

# Crosslinked Latex Blends Based on Gelatin: Synthesis, Morphology, Thermal, and Mechanical Properties

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## SYNOPSIS

Latex blends of different compositions of poly(methyl methacrylate-*co-n*-butylacrylate) and gelatin have been synthesised in latex form with crosslinking agents. These latex blends were characterized by thermal and mechanical properties. The morphology of cross-linked latex blends were studied by scanning electron microscopy (SEM).

## INTRODUCTION

During the last decade, remarkable advances have been made both scientifically and technologically in the area of polymer blends. Owing to strong economic incentives, modification of existing materials is becoming the best way to improve properties and to generate versatile polymeric products. This is manifested by the growing number of monographs and publications.<sup>1-6</sup> These "new" materials are typically blends of two or more polymers, wherein technological success is achieved either by exploiting the synergistic properties resulting from compatible mixing of two polymers or by additive properties.

Synergistic properties often result when components are truly miscible, whereas partially miscible or totally immiscible blends exhibit intermediate properties of the components. It is now well recognized in the polymer industry that immiscible polymer blends can lead to materials having superior performance and properties through relatively easy and straightforward blending techniques. The degree of compatibility and the morphology of polymer blends play an important role in determining ultimate properties. The degree of compatibility can be controlled by several techniques, depending upon

the interest and the desired performance characteristics of the system.<sup>7,8</sup>

One of the common methods to reduce the interfacial tension of components and increase their compatibility is to introduce interfacial agents. Such agents could be either an integral part of one of the components or an attached functional group capable of interacting with the other components. Thus, the addition of block or graft copolymers, whose components are known to be miscible with the blend components, has been demonstrated to enhance compatibility in otherwise incompatible polymer pairs.<sup>9-12</sup>

With the ongoing interest in our work on the modification of gelatin<sup>13-15</sup> by blending and grafting, here, we are reporting the synthesis and characterization of a new kind of blend from latex systems, which involves two different types of polymers, viz., gelatin and a copolymer of poly(methyl methacrylate-*co-n*-butylacrylate). Here, we have analyzed the crosslinking effect of glutaraldehyde on gelatin and diallylphthalate on MMA-*co-n*-BA polymer.

## EXPERIMENTAL

The raw materials used have been described in Table I. The monomers were freed from stabilizers by shaking with 10% NaOH solution (3×) and washing with distilled water until neutral. The monomer was dried for 24 h over fused granular CaCl<sub>2</sub> and distilled under vacuum.

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**Table I Raw Materials Employed and Their Source**

| Name and Description                    | Source                       |
|---|------------------------------|
| Gelatin from porcine skin-300 bloom     | Sigma Chem. Co.              |
| Methyl methacrylate (MMA)               | Aldrich Chemicals            |
| <i>n</i> -Butylacrylate ( <i>n</i> -BA) | Koch-Light Laboratories Ltd. |
| Glutaraldehyde                          | BDH Chemicals Ltd.           |
| Diallylphthalate                        | BDH Chemicals Ltd.           |
| Sodium metabisulfite (SMB)              | S.D. Fine Chem. Pvt. Ltd.    |
| Potassium persulfate (PPS), GR grade    | BDH Chemicals Ltd.           |
| Sodium lauryl sulfate (SLS)             | Local marker                 |

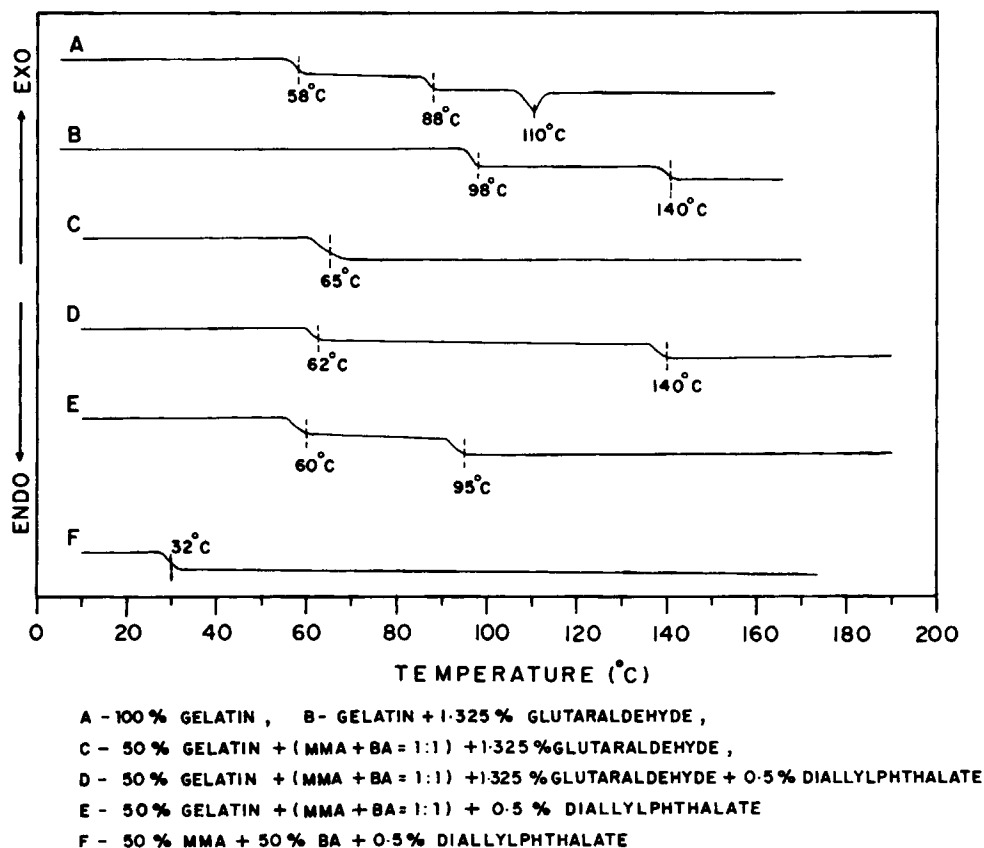
### Latex Blend Synthesis

The latex blend synthesis consisted of making a seed latex of crosslinked methyl methacrylate (MMA)–*n*-Butylacrylate (*n*-BA) copolymer and then intro-

ducing gelatin dissolved in deionized water and crosslinking it. This methodology is attempted in order to obviate the graft copolymerization when the acrylic copolymerization is carried out in the presence of gelatin as done with conventional IPN preparations.

To prepare the seed latex, 50 mL of deionized, deaerated water was stirred and gently warmed under nitrogen in a 500-mL three-necked reactor. At 40°C, 35 mL of deionized water containing 0.9 g sodium lauryl sulfate (SLS) (4.5% by weight of monomer) and 0.60 g potassium persulfate (3% by weight of monomer) were added while stirring at constant speed. At 60°C, 10 g MMA and 10 g *n*-BA containing 0.5% diallylphthalate as a crosslinking agent were added dropwise. The temperature was maintained at 60°C for 30 min and then gradually increased to 90°C and stirred at that temperature for 1 h. The emulsion was then allowed to cool to room temperature.

In order to complete the second stage, the emulsion was again heated to 60°C; the gelatin dissolved in deionized water (20%) was added for 5 min and maintained at 60°C for 30 min and gradually in-



**Figure 1** DSC of blends based on gelatin.

**Table II** Composition for Latex Blend System

| Sample Code | Gelatin Content (g) | MMA Content (g) | <i>n</i> -BA Content (g) | Crosslinker <sup>a</sup>  |
|-------------|---------------------|-----------------|--------------------------|---------------------------|
| A           | 20                  | —               | —                        | —                         |
| B           | 20                  | —               | —                        | 1.325% w/w GLU            |
| C           | 20                  | 10              | 10                       | 1.325% w/w GLU            |
| D           | 20                  | 10              | 10                       | 1.325% w/w GLU, 0.5% Dial |
| E           | 20                  | 10              | 10                       | 0.5% Dial                 |
| F           | —                   | 10              | 10                       | 0.5% Dial                 |
| G           | 20                  | 10              | 10                       | —                         |
| H           | 10                  | 10              | 10                       | 1.325% GLU                |
| I           | 16                  | 10              | 10                       | 1.325% GLU, 0.5% Dial     |
| J           | 12                  | 10              | 10                       | 1.325% GLU                |
| K           | 12                  | 10              | 10                       | 1.325% GLU, 0.5% Dial     |
| L           | 10                  | 10              | 10                       | 1.325% GLU                |
| M           | 10                  | 10              | 10                       | 1.325% GLU, 0.5% Dial     |
| N           | 10                  | 10              | 10                       | 0.5% Dial                 |
| O           | 8                   | 10              | 10                       | 1.325% GLU                |
| P           | 8                   | 10              | 10                       | 1.325% GLU, 0.5% Dial     |
| Q           | 6                   | 10              | 10                       | 1.325% GLU                |
| R           | 6                   | 10              | 10                       | 1.325% GLU, 0.5% Dial     |

<sup>a</sup> Dial = diallylphthalate; GLU = glutaraldehyde.

creased to 80°C where it was maintained for 1 h. The latex was filtered through cotton and 1.325% (w/w) glutaraldehyde with respect to gelatin was added. The emulsion was cast as a film on a mercury pool and dried for 50 h at 30°C. These films were taken for characterization.

### Physical Techniques

#### *Gel-Permeation Chromatography (GPC)*

Gel-permeation chromatography (GPC) was carried out with a Waters GPC instrument equipped with a  $\mu$ -styragel column set of  $10^5$ ,  $10^4$ , and  $10^3$  Å and

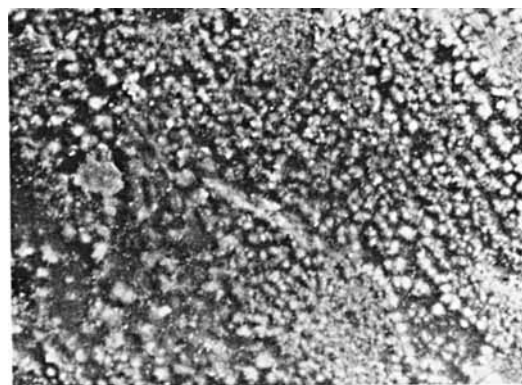
410 refractometric detector using tetrahydrofuran as eluent. (The polymer concentration was 2 mg/mL and the flow rate was 1 mL/min.) The calibration was carried out using polystyrene standards with narrow molecular weight distributions. The copolymer (MMA-*co*-*n*-BA) was precipitated with methanol and purified by repeated precipitation from THF. The pure sample was used to find the molecular weight distribution.

#### *Scanning Electron Microscopy (SEM)*

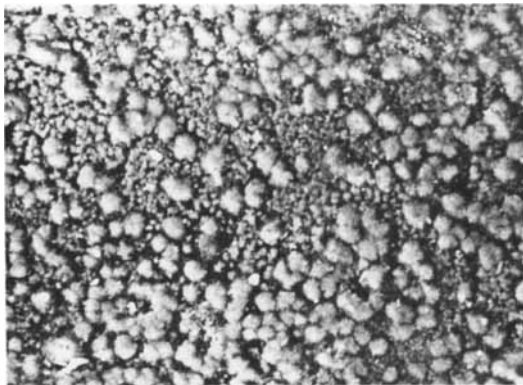
Approximately 6 × 6 mm sections were cut from fully crosslinked and partially crosslinked films.



**Figure 2** 50% gelatin + 1.325% GLU/50% [(MMA + BA = 1:1)].



**Figure 3** 50% gelatin + 1.325% GLU/50% [(MMA + BA = 1:1) + 0.5% dial].



**Figure 4** 50% gelatin/50% [(MMA + BA = 1:1) + 0.5% dial.

These samples were mounted on a specimen holder. A gold coating approximately 200 Å thick was deposited on the surface in a vacuum evaporator. Micrographs of the film surface were obtained with a Philips scanning electron microscope.

#### **Differential Scanning Calorimetry (DSC)**

DSC thermograms were recorded using a DuPont 910 thermal analyzer with a heating rate of 20°C/min under nitrogen atmosphere. Calibrations were performed using standards with well-known  $T_m$  and enthalpy.

#### **Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis was carried out with a DuPont 952 thermobalance in a nitrogen atmosphere on heating from ambient temperature to about 550°C at a heating rate of 10°C/min.

#### **Tensile Strength Analysis (TSA)**

Tensile tests were carried out on dumbbell specimens with an Instron universal testing machine (Model 4301) according to the ASTM 0638 (1977) at a constant extension rate of 20 mm/min.

## **RESULTS AND DISCUSSION**

One of the advantages of the latex system is the high molecular weight build up during the copolymerization of MMA and *n*-BA. The molecular weight distribution is given as follows:

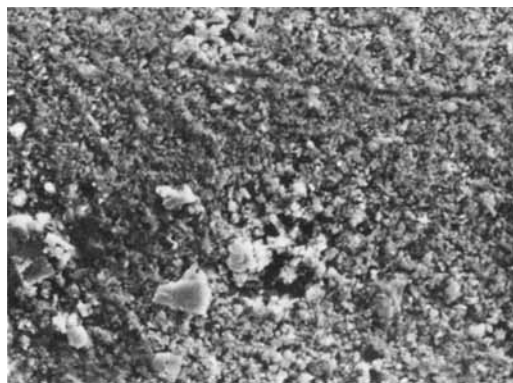
$$\bar{M}_n = 2.25 \times 10^4, \bar{M}_w = 28.51 \times 10^4$$

dispersity = 12.70, intrinsic viscosity = 0.29

The DSC results in Figure 1 shows that the sample A (Table II) corresponding to pure gelatin has two glass transition temperatures ( $T_g$ ) and one melting temperature ( $T_m$ ) at 58, 88, and 110°C, respectively. For the glutaraldehyde crosslinked gelatin, sample B  $T_g$ 's are 98 and 140°C, whereas the peak corresponding to  $T_m$  is missing, which may be due to crosslinking. The  $T_g$  for MMA-*co-n*-BA crosslinked copolymer is 32°C.

After blending the crosslinked polymers, the difference in glass transition temperature ( $T_g$ ) corresponding to the acrylic copolymer and gelatin decreases as shown for sample D at 62 and 140°C. When the gelatin network is crosslinked and the acrylic part is not crosslinked, the blend C has a single  $T_g$  at 65°C. However, this is not the case with fully crosslinked blends. This may be because when the gelatin is crosslinked with glutaraldehyde, the extent of hydrogen bonding of water with gelatin is reduced. This increased hydrophobicity brings about compatibility with MMA-*co-n*-BA, which is already hydrophobic. In the case of sample E, two glass transitions are observed, because, after crosslinking, the MMA-*co-n*-BA copolymer becomes more hydrophobic due to crosslinking causing distinct phase separation.

The above results are strongly supported by scanning electron micrographs. Figure 4, sample E, shows phase separation which is supported by the DSC results with two  $T_g$ 's at 60 and 95°C, where the copolymer part is crosslinked, but the gelatin is not. In case of sample D, Figure 3, the compatibility increased considerably where both polymers are crosslinked; when the copolymer MMA-*co-n*-BA is not crosslinked, there is a further increase in the compatibility, which is shown in Figure 2, sample C. Figure 5 (sample G) corresponds to the totally uncrosslinked blend, which shows randomness. Thermogravimetric analysis (TGA) of the above la-



**Figure 5** 50% gelatin/50% [(MMA + BA = 1:1)].

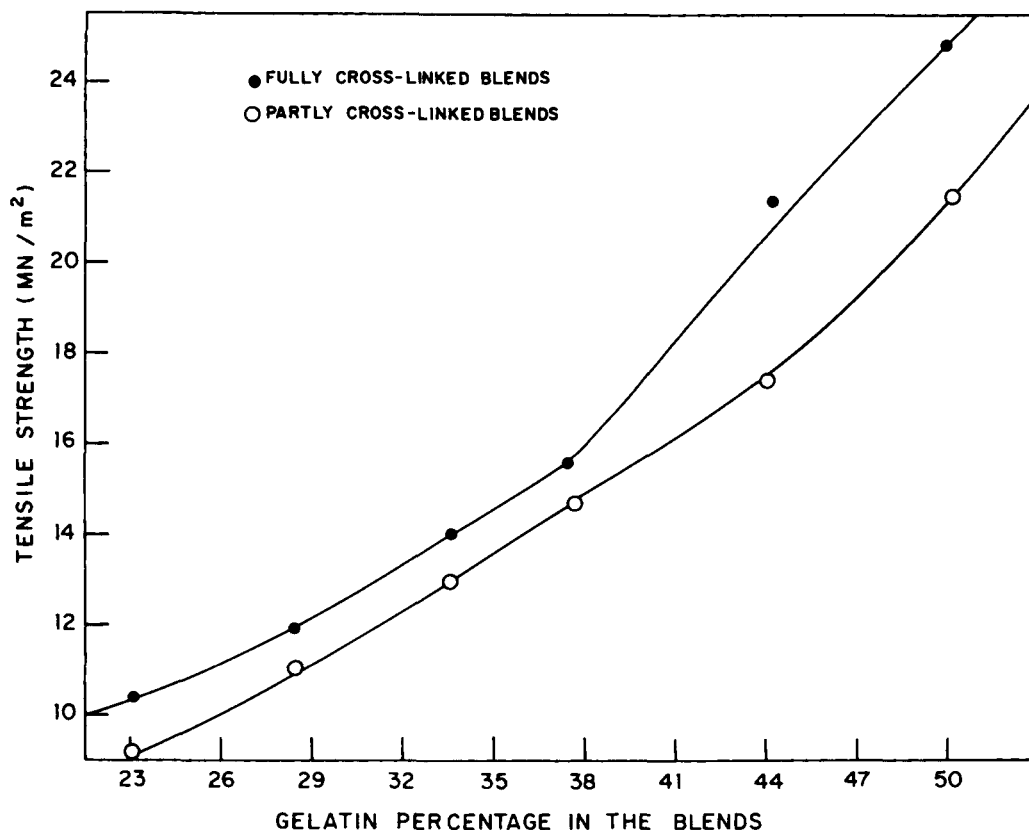


Figure 6 Plot of tensile strength vs percentage of gelatin.

tex blends are shown in Table III, where the percentage of weight loss for the crosslinked sample B is slightly less when compared to sample A, which is not crosslinked. The thermal stability of blends C, D, and E have been improved, suggesting that gelatin is thermally stabilized by blending with acrylates.

Figure 6 shows the mechanical properties of latex blends corresponding to the compositions given in Table II. The fully crosslinked latex blend shows a higher tensile strength than partially crosslinked

Table III Thermogravimetric Analysis of TGA of Blends Based on Gelatin

| Sample Code | Percentage of Weight Loss at |       |       |       |
|-------------|------------------------------|-------|-------|-------|
|             | 300°C                        | 350°C | 400°C | 450°C |
| A           | 34                           | 60    | 70    | 74    |
| B           | 34                           | 58    | 68    | 72    |
| C           | 18                           | 34    | 68    | 79    |
| D           | 20                           | 38    | 80    | 84    |
| E           | 24                           | 42    | 78    | 88    |
| F           | 20                           | 36    | 88    | 90    |

blends. The tensile strength of the blends decreased with decrease in the percentage of gelatin.

## CONCLUSIONS

By the synthesis of crosslinked latex blend from gelatin and methyl methacrylate (MMA) and *n*-butylacrylate (*n*-BA) copolymers, the thermal stability of gelatin is improved. Gelatin is made compatible with MMA-*co*-*n*-BA by crosslinking. The brittle film of gelatin is made flexible and the tensile strength analysis shows fully crosslinked blend has better tensile strength, when compared to partially cross-linked blends.

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