The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization
IAEA
International Atomic Energy Agency

2227-1c

Joint ICTP-IAEA Workshop on Radiation Resistant Polymers

14 - 18 March 2011

"The use of gamma irradiation for biopolymers development for food packaging application"

M. Lacroix
University of Quebec

Workshop on Radiation Resistant Polymers
Trieste, March 14-18, 2011

The use of gamma irradiation for co-polymerization of biopolymers and the development of food packaging

Monique Lacroix, Ph.D.
Professor
INRS-Institut Armand-Frappier
531 des Prairies, Laval, Qc, Canada H7V 1B7
Email: monique.lacroix@iaf.inrs.ca

Development of biodegradable packagings

Currently, synthetic polymers are using as packaging materials which are a threat to the environment.

Efforts are in progress to develop alternative packaging materials which are environment-friendly, cheap, light weight, possess good thermo mechanical properties and provide good moisture barrier.

Materials under consideration

Proteins: Soya, Milk, corn zein, wheat gluten, collagen

Polyssacharides: Cellulose, Chitosan, Alginate

Lipids: fatty acids, vegetable oils

Waxes

Crosslinking treatments

Enzymes: Transglutaminase

Physical treatments: ultrasound,
γ-irradiation

Grafting and compatibilization: Advantages of irradiation

Formation of strong bridges between macromolecules

Compatibilization of polymer blend by high energy radiation

Addition of multifunction monomers and inomers to polymer blends in order to accelerate and increase the crosslinking degree in polymer blends

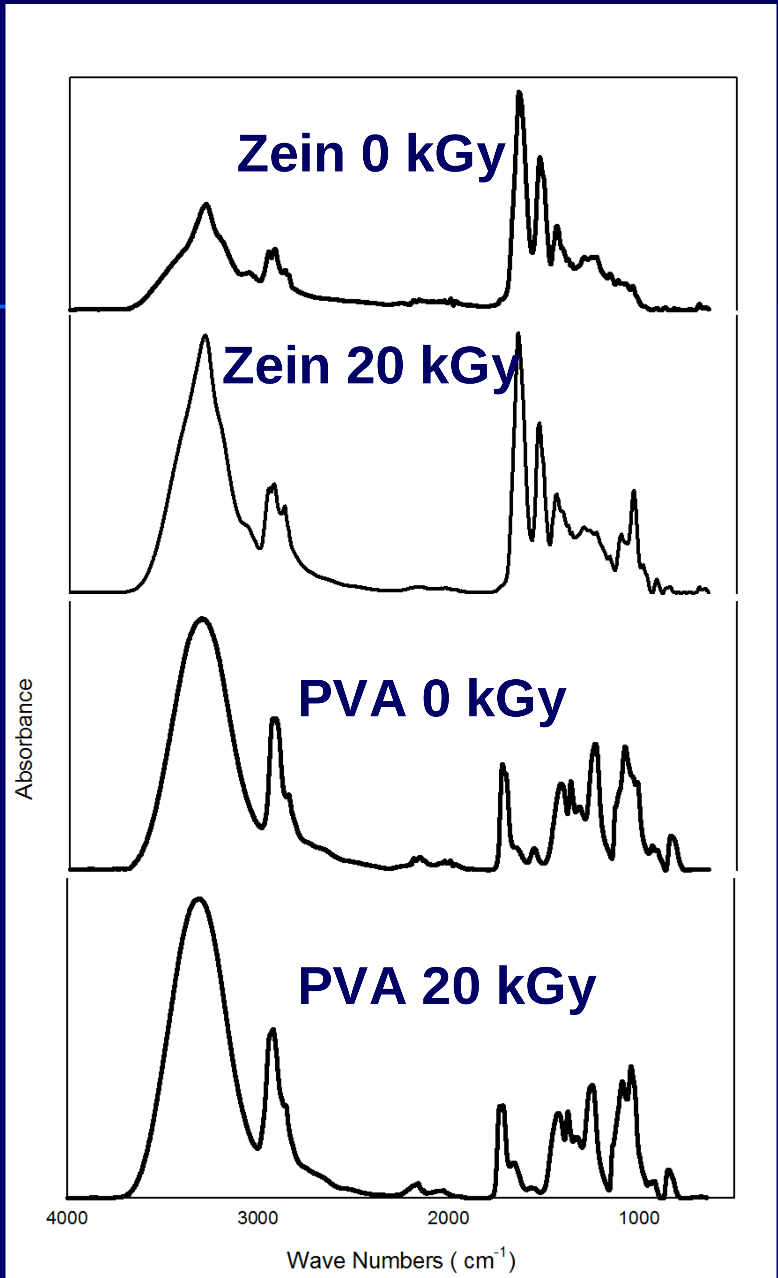
Zein / PVA blending

Zein/PVA: 100:0; 70:30
50:50; 0:100
+
Acrylic acid: 2, 5, 10%

↓

Gamma irradiation under
nitrogen atmosphere
at 20 kGy

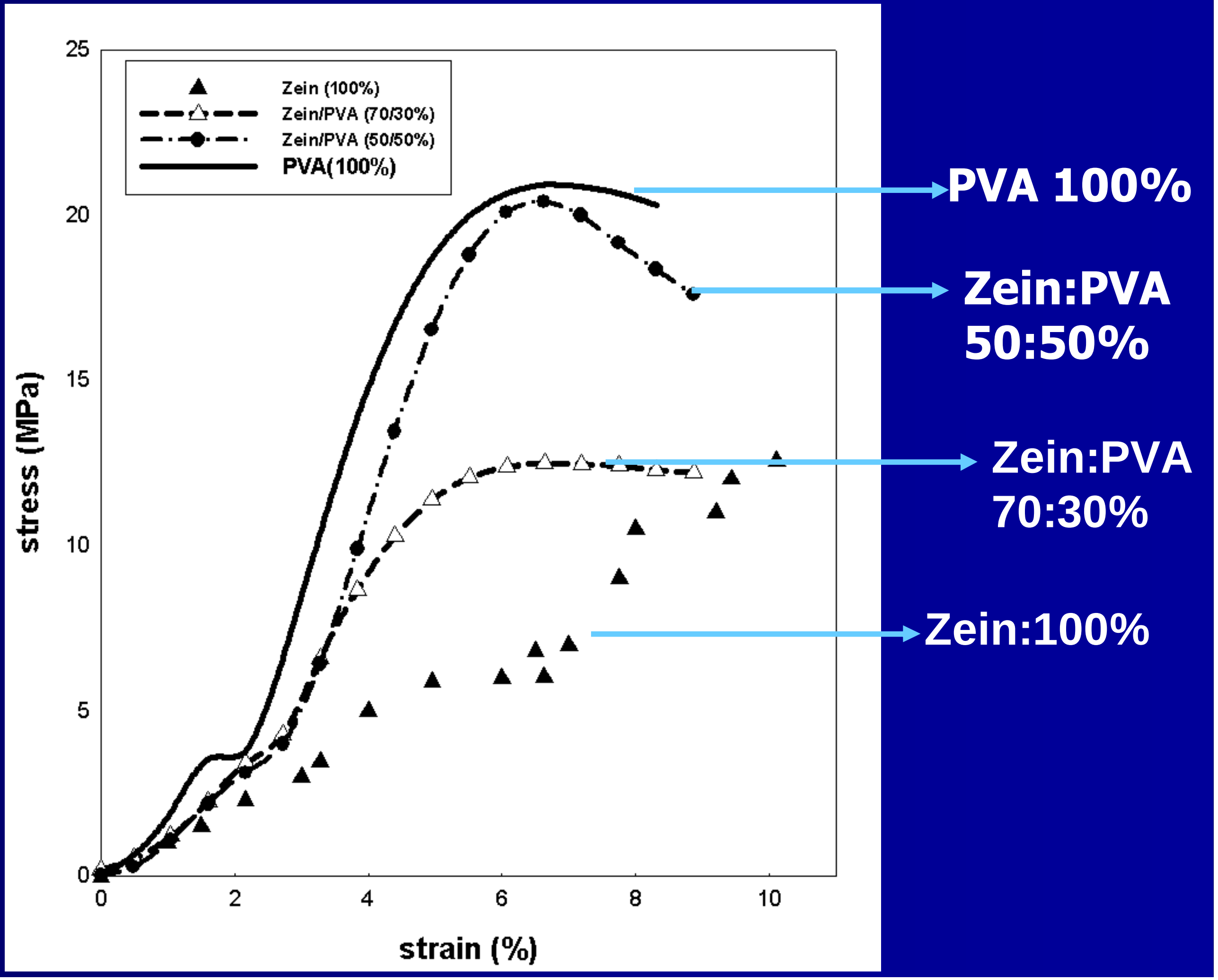
FT-IR spectra of ZEIN/PVA



Zein: Amine I: 1640 cm^{-1}
Amine II: 1550 cm-^{1}
O-H stretching intraintermolecular Hydrogen bond: 3200-3570 cm^{-1}
alkyl stretching: 2850-3000 cm-^{1}

PVA: C-OH: 1100 cm-^{1}

Stress-strain curves of unirradiated zein and PVA polymers and their blends of different ratio



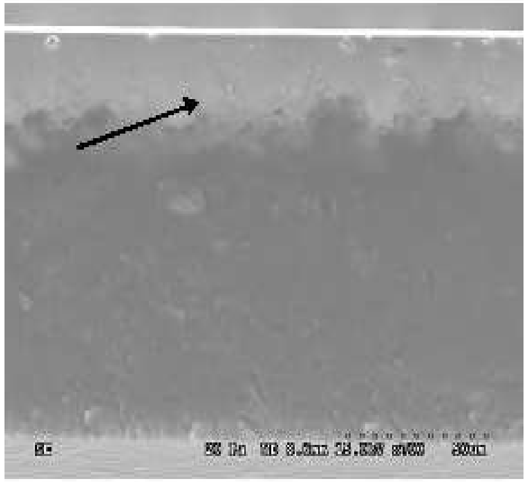
Mechanical properties

Zein/PVA ratio (%)	PS ($N.nm^{-1}$)	PD (mm)
70/30 0 kGy	29	2.6
70/30 70/30-AAc 5% 20 kGy	68* 40	6.5* 6.5
50/50 0 kGy	70	3.4
50/50 50/50-AAc 5% 20 kGy	234* 37	5.5* 9.8

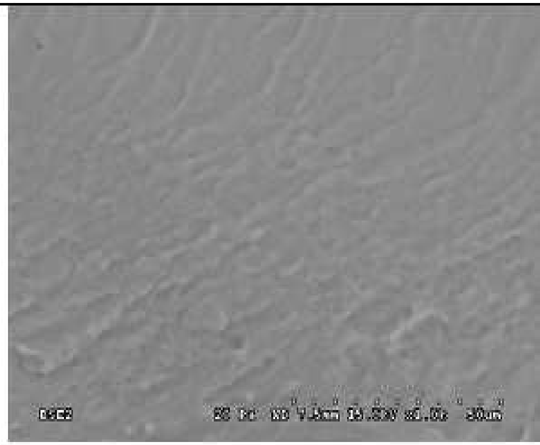
SEM

ungrafted

2% AAc



1.8% AAc +
0.2 % EGDA



5% AAc

DSC thermograms of Zein, PVA and their blends treated at 20 kGy

Blend composition	Tg (°C)	Tm (°C)	ΔH (J/g)
Zein/Glycerol	65.0	183	1.2
PVA/Glycerol	43.0	161	31.3
Zein/PVA 70/30/Glycerol	42.5	173	69.4
Zein/PVA 50/50/Glycerol	41.6	168	71.0
Zein/PVA 50/50/Glycerol, 2% AAc	57.0	167	42.7
Zein/PVA 50/50/Glycerol, 5% AAc	66.0	162	39.0

Methylcellulose and 2-Hydroxyethyl-methacrylate (HEMA)

Methylcellulose (MC) is a biodegradable and biocompatible cellulose derivatives.

Hydroxyethyl methacrylate (HEMA) is a vinyl monomer converted to polymer by ϒ-irradiation.

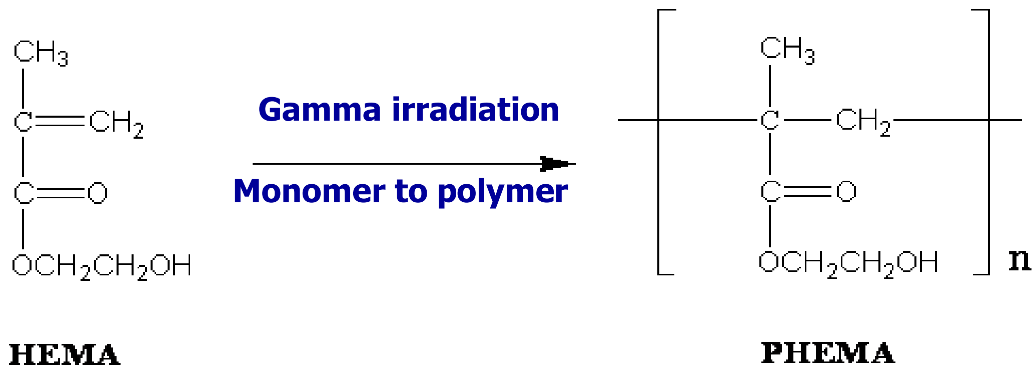
Poly(HEMA) has adequate biocompatibility and has many potential applications in medical sciences.

HEMA (0.1-1%, w/w) was incorporated into the MC-based Formulation Followed by Gamma Radiation

Methylcellulose: 1%
Vegetable Oil: 0.5%
Glycerol: 0.25%
Tween-80: 0.025%
(w/w, in aqueous solution)

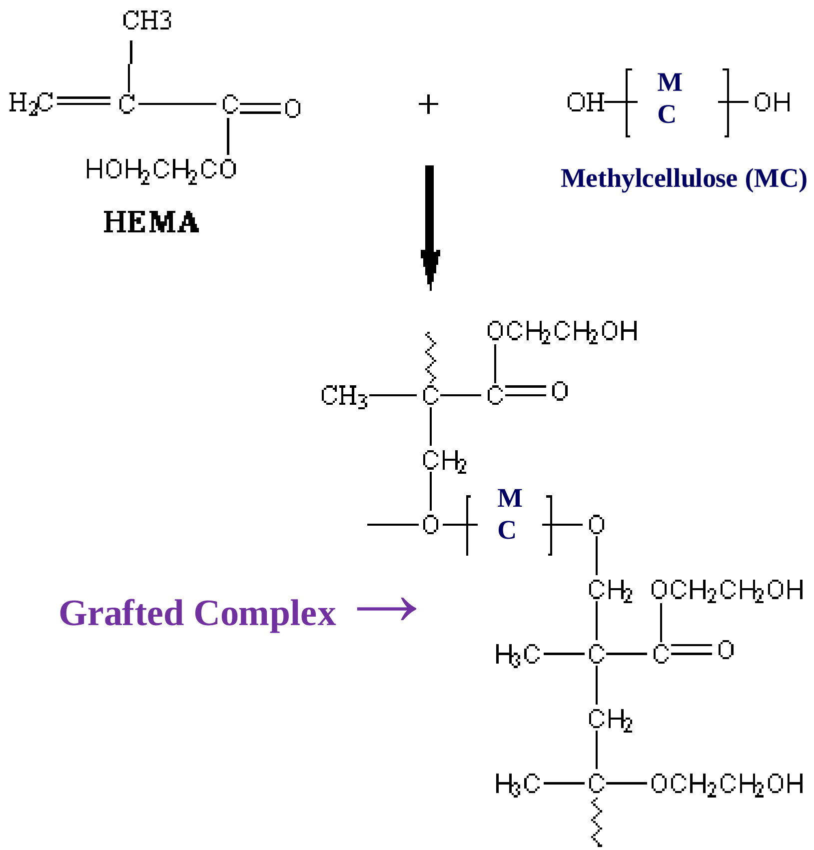
Using the above formulation, HEMA containing MC-based films were prepared by casting. Then films were irradiated (0.5-25 kGy dose). A 10 kGy dose was found to be optimal for the above formulation.

Effect of Gamma Radiation on HEMA



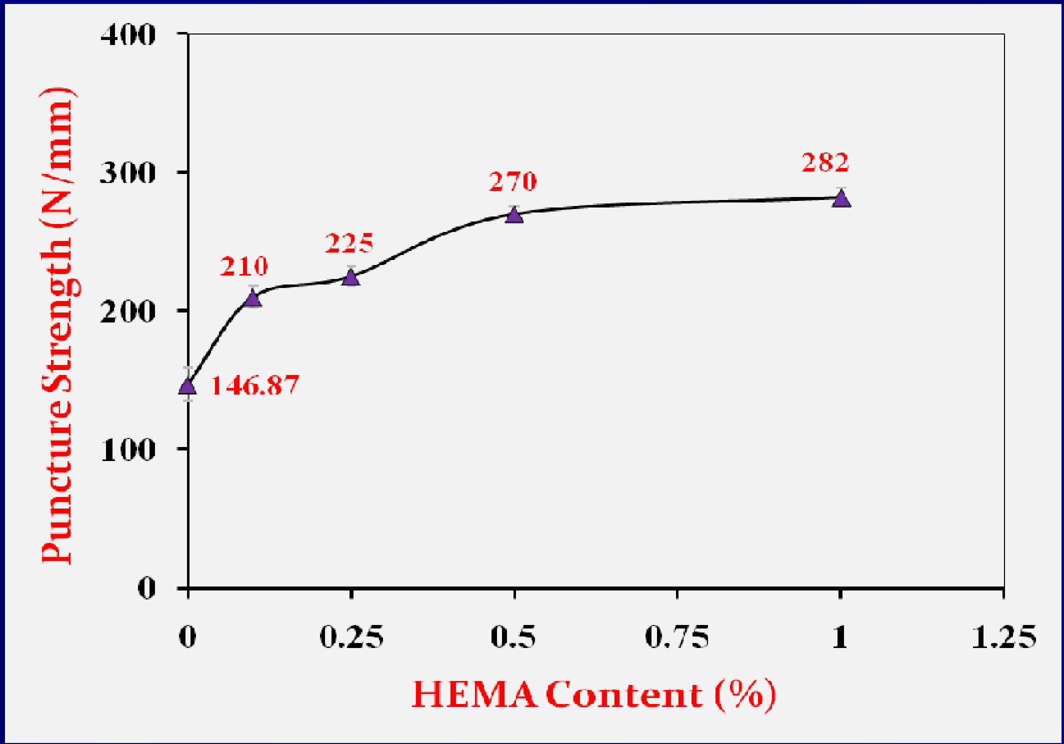
HEMA Monomer is converted to Poly (HEMA) when exposed to gamma Radiation

Grafting of HEMA with MC during irradiation



HEMA monomer reacted with OH groups of methylcellulose in presence of gamma radiation and thus formed grafted complex.

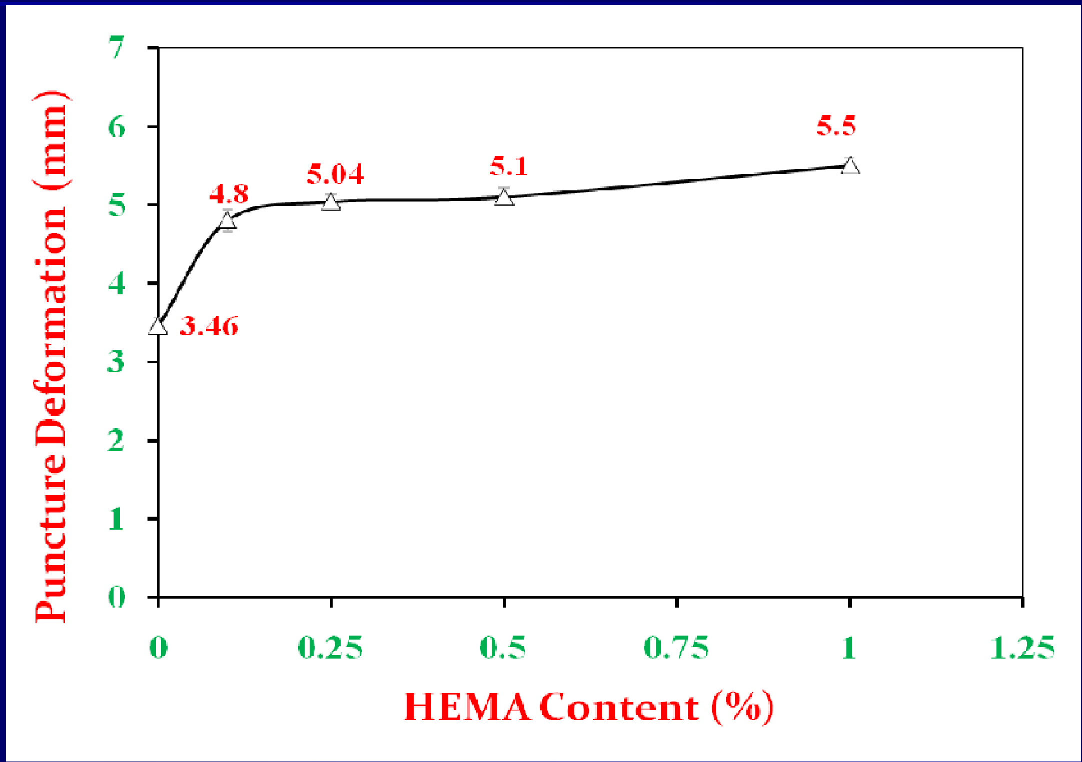
Effect of HEMA on Puncture Strength



The PS of the films improved significantly (92% improvement for 1% HEMA) when MC-based films were grafted with HEMA monomer at 10 kGy dose.

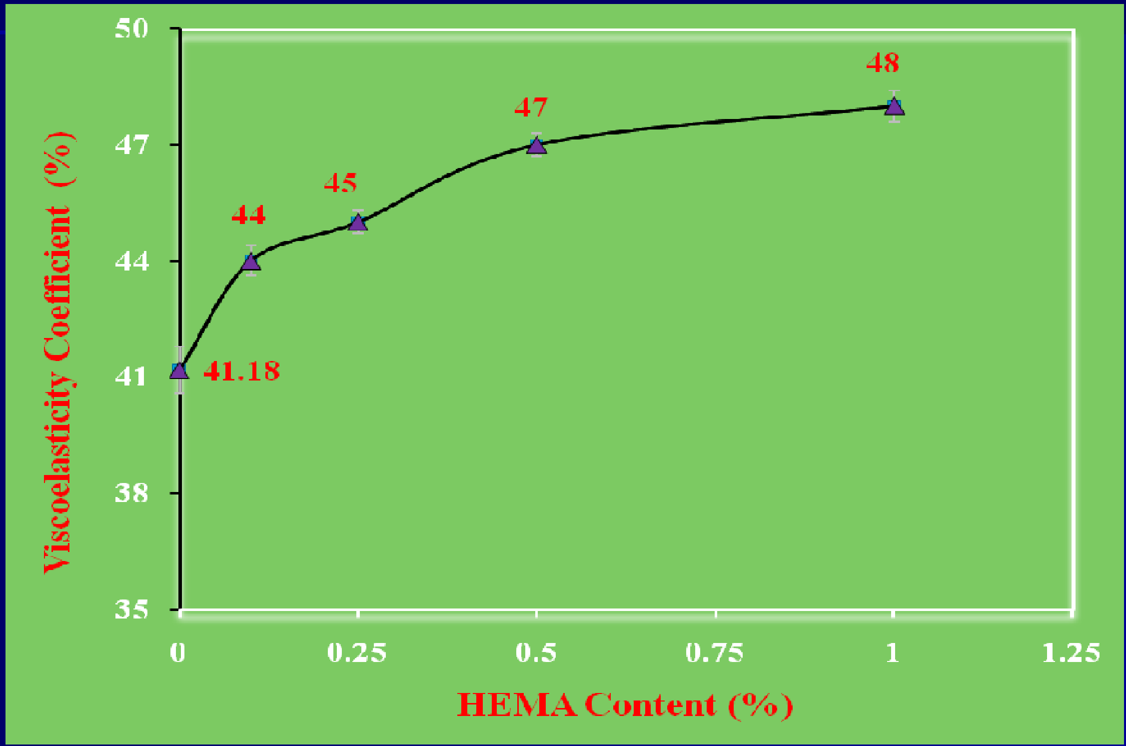
HEMA was successfully grafted with MC by gamma radiation.

Effect of HEMA on Puncture Deformation



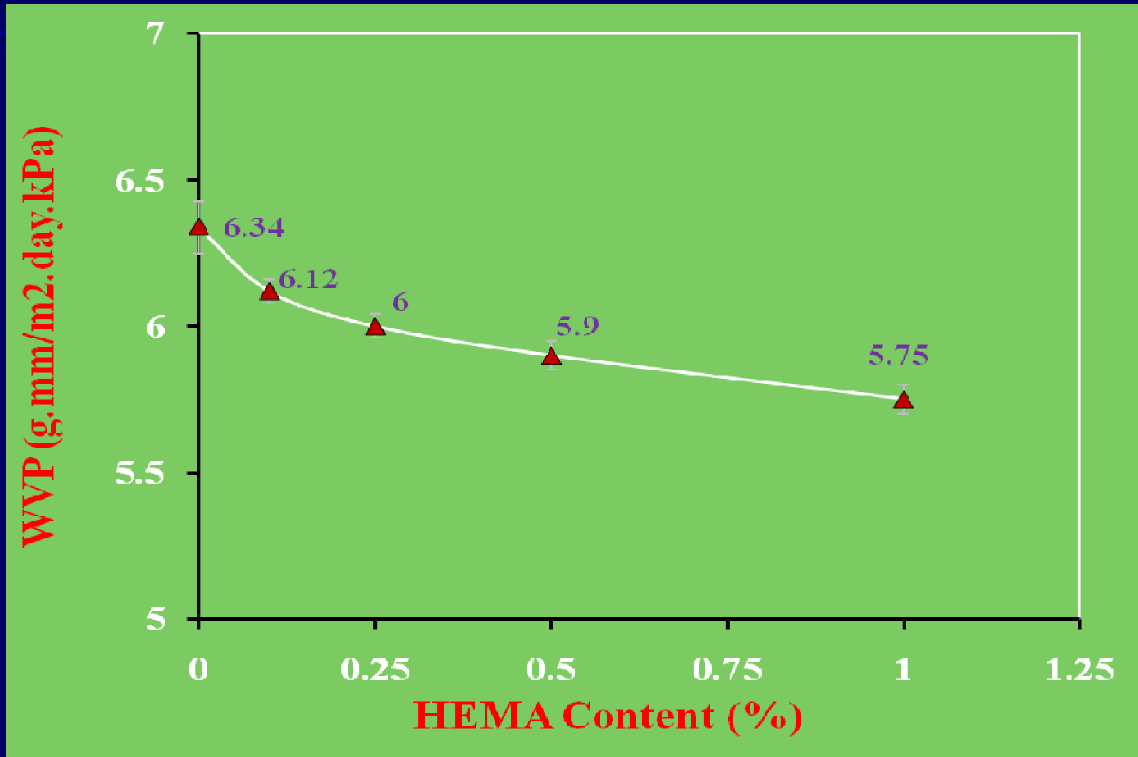
The values of PD of the films also improved significantly when MC-based films were grafted with HEMA monomer (1%) at 10 kGy dose.

Effect of HEMA on Viscoelasticity Coefficient



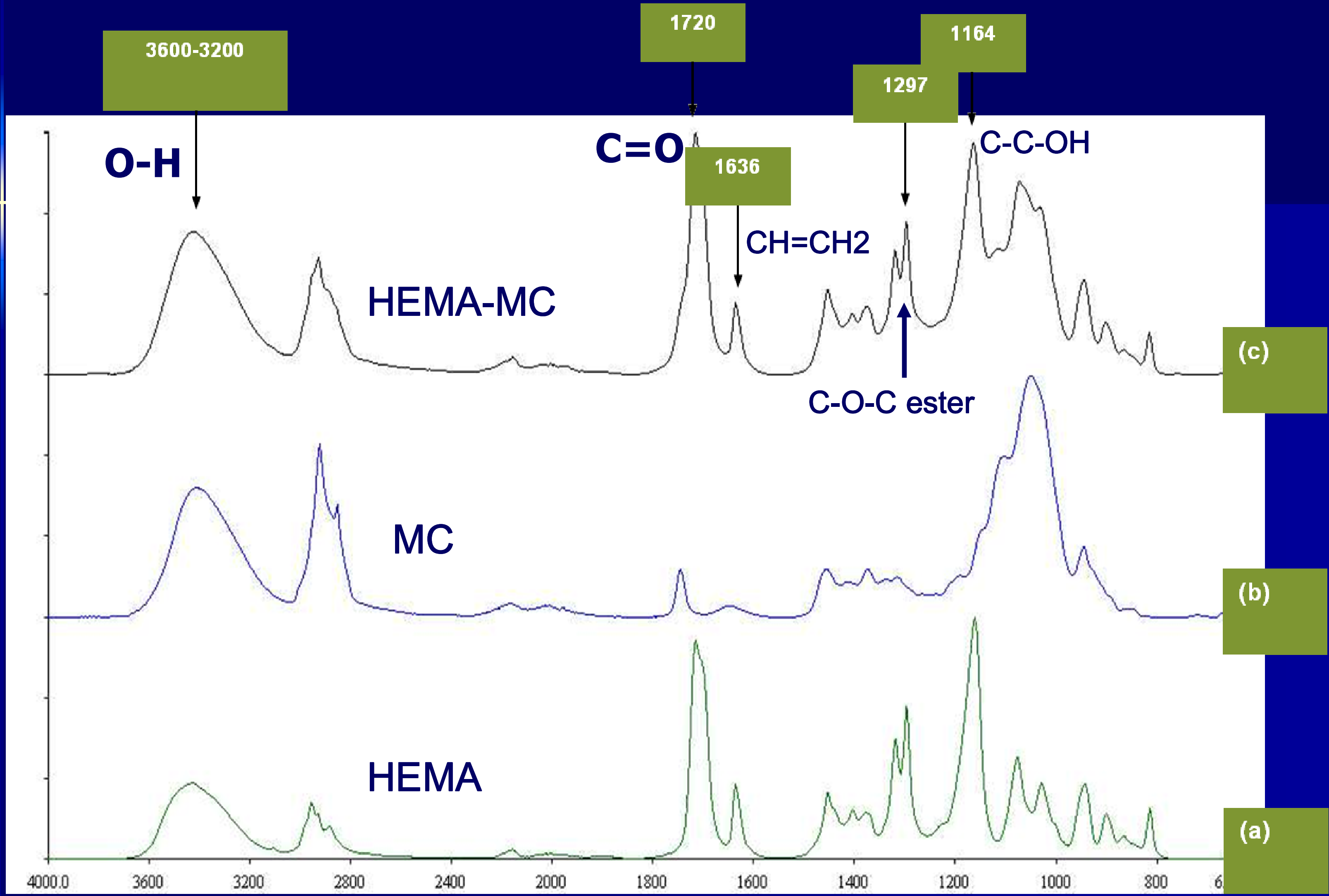
The values of viscoelasticity coefficient of the films also improved significantly when MC-based films were grafted with HEMA monomer at 10 kGy dose.

Effect of HEMA on WVP



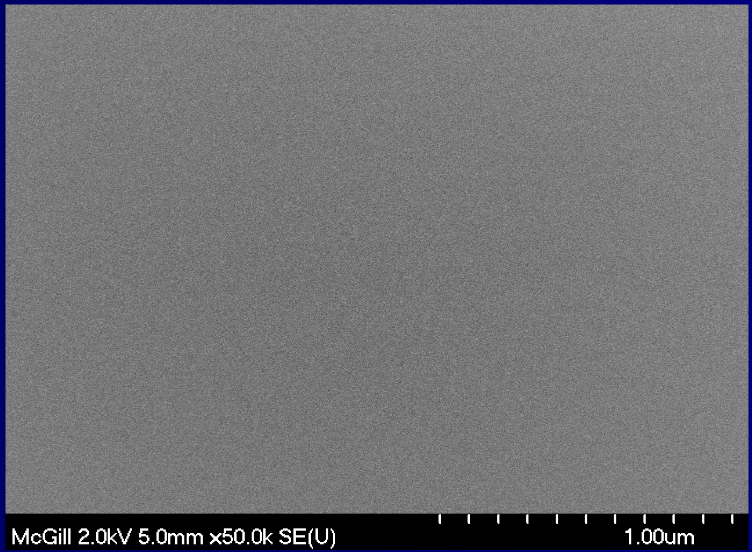
A continuous decrease of WVP values was observed with an increase of HEMA concentrations when exposed to 10 kGy which indicated better barrier properties of the grafted films.

FT-IR Analysis of the Films

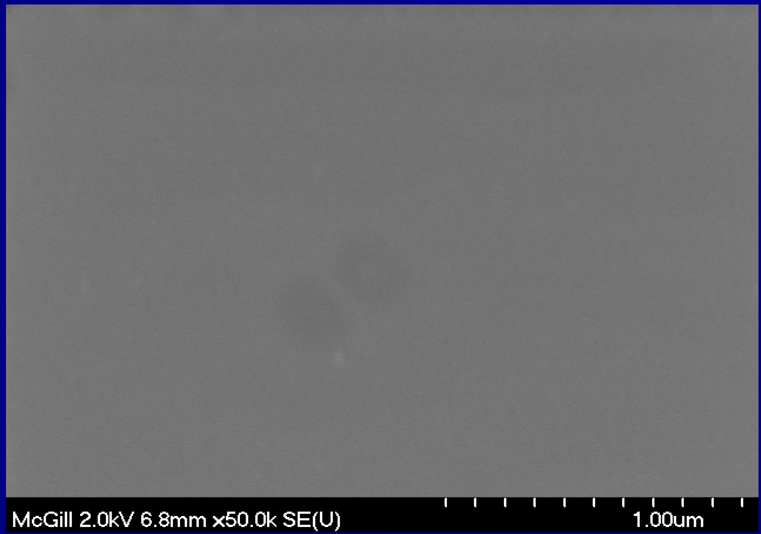


FTIR spectra of HEMA (a), non-grafted MC-based films (b) and grafted films (MC-g-HEMA) irradiated at 10 kGy.

Effect of HEMA on the Morphological Properties



MC-Based Films



HEMA +MC-Based Films

The surface of MC-based films was found quite even. But surface smoothness was significantly improved after HEMA grafting indicated better appearance.

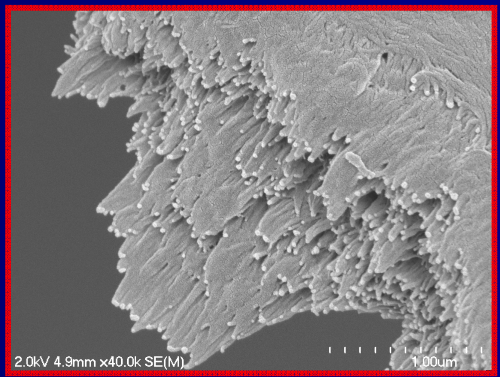
Nanocellulose reinforced methylcellulose based biodegradable Films

Methylcellulose

Methylcellulose (MC) is the derivative of cellulose and can be produced from cotton cellulose, wood and annual plant pulps.

Nanocellulose

Nanocellulose (NC) is also a cellulose derivative composed of a nano-sized fiber network.



Diameters varied: 2-20 nm, and lengths ranging from a few hundred nanometers up to a few micrometers.

Objectives: Evaluation the effect of incorporation of NC or chitosan on mechanical, barrier, thermal and interfacial properties of MC-based biodegradable films.

Methylcellulose: 1%
Vegetable Oil: 0.5%
Glycerol: 0.25%
Tween-80: 0.025%
(w/w, in aqueous solution)

Using the above formulation, MC-based films were prepared by casting.

Final Composition of the Films (dry weight basis):
MC (58.34%), Vegetable Oil (28.17%), Glycerol (14.08%), T-80 (1.41%)

Effect of NC or chitosan on Mechanical Properties of MC-Based Films

Aqueous NC solution (0.1-1%, w/w) was incorporated into the MC-based formulation

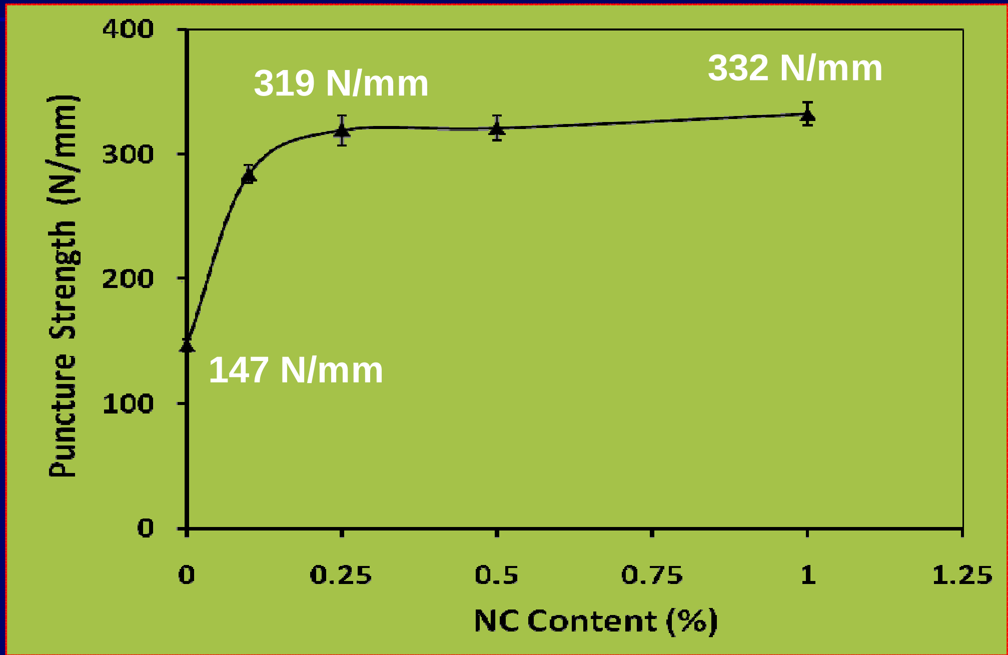
↓

Methylcellulose: 1%
Vegetable Oil: 0.5%
Glycerol: 0.25%
Tween-80: 0.025%
(w/w, in aqueous solution)

Using the above formulation, NC containing MC-based films were prepared by casting.

Final Composition (dry basis) of 1% NC + 1% MC-Based Formulation :
MC (36.04%), NC (36.04%), Vegetable Oil (18.01%), Glycerol (9.01%), T-80 (0.9%)

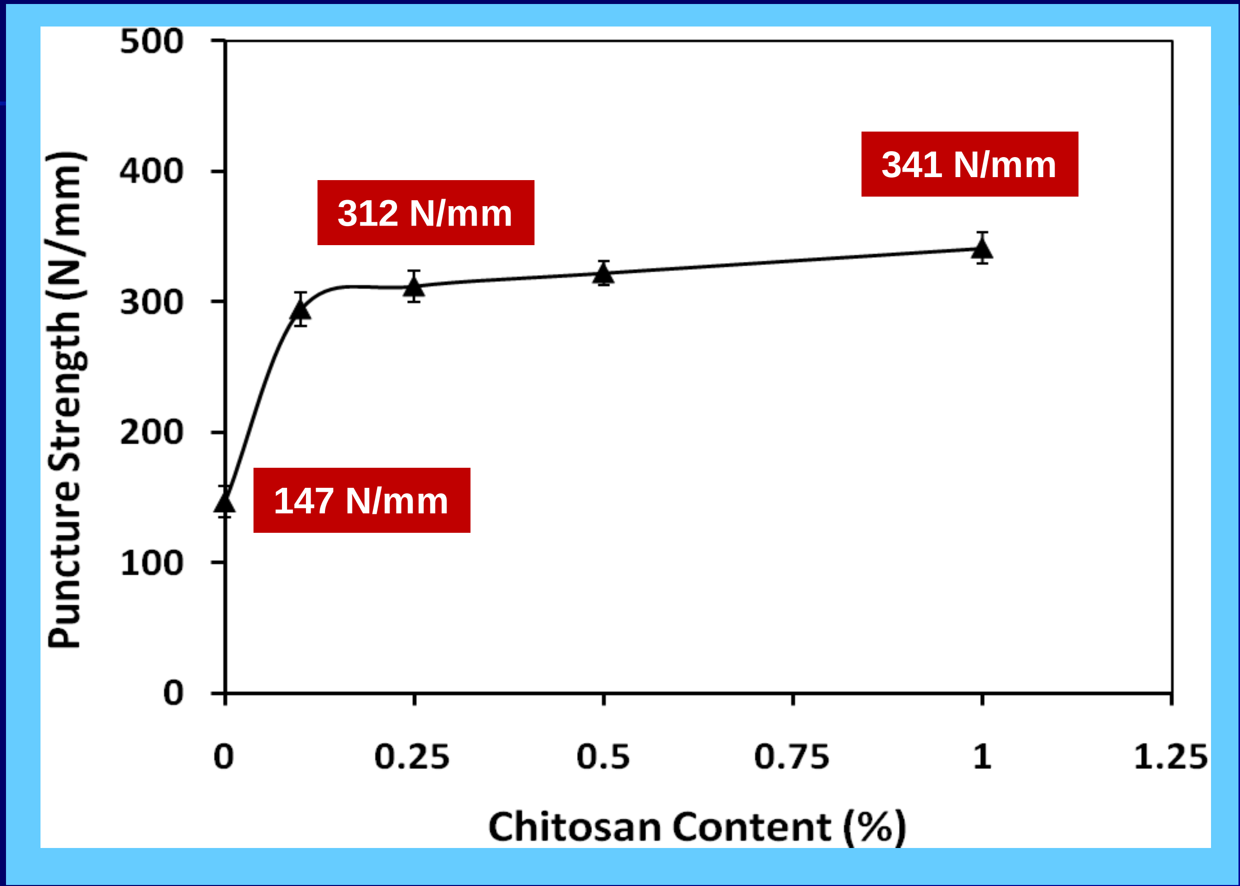
Effect of NC on Puncture Strength (PS) of MC-Based Films



PS of the films reached to 284, 319, 321, 332 N/mm, respectively for the incorporation of 0.1, 0.25, 0.5 and 1% NC solution. It was found that using 0.25% NC solution, PS improved 117%.

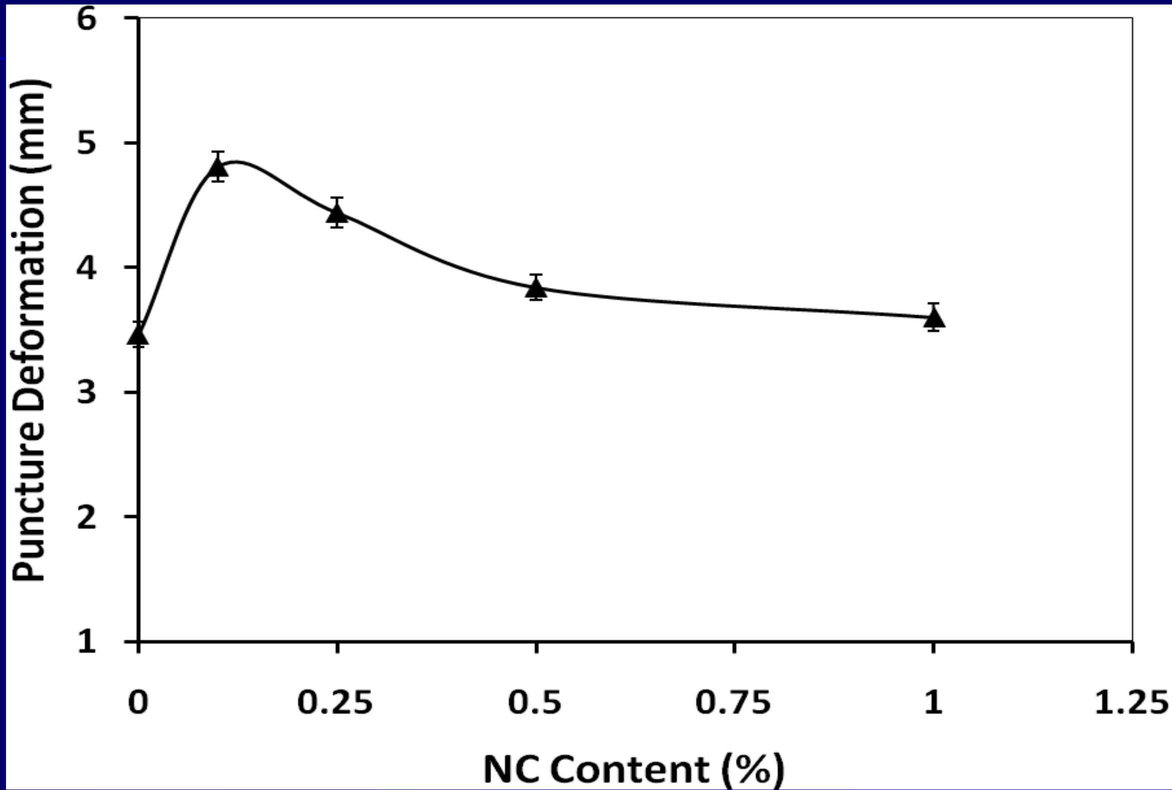
Nanocellulose (NC) acted as a reinforcing agent in MC-based formulation.

Effect of Chitosan on Puncture Strength of MC-Based Films



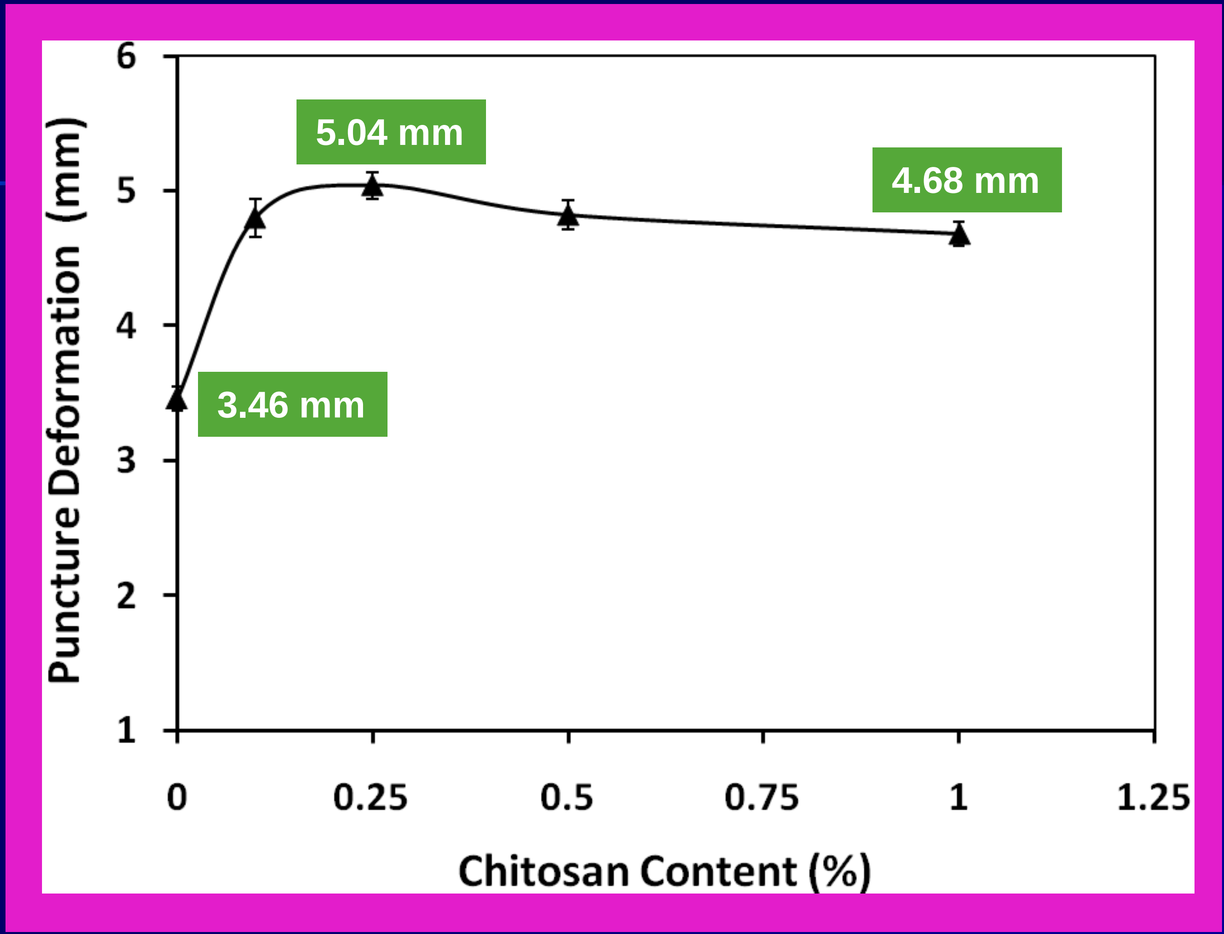
PS of the Chitosan containing films reached to 294, 312, 322, and 341 N/mm, respectively for the addition of 0.1, 0.25, 0.5 and 1% Chitosan solution.
It was found that using 0.25% Chitosan solution, the PS improved 117%.

Effect of NC on Puncture Deformation (PD) of MC-Based Films



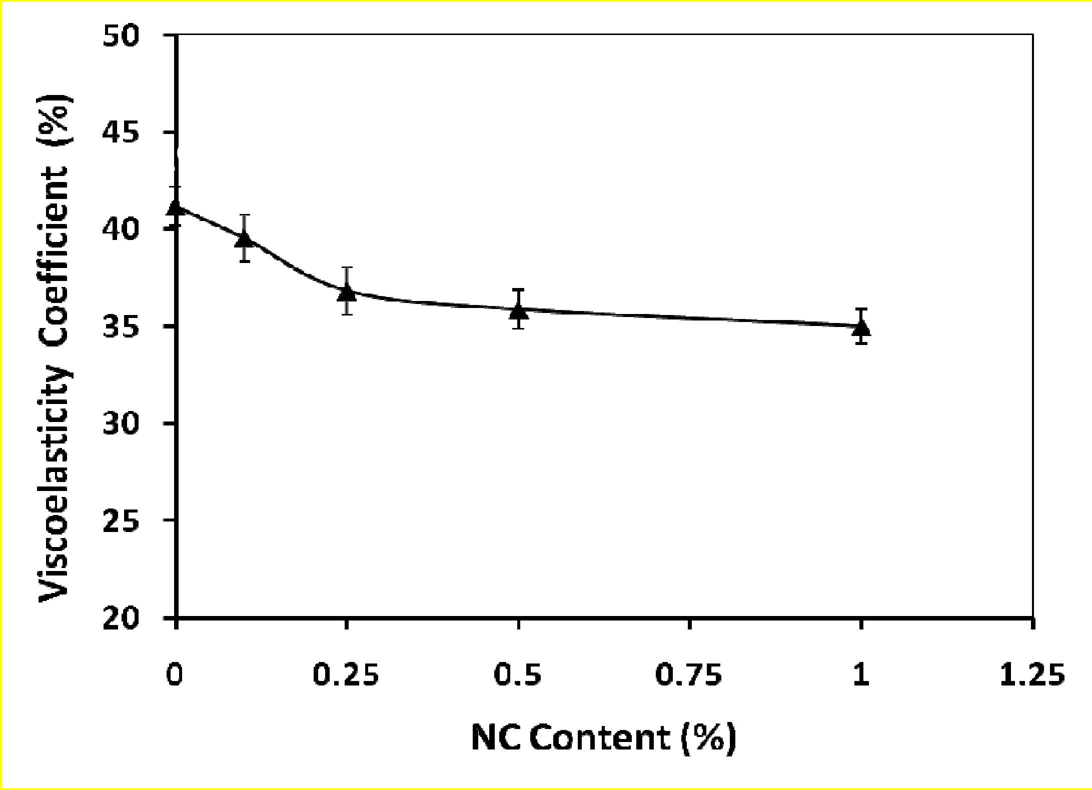
The incorporation of NC caused a significant rise of PD ($p \leq 0.05$). The largest deformation was 39% higher than control, which was observed for 0.1% NC concentration.

Effect of Chitosan on Puncture Deformation (PD) of MC-Based Films



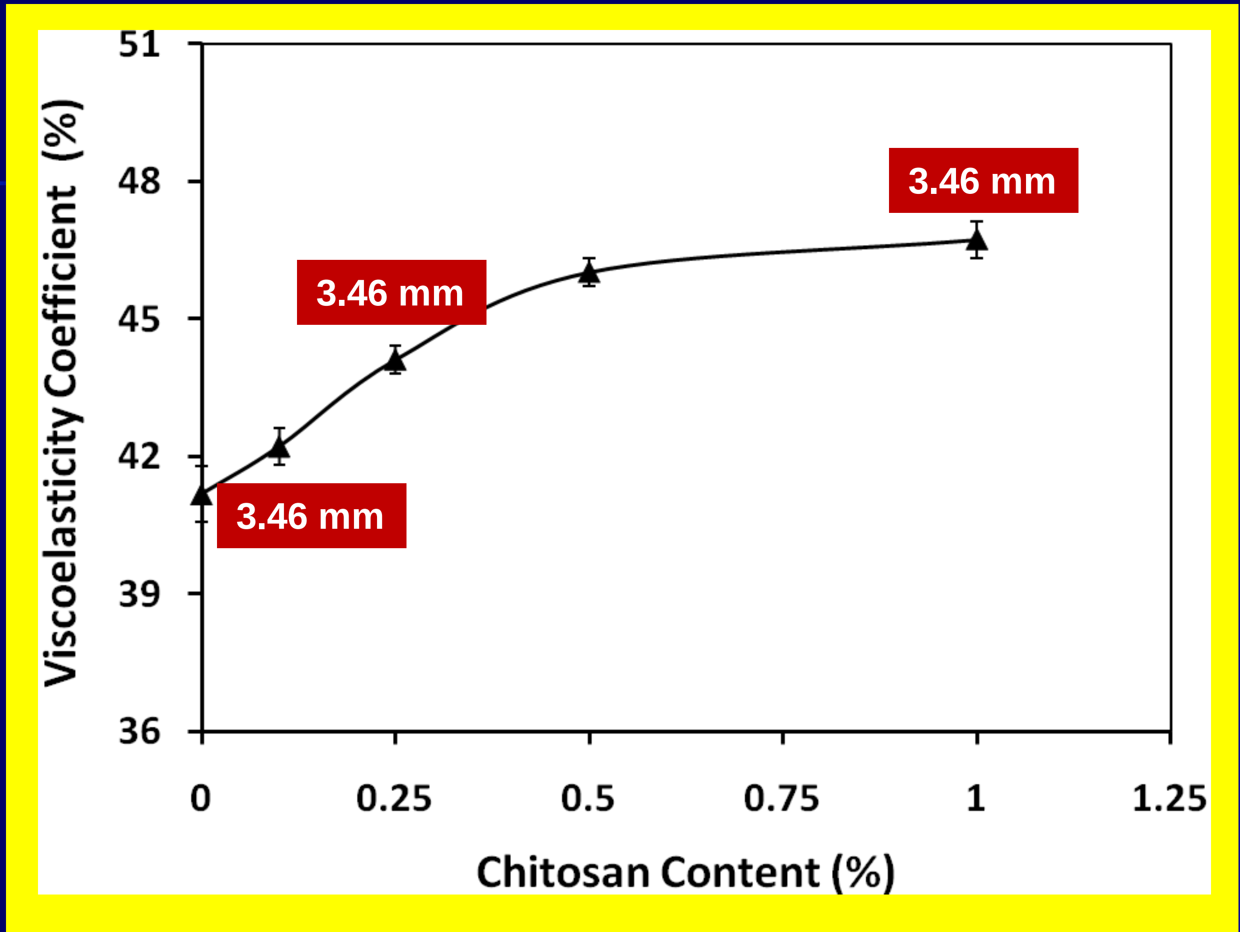
PD values of the Chitosan containing films reached to 4.8, 5.04, 4.82 and 4.68 mm, respectively for the incorporation of 0.1, 0.25, 0.5 and 1% Chitosan solution. It was found that using 0.25% NC solution, PS improved 46%.

Effect of NC on Viscoelasticity Coefficient of MC-Based Films



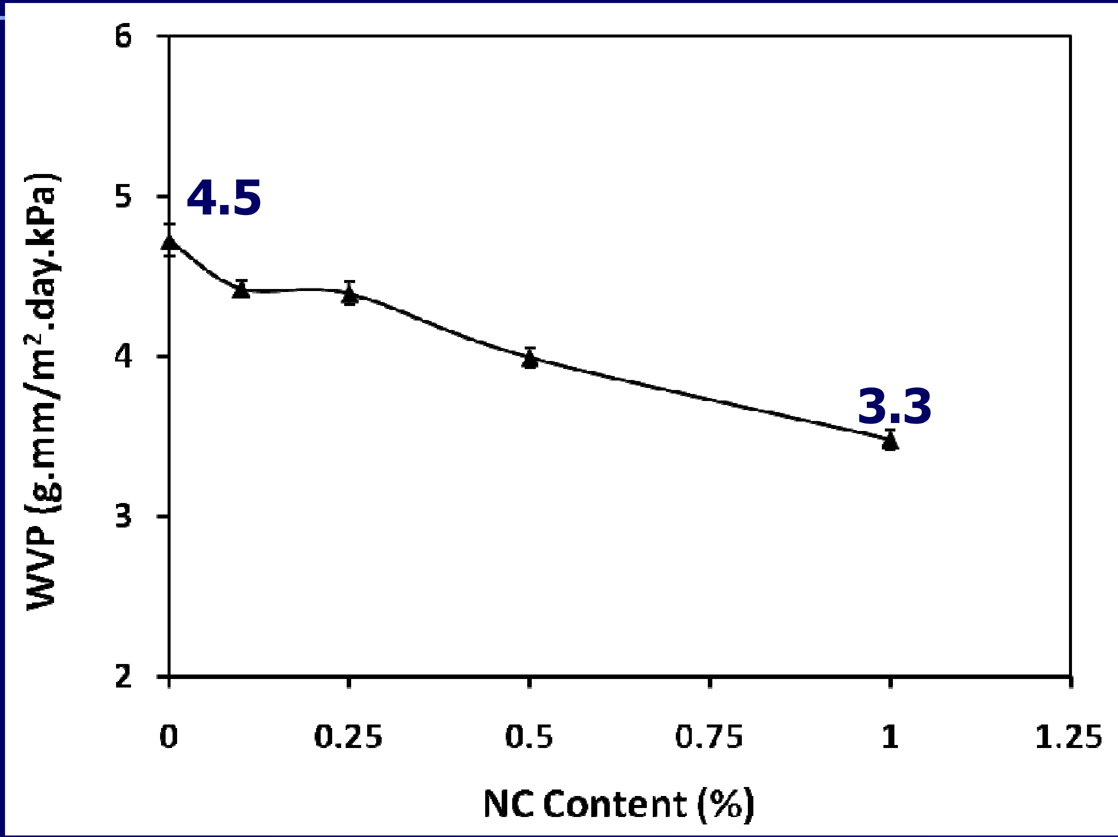
A monotonous decrease of viscoelasticity coefficient was observed with an increase of NC concentrations in MC-based formulation.

Effect of Chitosan on Viscoelasticity Coefficient of MC-Based Films



It was found that with the increase of chitosan concentration in the MC-based films, viscoelasticity coefficient values increased linearly.

Effect of NC on Water Vapor Permeability (WVP) of MC based films

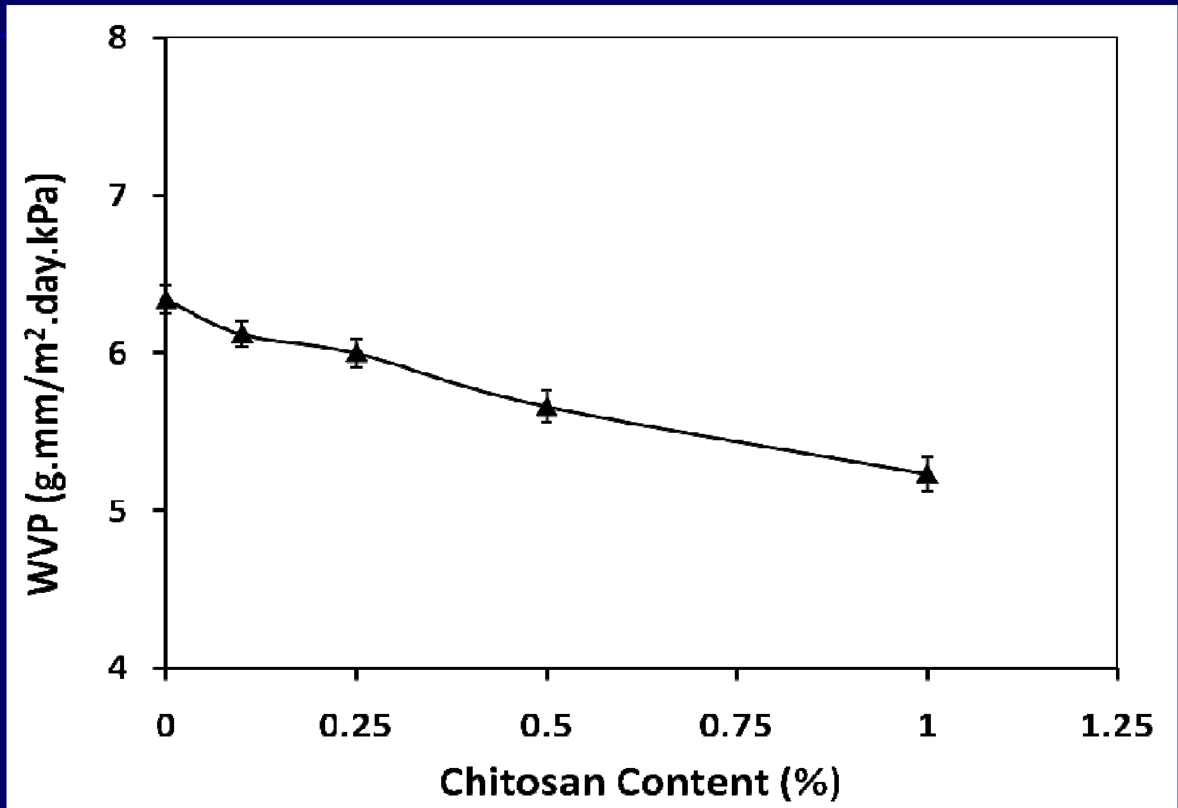


At 25℃ and 60% RH
For 24 h

ASTM -Method: 15.09:E96

A 26% reduction of WVP was obtained at 1% NC solution incorporation in MC-based films

Effect of Chitosan on Water Vapor Permeability (WVP) of MC-Based Films



A 26% reduction of WVP was obtained at 1% Chitosan solution incorporation in MC-based films

Effect of Gamma Radiation on mechanical properties: NC-MC based films

Dose	Puncture Strength (N/mm)	Puncture Deformation (mm)	Viscoelasticity Coefficient (%)	WVP (g.mm/m^2.day.kPa)
0	319 ± 16 [a]	4.4 ± 0.3 [a]	36.8 ± 0.9 [a]	5.9 ± 0.2 [a]
0.5	**346 ± 15 [b]**	4.4 ± 0.2 [a]	36.2 ± 1.2 [a]	5.9 ± 0.1 [a]
1	338 ± 12 [b]	4.5 ± 0.2 [a]	**33.1 ± 0.2 [b]**	5.9 ± 0.3 [a]
5	318 ± 19 [a]	4.4 ± 0.1 [a]	33.1 ± 0.8 [b]	5.3 ± 0.2 [a]
10	309 ± 22 [a]	4.3 ± 0.2 [a]	33.1 ± 1.2 [b]	**5.0 ± 0.1 [b]**
25	286 ± 15 [c]	**4.2 ± 0.2 [b]**	33.1 ± 0.5 [b]	4.8 ± 0.2 [b]
50	256 ± 23 [d]	4.2 ± 0.2 [b]	33.0 ± 1.0 [b]	**4.2 ± 0.2 [b]**

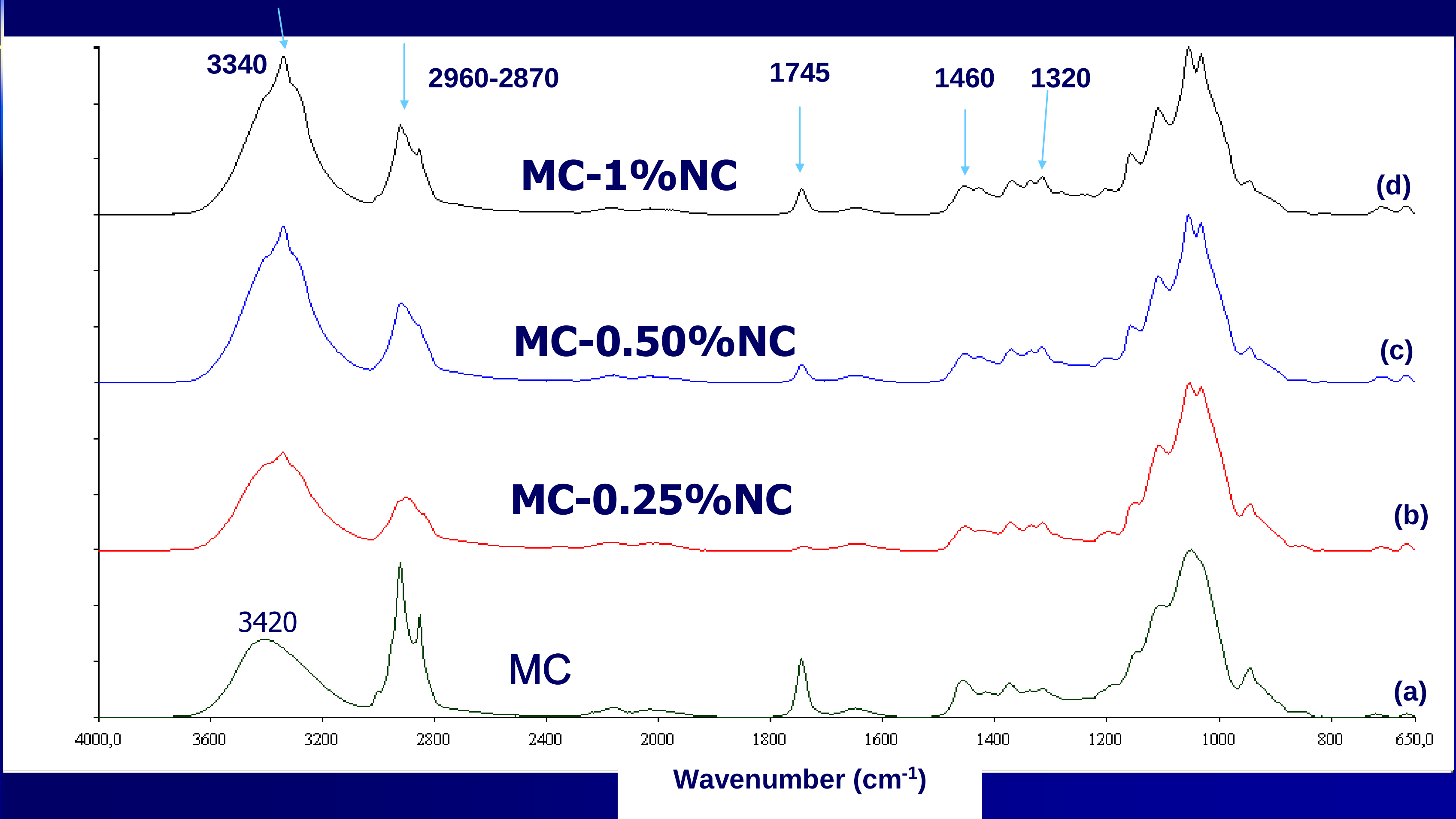
[a] Means followed by the same letter in each column are not significantly different at the 5% level.

Effect of Gamma Radiation Chitosan-MC based films

Dose	Puncture Strength (N/mm)	Puncture Deformation (mm)	Viscoelasticity Coefficient (%)	WVP ($g.mm/m^2.day.kPa$)
0	312 ± 11 d	5.0 ± 0.3 c	44.1 ± 0.3 d	6.0 ± 0.1 a
0.5	311 ± 8 d	5.3 ± 0.1 c	44.2 ± 0.2 d	6.1 ± 0.2 a
1	309 ± 9 d	5.1 ± 0.3 c	44.1 ± 0.4 d	5.8 ± 0.2 a
5	287 ± 11 c	4.6 ± 0.3 b	40.3 ± 0.2 c	5.8 ± 0.1 a
10	253 ± 15 b	4.6 ± 0.2 b	40.1 ± 1.3 c	6.0 ± 0.1 a
25	233 ± 12 b	4.5 ± 0.3 b	37.1 ± 0.4 b	5.8 ± 0.3 a
50	201 ± 10 a	4.0 ± 0.4 a	32.0 ± 1.2 a	5.8 ± 0.4 a

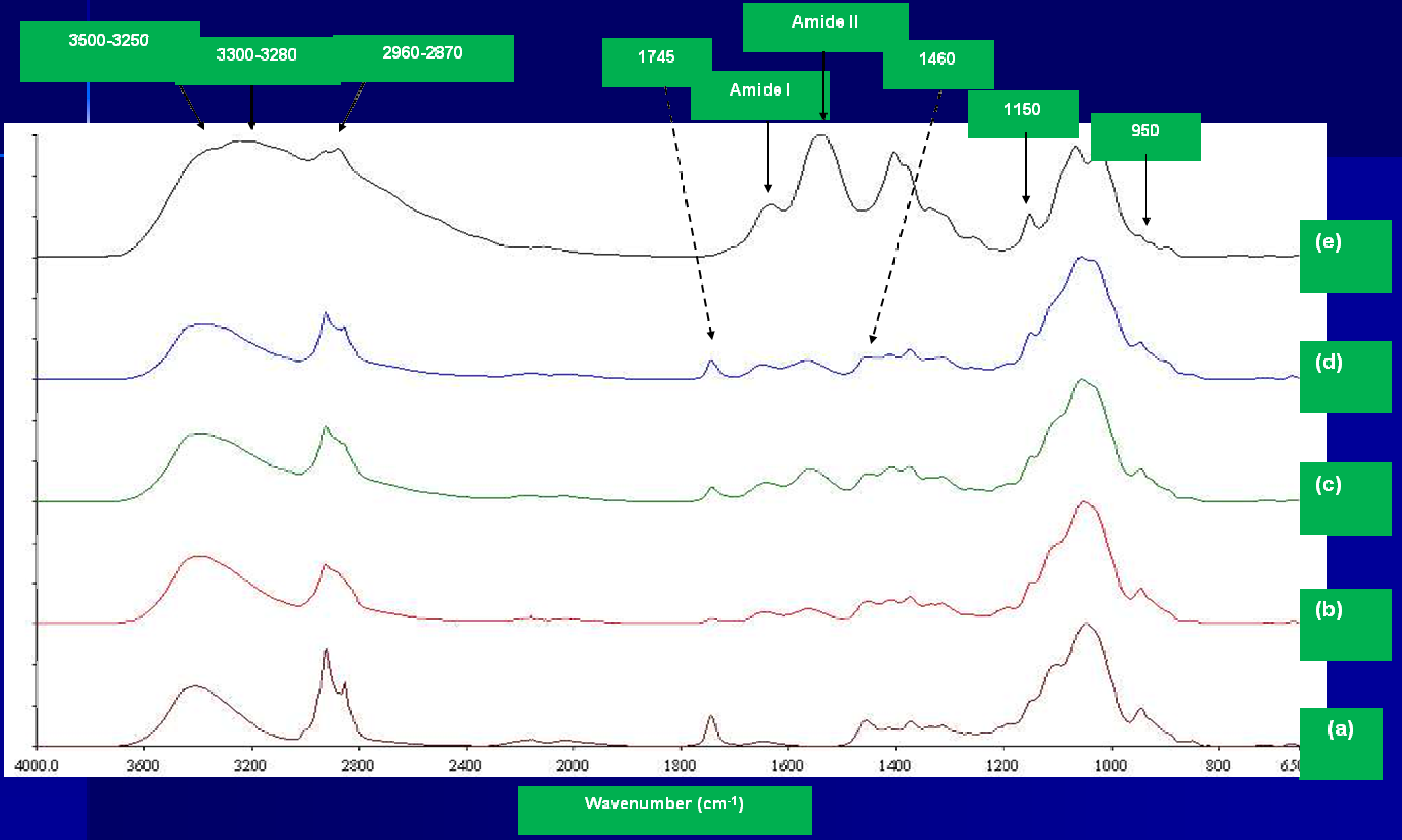
[a] Means followed by the same letter in each column are not significantly different at the 5% level.

FT-IR Analysis of the Films
NC-MC based films



FTIR spectra of MC- (a) and (MC+NC)-based films containing 0.25% (b), 0.5% (c), and 1% NC (d) respectively.

FT-IR Analysis of the Chitosan-MC based Films

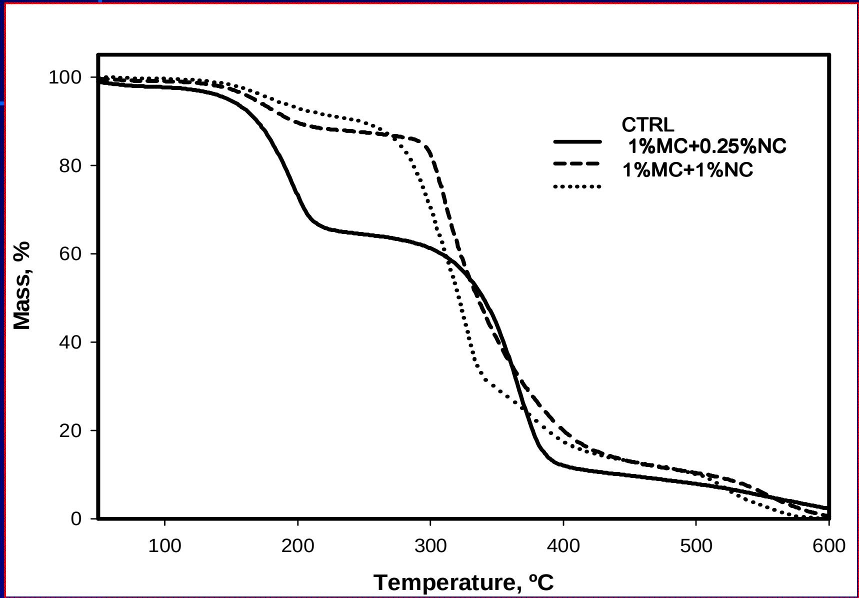


FTIR spectra of MC (a) Chitosan (b) (MC+Chitosan)-based films containing 0.25% (c), 0.5% (d), and 1% Chitosan (e) respectively.

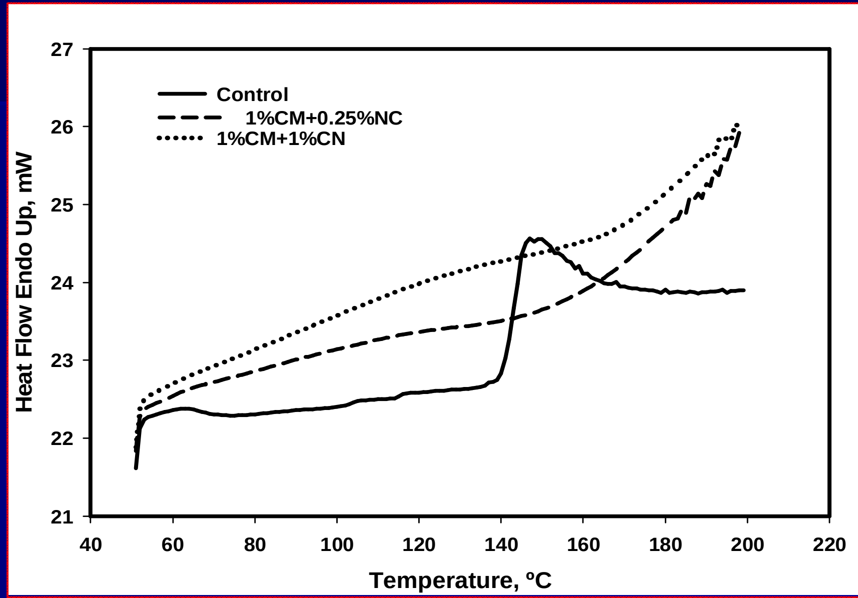
Effect of NC on DSC Thermograms Properties of MC-Based Films:Effects of NC

TGA Spectrum

TGA



DSC



DSC Spectrum

The control sample exhibited two major degradation steps (200 and 370℃). First decomposition: Vegetable oil. Second decomposition: Glycerol and MC. But NC-containing films found slower degradation.

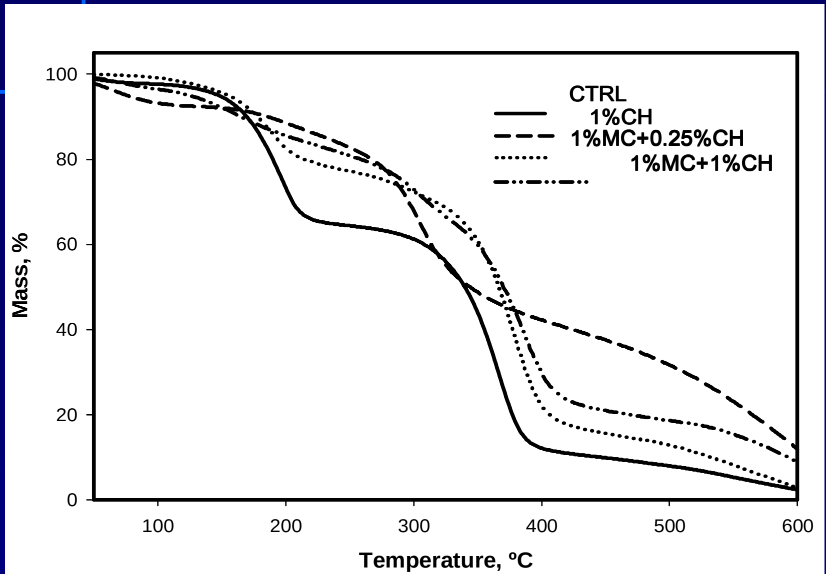
The control sample exhibited a melting peak (150℃) which is associated with evaporation of Vegetable oil. But this peak disappeared for NC-containing films.

NC has a good impact on thermal properties also

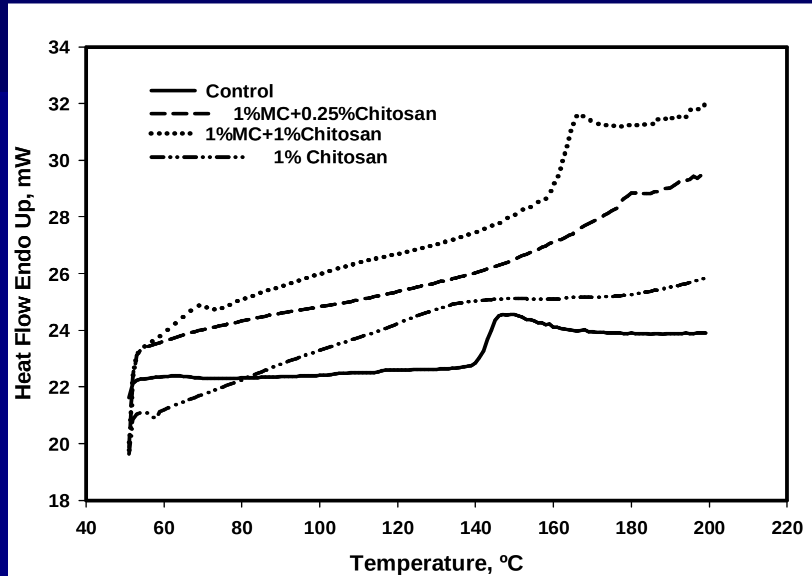
Effect of Chitosan on the DSC Thermograms Properties of MC-Based Films: Effect of Chitosan

TGA Spectrum

TGA



DSC

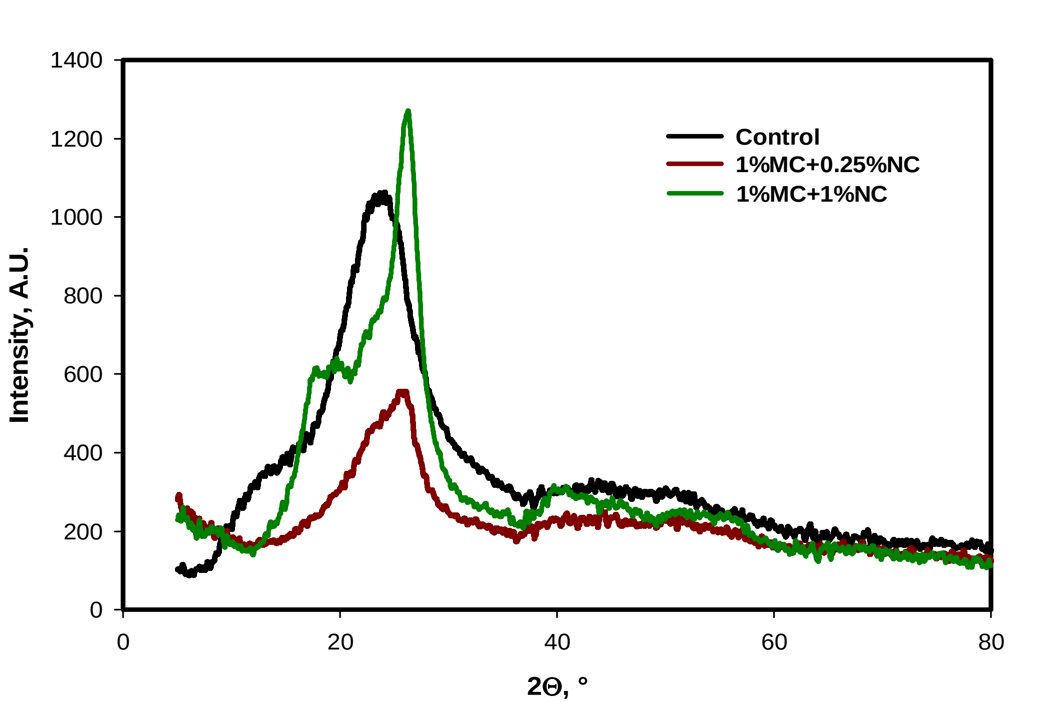


DSC Spectrum

The control sample exhibited two major degradation steps (200 and 370℃).First decomposition: Vegetable oil. Second decomposition: Glycerol and MC. But chitosan containing films found slower degradation.

The control sample exhibited a melting peak (150℃) which is associated with evaporation of Vegetable oil. But this peak disappeared for chitosancontaining films.

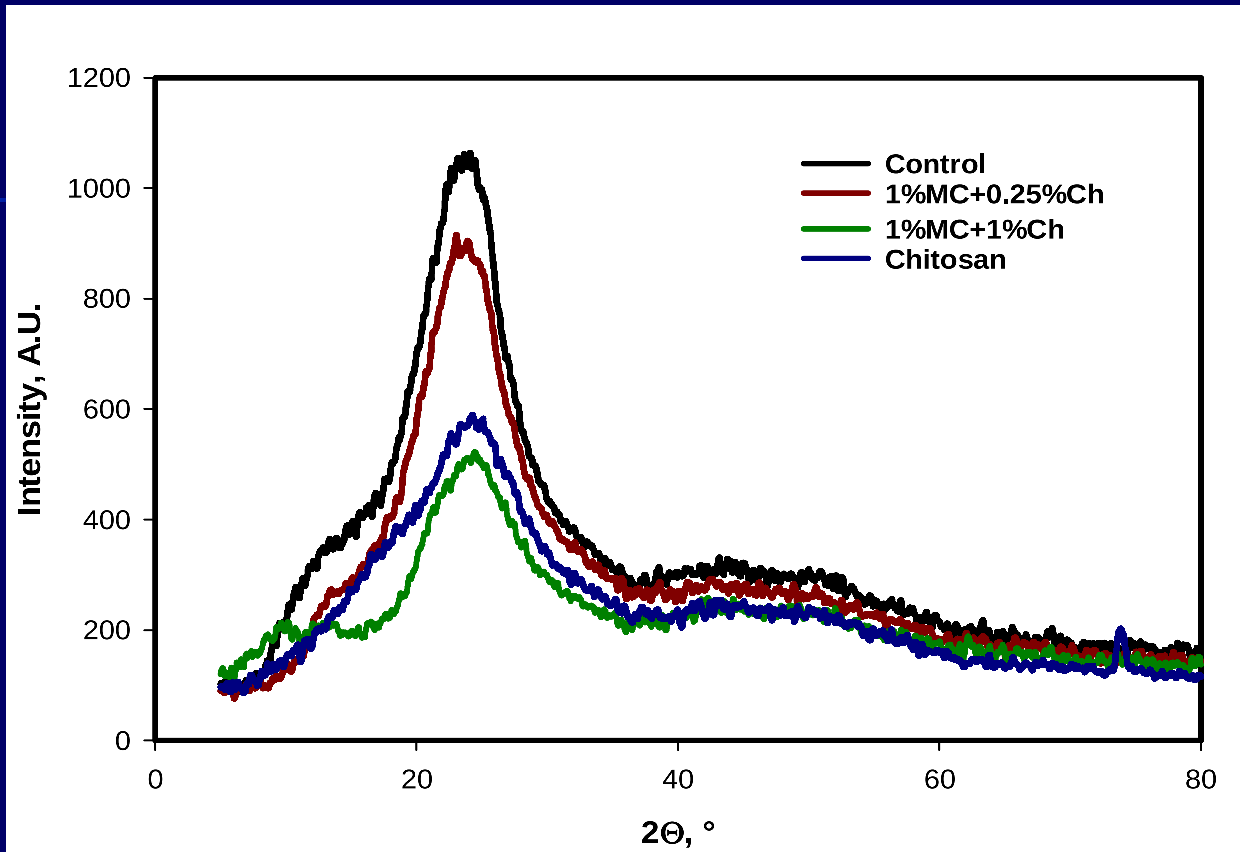
X-RD Analysis of the Films



X-Ray Diffractograms for MC- and (MC + NC)-based films.

Control films showed a broad halo which reflected the amorphous nature. Also, films containing lower amounts (0.25%) of NC exhibited similar patterns, but films containing 1% NC showed some crystalline peaks, which may be attributed to the NC fibers into the MC-based formulation.

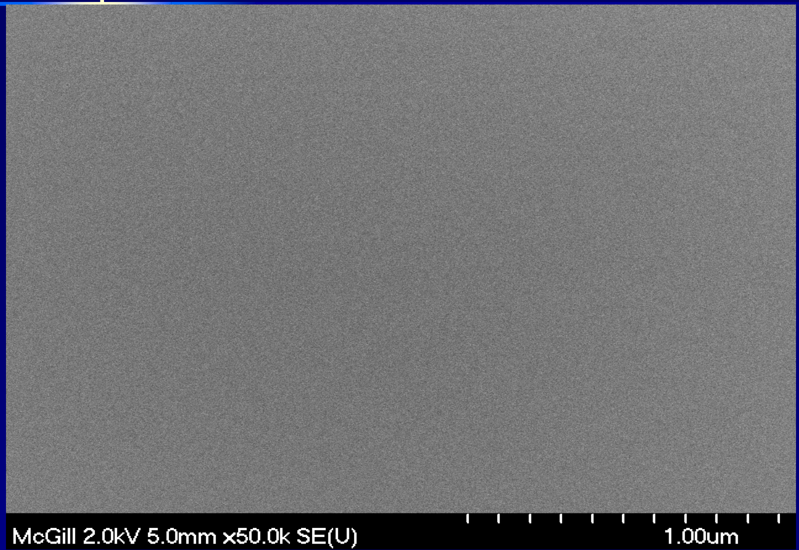
X-RD Analysis of the Films



X-Ray Diffractograms for MC- and MC + Chitosan-based films.

Control films showed a broad halo which reflected the amorphous nature. Also, films containing chitosan exhibited similar patterns.

Effect of NC on the Morphological Properties of MC-Based Films

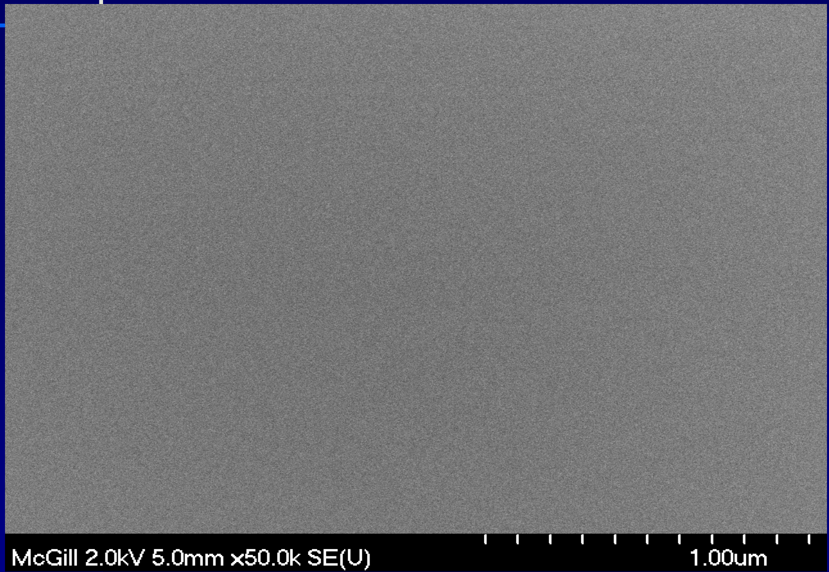


SEM Image of MC-Based Films

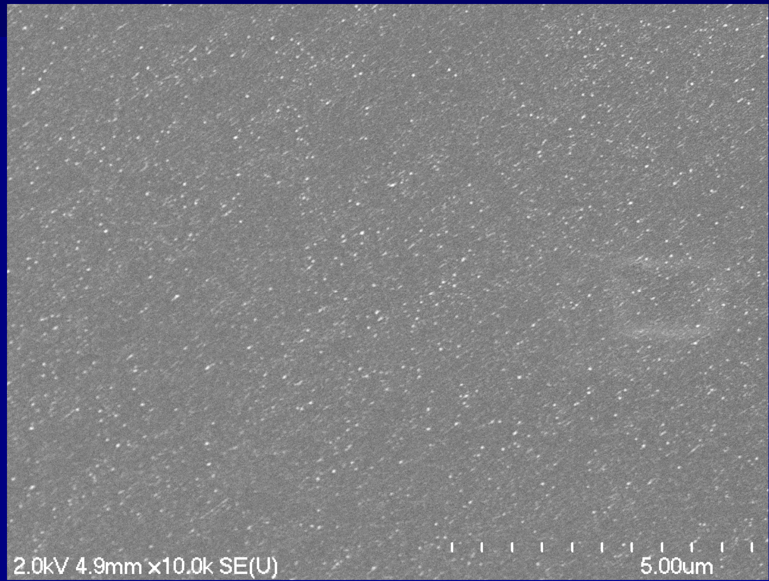
MC+NC (0.25%)-Based Films

The surface of MC-based films was found quite smooth. But surface smoothness was significantly affected after NC incorporation since the NC fibers are clearly visible at the film surface. These figures suggesting that NC fibers have kept much of their original properties. Thus, NC acted as a good reinforcing agent.

Effect of Chitosan on the Morphological Properties of MC-Based Films



SEM Image of MC-Based Films



MC+Chitosan (0.25%)-Based Films

The surface of MC-based films was found quite smooth. But surface smoothness was significantly affected after chitosan incorporation. Moreover, the surface of films containing chitosan appears to be rougher and more dense. Thus, chitosan acted as a good reinforcing agent.

Conclusion

γ-irradiation and graft copolymerization

- enhanced the compatibility and improves the film formation
- Improve the physico-chemical and barrier properties (WVP) of the films
- SEM analysis of the film surface suggested also better films appearance

CONCLUSIONS

Addition of NC or Chitosan content in MC-based films

allowed increasing the physico-chemical and barrier properties of the films.

Significantly improved the thermal stability.

NC-MC or Chitosan-MC based films exposed to gamma radiation improve significantly the barrier properties with a minor decrease of PS.

ACKNOWLEDGEMENT

- International Atomic Energy Agency (IAEA) for financial support for a fellowship and a training support offered to Dr Ruhul A. Khan, Bangladesh Atomic Energy Commission

- Nordion, Canada for irradiation procedures.

- Natural Sciences and Engineering Research Council of Canada (NSERC) through the RDC program and by a research contract under a research agreement with FP Innovation (Pointe-Claire, Quebec, Canada).

- Winpak (Winnipeg , MB , Canada) for providing the packaging material.

- Mrs. Line Mongeon, Technician of Biomedical Engineering Department, University of McGill for SEM support.

Thank you

Monique Lacroix

INRS-Institut Armand-Frappier

Canadian Irradiation Centre

531 des prairies

Laval

Québec, Canada H7V 1B7

Email: monique.lacroix@iaf.inrs.ca

Tel 1 450 687 5010 ext 4489