How cottonseed protein concentrate can form a film ?

FINAL WORKSHOP OF THE PROJECT COTONBIOMAT
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PROTEIN-BASED BIODEGRADABLE MATERIAL MANUFACTURE

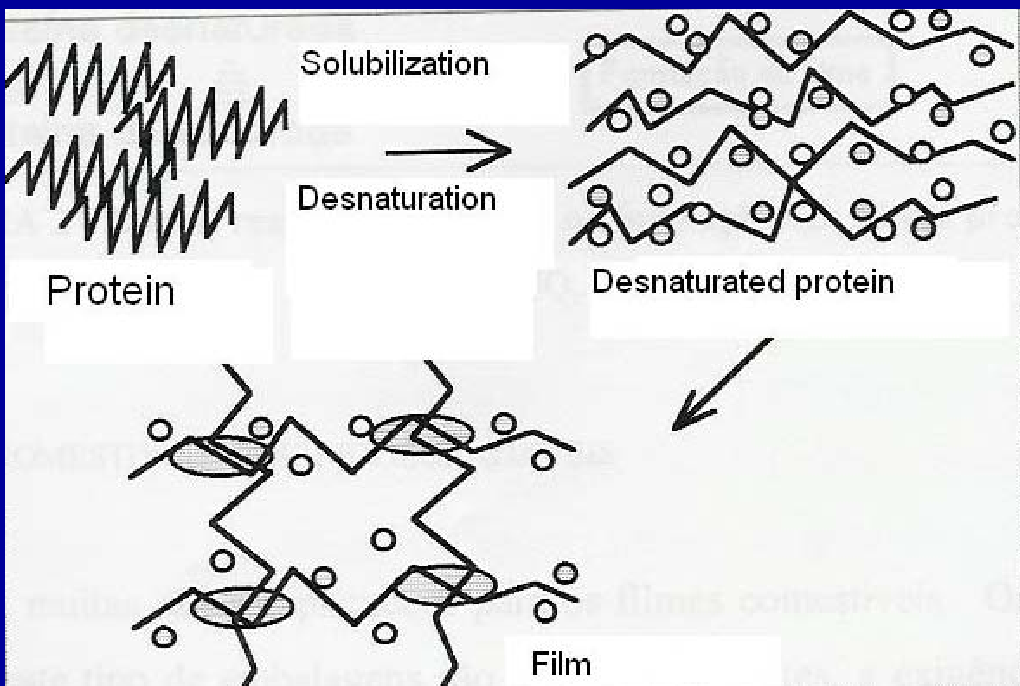
- **Wet processing technologies**
- **Low-moisture processing technologies**

FILM FORMATION

One component able to form a suitably cohesive and continuous matrix

Involved inter- and intra molecular associations or cross-linking of polymer chains

FILM FORMATION



Font: Cuq, 1993

Fomation a semi-rigid 3D network that entraps and immobilizes the solvents

Degree of cohesion

- Polymers structure
- Solvent used
- Temperature
- Type of plasticizer
- Presence of other molecules
- Degree of crosslinking

Formulation of protein based film

Incorporation of a plasticizer to avoid brittleness → **Decrease in the molecular forces**

Solution: increase of the degree of crosslinking

PROTEIN CONTENT

Flour cottonseed

PB = 32.5 g/100g of dry matter

COTPROT solution

PB = 56.3 g/100g of dry matter

ADDITIVES

Crosslinking agents

Glutaraldehyde

Glyoxal

Plasticizers

Ethylene glycol
Propylene glycol
Glycerol
Diethylene glycol
Sorbitol
Polyethylene glycol 300
Polyethylene glycol 400

PLASTICIZERS : MOLAR CONCENTRATIONS AND MOLECULAR MASS

Plasticizer type	Formula	MW	mol plasticizer / 100g dry matter	g Oxygen / 100g dry matte	mol Oxygen in plasticizer / 100g dry matter
Ethylene glycol	$C_2H_6O_2$	62	0.32	10.32	0.166
Prolpylene glycol	$C_3H_8O_2$	76	0.26	8.42	0.111
Glycerol	$C_3H_8O_3$	92	0.22	10.43	0.113
Diethylene glycol	$C_4H_{10}O_3$	106	0.19	9.06	0.085
Sorbitol	$C_6H_{14}O_6$	182	0.11	10.55	0.058
PEG 300	$H(OCH_2 - CH_2)_6 OH$	300	0.07	7.47	0.025
PEG 400	$H(OCH_2 - CH_2)_8 OH$	400	0.05	7.20	0.018

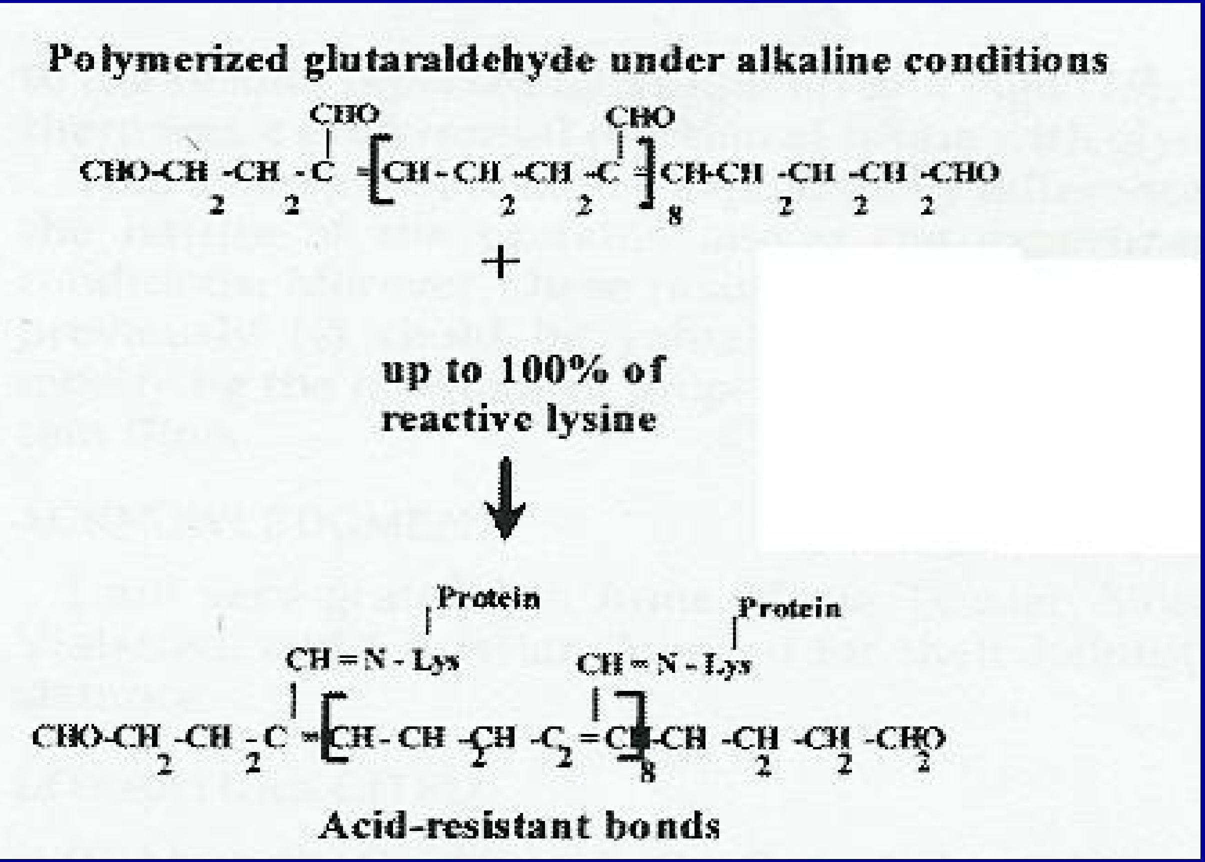
COTTONSEED CROSSLINKED FILMS PRODUCTION

COTPROT → COTPROT dry matter determination

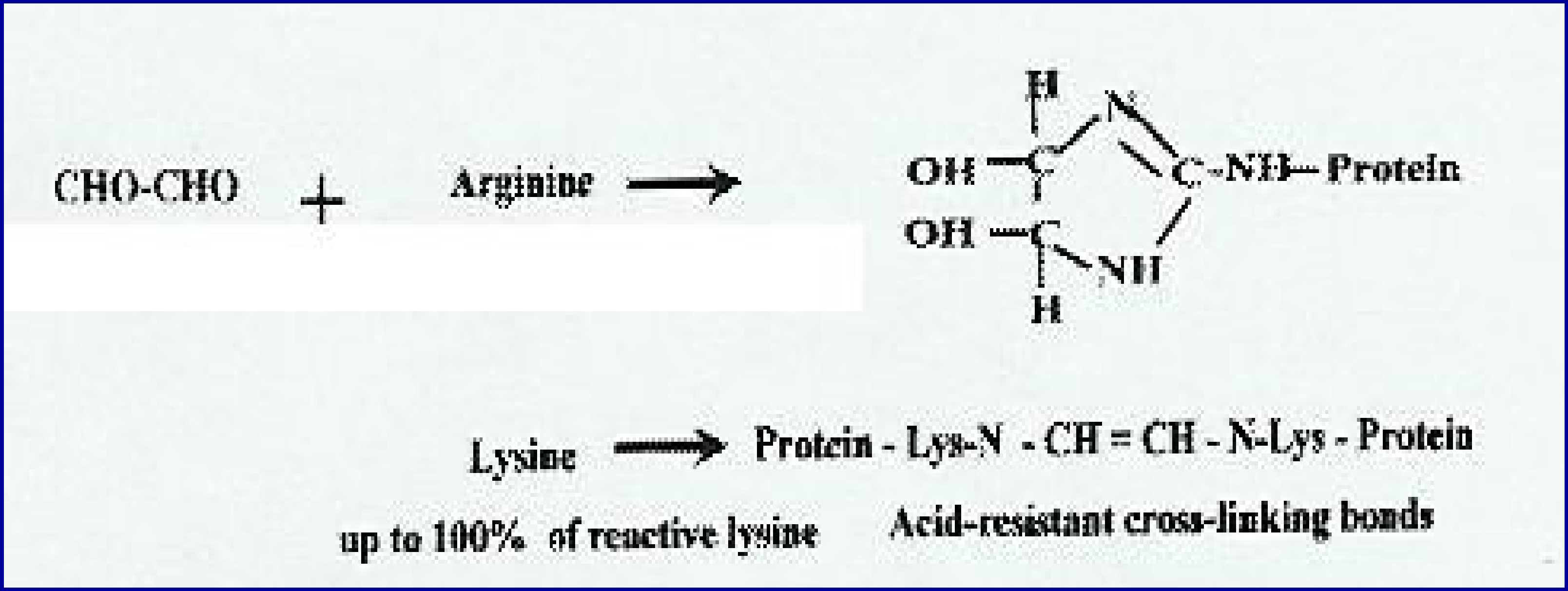
1. COTPROT
2. Glutaraldehyde or glyoxal addition
3. Agitation
4. Plasticizer addition
5. Agitation
6. Casting in suport
7. Drying

Drying → Films conditioned in NaBr (25^{0}C) for 72h

Postulated mechanism of protein cross-linking by glutarldehyde (Marquié, 2001)

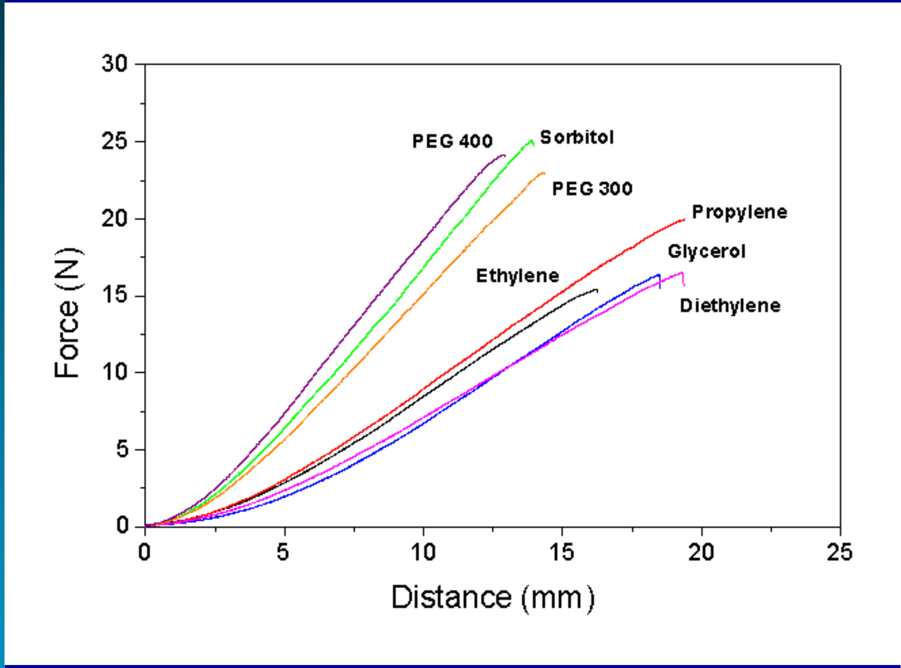


Postulated mechanism of protein cross-linking by glyoxal (Marquié, 2001)

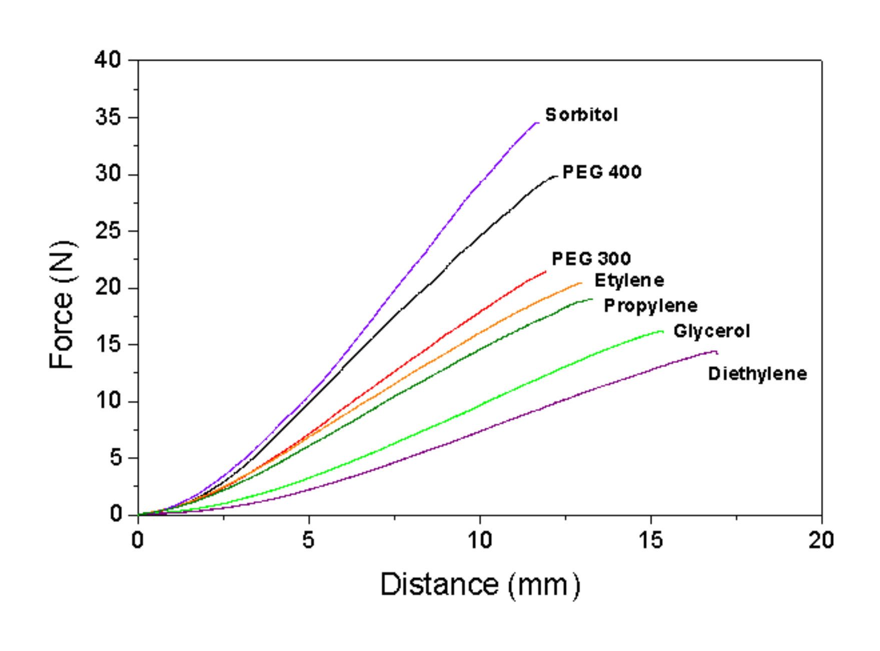


EXAMPLES OF PUNCTURE CURVES

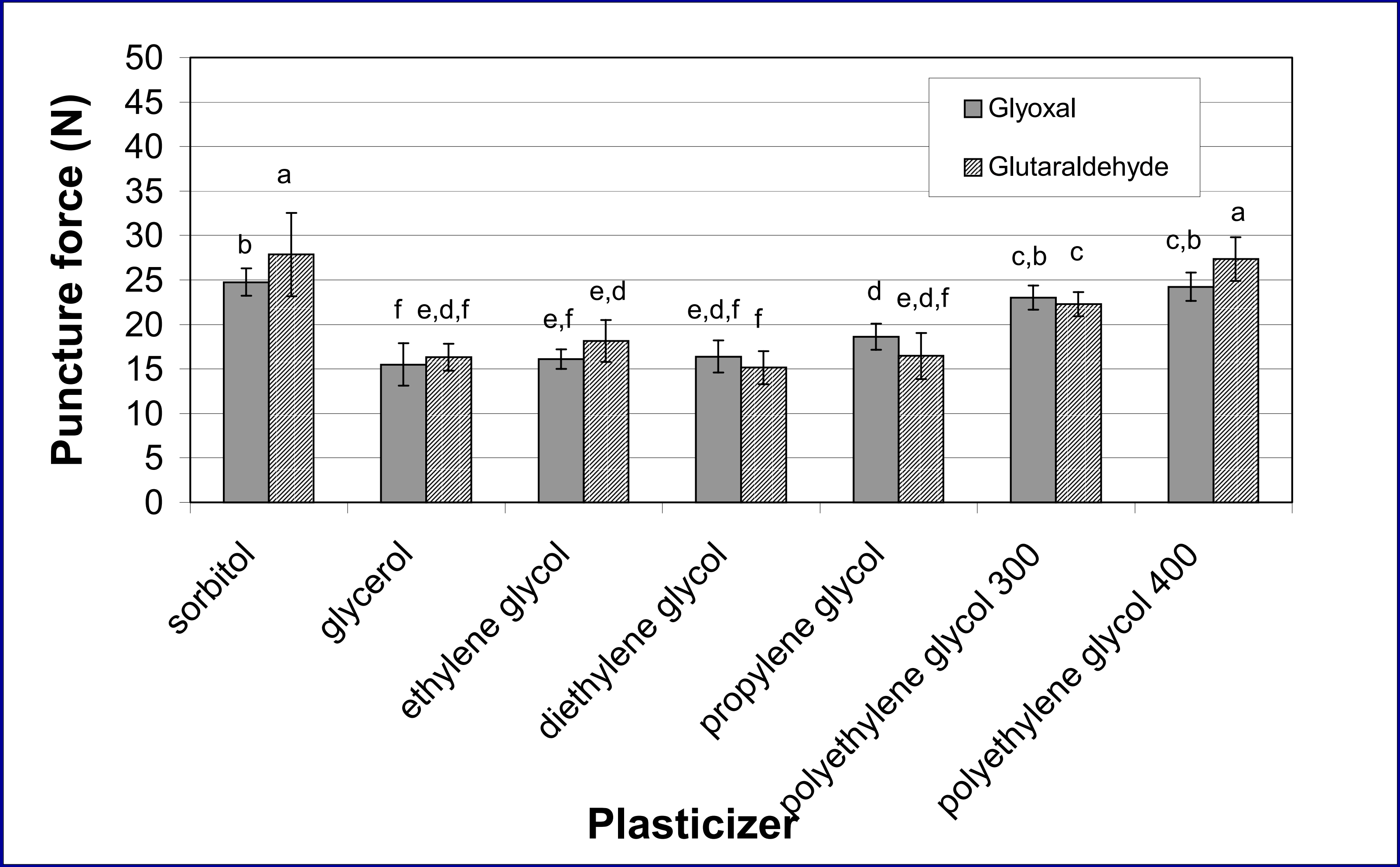
Glyoxal



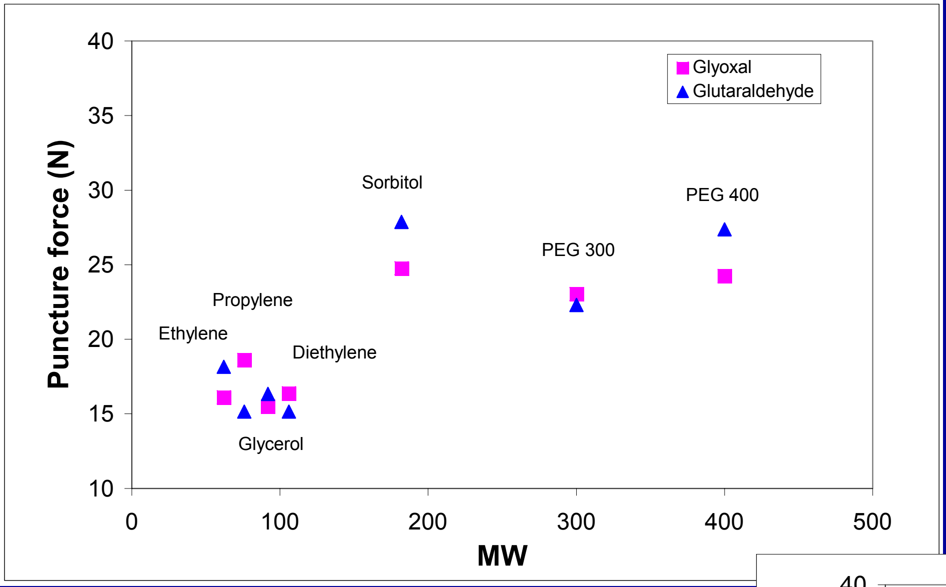
Glutaraldehyde



EFFECT OF PLASTICIZER ON PUNCTURE FORCE



Puncture force as function of: molecular weight of the plasticizer and molar concentration of plasticizer



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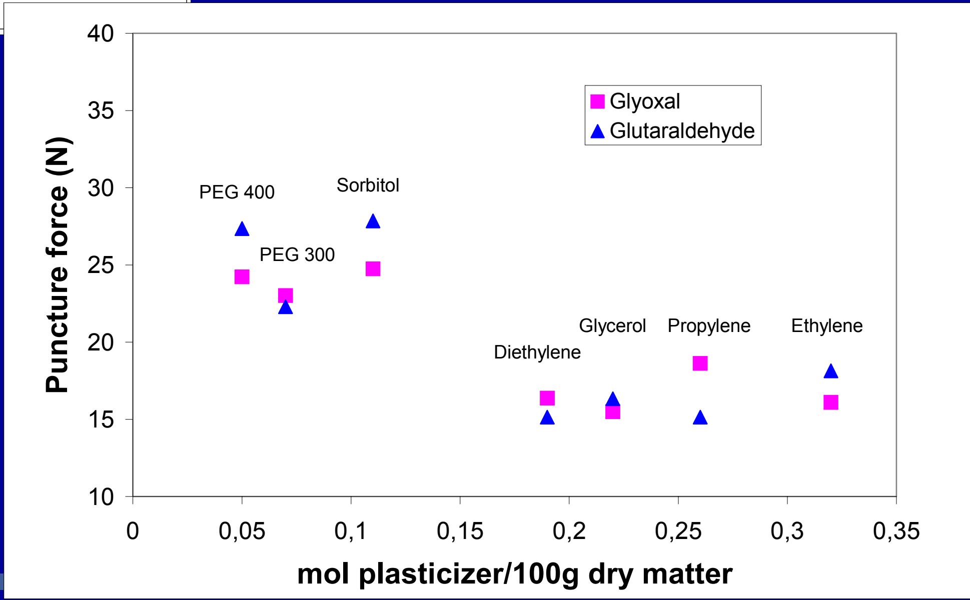
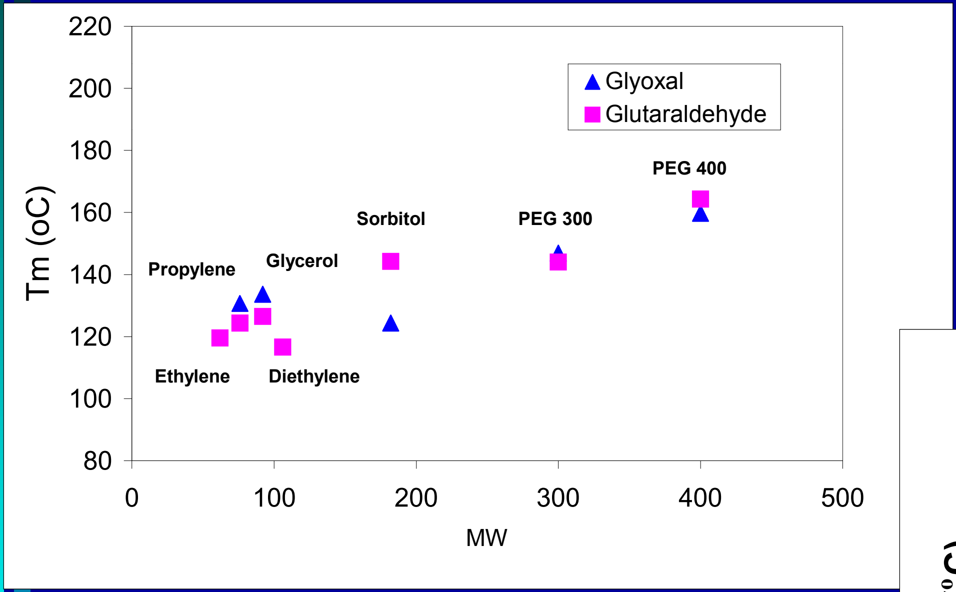
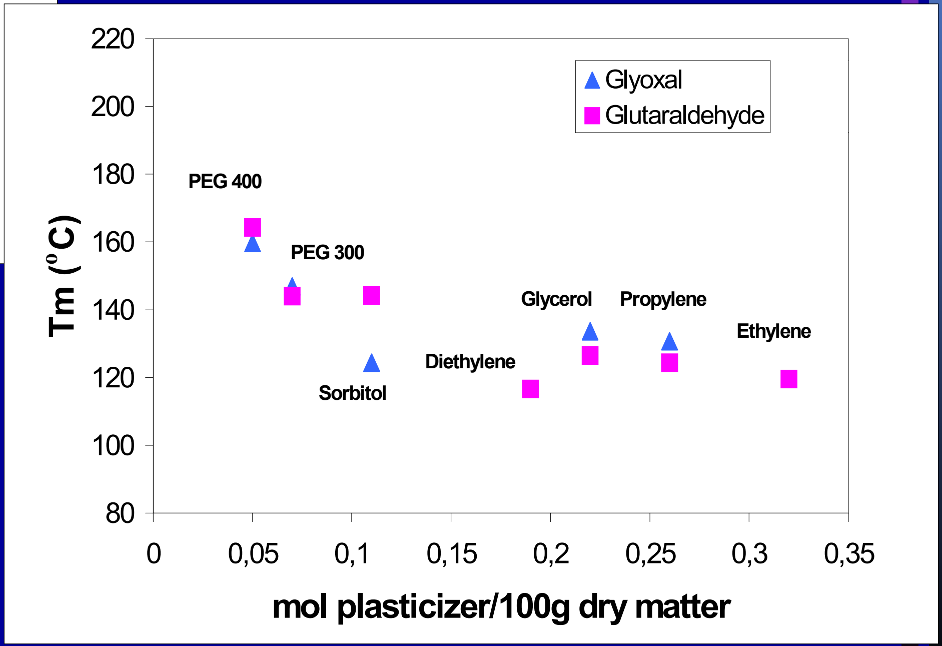
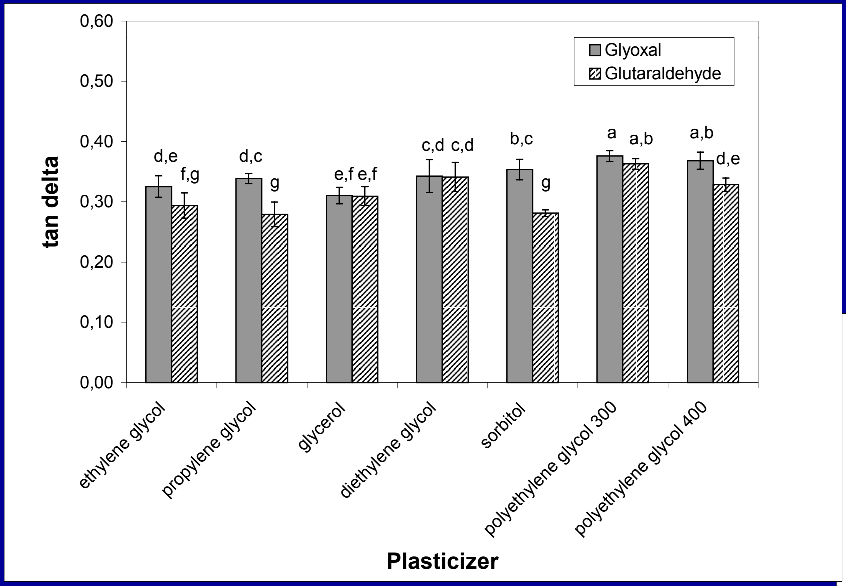


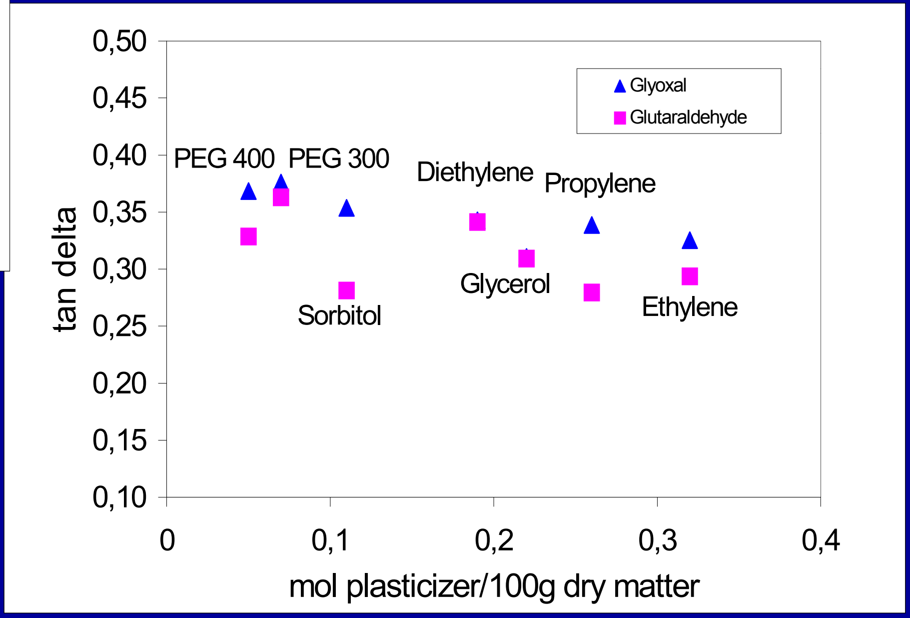
Melting temperature (Tm) as function of: molecular weight of the plasticizer and molar concentration of plasticizer





Effect of the type of plasticizer on Loss modulus (MPa) of glutaraldehyde and glyoxal cross-linked cottonseed protein films



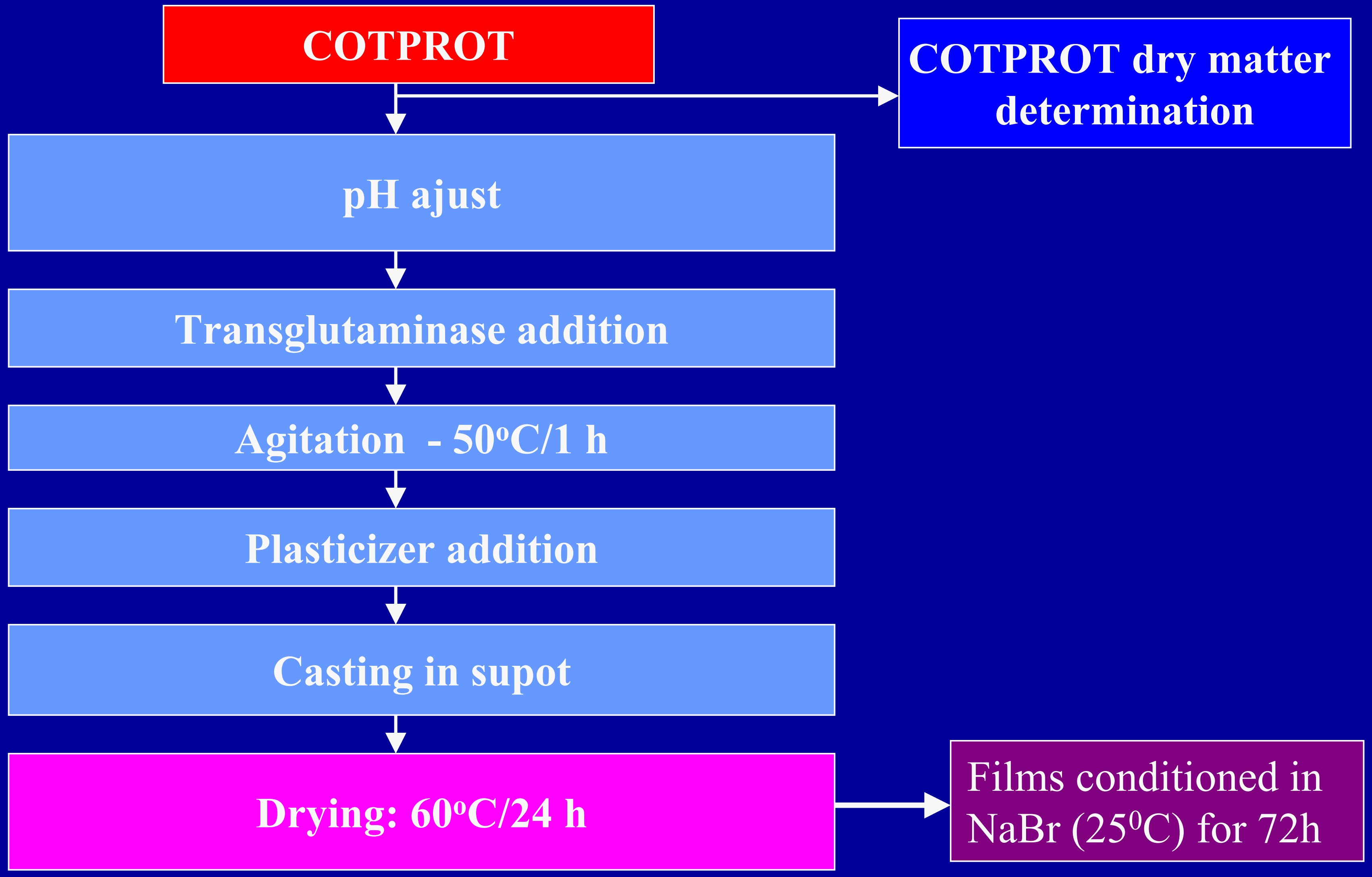


TRANSGLUTAMINASE CROSSLINKED FILM

Properties

Puncture force - 4.46±0.56 N -	L^* - 35.3±3.5
Puncture deformation - 12.33±0.99 %	a^* - 31.2±1.4
Tensile strength - 0.27±0.03 Mpa	b^* - 54.6±4.1
Deformation at break - 100.58±21.80 %	ΔE^* - 86.2±0.8
Elastic modulus - 0.023±0.007(MPa)	Opacity - 23.4±2.3

FILM PRODUCTION USING TRANSGLUTAMINASE



CONSIDERATIONS

- **In relation to the cross-linking agent, an interesting, is the increasing of viscosity during cross-linking observed when gluraraldehyde is used contrary to the glyoxal.**

- **The viscosity of the filmogenic solution after the crosslinking reaction with transglutaminase did not increased.**

Reactive Lysine Content (by CIRAD) of the Cottonseed Flours

	Reactive lysine (g/100g dry matter)	
Flour	**Repetitions**	**Average value**
September/2003	0.92	
	0.89	
	Solubilization 12h, T = ambient - 0.96	
	Solubilization 12h, T = ambient - 1.28	1.06 ± 0.17
	Solubilization 48h, T = ambient - 0.89	
	Solubilization 48h, T = ambient - 1.30	
	Solubilization 48h, T = 4 ^{o}C - 1.08	
	Solubilization 48h, T = 4 ^{o}C - 1.14	
October/2003	0.76	
	1.26	1.12 ± 0.28
	1.03	
	1.41	
November/2003	0.79	
	1.24	
	0.98	1.02 ± 0.17
	0.97	
	1.12	

Critical point in Film Production by Casting Technique

Significant variation on the solution viscosity