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CHEMICAL MODIFICATION OF UREA-FORMALDEHYDE RESIN

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ABSTRACT

In this study, the effects of the concentration of some additives (ethylene glycol, glycerol, poly (vinyl alcohol) PVA, and starch) on some physical properties (shelf life time) of uncured urea formaldehyde resin (UF) and on some of mechanical properties of cured urea formaldehyde were determined. It has been found that the elasticity of cured resin increases with increasing the amount of (ethylene glycol, glycerol and PVA.). However, it decreases with increasing of the amount of starch. Whereas the elasticity has been improved, fracture resistance decreases with increasing the concentration of ethylene glycol, glycerol and PVA and increases with increasing the amount of starch. When Glutardialdehyde, was added with ethylene glycol, glycerol and PVA, the stress of fracture resistance has been improved with maintaining the elasticity gained by these additives. Also, with these additives the shelf life of uncured – UF has been increased. The best results were obtained in case of ethylene glycol.

Keywords: Urea formaldehyde, PVA, Glutardialdehyde, shelf life,

1. INTRODUCTION

The term amino plastics have been coined to cover a range of resinous polymers produced by interaction of amines or amides with aldehydes. Amino plastics include various polymers of this type that have been produced there are two of current commercial importance in the field of plastics, the urea-formaldehyde and the melamine-formaldehyde resins [**Baun, et al. (2005)**]. Of the various amino-resins that have been prepared, the urea-formaldehyde (UF) resins are by far the most important commercially, and urea - formaldehyde resin comprise about 80 % of the amino resins produced worldwide. Like the phenolic resins, they are, in the finished product, cross-linked thermoset which are insoluble, infusible materials. For application, a low molecular weight product or resin is first produced and this is then cross-linked only at the end of the fabrication process. In a general comparison with phenolic resins, the use of urea- formaldehyde resins as a major adhesive by the forest products industry is due to a number of advantages, including low cost (cheaper), ease of use under a wide variety of curing conditions, low cost temperature, water solubility, resistance to microorganisms and to abrasion, hardness, excellent thermal properties, light in color, especially of the cured resins, lacking in odor, and have better resistance to electrical tracking but have an inferior heat resistance and higher water absorption **[Brydson, (1995,1997)]**. UF is known long time ago so, a great number of studies has been carried out to improve its applications, properties and decrease its disadvantages. Thus, UF is used in manufacturing of artificial woods from different raw materials **[Daisy Biswas, (2011)]**. Modifications of UF have been carried out in order to decrease the formaldehyde emission **[Boran, (2011)]**. UF has been also modified in order to increase its water resistance **[Byung-Dae Park, (2011)]**. and for preparation of carbon dioxide adsorbents **[Drage, et al., (2007)]**. UF could be use also used as a continuous bed in chromatographic column **[Xuefei Sun & Zhikuan Chai (2002)]** and to prepare monodispersed polymeric microcapsules **[Kubota, et al., (2007)]**. The most important disadvantage of UF is the short shelf life of uncured- UF and the elasticity deficiency of cured-UF., Improving the storage life properties of UF makes it more significant commercially and industrially important material in manufacturing and applications.

2. EXPERIMENTAL

2.1. Materials and techniques

- Urea formaldehyde (UF) Manufactured by: **"Mansoura for Resins & Chemical Industries Co. (MRI)"** (El-Mansoura- Egypt). Ethylene glycol, (HOCH2CH2OH, Liquid, m.p.-13°C, b.p.196-198°C, d. 1.113, EL Nasr Pharmaceutical Chemicals CO., Abu Zaabal, EGYPT.). Glycerol, (HOCH2CH(OH)CH2OH, Liquid, b.p. 182°C, d. 1.260, EL

Nasr Pharmaceutical Chemicals CO., , Abu Zaabal, EGYPT) Poly vinyl alcohol (PVA [-CH2CH (OH)-]**n**, Poly(vinyl alcohol) PVA 8-88(Mw_67,000 mol/g, degree of hydrolysis 86.7-88.7 mol.%); Fluka.

PVA (soln. 6%), was prepared by adding 12 gm of solid PVA to 200 ml distilled water in water bath and heated at 80° C, , with stirring until complete dissolution.
- Starch powder). (Commercial)
Some technical characteristics belonging to UF are given in Table 1.

Table (1): Technical characteristics of used Urea- Formaldehyde.

Test	Unit	Result
Appearance		Milky Liquid
Solid Content	%	60.5
Gel. Time	sec.	60
pH at 20 ° C		8.3
Viscosity	cps	385

UF Samples were prepared by mixing UF with the additives and with ammonium chloride (NH_4Cl, 20 wt % soln.) used as a hardening agent and was added into the liquid UF in 5 vol. % ratio. Each was added into UF in two concentrations, low concentration 0, 1, 2, 3, 5, 10 vol. % and high concentration 0, 5, 7.5, 10, 12.5, 15. Vol. % in presence and in absence of glutardialdehyde added as crosslinking agent..

The solution of each sample was poured in clean and dried stainless steel mould and left until complete curing under room temperature. The samples have the dimension of the mould (270x20x15 mm). The prepared samples should have smooth surfaces and without any notches at their edges.

2.2. Measurements

1-Bending tests of samples were carried out according to ASTM: D 790 "Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials" the following equation has been used in the bending strength calculations:

$$\sigma e = 3FL / 2ba^2 \ (N/mm^2)$$

Where σe is the bending stress (N/mm^2), F the max. force at the moment of breakage, L the distance between points of support (mm), b the width and a is the thickness of the sample piece (mm).
Flexural modulus was calculated according to the following equation;

$$EB = L^3m / 4ba^3 \ (N/mm^2)$$

Where EB, is the modulus of elasticity (N/mm^2) and m is the slop of tangent of stress - strain curve of bending.

2- Shelf life measurements were conducted in the laboratory circumstances until gelling of the resin occurred.

3. RESULTS AND DISCUSSION

1. Effect of additives on Bending strength and modulus of elasticity of UF resin

The values of the modulus of elasticity in presence of the additives were expressed as a ratio of that of the blank sample. This helps to determine the effect of different concentrations of the additives in UF in on the modulus of elasticity (i.e. on the elasticity of cured samples). The results obtained are given in Table 2.

From Table 2It can be seen that the modulus of elasticity of samples decreases with increasing the concentration ethylene glycol, glycerol and PVA. In case of starch, opposite effects have been detected. for instance, the samples becomes more brittle.

Table (2): Effect of additives on modulus of elasticity.

% of Additive	Ethylene Glycol, Modulus, %	Glycerol, Modulus, %	PVA Modulus, %	Starch, Modulus, %
0.0	100.00	100.00	100.00	100.00
5.0	98.86	99.96	84.36	106.62
7.5	98.12	89.47	78.94	110.13
10.0	83.60	76.46	67.12	112.28
12.5	78.55	69.99	67.38	116.47
15.0	68.06	60.34	57.62	120.66

2- Effects of modifiers on the bending stresses of samples

The changes in the tensile stress of the samples under the effect of investigated additives are shown in Table 3.It can be seen that the stress increases firstly up to certain concentration of the additive and then the stress decreases after that. This behavior is shown obviously in the case of using ethylene glycol and glycerol. Effects of Glutardialdehyde in this case on the stresses and elasticity of cured urea formaldehyde in presence of high concentration s of ethylene glycol and glycerol are shown in Table 4. Such increase could be attributed to the possible additional crosslinks between bihydroxyl (ethylene glycol) and trihydroxyl (glycerol) with glutardialdehyde and the resin. This can be represented as follows:

Glycerol or (ethylene glycol) --- OCH--------CHO -- Resin OCH---CHO----Glycerol

It is seen that, by the addition of high concentration of modifier (10 vol. %) the stress decreases and the elasticity increases (the value of modulus of elasticity decrease) with each modifier due to the increase of crosslinking density of the resin. However, with the addition of (Glutardialdehyde) with different ratios into modified UF mixture, it has been found that the stress increases and the elasticity still increases. This behavior is shown obviously in the presence of ethylene glycol and glycerol. This behavior may be attributed to the length of crosslinks which should improve the elasticity of the resin as the length increases.

Glutraldialdehyde has two terminal aldehydic group each of them may nearly acts as formaldehyde (or formaldehyde derivatives) leading to expressed similar effect as increasing the concentration of the reactants, hence, increasing the rate of reaction, (i.e., increase the percentage of yield in final cured resin .

Due to the bialdehydic functional group glutraldialdehyde (OHC-CH2-CH2-CH2-CHO), may also, react in a way leading to crosslinking in the final cured resin, where the crosslink contains a straight chain of five carbon atoms, which improves the elasticity in the final cured resin.

3- Shelf life

The Effects of additives on the storage period of UF before gelling starts (known as shelf life) are taken as indication of the effect of each additive. The results are shown in Tables 5and 6.

It can be seen that, the time of gelling of the samples increases with increasing the additive concentration in presence of the hardener. crosslinking agent (Glutardialdehyde) decreases the time of gelling of modified samples see tables 7 and 8. The results of stored and modified UF samples given in table 9 are compromise with the data of times of first curing of modified samples.

Table (3): Effect of modifiers on the stresses of UF samples.

% addition	Ethylene Glycol %	Glycerol %	Starch %	PVA, 6% %
0	100	100	100	100
1	126.64	116.73	179.47	110.55
2	137.75	126.23	203.99	112.71
3	122.89	135.73	228.51	114.49
4	122.45	120.46	190.32	121.28
5	107.25	105.19	143.70	128.29
10	80.37	68.85	101.29	111.58

Table (4): Effect of concentration of (Glutardialdehyde) on the tensile stresses and elasticity of cured urea formaldehyde in presence of high modifier contents.

% Dehydrating Agent	% modifier	Ethylene Glycol		Glycerol		PVA, 6%	
		Stress %	E %	Stress %	E %	Stress %	E %
0.0	0.0	100.00	100.00	100.00	100.00	100.00	100.00
0.0	10.0	111.46	74.34	64.96	76.06	86.11	79.31
1.0	10.0	126.84	70.14	81.76	75.97	89.64	77.83
2.0	10.0	141.53	65.73	97.12	70.31	87.84	71.81
3.0	10.0	161.51	66.20	85.44	67.66	89.10	73.09
4.0	10.0	159.16	64.10	98.56	64.33	75.83	63.97
5.0	10.0	138.49	62.17	107.92	59.20	91.44	73.83

Table (5): Effect of concentration of additives on the time of complete curing.

% addition	Ethylene Glycol Time(hr)	Glycerol Time(hr)	PVA, 6% Time(hr)
0.0	36	36	36
5.0	42	42	34
7.5	42	96	72
10.0	42	96	72
12.5	72	120	96
15.0	72	120	96

Table (6): Effect of dehydrating agent (Glutardialdehyde) on the time of complete curing of non-modified UF.

% Addition	Time of complete curing (hr)
0	24
2	18
4	12
6	10
8	8
10	6

Table (7): Effect of dehydrating agent (Glutardialdehyde) on the time of first curing of urea formaldehyde samples in presence of high modifier contents.

% Dehydrating Agent	% modifier	Curing time (hr)		
		Ethylene Glycol	Glycerol	PVA, 6%
0.0	0.0	48	48	48
0.0	10.0	96	96	48
1.0	10.0	57	48	44
2.0	10.0	45	44	40
3.0	10.0	45	44	28
4.0	10.0	33	38	24
5.0	10.0	33	38	19

Table (8): summary of monitoring of stored - UF in absence / presence of modifiers.

Component	Urea formaldehyde / Modifier						
ml/ml	100/--	100/--	100/--	100/--	100/--	100/--	100/--
Storing life (month)	6	6	6	6	6	6	6
Component	**Urea formaldehyde / (dehydrating agent)Glutardialdehyde**						
ml/ml	100/1	100/2	100/3	100/4	--------	-------	------
Storing life (month)	4	3	2	1			
Component	**Urea formaldehyde / Ethylene Glycol**						
ml/ml	100 / 5	100 /7.5	100 / 10	100/12.5	100/ 15	100/1 7.5	100 / 20
Storage time (month)	6	7	8	9	10	11	11
Component	**Urea formaldehyde /Glycerol**						
ml/ml	100 / 5	100 /7.5	100 / 10	100/12.5	100/ 15	100/1 7.5	100 / 20
Storing life (month)	6	6	6.5	6.5	6.5	7	7
Component	**Urea formaldehyde / PVA, 6% soln.**						
ml/ml	100 / 5	100 /7.5	100 / 10	100/12.5	100/ 15	100/1 7.5	100 / 20
Storing life (month)	6	6	6	6	6	6	6

CONCLUSION

From the results obtained it has been found that, the addition of the modifiers investigated (ethylene glycol, glycerol and PVA.) improves the elasticity of cured-UF, decreases its stress and increases the storage life time of UF solution. Besides, the presence of dehydrating agent (glutardialdehyde) maintains the elasticity gained and increases the stress lost of modified and cured UF. Also, glutardialdehyde decreases the curing time of modified samples. The best results were obtained with ethylene glycol.

REFERENCES

Baun, D. Cherdon, H.. Rehahn, M. Ritter, H., Voit, B. Polymer Synthesis: Theory and Practical, Fundamentals, Methods, Experiments. Fourth Edition, (2005), Berlin: Springer, p: 39-64.

Boran, S., Usta, M. Gumuskaya, E. International Journal of Adhesion & Adhesives **31** (2011) 524 -529.

Brydson, J.A) PLASTICS MATERIALS, SEVENTH EDITION, (1995,1997), Chapter 24(p 669-671).

Byung-Dae Park, Ho-Won Jeong, International Journal of Adhesion & Adhesives **31** (2011) 524 -529.

Daisy Biswas, Samar KantiBose. Mozaffar Hossain, M International Journal of Adhesion & Adhesives **31** (2011) 84-87.

Drage, T.C, Arenillas, A. , Smith , K.M. Pevida, C., Piippo, S., Snape C.E., Fuel **86** (2007) 22-31.

Kubota J, N. Hirabayashi, A. Kato, H. Yoshizawa, Colloids and Surfaces A: Physicochem. Eng. Aspects **302** (2007) 320-325

Xuefei Sun, Zhikuan Chai, R, Journal of Chromatography A, **943** (2002) 209-218.

تحورات كيميائية لبلمرات اليوريا فورمالدهيد

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فى هذه الدراسة تم تحديد تأثيرات تركيزات بعض الإضافات من المواد المـــعدلة (الإيثيلين جليكول والجليسرول والبولى فينيل الكحول والنشا) على بعض الخواص الفيزيائية (فترة التخزين) لليوريا فورمالدهيد السائلة وكذلك تأثيرها على بعض الخواص الميكانيكية لليوريا فورمالدهيد الملتئمة (المتصلبة)، وقد وجد أن مرونة الراتنج المتصلب تزداد مع زيادة كمية (الإيثيلين جليكول والجليسرول والبولى فينيل الكحول) فى حين أنها انخفضت مع زيادة كمية النشا، ومع أن المرونة قد تحسنت إلا أن مقاومة الكسر انخفضت مع زيادة تركيز كل من (الإيثيلين جليكول والجليسرول والبولى فينيل الكحول) كل على حدة وأيضاً على العكس ازدادت مقاومة الكسر مع زيادة كمية النشا. وعندما تمت إضافة الجلوتار ثنائى الألدهيد مع كل من (الإيثيلين جليكول والجليسرول والبولى فينيل الكحول) وجد أن إجهاد الكسر قد تحسن مع المحافظة على المرونة المكتسبة من إضافة المواد المعدلة، وأيضاً مع هذه الإضافات إلى اليوريا فورمالدهيد السائلة فقد وجد أن فترة تخزينها تطول وتم الحصول على أفضل النتائج مع إضافة الإيثيلين جليكول.