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Preperation and Characterization of Cross-linked Guar-Gum Poly(vinylalcohol) Green Films

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ABSTRACT

Guar –gum/ Polyvinyl alcohol (GG/ PVA) blend films were prepared by using Guar –gum , polyvinyl alcohol (PVA) and Citric acid (CA) as additive and gluteraldehyde as crosslinking agent for the mixing process . The additives , drying temperature , and the influence of crosslinker of films on the properties of the films were investigated . The mechanical properties tensile strength , elongation at break (% E) and thermal properties includes thermogravemetric analysis , degree of swelling (DS) of GG / PVA films were examined by using CA as additives .when the film was dried at low temperature , physical properties of the films were clearly improved because the hydrogen bonding was activated at low temperature ..

Key Words: Guar- Gum, Polyvinyl alcohol , Citric Acid, Gluteraldehyde crosslinking

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INTRODUCTION

There has been a growing intrest in the use of biodegradable polymers in order to reduce the environmental pollution caused by plastic waste. The disposal of waste plastic has become a serious problem therefore development of novel plastic that could be degraded by microorganism in soil and sea water has recently been attracted much attention . Among the several candidates including natural polymers and their derivatives, guar gum is very cheap , produced in abundance , and easily available from many renewable sources guar gum (GG) is a natural polymer extracted from the endosperm of the plant cyamopsis tetragonalobus .and chemically is a galactomannans with a galactose to mannose ratio of 1:2 [1], which consist of a (1-4) linked β D mannopyranosyl backbone partially substituted at O-6 with α- D- galactopyranosyl side groups In recent years , modified guar gum has been found numerous application in water based paints (2) , food (3) ,textiles (4,5), cosmetics (6),pharmaceuticals (7) and oil recovery and drilling [8,9] . Guar gum is a natural polysaccharide which is capable of forming films by using the solution casting technique. In the case of guar gum the solvent used is most commonly water. Guar gum is known to give brittle films with extremely poor flexibility and high moisture sensitivity [12] . To overcome these drawbacks guar gum is modified or blended with other materials (13-17) . Poly vinyl alcohol (PVA)which is biodegradable and water processable synthetic biodegradable polymers is blended with guar gum to modify their properties . It would seem , therefore that further investigations are needed in order to reduce water sensitivity and increase mechanical properties of the films. among many chemically modified methods chemical crosslinking is a convenient and feasible method to modify the structure of natural polymers and

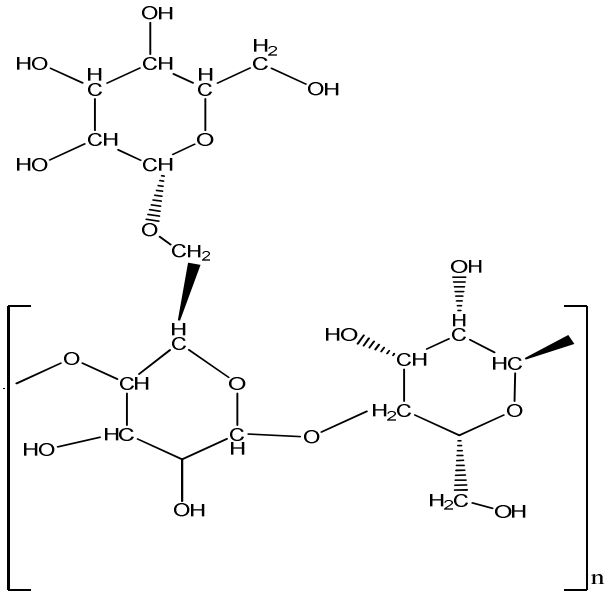


Fig-1 structure of Guar –gum

thus make them attractive biomaterial for further application(18,19). In Previous papers through Crosslinking with gluteraldehyde , phosphate , urea formaldehyde and borax , modified guar gum was applied in various field , such as controlled drug release (7), liquid pesticide (10) , However, the high water sensitivity and and bad form-film ability of guar gum and its derivatives limit their application as useful film material there are several ways to overcome these problems , one of them is mixture of synthetic polymers with natural polymers ;another option is the synthesis of polymer with use of products from natural resources (11) .The aim of this study was to make biodegradable films based on Guar gum (GG) , Polyvinylalcohol(PVA) blends by using citric acid as additive and gluteraldehyde as a crosslinking agent to determine the mechanical properties , degree of swelling , and its characterization by FTIR , TGA , and SEM of these films .

2.3 -Characteristics of Films

2.3.1 Fourier -Transform Infrared (FT-IR) Spectroscopy -

The FTIR spectra were recorded on Thermo- Nicollet Spectrophotometer using ATR assembly the spectra were taken of the respective films after being cast on a Poly propylene sheet, dried at room temperature , from an aqueous solution. Films made of GG/PVA blends were recorded in a similar manner.The spectra were obtained at a resolution of 4 cm^{-1} in the $4000cm^{-1}$ to -400 cm^{-1}

2.3.2 Mechanical Testing

Tensile properties --The % elongation at break and the tensile strength of the films were determined at 23^{o} c and 50% RH using an Universal testing machine . The initial grip distance was 50 mm and the rate of grip separation was 5mm/minute .When continuous films were formed, at least two films of each type and six replicate specimens from each film were measured. The specimens were 10 mm wide and approximately 100mm long. The thickness of the specimens was measured with a micrometer.

2.3.3 Thermogravimetric (TG)analysis-Thermogravimetry analyses were carried out by Instrument TA About 10mg sample was positioned in silica pans and the samples were heated at 10^{o} Celcius / Minute from ambient Temp to 600^{0} celcius . Thermal analysis was performed under the nitrogen flow .

2.3.5 SEM Study .-The surface Morphology of the Film samples were investigated with HITACHI S 3700N using a Voltage of 15KV by Coating with Au.

2.3.6 Swelling analysis: The swelling analysis of dried specimen films were carried in distilled water the film samples were conditioned at 50^{0} Celsius for 24 Hrs in an oven , and the conditioned samples were weighed on a digital balance with a precision of 0.0001 gm . The specimen were than immersed in Distilled water .

$$\frac{Ww-Wd}{Wd} X100$$

Ww and Wd are the weight of wet and air dried samples

MATERIALS AND METHODS

2.1 Materials

Guar gum was supplied as a sample by Dabur India Ltd having Viscosity 5000cps (1% solution at 30^o celcius) , Polyvinyl alcohol was Purchased from CDH chemicals with an average Molecular Weight of 1,25000 , Citric acid was Purchased from Thomas Baker Chemical Ltd . Gluteraldehyde 25% w/v was Purchased E Merck India .The water used to prepare Guar Gum / PVA blend films was redistilled after deionization .

Preperation of Guar-gum/PVA blend Films

Guar gum and Polyvinylalcohol solution were prepared by dissolving them separately in water .Guar gum and Polyvinylalcohol solution are intermixed in required wt fraction and add citric acid and cross-linking agent (Guar gum and PVA dried weight basis) .The above solution were blended to form a homogenous gel like solution with a mechanical stirrer for 4 Hrs The gel like solution were casted on a polypropylene disc and allowed to dry at 40 ^{0} celcius .

Table1 .Composition of Guargum – PVA blend films

Sample Name	GG-PVA (Wt Fraction)	Citric Acid Wt % (Dried basis)	Gluteraldehyde wt% (Dried Basis)
GP	0.6-0.4	-	_
GPC	0.6-0.4	20	_
GPC3	0.6-0.4	30	_
GPC4	0.6-0.4	40	_
GPC GLU1	0.6-0.4	20	0.3%
GPCGLU2	0.6-0.4	20	0.6%
GPCGLU3	0.6-0.4	20	0.9%
GPCGLU4	0.6-0.4	20	1.2%

RESULTS AND DISCUSSION

Guar Gum and polyvinylalcohol molecules , having a large number of hydroxyl in their structures , remain associated with one another by inter- and intramolecular hydrogen bonding in the blend , The plasticizer molecule enter between the guar gum and the polyvinylalchol molecules , reduce the intermolecular force of attraction and also take part in hydrogen bonding with them . The crosslinking agents react with the –OH groups present in guar gum and polyvinylalchol and make ether linkages with the available hydroxyl groups . this help in increasing the mechanical properties of the films

3.1 Mechanical properties of Guar Gum / PVA blend Films Table 2. Showed TS and % E of film using GG and PVA with varying concentration of Citric Acid from 10% to 40% (% wt of dried GG and PVA) and gluteraldehyde 0.2 to 0.6% (% wt of dried GG and PVA). The tensile strength and % elongation at break as the function of CA concentration are shown in Table 2. The citric acid reacts with hydroxyl group of Guar Gum and the hydroxyl group of PVA .The free carboxyl group attached could increase the solubility of GG and prevent Crystallization , CA reacted with GG can be considerd as the internal plasticizer while the residual CA in the blend plays the role of external Plasticizer. The tensile strength of film were increased and % E were decreased and gluteraldehyde react with the hydroxyl group present in Guar Gum , PVA and Citric acid and it crosslinks the polymer films .

Table -2 Effect of citric acid and Gluteraldehyde on the Mechanical Properties of GG/ PVA Blends

Sample Name	Tensile Strength (MPa)	% Elongation at Break
GP	18.5	0.9
GPC1	23.2	1.5
GPC	21.4	1.9
GPC3	17.8	2.2
GPC4	11.4	2.7
GPCGLU 1	14.8	1.31
GPCGLU 2	16.35	1.04
GPCGLU 3	17.76	0.78
GPCGLU4	21	0.571

3.2 FTIR Analysis –The FTIR spectra of noncrosslinked are shown in Fig -2 . From the fig2 it may be observed that peak intensity at 1709 cm^{-1} increases as the content of citric increases into the system , which is attributed to C=O stretching vibration in carboxyl groups has only found in the spectra of pure citric acid . thus the result from the FTIR sujjest that the esterification not occurred during blending when the films were cast at 40 ^{0} Celcius after the addition of gluteraldehyde no any change in FTIR spectrum occurs .The peak intensity at 1709 cm^{-1} was increased as the concentration of gluteraldehyde was increased .

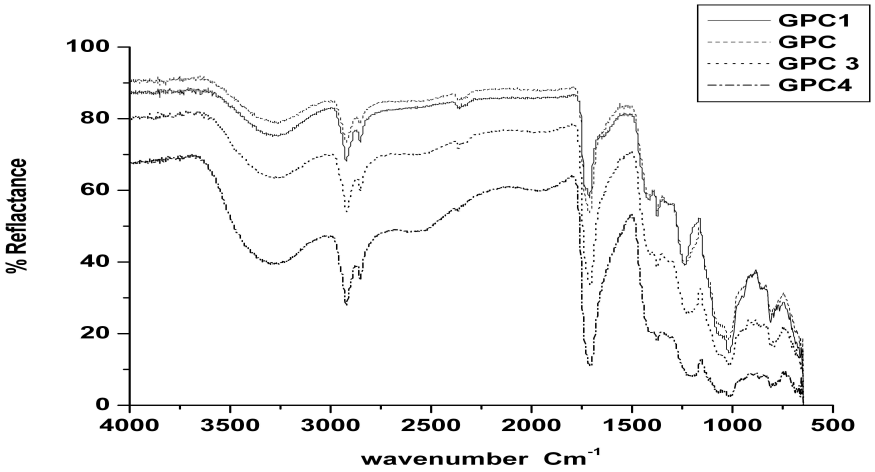
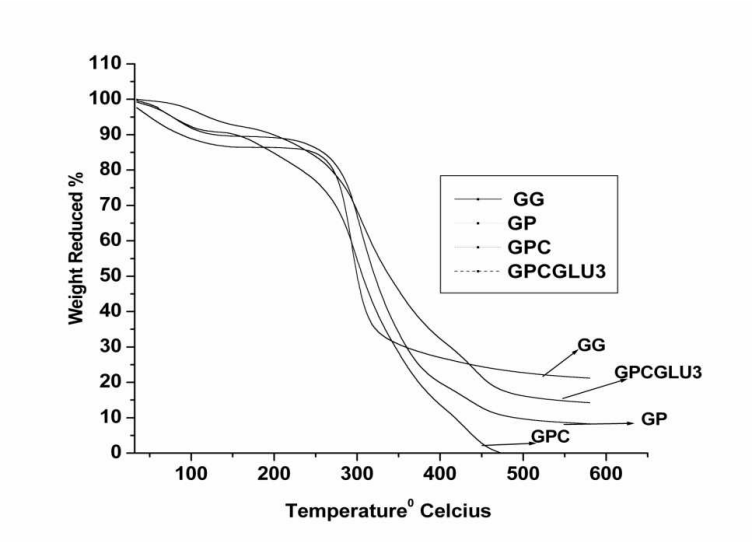


Fig 2 : FTIR of Guar gum –PVA Fims treated with Citric Acid GPC, GPC3, GPC4

3.3Thermogravimetric Analysis :

The thermal degradation behavior of individual components such as Guar Gum , and PVA of GPC non-crosss-linked, as well as crosslinked with gluteraldehyde , GPCGLU3 are shown in Figure 3. There was a remarkable difference in the thermal degradation of the crosslinked film compared to that of non crosslinked films . The TGA graph exhibited that the Cross-linked Guar-Gum films have about 14% lower Weight loss than noncross -linked films after heating the films to 600^o celcius indicating much improved resistance to thermal degradation . The effect of Citric acid on TGA graph of GG/PVA were found that the addition of Citric acid increases the wt loss and decreases the residue % . It means that citric alone not crossslink the film at low temperature .The effect of gluteraldehyde in GPC2 films were found that the addition of gluteraldehyde lowers the wt loss , and increase the residue % , due to the crosslinking of film at low temperature ,



Fig(3) TGA Thermogram of non -cross-linked GG.GP .GPC.and crosslinked GPCGLU3

Table 3-Effect of Citric acid and gluteraldehyde on theral stability of GG/ PVA film samples

Sample Name	Weight Loss %					Residue at 550 ^{0} C
	100	200	300	400	500	
GG	12	14	50	73	77	21.9
GP	9	11	14	61	90	8.27
GPC	8	16	46	63	100	-
GPCGLU3	3	11	33	69	84	14.23

Swelling analysis : -The water absorbency of the film was decreased. A higher concentration of crosslinker produces a larger degree of polymer chains branching and generates an additional network. thereby, with the crosslinker content increasing, the crosslinking density increases the network space gets diminished, and less water enters the films .

Table 4 – Degree of swelling of crosslinked films

Sample Name	Swelling % after 2 Hrs	Swelling % after 4Hrs	Swelling % after 6Hrs
GPCGLU1	780	866	--
GPCGLU2	611	700	804
GPCGLU3	552	567	556
GPCGLU4	410	434	455

3.4 Morphological Structure – From the SEM micrographs , the porosity of uncrosslinked GP and GPC is reduced as gluteraldehyde concentration increases . The most of the porosities are eliminated by increasing gluteraldehyde concentration .It confirms the film strength and decreasing the swelling percentage of the guar gum films on increasing gluteraldehyde concentration .

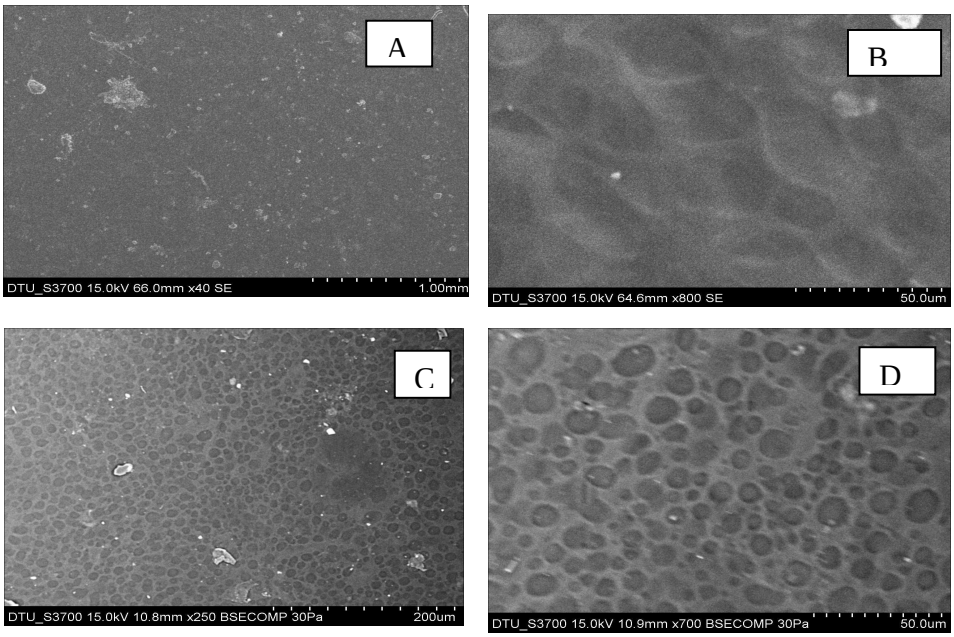


Fig 5- SEM images, Magnified 40 x (A) and 800 x(B)for sample GP, 55 x (C) and 250x(D) for sample GPCGLU3

CONCLUSION

Guar gum – PVA blends were crosslinked with gluteradehyde in the presense of citric acid with different wt % gluteraldehyde . These films were analyzed by FTIR , TGA and SEM and the mechanical properties including Tensile strength and % Elongation were also evaluated .The results showed that as the content of gluteraldehyde increases , the tensile strength increases and % Elongation and degree of swelling decreases , the addition of gluteraldehyde decreases the wt loss % and increases the % residue , and reduces porosity than the noncrosslinked films .This study demonstrate that gluteraldehyde is an effective crosslinker in the presence of citric acid into the Guar –gum –polyvinylalcohol films .

REFERENCES

[1] R.H.W. Wientjes, M.H.G. Duits, R.J.J. Jongschap, J. Mellema , Macromolecules, **2000**, 33, 9594, .
[2] Lapasin, R., & Pricl, S. . Rheology of industrial polysaccharides:Theory and applications. London: Blackie **1995** (pp. 134–160).
[3] T. Funami, Y. Kataoka, T. Omoto, G. Yasunori, I. Asai, K. Nishinari, Food Hydrocolloid **2005** ,19(1), 15.
[4] S. Sostar, R. Schneider, Dyes. Pigm., **1999**, 41(3), 167.
[5] R. Schneider, S. Sostar-Turk, Dyes. Pigm. **2003** ,57(1), 7.
[6] V. Maurin, B. Beauquey, United States of America Patent **2002 ,**6,383,993.
[7] K.S. Soppimath, A.R. Kulkarni, T.M. Aminabhavi, J. Controlled Release,**2001**, 75 (3), 331
[8] R. Moorhouse, L.E. Matthews, Unites States of America Patent **2004 ,** 6, 737,386.
[9] C.G. Mothe, D.Z. Correia, F.P. de Franca, A.T. Riga, J. Therm. Anal.Calorim.,**2006** , 85 (1), 31,
[10] Anand rao , R.K ., Kumaresh , S.S ., Tejraj , M.A ., Ashok , M ., & Mahesh H.M . Urea –formaldehyde crosslinked starch and guar gum matrices for encapsulation of natural liquid pesticide [azadirachta indica a.juss . (neem) seed oil]:swelling and release kinetics , Journal of Applied Polymer Science , **1999,** 73 (12) , 2437-2446.
[11] Aravintoyannis , I ,Totally and partially biodegradable polymer blends based on natural and synthetic macromolecules : preparation and physical properties and potential as food packaging materials . journal of Macromolecular science – Reviews in Macromolecular chemistry and physics **1999**, C39 (2) , 205-271
[12] T.Thimma Reddy ,Shekharam Tammishetti Free radical degradation of guar gum . polymer degradation and stability, **2004** , 86 ,455-459.

[13] Mikkonen, K.S. Rita, H., Helen, H., Talja, R.A., Lea Hyvonen, Tenkan, M, Effect of Polysaccharide , Structure on mechanical and thermal properties of Galactomannan based films Biomacromolecules, , **2007** ,*8* (10), 3198–3205
[14] Chaobo Xiao, Jinhua Zhang, Zhenjun Zhang, Lina Zhang Study of Blend Films from Chitosan and HydroxypropylGuar Gum Journal of Applied Polymer Science, **2003**, 90, 1991–1995 Wiley Periodicals, Inc
[15] Yihong Huang , Chaobo Xiao Miscibility and mechanical properties of quaternized polysulphone / benzoylguar gum blends polymer **2007** ,48 ,371-381
[16] Ju-Zhen Yi , Li -Ming Zhang , Biodegradable Blend films based on two polysaccharide Derivatives and their use as Ibuprofen – Releasing Matrices . Journal of Applied polymer Science vol 103 , 3553- 3559
[17] Yihong Huang , Huiqun Yu , Chaobo Xiao , Effect of Ca^{2+} crosslinking on structure and properties of waterborne polyurethane – carboxymethylated guar gum films Carbohydrate polymers **2006** 66, 500-513
[18] Reddy T . Thimma , Shekharam Tammishetti , Barim chlororide Crosslinked Carboxymethyl Guar gum Beads for Gastrointestinal drug delivery Journal of Applied polymer Science **2001** , 82 , 3084 -3090