl-C3	0.33	97	24	307.8	20.36	4,683
Gl-C4	0.5	57	24	313.9	19.7	4,839
Gl-C5	0.5	77	2	602.1	6.64	12,662
Gl-C6	0.5	97	6	550.7	7.71	11,592
Gl-C7	1.0	57	6	434.9	11.43	8,338
Gl-C8	1.0	77	24	302.1	21.01	4,539
Gl-C9	1.0	97	2	666.7	5.6	14,581
EG-C samples	[OH]$_{EG}$/[COOH]$_{GT}$					
EG-C1	0.25	57	2	657.1	3.59	–
EG-C2	0.25	77	6	423.4	7.48	–
EG-C3	0.25	97	24	368.5	9.43	–
EG-C4	0.5	57	24	409	7.93	–
EG-C5	0.5	77	2	622.5	3.93	–
EG-C6	0.5	97	6	540.2	4.98	–
EG-C7	1.0	57	6	495	5.76	–
EG-C8	1.0	77	24	326.4	11.55	–
EG-C9	1.0	97	2	543.4	4.93	–
TEG-C samples	[OH]$_{TEG}$/[COOH]$_{GT}$					
TEG-C1	0.5	77	6	649.1	3.67	–
TEG-C2	0.5	97	24	443.4	6.93	–
TEG-C3	1.0	77	24	935.4	1.99	–
TEG-C4	1.0	97	6	380.2	8.96	–

TABLE VI
Taguchi Method of Experimental Design Applied to Evaluate the Effects of Different Variables on the Properties of GT Hydrogels Belonging to Glt-C Series

| Glt-C samples	Glt (µmol)/100 mL of 1% w/v GT solution	T (°C)	Q_∞ (g/g)	n_x (mol/cm^3)	$\overline{M_c}$ (g/mol)
Glt-C1	3.72	75	186.2	12.57	7,650
Glt-C2	3.72	80	179.2	12.98	7,297
Glt-C3	3.72	85	128.9	22.85	4,016
Glt-C4	3.72	90	160	15.19	6,276
Glt-C5	7.44	75	172.2	13.31	6,326
Glt-C6	7.44	80	125.6	23.62	3,783
Glt-C7	7.44	85	131.1	21.59	4,416
Glt-C8	7.44	90	120.3	26.41	3,611
Glt-C9	18.6	75	183.8	12.86	7,355
Glt-C10	18.6	80	165.5	14.33	6,300
Glt-C11	18.6	85	129.3	22.6	4,172
Glt-C12	18.6	90	143.2	17.74	5,374
Glt-C13	37.2	75	185.1	12.64	7,540
Glt-C14	37.2	80	189.9	12.36	7,804
Glt-C15	37.2	85	124	23.87	3.745
Glt-C16	37.2	90	176.8	13.06	6,996
Glt-C17	55.8	75	262.5	6.91	13,793
Glt-C18	55.8	80	233.4	8.44	12,200
Glt-C19	55.8	85	213.2	9.72	9,500
Glt-C20	55.8	90	195	11.38	7,977
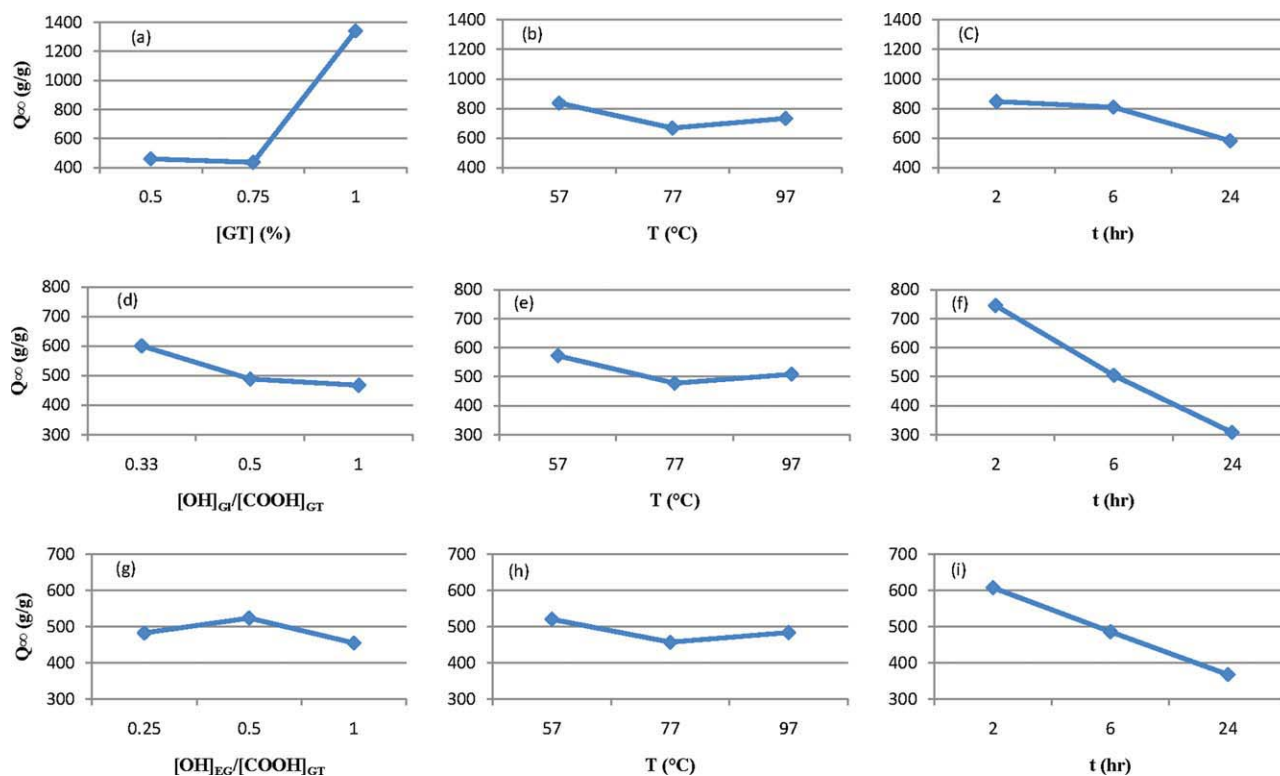
Figure 3 The effects of different variables on the equilibrium swelling of GT hydrogels prepared by heating via Gl and via EG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3(b) shows that the increase in the crosslinking temperature initially led to a decrease in swelling value of the gum film followed by a slight increase. This observation could be simply assigned to the fact that esterification reaction occurring in the gum was improved by increasing the temperature. The increase in swelling value of the film beyond 97°C could be discussed in terms of the fast evaporation of water from the wet film. Therefore, decreasing the gum molecular mobility led to lower crosslinking density. Figure 3(c) shows that by the extension of heating time, the swellability of the film was decreased, mainly, due to the enhanced occurrence of crosslinking reaction. Therefore, the crosslinking density of the film was increased which lowered its absorption capacity.

The experimental design chosen for evaluation of the effects of different variables on equilibrium swelling (Q_∞) of the crosslinked GT films with the aid of Gl, EG, and TEG were made based on L9, L9, and L4 OA of Taguchi method, respectively, and are presented in Table V. In the case of these series of membranes, again, FTIR spectrum of the prepared samples provided a weak evidence of the occurrence of crosslinking in GT film, as discussed for H-C series. The values of Q_∞ of the films and the effects of the variables on them are given in the same table and Figure 3(d–i). As it is observed, by increasing the crosslinking temperature from 57°C to 97°C and

the crosslinking time from 2 h to 24 h, the Q_∞ values changed with similar trends to that observed previously in the case of the GT films prepared by heating the gum.

The data in Table V and the corresponding curves in Figure 3(d,g) show that by changing the Gl and EG concentrations for preparation of crosslinked GT (in fact, changing the $[OH]_{Gl}/[COOH]_{GT}$ or $[OH]_{EG}/[COOH]_{GT}$ ratios), the equilibrium swelling of the resultant films were changed. However, interpretation of the results obtained was not straightforward as there was a competition between internal esterification reactions (through OH and COOH groups existing in the gum) and inter-esterification reactions between these groups with those of the crosslinking reagents. Moreover, all functional groups of the crosslinking reagents might not undergo reactions with the gum functional groups. As a whole, the increase in concentration of the crosslinking reagents would result in decrease in the swelling capacity of the hydrogels.

In this study, a comparative investigation has been made between the swelling properties of crosslinked GT film with EG and TEG to evaluate the effect of the crosslinking reagent molecular size on its swelling behavior. The results obtained are presented in Table V. As it was seen, Q_∞ values of GT crosslinked films prepared by reaction with TEG was higher than that of the crosslinked GT prepared
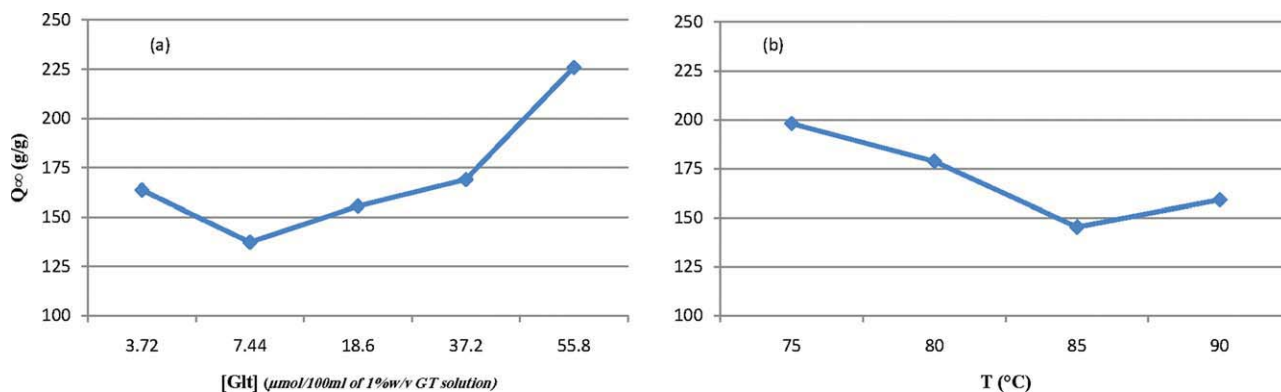
Figure 4 The effects of different variables on the equilibrium swelling of GT hydrogels prepared via Glt. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by reacting with EG under the same conditions. This could be attributed to the lower retracting elastic forces of TEG residues in the crosslinked film in comparison with the EG residues.

Crosslinking reaction of GT with Glt was conducted in presence of H_2SO_4 (pH $\sim$ 3.32) for a fixed reaction time of 24 h. The crosslinking reaction was performed on the basis of a full factorial design to evaluate the effects of Glt concentration (at five levels) and reaction temperature (at four levels) on Q_∞ of the crosslinked films, as given in Table VI.

The FTIR spectra of the products obtained (Glt-C series), as shown in Figure 1(c) for Glt-C17 sample, proved that the concentration of carboxylate ions (as determined by measuring the ratio of band intensity at 1624 cm^{-1} due to carbonyl groups vibration of COO^- to the band intensity at 1755 cm^{-1} due to carbonyl groups vibration of COOH) were quite less than the crosslinked products prepared through reaction of GT with other crosslinking reagents or the raw gum. This was due to the removal of some parts of metallic ions existing in the natural gum with added H_2SO_4 to the solution. This was responsible for reduction of Q_∞ values of the Glt-C series in comparison with those of the other samples as presented in Table VI. The other observation was the appearance of an absorption band at 1500 cm^{-1} due to the acetal formation via reaction of aldehyde groups of Glt and hydroxyl groups of the gum. This finding could prove the crosslink formation in GT film through reaction with Glt.

Figure 4(a,b) show the variation of Q_∞ values of the crosslinked GT by Glt in terms of the Glt concentration and the reaction temperature, respectively. One should take into consideration that GT was able to undergo acetalization reaction with Glt and also internal esterification reaction, simultaneously. Thus, increasing of Q_∞ values obtained for Glt-C samples by increasing the Glt concentration could be due to the acetalization reaction exceeding over the internal

esterification reaction. Therefore, the retracting elastic forces in the network were reduced due to the longer distance formed between the crosslink points via acetalization reactions. The variation of Q_∞ value of the crosslinked GT in terms of the reaction temperature and the extent of the acetalization and esterification reactions [Fig. 4(b)] could be interpreted in the same way that explained previously in the case of the crosslinking of GT with the other crosslinking reagents.

Thermogravimetric analysis (TGA) is a simple and accurate method of evaluating the decomposition pattern and the thermal stability of polymers.[25] The evaluation of the effect of crosslinking methods on the thermal stability of the gum was assessed by the aid of TGA analysis as shown in Figure 5. It could be perceived from Figure 5(a) that thermal stability of the membranes prepared under the action of heat only and Gl, EG, and TEG reagents varies slightly compared with each other just due to the different nature of the crosslinking reagents used. All of these samples underwent an initial degradation at about 230°C with slightly higher value obtained for H-C sample mainly due to the formation of shorter crosslinks and slightly lower value obtained for TEG-C sample possibly due to TEG chemical structure bearing ether bonds. Besides, one should note that non-reacted Gl and TEG would act as plasticizer in the gum and could impact its thermal stability. However, EG-C sample withstand higher temperatures during the second degradation stage which could be attributed to the length and chemical nature of the crosslinks obtained through the action of EG reagent on the gum. Moreover, Glt-C sample, as shown in Figure 5(b), revealed a different trend of weight loss at temperatures above 380°C which could be due to the different chemical reaction occurred in this series. Furthermore, almost no char yield could be observed for Glt-C sample due to the wash-out of metal ions by sulfuric acid added as the catalyst to the reaction medium. This was in
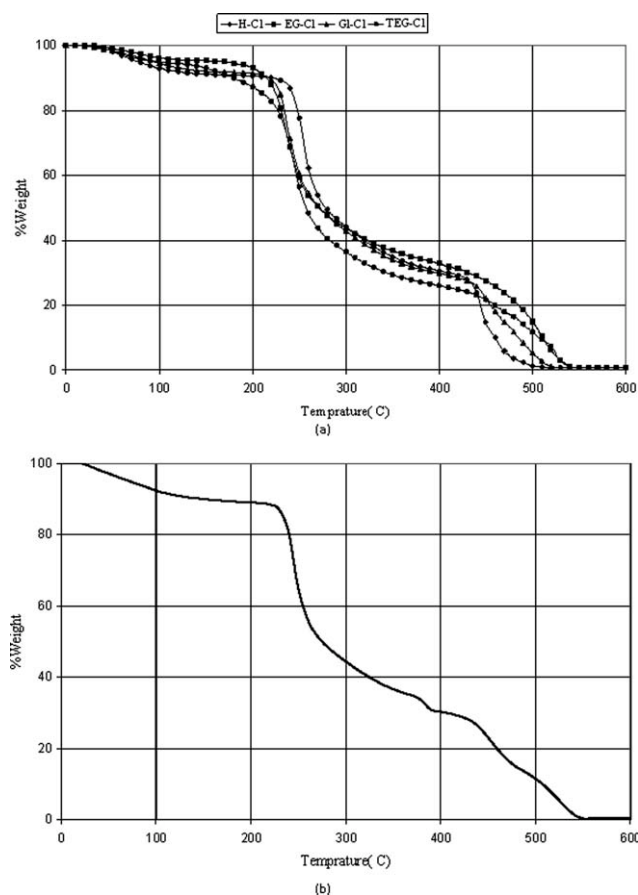
Figure 6 Modulus variation versus frequency for Gl-C4 swollen gel.

Figure 5 TGA thermograms for crosslinked GT samples: (a) H-C1, Gl-C1, EG-C1, and TEG-C1 samples and (b) Glt-C17 sample.

complete agreement with FTIR results for Glt-C series [Fig. 1(c)].

To evaluate the viscoelastic characteristics of the crosslinked GT films prepared under different conditions, some of the films were subjected to RMS analysis. A typical result obtained for variation of G' and G'' versus frequency is shown in Figure 6. The changes of both G' and G'' in terms of frequency were almost in a parallel mode and insensitive to frequency. Furthermore, G' values were always higher than G''. Observation of such behavior has been reported as a characteristic of the polymeric networks containing chemical crosslinking bonds.[48,49] Therefore, the RMS results were taken in benefit of the crosslinking reaction occurrence in GT by treating the gum with and without the use of Gl, EG, TEG, and Glt reagents.

The values of Flory-Huggins interaction parameter (χ_1) for different series of the crosslinked GT samples, as calculated from the results of RMS tests, are presented in Table VII. Knowing that the lower value of χ_1 is representative of a higher tendency of a polymer to swell in a given solvent,[50] the data in Table VII implies that Glt-C series with a higher
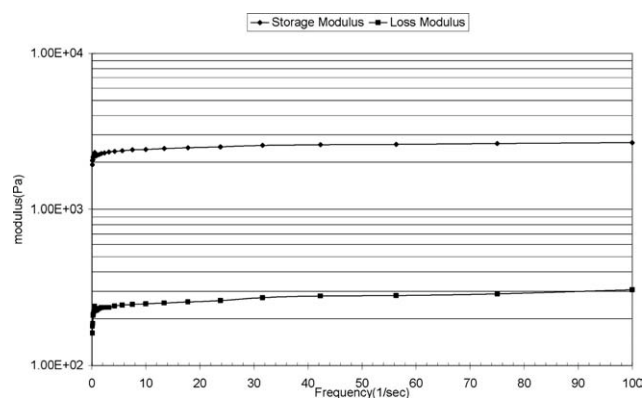
value of χ_1 should imbibe less water than the other series, mainly due to the less ionic nature of the Glt-C series. The values of crosslinking densities (n_x) for different series of the crosslinked GT samples, given in Tables V and VI, were evaluated based on the calculated values of χ_1. Having the values of n_x, the average molecular weight between crosslinking points ($\overline{M_c}$) were obtained, by the aid of eq. (3), for samples of Gl-C and Glt-C series. The results of such calculations are also presented in Tables V and VI.

By considering the values calculated for $\overline{M_c}$, besides the value of molecular size (4500*19 Å) reported for GT[27] and the value reported for the molecular mass of the gum (850,000),[41] the network mesh sizes were roughly calculated to be in the range of 23–110 Å for Gl-C series and 18–70 Å for Glt-C series. These results confirmed that we have prepared different series of crosslinked GT (hydrogel networks) with various structures, successfully. Regarding the porosity size (10–100 Å) of the crosslinked products obtained based on GT; all of these products were considered as non-porous hydrogel membranes.

The characteristics of the prepared gels in this work including swelling kinetics, swelling in aqueous media with different pH and ionic strength, swell–deswell behavior in repeated cycles, and absorbency under load would be reported in the next article.

CONCLUSIONS

GT was proved to be a suitable starting material for preparation of various crosslinked products with

TABLE VII
χ_1 Values Calculated for Various Cross-Linking Reactions of GT

Sample series	H-C	Gl-C	EG-C	TEG-C	Glt-C
χ_1	−0.93	−0.84	−0.79	−0.91	−0.32

TABLE VIII
Swelling Capacities and Cross-Linking Densities of Different Series of the Prepared Hydrogels

Reaction route	Equilibrium swelling g/g	Cross-linking density 10^6 mol/cm^3
Heat	320–1580	0.83–11.85
Glycerin	302–968	3.01–21.01
Ethylene glycol	326–657	3.59–11.55
Triethylene glycol	380–935	1.99–8.96
Glutaraldehyde	120–260	6.91–23.87

different equilibrium swelling characteristics, via reacting the gum with Gl, EG, TEG, and Glt, as well as through heating the swollen gum for various periods of time in 57–97°C temperature range. The measured equilibrium swelling values (Q_∞) and crosslinking densities (n_x) calculated for the prepared products (Table VIII) proved that hydrogel membranes with porosity sizes of 10–100 Å could be obtained based on GT.

The results showed that while crosslinking of GT on heating resulted in production of hydrogels with a broad range of equilibrium swelling, the hydrogels prepared via reacting of GT with Glt addressed swelling values lower than other series mainly due to their less ionic nature.

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