Water Swellability and Tensile Properties of Plasticized Cured Gelatin–Trimethylolphenol Blends

T. H. GOSWAMI,¹ M. M. MAITI²

¹ Defence Research & Development Establishment, Gwalior 474 002, India

² Indian Institute of Technology, Department of Chemistry, Kharagpur 721 302, India

Received 7 November 1997; accepted 31 March 1998

ABSTRACT: Gelatin has been chemically modified by crosslinking with timethylolphenol (TMP), which represents the smallest molecule of the phelol-formaldehyde resins, and exhibits high reactivity towards gelatin. Although gelatin is soluble in water in all proportion, the cured gelatin–TMP blends only swell in water, swellability decreasing with increasing resin content. They exhibit moderate tensile strength, but very low elongation at break. Elongation is substantially improved by using a polyethylene glycol, PEG 400, as cosubstrate to gelatin, which serves as a plasticizer. Binding efficiency of PEG 400 to the cured blend network, and the water swellability and tensile properties of the cured plasticized blends have been reported. Some practical advantages and possible areas of application have also been highlighted. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1721–1729, 1999

Key words: gelatin; trimethylolphenol; gelatin–trimethylolphenol blends; water swellability; tensile properties

INTRODUCTION

Gelatin is a protein that is highly amenable to chemical modification at a variety of reactive sites along the chains. One of the most common and commercially important chemical modification involves crosslinking on gelatin, best exemplified by the gelatin coating on photographic paper and films. Crosslinking of gelatin in general ensures dimensional stability, surface gloss, adhesive strength to the substrate, and improved resistance to mechanical damage and aerobic biodegradation. The most common crosslinking agents are aldehydes, formaldehyde¹⁻⁴ being the most potent one by virtue of its smaller mass and size, very high reactivity towards abundant amine functionalities on gelatin chain, high solubility in aqueous medium, and being capable of imparting no undesired coloration to the cured gelatin coatings. But a common disadvantage with formaldehyde as a crosslinker is the low hydrothermal stability of the crosslinks, resulting in slow release of formaldehyde, which has proven human toxicity.

Besides formaldehyde and other aldehydes, a host of other agents have been reported^{5–19} to be used for the crosslinking of gelatin. A potential agent for the crosslinking of gelatin is the phenolformaldehyde resin,^{20,21} which is soluble in water with or without the aid of an alkali. For PF resins, solubility in water is drastically reduced with increasing molecular weight. Use of an alkali increases their solubility by producing phenolate ions. In this regard, trimethylolphenol (TMP) is particularly suitable as a crosslinker over the conventional PF resins. It has low molecular weight, has the maximum possible functionality of three, and is freely soluble in water. It is for these rea-

Correspondence to: M. M. Maiti.

Journal of Applied Polymer Science, Vol. 71, 1721-1729 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/111721-09

sons that trimethylolphenol has been chosen as the crosslinking agent of gelatin in this investigation. Trimethylolphenol has been reported to react more completely with proteins than any PF resins.²² Thus, gelatin–TMP condensates offer higher resistance to heat and water swellability. However, some inherent disadvantage with these condensates is the light yellow to deep brown coloration imparted by the resin component.

Although the use of PF resin as a potential crosslinker of gelatin has been reported in the published literature, systematic studies relating to the physical, mechanical, and thermal behavior of the condensates are very lacking. Because of very high reactivity, lowest molar mass (compared to other PF resins), and greater average number of reactive functional groups (three CH₂OH groups per phenol moiety in trimethylolphenol), it is envisaged that a high crosslink density on gelatin will be achieved by employing even a small proportion of TMP. This, in turn, will induce brittleness (lack of flexibility) into the blends, which is undoubtedly a practical disadvantage. In fact, the cured unplasticized gelatin-TMP blends have poor tensile properties characterized by low tensile strength, very low elongation at break, moderately high tensile modulus, and low flexural strength, which are characteristic of brittle materials. It was, therefore, imperative that a suitable plasticizer be used to improve the flexibility of the cured blends.

The plasticizer to be employed should preferably remain chemically bound to the crosslinked network to check against its loss under usage condition. Also, it should not impair other properties of the blends like water swellability and thermal stability. Several plasticizers 2^{23-26} are known for gelatin. They include ethylene glycol, glycerol, acetic acid, dimethyformamide, and dimethylsulfoxide, besides water. We have chosen polyethyleneglycol (PEG) of various molecular weights as the plasticizer for the blends, because of certain advantages it is likely to offer. First, being a long chain molecule, the plasticizing capacity of PEG is likely to be better than other small molecular agents. Second, it is known to chemically combine with PF-resin. Third, it is soluble in most of the polar solvents like methanol, ethanol, and acetone, in which gelatin is not soluble. Thus, any uncombined PEG in a cured plasticized gelatin-TMP blend can be easily extracted. Further, it has higher molecular weight and, hence, much lower volatility, and is freely soluble in water; but it is much less hygroscopic

than other agents like glycerol. Among various PEGs tested as a plasticizer in this investigation, PEG 400 appeared to be the best compromise, considering such factors as (a) moderate plasticizing ability because of moderate oxyethylene chain length, and (b) moderately reduced hygroscopicity (hygroscopicity decreases with increasing molecular weight), which helps in retaining moderately high residual moisture in the cured blends but improves upon flexibility without sacrificing much of its tensile strength.

In this communication we report a comprehensive study on the condensation efficiency of plasticizer as a cosubstrate to the gelatin in the gelatin—TMP blends and evaluation of the cured plasticized blends in respect of their swelling behavior (in water) and tensile properties. A comparison of the properties of the plasticized and unplasticized blends is also reported.

EXPERIMENTAL

Materials

Gelatin of bacteriological grade (BDH, $\overline{M}_n \sim 90,000$) was used as received. Analytical grade polyethyleneglycol of average molecular mass of 400 (PEG 400, s.d. fine chem., India) was used without further purification. Trimethylolphenol (TMP) was synthesized according to reported methods.^{27–30}

Preparation of Plasticized Gelatin-TMP Blends

Plasticized gelatin–TMP blends were prepared by adding different wt % of plasticizer on a fixed weight of gelatin in the blends. Polyethylene glycols (PEG) of various average molar mass like PEG 200, PEG 300, and PEG 400 were tested for their suitability as a plasticizer. Among these, PEG 400 was found to be most suitable. To ascertain the optimum plasticizer loading, the blends containing various proportion of plasticizer (PEG 400) were prepared, keeping the gelatin-to-resin ratio fixed at 5 : 5. The plasticizer content was varied from 10 to 50% w/w on gelatin.

Weighed amounts of dry gelatin and TMP were dissolved separately in predetermined minimum volumes of water and concentrated ammonia solutions (25% w/v), respectively. Gelatin was allowed to swell overnight in water at room temperature (27° C), which was then homogenized to a clear mobile liquid by continuous stirring at a moderate temperature of about 40°C by warming in a water bath. Exact amount of plasticizer was then mixed throughly into the gelatin solution by continuous stirring at room temperature. The ammonical TMP solution and the gelatin–PEG mixture were then mixed thoroughly by continuous stirring. The mixture was then suitably diluted with water a give a total solid content of $\sim 10\%$ w/v.

Wet films were cast from this solution on a clean dry glass plate by dipping, followed by slow evaporation in an oven at about 40°C holding the glass plate in a perfectly horizontal position. The glass plates along with the dry adhered films of the blends were then subjected to thermal curing in an air oven maintained at 120°C for an optimum period of 4 h. The curing time was optimized by trial and error to constant weight.

Cured films of the blends of varying compositions were then removed from the glass plate by immersing them in warm ($\sim 60^{\circ}$ C) water for about an hour, at which time the films easily peeled off the glass plate. The wet films were then placed between filter papers and stored in a desiccator under mild pressure between two small rigid steel plates.

Unplasticized gelatin–TMP blends were prepared by casting films from the aqueous ammonical solution of gelatin and TMP mixtures. Films were cast to give final compositions in the gelatinto-TMP ratios of 10: 1, 8: 2, 7: 3, 6: 4, 5: 5, 4:6, 3: 7, 2: 8, 1: 9, and 0: 10, w/w.

Condensation Efficiency of the Plasticizer

The unreacted plasticizer in the cured blends were removed by subjecting the cured plasticized films to soxhlet extraction in methanol for 10 h. The amount of unreacted plasticizer was determined using the relation:

Percent unreacted plasticizer = $(W_1 - W_2)100/W_p$

where W_1 is the weight of the cured plasticized blend before methanol extraction; W_2 is the weight of the cured plasticized blend after methanol extraction; and W_p is the calculated weight of plasticizer originally present in W_1 g of the cured plasticized blend.

Percent plasticizer loading on gelatin

$$= X \frac{(W_1 - W_2)(100f_g \cdot X)}{W_1 f_g}$$

where X is the original loading of plasticizer as percent gelatin w/w, and f_g is the fraction of gelatin in the base blend

 $= \frac{\text{wt of gelatin}}{\text{wt of gelatin} + \text{wt of TMP}}$

Swelling Behavior of Plasticized Cured Gelatin–TMP Blends

Dimensional stability under hydrothermal usage conditions were tested for plasticized cured gelatin-TMP blends. In a typical test method, a weighed amount of a cured film of fixed composition that had been previously dried to constant weight under specified conditions was kept immersed into 100 mL of boiling water ($\sim 100^{\circ}$ C) for 2 h, and then left sealed against aerial microbial contamination at room temperature for 2 days to attain equilibrium swelling. The swelled film was then removed from water and superficially washed against a draining acetone for a short period. The surface of the film was then air dried for a few seconds and then subsequently weighed. The percentage of swelling was then calculated using the relation:

percent swelling = $(W_s - W_i)100/W_i$,

and, percent unreacted gelatin = $100(W_i - W_f)/f_g$

where W_i is the initial dry weight of the cured blend; W_s is the weight of the cured blend after equilibrium swelling in water; and W_f is the weight of the equilibrium swelled cured blend after drying to a constant weight.

Tensile Properties

Tensile properties of the cured films were measured on a universal testing machine, Zwick, UTM No. 1445. All the testings were carried out under fixed conditions of temperature $(27 \pm 1^{\circ}C)$ and an ambient relative humidity of 75 \pm 2%. Before subjecting to mechanical testing, the test specimens were left for 48 h to equilibrate at the test temperature and relative humidity. Test specimens were of approximately 75×25 mm with thickness, varying around 0.25 mm for the unplasticized and around 0.05 mm for the plasticized blends. Operating conditions were as follows: grip separation 35 mm, extension rate 50 mm/min, dumb-bell specimen as per ASTM, D-412, type 2. At least six specimens were tested for each blend compositions.

RESULTS AND DISCUSSION

Physical Appearance

The cured films, thus obtained, were free standing, transparent, smooth, and glossy without any

		Weight of Cured Plasticized Blends			
Original PEG 400 Loading (% w/w on Gelatin)	Before Methanol Extraction (w_1/g)	After Methanol Extraction (w_2/g)	Loss of PEG (% w/w on Cured Blend)	PEG 400 Loading (% w/w on Cured Blend)	Modified Substrate to TMP Ratio (w/w)
0	4.96	4.96	0	0	5 : 5
10	1.508	1.459	3.20	3.28	5.1:4.9
15	1.466	1.416	3.41	7.68	5.2:4.8
20	1.555	1.492	4.05	11.2	5.3:4.7
30	1.587	1.512	4.73	19.12	5.4:4.6
40	1.395	1.323	5.16	27.61	5.6:4.4
50	1.337	1.302	5.45	36.38	5.8:4.2

Table ICondensation Efficiency of PEG 400 as a Cosubstrate to Gelatin in the Blend of 5 : 5 Gelatin-
to-TMP Ratio

apparent wrinkles. They were from light yellow to brown in color, with increasing contents of TMP. The films were found to be reasonably uniform in thickness, within the limit of $\pm 2\%$ as measured by a micrometer. The film thickness, however, varied with composition of the blends.

Crosslinking Efficiency of PEG 400 in the Curing of Gelatin–TMP Blends

Table I summarizes the crosslinking efficiency of PEG 400. The base composition of the blend was kept at a 5 : 5 gelatin-to-TMP ratio. The choice of this composition has been justified in the course of discussion in a following section. It is seen from the data in Table I that complete binding of PEG 400 originally taken could not be effected. In Figure 1, the extent of PEG 400, cocured with gelatin



Figure 1 Binding efficiency of PEG-400 to gelatinresin blend (5 : 5).

at its various levels of initial loading, have been plotted. There is a critical PEG 400 loading, below which it could not bind itself onto the cured gelatin–TMP matrix. This critical loading is about 5.5% w/w on gelatin. Beyond this critical loading, the extent of bound PEG 400 increased steadily with increasing proportion of PEG. The results indicate that possibly PEG 400 has lower reactivity than gelatin in its condensation with TMP. It may be mentioned that PEG 400 is difunctional with two hydroxyl groups at the chain ends, whereas the gelatin chain is multifunctional, involving a large number of pendent reactive functionalities like —NH₂, —OH, —COOH, etc.

Swelling Behavior of Plasticized Cured Gelatin–TMP Blends

The results of the swelling behavior of the unplasticized cured gelatin–TMP blends in water have been presented in Table II and those of plasticized blends in Table III. Because PEG 400 has been used as a cosubstrate to gelatin, the original gelatin to TMP ratio of 5 : 5 has been redesignated as modified substrate to TMP ratio. This modified substrate to TMP ratio is not a constant quantity but varies with PEG 400 loading as a cosubstrate. The swelling behavior of these cured plasticized blends have been compared with the swelling behavior of gelatin–TMP blends of the same TMP contents, which have been computed from the data obtained from the swelling behavior of cured unplasticized blends (Table II, Fig. 2).

Figure 2 shows that beyond an original loading of about 18%, the swelling increases linearly with PEG 400. This indicated that plasticized gelatin–

Blend Compositions (Gelatin : TMP, w/w)	Initial Weight (w_i/g)	Weight of Swelled Film (w_s/g)	Percent Equilibrium Swelling = $\{(w_s - w_i)/w_i\}$ \times 100	Weight of Swelled Film after Drying to Constant Weight (w _f /g)
1:9	3.62	3.72	2.2	3.61
2:8	8.35	9.07	8.6	8.35
3:7	1.54	1.72	11.7	1.54
4:6	4.92	5.96	21.1	4.92
5:5	5.45	7.08	30.0	5.46
6:4	4.30	6.28	46.0	4.29
7:3	4.93	8.13	65.0	4.91
8:2	3.99	10.97	175.0	3.54

Table II Equilibrium Swelling of Unplasticized Cured Gelatin-TMP Blends

TMP blends still retains perceptible hydrophilicity but of a much reduced magnitude compared to the corresponding unplasticized blends (Table III). This may be attributed to much reduced hydrophilicity of PEG 400 compared to the base substrate, gelatin. An interesting observation is the occurrence of a minimum in the PEG 400 loading at around 5.5%. The observation is somewhat unusual, but can be explained on the following premises. It is possible that PEG 400 itself may bind through its terminal hydroxyl groups onto the gelatin chain through some chemical reactions like esterification, with the pendent acid groups on gelatin chain. This may significantly attenuate the hydrophpilicity of gelatin. Further, PEG 400 may act as a stronger solvating agent for gelatin compared to water, and thereby effectively shield gelatin against hydration in aqueous medium. When the gelatin chains are maximum

solvated by PEG 400 (which is believed to occur at around 5.5% of PEG 400 loading), the percent swelling goes down to a minimum value of about 15%. Beyond this critical PEG 400 loading, the normal hydrophilicity of PEG 400 contributes to gradual increase in percent swelling.

Tensile Properties of Unplasticized Blends

Table IV lists the tensile breaking stress and the percent elongation at break data averaged over at least six specimens of each blend. The extent of scattering has been shown as error bars along with the average values in Figure 3. In spite of wide scattering, a definite trend is clearly reflected as the blend composition is varied. Blend composition was varied between 1 : 9 and 6 : 4 of the gelatin-to-TMP ratio. With the increase in gelatin content, the breaking stress gradually in-

Original PEG 400 Loading (% w/w on Gelatin)	Modified Substrate to TMP Ratio ^a (w/w)	Initial Weight (w_i/g)	Weight of Swelled Film (w_s/g)	Swelling (% w/w on Cured Blend)	Swelling ² of Unplasticized Blends (% w/w on Cured Blends)
0	5:5	5.45	7.08	30.0	30.0
10	5.08:4.92	1.46	1.72	17.9	31.0
15	5.18:4.82	1.43	1.65	15.4	32.0
20	5.26:4.74	1.39	1.65	18.7	33.0
30	5.44:4.56	1.53	1.87	22.2	36.0
40	5.61:4.39	1.67	2.07	24.0	38.0
50	5.77:4.23	1.30	1.65	26.9	39.5

Table III Swelling Behavior of Plasticized and Unplasticized Cured Gelatin-TMP Blends

^a Data from Table I.

^b Data computed from Table II.



Figure 2 Variation of equilibrium swelling of the cured plasticized gelatin-resin blends with PEG-400 loading. Temperature, 27°C.

creased from about 15 Mpa for 1:9 blends to a maximum of about 37 Mpa for 5:5 blends. On further increase of gelatin content, the stress registered a decline to about 30 Mpa for the 6:4 blends.

In regard to the elongation at break, a distinct trend is again apparent, which is, however, opposite to the one observed with the breaking stress. In general, the elongation decreased with increase in gelatin content, from about 9% for 1:9 blends to about 5.7% for 5 : 5 blends. Beyond the 5 : 5 gelatin-to-TMP ratio, the elongation increased again to about 8.3% for the 6:4 blends. Low values of elongation of the blends are representative of ideal elastic behavior of the materials. The experimental stress-strain curves (Fig. 4) clearly show almost linear Hookean behavior up to the breaking point without any marked impression of plastic flow. Data in Table II and Figure 3 show that equilibrium swelling of the blends is small and almost linear up to an increased gelatin-to-TMP ratio of 5 : 5, beyond

Table IVTensile Properties of CuredUnplasticized Gelatin-TMP Blends

Blend Compositions (Gelatin : TMP)	Tensile Strength (MP _a)	Elongation at Break (%)
1:9	15.21	9.40
2:8	22.60	7.50
3:7	27.47	6.00
4:6	34.34	5.14
5:5	37.28	5.70
6:4	30.40	8.27



Figure 3 Tensile properties of cured unplasticized blends at various gelatin to resin ratios. Temperature, 27°C; relative humidity, $75 \pm 2\%$.

which equilibrium swelling increases sharply with increasing gelatin content. This clearly shows that the blends with a gelatin-to-TMP ratio greater than 5 : 5 have much higher proportions of retained moisture. This moisture may very effectively act as plasticizer to the matrix. It may be mentioned that these water molecules are not covalently bound to the crosslinked gelatin network, and are quite labile within the matrix of the blends. As a result, they offer unrestrained plas-



Figure 4 Typical tensile stress-strain profile of cured unplasticized gelatin-resin blends. Base blend composition, 5:5 gelatin to resin ratio; Temperature, 27° C; relative humidity, $75 \pm 2\%$.

PEG Loading (wt % on Gelatin)	Tensile Strength (MP _a)	Elongation at Break (%)
0	37.28	5.7
3.28	46.1	13.3
7.68	51.68	15.0
11.2	55.87	17.5
19.12	67.5	21.6
27.61	47.14	15.7
36.38	26.0	5.0

Table VTensile Properties of CuredPlasticized Gelatin-TMP Blends

ticization of longer gelatin chain segments (because of lower crosslink density at lower resin contents) between two successive crosslink sites. This enhanced plasticization results in lower tensile strength and higher elongation at break. The observed tensile properties of the blends, therefore, can be explained in terms of two important parameters, viz., the crosslink density in gelatin, and the retained moisture content. In general, a decrease in crosslink density tends to increase tensile strength and decrease elongation. On the other hand, retained moisture content (which increases with decrease in crosslink density) tends to plasticize the matrix, bringing about a decrease in tensile strength and an increase in elongation.

Tensile Properties of Plasticized Blends

As discussed in an earlier section, the blends offer an optimum gelatin-to-TMP ratio of 5 : 5 in respect of their tensile properties (Table IV, Fig. 3) and equilibrium swelling (Table III). The studies on the tensile behavior of plasticized blends have, therefore, been made at only one blend composition of 5 : 5 of the gelatin-to-TMP ratio.

Table V summarizes the data on tensile strength and elongation of the 5 : 5 gelatin–TMP blends with varying PEG contents. As will be apparent from Figure 5, the extent of scattering of the data is far less compared to that recorded with unplasticized blends. A definite trend in the variation of breaking stress and elongation with PEG content is also clearly reflected in Figure 5. In general, the tensile strength registered a sharp and almost linear increase with PEG content up to about 19% (on gelatin). Beyond this, the strength again fell off. The increase in tensile strength is quite steep, and is more than 80% over the control 5:5 blend. The elongation at break also followed a parallel trend, the highest elongation recorded being about 22.5% at about 19%PEG loading, which is about 300% increase over 5.7% recorded for the control 5:5 blend.

The PEG loadings referred to here correspond to the ones calculated as chemically bound PEG after extraction of the original cured blends with methanol. The plasticized blends up to about 19% PEG loading were all found to be transparent, while those with higher PEG loading (up to $\sim 36\%$) were all translucent, the transparency decreasing with increasing PEG loading. Further, it has been shown that plasticized blends have considerably lower moisture retention capacity compared to their unplasticized analogs. These two facts possibly suggest that at higher PEG loadings, phase separation of the plasticizer might have taken place. This phase separation may be attributed to its incomplete chemical binding to the crosslinker (i.e., only one terminal hydroxy group being used for condensation with TMP), which allows it to segregate within the matrix.

Another possibility is that PEG content of about 19% on gelatin is just sufficient to effect maximum solvation to the crosslinked gelatin chain segments. Any excess over this amount may segregate as a separate phase to make the blends translucent. This phase segregation might be re-



Figure 5 Tensile properties of cured plasticized blends at various PEG-400 loadings. Base blend composition, 5:5 gelatin to resin ratio. Temperature, 27°C; relative humidity, $75 \pm 2\%$.

sponsible for generating local stress that eventually leads to lower tensile strength and elongation.

In this context, the role of water and PEG 400 as plasticizers may be contrasted. In explaining the tensile behavior of unplasticized blends at higher gelatin contents beyond the 5:5 gelatinto-TMP ratio, it was argued that the higher moisture contents were responsible for decrease in tensile strength and increase in elongation. In the case of plasticized blends, however, the trend is reversed; the higher the plasticizer content (without any phase segregation up to about 19%), the higher were the elongation and tensile strength. This apparent anomaly is readily rationalized if one looks into the state of existence of the plasticizing moieties in the matrix. In the case of water, the molecules are small, mobile, and only quasibound to the matrix by the force of solvation, without any firm covalent bonding. In the case of PEG 400, the molecules are long, flexible in respect of chain bending, and hence, capable of solvating the gelatin chains, but bound to the matrix by a firm chemical bond at either or both terminals of the chains. As a result, water offers only plasticization but no reinforcement to the matrix. Further, this plasticizing effect of water is perceptible only at higher gelatin content. On the other hand, PEG offers both plasticization and reinforcement.

GENERAL REMARKS AND CONCLUSIONS

The present study shows that a fairly homogeneous, glossy, transparent films can be obtained from gelatin-TMP blends, that offer significant hydrothermal stability in respect of retaining shapes and sizes. Appreciably low moisture uptake and moderate tensile properties make these blends particularly suitable for use as a coating material onto polar substrates like paper and cellulosic fabrics with improved mechanical strength and surface gloss. A simple coating technique to which the blends are amenable and strong adhesion between the substrates and the blends would be the added attractions in such applications as biodegradable agricultural mulch, strong and moisture resistant packaging materials, protective and attractive coating for book covers, and also as moisture-resistant binders for match stick heads. Ordinary papers coated with the blends have been found to develop a high-surface gloss, and improved tear strength, and resistance to

moisture, but with yellow to brown hues, depending upon the TMP content of the coated blends. This color development, though apparently disadvantageous, may very well help in imparting composite color to the coated paper to improve its aesthetic appeal. Thus, an originally blue colored paper may develop a pleasant glossy turquoise to light green shade on being coated with a 5 : 5 gelatin–TMP blend. The coating has been found to very strongly adhere to paper but rendered the paper to some extent brittle. Sharp folds on the paper left permanent cracks and general irrecoverable loss of gloss along the folds.

Admittedly, brittleness of the cured blends is the greatest disadvantage. But plasticization of the blends with suitable agents to any optimum level, may significantly overcome this difficulty. Low-grade gelatins and animal glues that are simply regarded as waste may be rendered more usable by blending and curing them with TMP.

REFERENCES

- 1. French, D.; Edsall, J. T. Adv Protein Chem 1945, 2, 278.
- 2. Kragh, A. M. Manuf Chemist 1958, 29, 103.
- 3. Fuchs, E. Adhesion 1961, 5, 225.
- 4. Sutton, D. A. Nature 1962, 196, 223.
- Allen, C. F. H.; Carroll, B. H. U.S. Pat. 2725294 (1955).
- Minsk, L. M.; Cohen, H. L. U.S. Pat. 3330664 (1967).
- Henkel and Cie. G. M. b. H., Ger. Pat. 1149517 (1963).
- Allen, C. F. H.; Carroll, B. H. U.S. Pat. 2725295 (1955).
- Kenchington, A. W.; Lauder, W. W. Recent Advances in Gelatin and Glue Research; Stains, G., Ed.; Pergamon Press: London, 1958, p. 191.
- Gevaert Photo-Production N. V., Can. Pat. 715561 (1965).
- Fanta, P. A. The Chemistry of Heterocyclic Compounds: Heterocyclic Compounds with Three and Four Member Rings, Part 1; Weissberger, A., Ed.; Interscience Publishers: London, 1964, p. 524.
- 12. Burness, D. M. U.S. Pat. 3338715 (1967).
- Allen, C. F. M.; Webster, E. R. U.S. Pat. 2950197 (1960).
- 14. Burness, D. M.; Wilson, B. D. U.S. Pat. 3232763 (1966).
- Rosowsky, A. The Chemistry of Heterocyclic Compounds: Heterocyclic Compounds with Three and Four-Membered Rings, Part 1; Weissberger, A., Ed.; Interscience Publishers: London, 1964, p. 1.

- 16. Merrill, R. E. U.S. Pat. 3207613 (1965).
- 17. Burness, D. M. U.S. Pat. 3189459 (1968).
- 18. Venner, H. A. L. Br. Pat. 1109546 (1968).
- Kenyon, W. O.; Smith, D. A.; Taylor, E. W. U.S. Pat. 3220864 (91965).
- 20. Nakamoto, Y.; Ikeda, T.; Ishida, S. Netsu Kokasci Jushi 1987, 8, 1.
- 21. Monier, J. B. U.S. Pat. 23638892 and 2732303 (1944).
- 22. Barth, B. P. U.S. Pat. 3046103 (1962).
- 23. Kodak Ltd., Br. Pat. 908777 (1959).

- 24. Union Carbide Corp. U.P. Pat. 3164560 (1965).
- 25. Eastman Kodak Inc., U.S. Pat. 2772166 (1957).
- 26. Gevaert Phot-Prod. N. V., Belg. Pat. 565861 (1959).
- Myers, C. Y. (to Union Carbide Corp.), U.S. Pat. 2,889,374 (1959).
- Senior, G. A. (to Union Carbide Corp.) U.S. Pat. 3,109,033 (1963).
- Senior, G. A. (to Union Carbide Corp.) U.S. Pat. 3,023,252 (1962).
- Conley, R. T.; Bieron, J. J Appl Polym Sci 1963, 7, 105.