

POLYANILINE/CARBOXYMETHYL GUAR GUM NANOCOMPOSITES: AS BIODEGRADABLE, CONDUCTIVE FILM

J. Meena¹, S. K. Verma², R. Rameshwari³ and D. K. Verma⁴, ✉

¹Department of Chemistry, Gurukul Kangri (Deemed to be University),
Haridwar-249404 (Uttarakhand), India

²Department of Chemistry, Dayalbagh Educational Institute (Deemed University), Agra, India.

³Department of Biotechnology, Manav Rachna International Institute of Research and Studies,
Faridabad, India

⁴Department of Chemistry, Sri Venkateswara College, University of Delhi (South Campus),
Delhi, India.

✉Corresponding author: vermadev148@gmail.com

ABSTRACT

Biomaterial-based nanocomposites have been increased in demand in industries for a purpose of packaging and sensing because of their low cost and environmentally friendly nature. But less work has been done on conductive, biodegradable film preparations. This article is devoted to the preparation of Polyaniline/ Carboxymethyl guar gum nanocomposites film and their applications. Controlled synthesis of polyaniline in the presence of carboxymethyl guar gum solution has been carried out for the synthesis of these nanocomposites. Then nanocomposite films have been obtained by solution casting method in one step. The object of this research work was to prepare a conductive, biodegradable, flexible film. Such made nanocomposites film has been further tested for FTIR, SEM, UTM, Conductivity, Swelling behavior and biodegradability. The results have been concluded that by this method a fine flexible, conductive, biodegradable film may be prepared that can be applied in different fields for further study.

Keywords: Carboxymethyl Guar Gum, Polyaniline, Biodegradable, Nanocomposites Film.

RASĀYAN J. Chem., Vol. 15, No.2, 2022

INTRODUCTION

A variety of nanostructure materials have been prepared so far with different synthesis approaches. Some of the research findings show that electrical stimulation affects a lot of cellular activities.¹⁻² On this basis, conductive polymers like polyaniline, polypyrrole, etc. have been used in biomedical applications.³ Polyaniline is the most studied polymer because of its easy synthesizing, low cost of formation, and easy combining property.⁴ But even this, polyaniline has some drawbacks like non-biodegradability, not being soluble in common salts, and being unable to form thin films. This limits polyaniline in biomedical applications, but it has been found that this problem can be removed by replacing polyaniline with short chains aniline oligomers.⁵ This short-chain oligomers may be obtained by control synthesizing. Researchers have found that conductivity, yield, and chain length may be controlled by using different doses of initiator, monomer, pH value of the medium, viscosity of the medium, temperature, and time of the reaction⁶. Polysaccharides have been found very useful for biomedical applications because of their biocompatibility and biodegradable behavior. CMGG (Carboxymethyl guar gum) is also a polysaccharide.⁷ It has also a guar gum-based backbone.⁸⁻⁹ Among the derivatives of the guar gum, CMGG has some specific properties which make this suitable for use in biomedical and drug delivery.⁹⁻¹¹ Some of the specific properties include good film-forming property, low cost, easy to synthesize, good stabilizing and reducing agent, biodegradable and biocompatible, soluble in acidic water, and vicious than guar gum. In this research article Polyaniline/ Carboxymethyl guar gum (PANI/CMGG) nanocomposites biodegradable, flexible, conductive film was prepared by controlled synthesizing, which might be used in biomedical application like tissue engineering and control drug delivery applications. For these, following points were considered:

- An acidic medium is required to polymerize aniline to polyaniline.
- The minimum amount of CMGG is sufficient to stabilize Polyaniline nanoparticles.
- Short-chain polyaniline or oligomers are formed during 1 h of reaction.
- Oligomers or short chains of polyaniline are degradable and can be consumed by different macrophages. They are found in all tissues. They are generally found in the liver, spleen, and connective tissues of the body.
- Guar gum becomes soft and breaks in short chains at a low pH value.
- The minimum amount of Potassium dichromate is sufficient to polymerize aniline to polyaniline.
- In pH range 5 to 7, guar gum entanglements with other polymers.

EXPERIMENTAL

Guar gum derivative CMGG was purchased by Hariom Gum Industry, Gujarat, India. $K_2Cr_2O_7$ and aniline were obtained from Merk Germany. All the solutions were made using deionized water without any refinement of chemicals.

Synthesis of Nanocomposites

The in-situ method has been used for the synthesis of polyaniline/carboxymethyl guar gum nanocomposite. 0.75 g of CMGG powder has been dissolved in 100ml of DI water with stirring to obtain a clear viscous solution. Then 1.2ml of aniline and 1 ml of conc. hydrochloric acid has been added to this solution with constant stirring. After this 1ml of 1.13 % (w/v) potassium dichromate solution (as an initiator for polymerization of aniline to polyaniline) has been added to the solution with constant stirring. As the reaction proceeds, the reaction solution converts to greenish-Brown. This confirms polymerization of aniline to polyaniline. The reaction has been kept in the same position for one hour. Thus a viscous greenish-brown PANI/CMGG entanglement nanocomposites solution has been obtained. Different compositions have been changed to optimize the best conductivity (Table-1). The conductivity of all the films has been tested by four-probe methods.

Table-1: Various Compositions for the Synthesis of PANI/CMGG Nanocomposites Films

Film Code	CMGG Powder (g)	Aniline (ml)	Potassium dichromate (0.5N solution) ml	Hydrochloric Acid (HCl) (ml)	Time (Hour)
P ₁ C ₁	0.75	1	1	1	1
P ₁ C ₂	1.00	1	1	1	1
P ₁ C ₃	1.25	1	1	1	1
P ₂ C ₂	1.00	2	1	1	1

Film Preparation

PANI/CMGG nanocomposites film has been prepared by solution casting method. PANI/CMGG nanocomposites solution has been synthesized by the using method described in the literature.¹²⁻¹⁴ Then this solution has been transferred into a Teflon plate for drying in an oven at 30°C. Thus a very fine PANI/CMGG nanocomposites film has been obtained (Fig.-1). Then it has been stored in the desiccators for further testing.

RESULTS AND DISCUSSION

Conductivity Measurement

To obtain the highest conductive PANI/CMGG nanocomposites film, CMGG and aniline concentrations have been changed by keeping initiator concentration and time of polymerization reaction constant (Table-2).

Table-2: Change in Conductivity of PANI/CMGG Nanocomposites Films

Sample Code	Conductivity (S/cm)	Color
P ₁ C ₁	0.17×10^{-5}	Greenish brown
P ₁ C ₂	0.51×10^{-6}	Greenish brown
P ₁ C ₃	0.85×10^{-6}	Greenish brown
P ₂ C ₂	0.10×10^{-5}	Greenish brown

CMGG Concentration

CMGG concentration was varied, keeping others concentration of potassium dichromate, HCl and aniline as constant. An increase in concentrations of CMGG has been found inversely proportional to the conductivity of PANI/CMGG nanocomposites films. As the concentration of CMGG powder has been increased from (0.75 to 1.25) g/100ml, conductivity decreased from (0.17×10^{-5} to 0.85×10^{-6}) S/cm. An increase in the viscosity of the reaction medium might be created a hindrance in the polymerization of aniline. The insulating nature of CMGG may also be the cause of a decrease in conductivity.

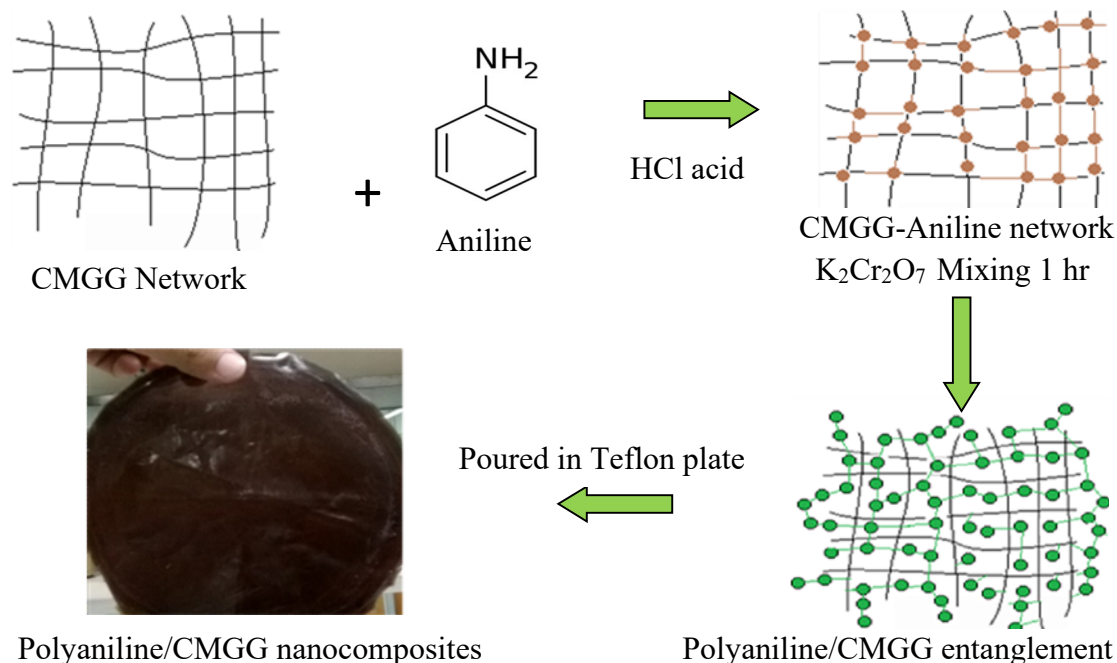


Fig.-1: Synthesis of PANI/CMGG Nanocomposites Film

Aniline Concentration

An increase in conductivity from (0.51×10^{-6} to 0.60×10^{-5}) S/cm has been found with an increase in the concentration of the monomer (Aniline) from 1 to 2 ml keeping others concentration of potassium dichromate, conc. HCl acid and CMGG powder as constant.

The Mechanism for PANI/CMGG Nanocomposites Film Formation

Guar gum has a tendency to entanglement with other polymers at a pH range of 5 to 7 and polyaniline cannot be polymerized without an acidic medium. But below the pH range (5-7) CMGG starts to dissolve in water. So the medium of the solution has been fixed at pH (5-7). At this pH value, aniline has been polymerized in the presence of CMGG solution. Thus aniline has been mixed in CMGG solution in this pH range to form a CMGG-Aniline network. Then potassium dichromate has been mixed as an initiator to this solution. This started the polymerization of aniline to polyaniline. As the reaction has been commenced, the solution changed to greenish-brown that confirming the polymerization of aniline. CMGG stabilizes the polyaniline on the nanoscale because of its good stabilizing property, but it has also a tendency to entanglement with the chains of polymers. So PANI/CMGG entanglement nanocomposites have been formed. After drying this solution in a Teflon plate, a very fine PANI/CMGG nanocomposites film has been prepared successfully (Fig.-1).

FTIR Analysis

Nanocomposite films, CMGG, and polyaniline have been tested by FTIR spectroscopy. In the FTIR spectrum of PANI/CMGG nanocomposites films, both peaks of polyaniline and CMGG have been found (Figs.-2a to 2d). Table-3 shows the various peaks of PANI/CMGG nanocomposites films, polyaniline, and CMMG. All peaks of CMGG and Polyaniline were present in PANI/CMGG nanocomposites film with one extra shoulder peak at 1731 cm^{-1} . This was found because of moisture contents. This favors that there is no grafting and supports the formation of PANI/CMGG nanocomposites films.

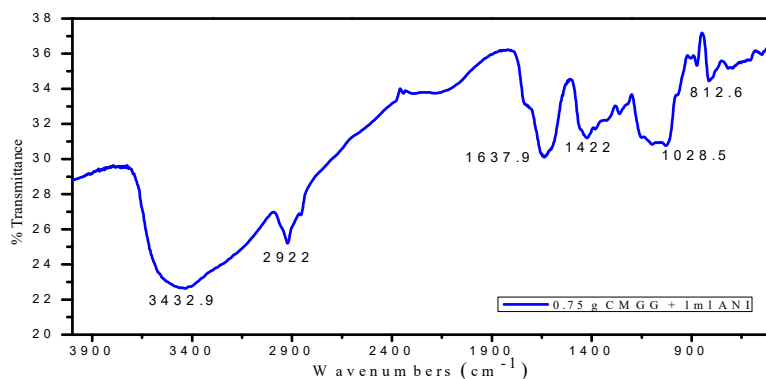


Fig.-2a: FTIR Spectrum of P₁C₁ Nanocomposites film

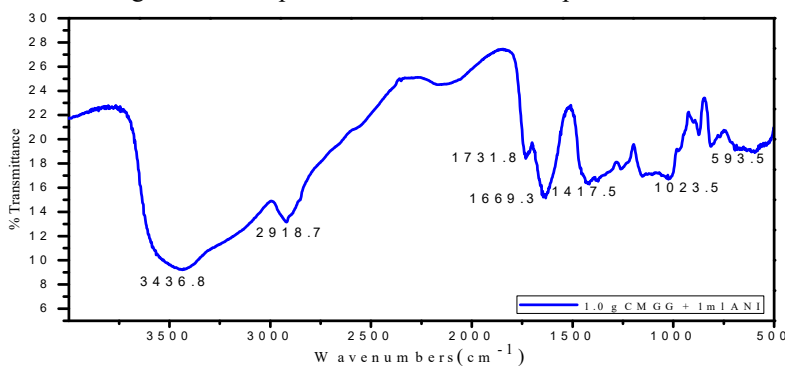


Fig.-2b: FTIR spectrum of P₁C₂ Nanocomposites Film

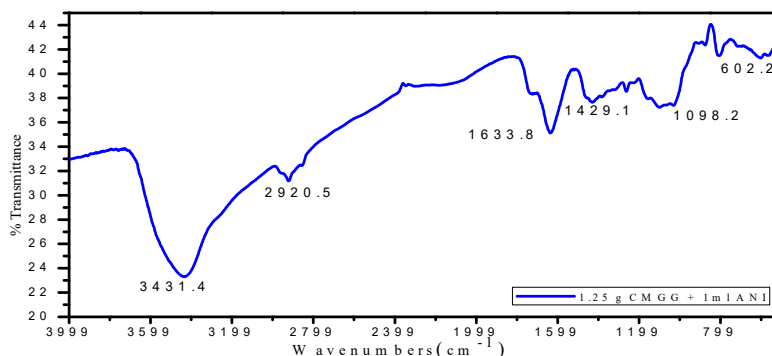


Fig.-2c: FTIR Spectrum of P₁C₃ Nanocomposites Film

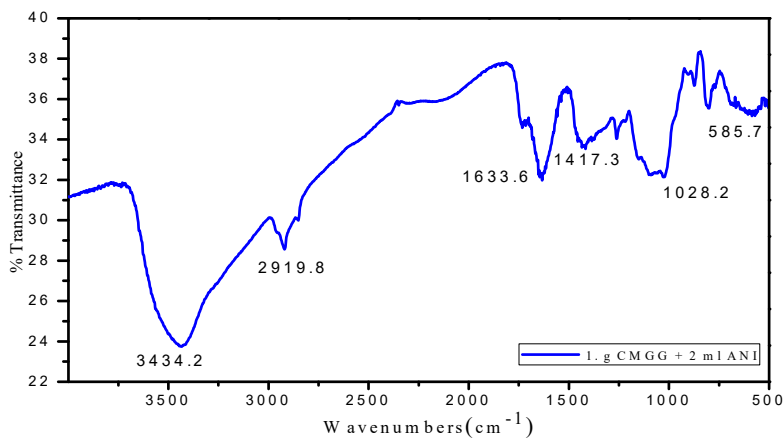


Fig.-2d: FTIR Spectrum of P₂C₂ Nanocomposites Film

Table-3: FTIR Spectrum Peak Positions of CMGG, PANI and PANI/CMGG Nanocomposites Films made from Various Concentrations of CMGG and Aniline

CMGG peak (cm ⁻¹)	Groups	PANI peak (cm ⁻¹)	Groups	PANI/CMGG Nanocomposites with different concentrations of CMGG (g) and Aniline (ml)			
				P ₁ C ₁	P ₁ C ₂	P ₁ C ₃	P ₂ C ₂
3436.7	O-H	3445.6	N-H Stretching	3432.9	3432.9	3431.4	3434.2
2922.1	C-H	1558.6	Bezenoid	2922	2922	2920.5	2919.8
1604.1	COOCH ₂ -	1473.5	Quinoid	1637.9	1637.9	1633.8	1633.6
1423.3	Asymmetric & Symmetric vibrations	1292.5	C-H	1422	1422	1429.1	1417.3
1022.8	C-O	1116.1	N-H vibration	1028	1028	1098.2	1260.9
814.5	C-O-C	801.7	C-H out of the plane bending vibrations	812	812	808.2	801.3

SEM Analysis

SEM images have been analyzed for the morphology of the PANI/CMGG nanocomposites film (Fig.-3a to 3e). The presence of nanoscale particles of polyaniline in the CMGG matrix has been confirmed by SEM images of PANI/CMGG films at various scales. This supports the formation of PANI/CMGG nanocomposites film.

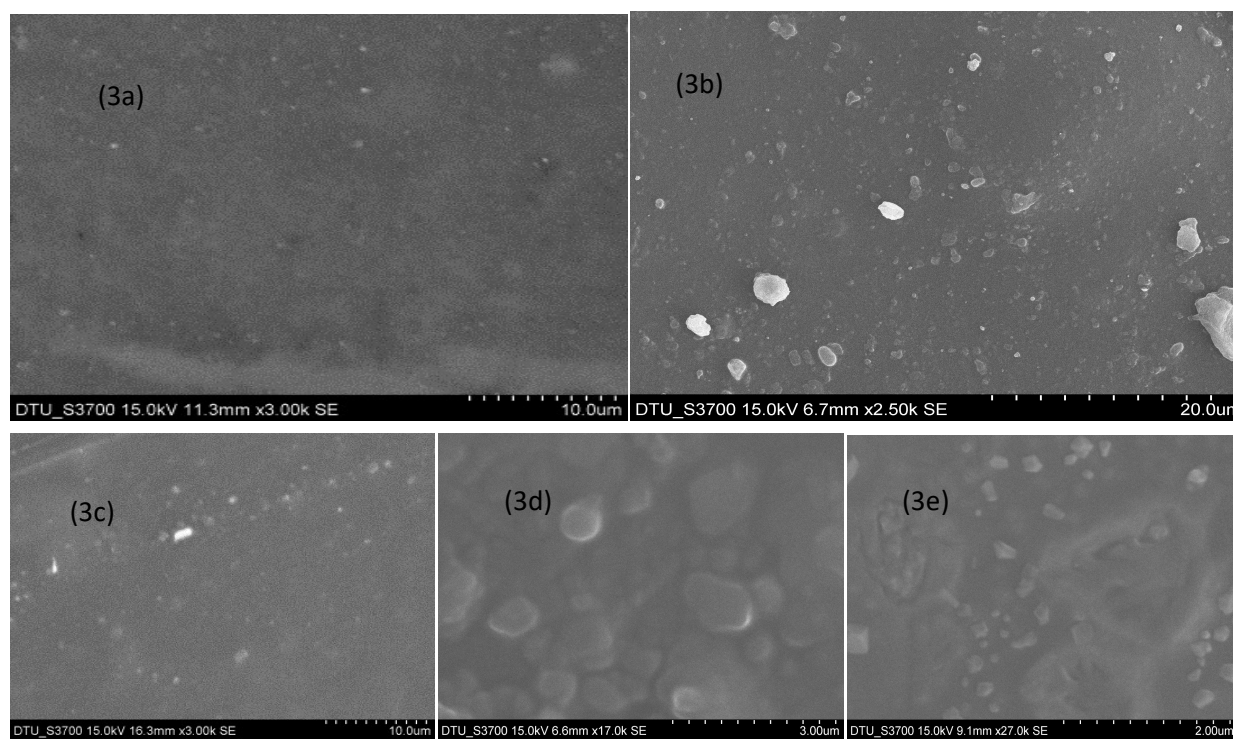


Fig.-3(a to e): SEM Images of PANI/CMGG Nanocomposites Film at (a, c) 10µm scale, (b) 20µm scale, (d) 3µm scale and (e) 2µm scale

Tensile Strength Analysis

The tensile strength of the nanocomposites films was analyzed using UTM (Universal Testing Machine). Concentrations of CMGG and aniline were also varied for the preparation of films. All these films were tested for optimum tensile strength of the PANI/CMGG nanocomposites films (Figs.-4a to 4d). Tensile strength was found directly proportional to the CMGG concentration. Tensile strength was found maximum 34.11MPa corresponding to PANI/CMGG nanocomposites film P₁C₃. While there was no significant change in Tensile strength of PANI/CMGG nanocomposites film by changing the concentration of aniline (Fig.-4d).

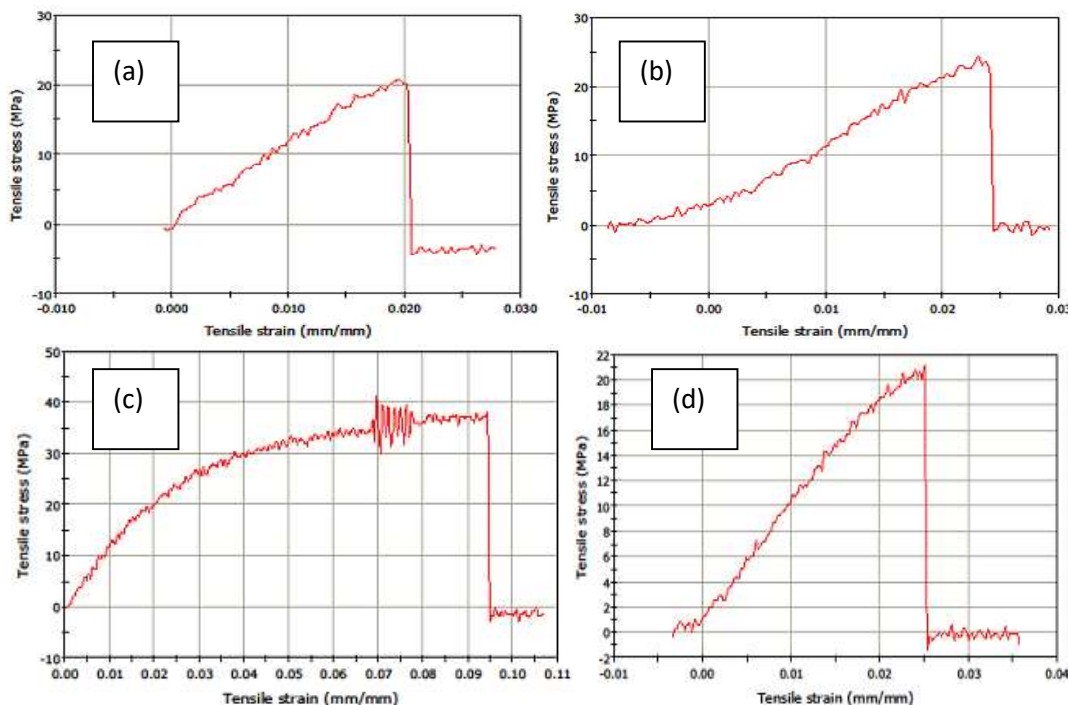


Fig.-4(a to d): Tensile Strength Graph of PANI/CMGG Nanocomposites Film for Different Concentrations: (a) P_1C_1 , (b) P_1C_2 , (c) P_1C_3 , (d) P_2C_2

Swelling Testing

Swelling testing of the PANI/CMGG nanocomposite films in water has been analyzed to obtain the maximum swelling percentage with time. The effect of variation in concentrations of CMGG and aniline has been studied on the swelling percentage of the PANI/CMGG nanocomposites films. The swelling percentage of the PANI/CMGG nanocomposites films has been found directly proportional to the CMGG concentration. After 24 hours, the Swelling percentage has been increased from (100 to 150) % on increasing CMGG from 0.75g to 1.25 g. Equilibrium percentage swelling was found to increase from (270 to 310) % on increasing the concentration of CMGG from 0.75g to 1.25 g. Swelling percentage, after 24 hours has been found to slight decrease on increasing the aniline concentration from 1-2ml. On increasing the aniline, polyaniline concentration increases. Polyaniline is hydrophobic in nature. So it resists the water to swelling in nanocomposites film. This may be the cause of less swelling of PANI/CMGG nanocomposites on increasing the aniline concentration.

Biodegradable Analysis

PANI/CMGG nanocomposites films prepared from various concentrations of CMGG and aniline have also been tested for biodegradable analysis. The Biodegradability of the nanocomposites films was tested by the laboratory method. The laboratory method has been considered the best method for determining the biodegradability of any material¹². In this method, a defined media has been used and then inoculated with the fixed microbial strain which might degrade the specific polymer. In many systematic investigations laboratory method has been used widely. In the present study, Luria Broth media has been used and then it has been inoculated with *E. coli* bacteria. After this, all PANI/CMGG nanocomposites films with a circular size have been cut and put in the inoculated Petri discs, Fig.-5a. Then these Petri discs have been put in the desiccators for 24 hours at 37°C to see the effect of microbes on the PANI/CMGG nanocomposites film. From Fig.-5b, it has been cleared that all the PANI/CMGG nanocomposites films are biodegradable in the presence of *E.coli*. It has been also found that biodegradability increased by increasing the CMGG concentration.

CONCLUSION

PANI/CMGG nanocomposites biodegradable, conductive, flexible films have been synthesized successfully by solution casting method, which was confirmed by FTIR, SEM, Conductivity analysis, and

biodegradability testing. The conductivity of the PANI/CMGG nanocomposites film has been found inversely proportional to the CMGG concentration and directly proportional to the aniline concentration. Maximum conductivity has been obtained at 0.17×10^{-5} S/cm for P_1C_1 film. Tensile strength was also found directly proportional to the CMGG concentration and vice versa for aniline concentration. Because of the great availability of guar gum and its derivatives this method has the new possibility for large-scale synthesis of biodegradable, conductive, and flexible nanocomposites films.

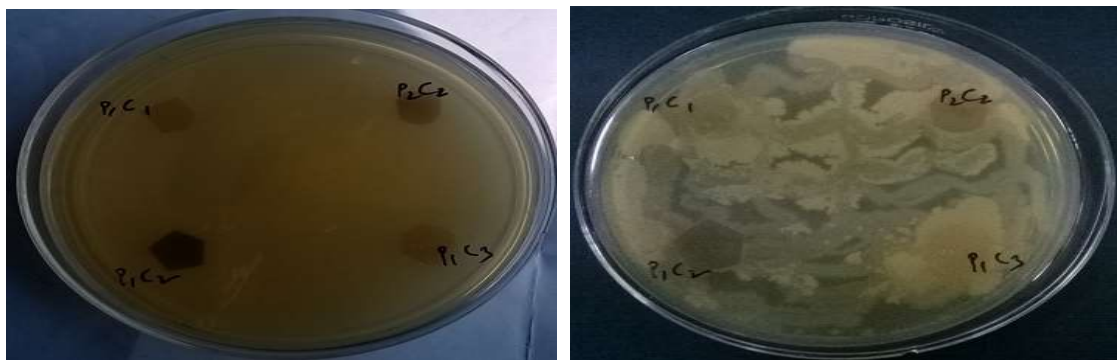


Fig.-5: Biodegradable Testing: PANI/CMGG Nanocomposites Inoculation with *E.coli* Bacterial (a) Just after Inoculation With *E.coli* Bacterial, (b) After 24 hours of Films Inoculation with *E.coli* Bacterial.

ACKNOWLEDGEMENT

As a corresponding author, I acknowledge to Department of Applied Chemistry and Polymer Technology and Delhi Technological University, Delhi, India, for providing me with the testing facility for doing this work.

REFERENCES

1. J. Y. Wong, R. Langer, D. E. Ingber, *Proceedings of the National Academy of Sciences of the United States of America*, **91**, 3201(1994), <https://doi.org/10.1073/pnas.91.8.3201>
2. N. K. Guimard, N. Gomez, C. E. Schmidt, *Progress in Polymer Science*, **32**, 876 (2007), <https://doi.org/10.1016/j.progpolymsci.2007.05.012>
3. R. Ravichandran, S. Sundarajan, J. R. Venugopal, S. Mukherjee, S. Ramakrishna, *Journal of the Royal Society Interface*, **7**, S559 (2010), <https://doi.org/10.1098/rsif.2010.0120>
4. I. S. Budi, S. J. Santosa, E. S. Kunarti, *Rasayan Journal of Chemistry*, **13(1)**, 202(2020), <https://doi.org/10.31788/RJC.2020.1315509>
5. B. Guo, A.F. Wistrand, A.C. Albertsson, *Biomacromolecules*, **12**, 2601(2011), <https://doi.org/10.1021/bm200389t>
6. P. Chowdhury, B. Saha, *Indian Journal of Chemical Technology*, **12**, 671(2005).
7. H. Gong, M. Liu, J. Chen, F. Han, C. Gao, B. Zhang, *Carbohydrate Polymers*, **88(3)**, 1015(2012), <https://doi.org/10.1016/j.carbpol.2012.01.057>
8. A. P. Gupta, D. K. Verma, *International Journal of Advanced Research*, **2(1)**, 680(2014).
9. A. P. Gupta, D. K. Verma, *International Journal of Biological Macromolecules*, **68**, 247(2014), <https://doi.org/10.1016/j.ijbiomac.2014.05.012>
10. P. Garg, *Studies on Hydrogels based on Polyacrylamide and Guar Gum Derivatives. A Major-II Dissertation*, Delhi Technological University, India, (2013).
11. S. N. Murthy, S. R. R. Hiremath, K. L. K. Paranjothy, *International Journal of Pharmaceutics*, **272(1-2)**, 11(2004), <https://doi.org/10.1016/j.ijpharm.2003.11.019>
12. R. J. Muller, *Biodegradability of Polymers: Regulations and Methods for Testing*, Book Chapter **12**, 365, 2005.
13. U. D. Lingewari, T. Vimala, *Rasayan Journal of Chemistry*, **13(3)**, 1544(2020), <https://doi.org/10.31788/RJC.2020.1335722>
14. U. Stamenović, S. Davidović, S. Petrović, A. Leskovic, M. Stoilković, V. Vodnik *New Journal of Chemistry*, **28**, 12711(2021), <https://doi.org/10.1039/D1NJ02729H>

[RJC-6820/2021]