

Study of the Degree of Crystallinity in Eudragit/Poly(methyl methacrylate) Polyblends by X-Ray Diffraction

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ABSTRACT: Plaques of blends of Eudragit RL 100 (EU) and poly(methyl methacrylate) (PMMA) with different weight-per-weight ratios were prepared by compression molding at 150°C. The X-ray diffraction profiles of the blends were studied and compared, and the interplanar distance, crystallite size, and crystallinity were computed for

various peaks. The Eu/PMMA blend with a 70:30 (w/w) ratio had the maximum crystallinity. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1835–1838, 2005

Key words: blends; X-ray

INTRODUCTION

Polymeric blends have widespread industrial applications because of their improved properties, ease of preparation, and economic advantages. They can be processed like thermoplastics, and certain properties of amorphous polymers can be enhanced through an increase in the crystallinity order.^{1,2} X-ray diffraction is one of the most powerful techniques for the analysis of the regular arrangement of lattice units. Even if the regular arrangement is very imperfect, X-rays produce maxima. Many plastics are partly crystalline and composed of very long molecules, generally being in a state of great disarray but organized into ordered regions called *crystallites*. These regions produce broad diffraction lines. By comparing the intensity and width of the line, researchers can estimate the degree of crystallinity (C_r) and crystallite size (C_s).³ Many researchers have reported X-ray diffraction studies on polymers and polymeric blends that show the existence of ordered regions.^{4–9}

Eudragit RL 100 (EU) is an amorphous copolymer used in pharmaceutical preparations for coating tablets, granules, powders, and drug crystals. It has many prospective uses in technical applications. Current studies have shown that compatible, miscible blends of Eudragit and poly(methyl methacrylate) (PMMA) can be formed via compression molding. This tech-

niques imparts thermal stability and a crystalline structure to polyblends for appropriate applications; with solution casting, however, the problem of dispersion arises during the mixing of polymers. It may, therefore, be useful to blend Eudragit RL with different amounts of PMMA, which increases the crystalline phase, and to study the blends for various properties. This article reports a comparative study of the X-ray diffraction of polyblends of Eudragit RL and PMMA with different weight-per-weight ratios.

EXPERIMENTAL

Materials

Eudragit RL is a copolymer synthesized from acrylic and methacrylic acid esters with a low content of quaternary ammonium groups. The ammonium groups are present as salts and lead to the permeability of lacquer films. They afford water-insoluble but permeable film coatings. The molar ratio of these ammonium groups to the remaining neutral (meth)acrylic acid esters is 1:20 for Eudragit RL (mean molecular weight \approx 15,000; RL is related to the initial letter of the German word *leichtdurchlassig*, which means “freely permeable”). Eu is used for coating crystals, rounded granules, microtablets, and pellets. It is also used for granulation as the first stage in building up matrix structures, particularly with freely soluble drugs. It acts as a film former or binding agent for the pelletizing of drugs. The addition of plasticizers is recommended to enhance the characteristics of Eu in film form. PMMA is an engineering thermoplastic that is hard, rigid, heat-resistant, and transparent. It

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also possess high tensile and flexural strength and good weather resistance. It is a methyl ester of poly(methacrylic acid) with a molecular mass of 50,000–200,000. Its specific gravity, melting point, and glass-transition temperature are 1.17–1.2, 225°C, and 105°C, respectively.

Preparation of the blends

For the preparation of the Eu/PMMA polyblends, granules of Eu from Rohm Pharma GmbH (Weiters-tadt, Germany) were used. PMMA powder was supplied by the Chemical Agency (Bombay, India). Eu granules were crushed into a powder form in a mortar. For each particular blend, amounts of Eudragit and PMMA were measured with an electronic balance so that the total amount was 2 g. The materials were mixed properly with a hand rotor, and plaques of the blends were prepared with a Buchler Simplimet II compression molder (Patiala, India). The temperature was kept a little above the melting point, and a pressure of 3–4.2 ksi was applied for molding. After about an hour, the samples were cooled to room temperature and then were removed from the molding unit. The prepared plaques of each blend were about 2–3 mm thick. All the samples were crystallized from the molten state from a temperature a little higher than the melting point, which also covered the glass-transition temperature. The crystallization time was almost the same for all the samples. Thus, a series of polyblends of Eu and PMMA were prepared with compositions of 100:0, 70:30, 50:50, 30:70, and 0:100 (w/w).

X-ray diffraction

The X-ray diffraction studies were carried out on a Ribacu rotating-crystal diffractometer at the Thaper Center for Research and Development (Patiala, India). The intensity– 2θ profile was obtained with an automatic step-scanning and strip-chart recorder.

RESULTS AND DISCUSSION

The X-ray diffraction profiles of Eu/PMMA blends with different weight-per-weight ratios are shown in Figure 1. Comparing the diffraction patterns, we observed the following:

1. For pure Eudragit RL, there were two narrow peaks at $2\theta = 6.5^\circ$ and $2\theta = 23^\circ$ and two broad peaks at $2\theta = 14^\circ$ and $2\theta = 20^\circ$.
2. With PMMA in the blends, the peak at $2\theta = 14^\circ$ was intensified, and the intensity increased with the PMMA percentage; the peak at $2\theta = 23^\circ$ disappeared, and the peak at $2\theta = 6.5^\circ$ was very

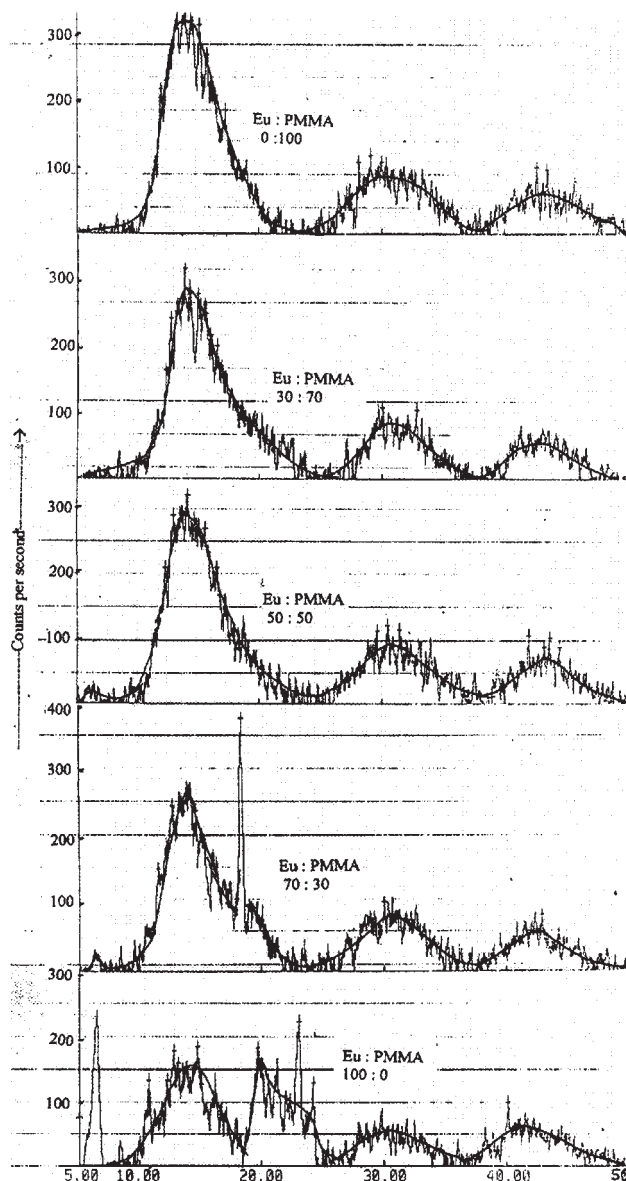


Figure 1 X-ray diffraction patterns of Eu/PMMA blends.

much reduced and disappeared with more than 50% PMMA.

3. For a 70:30 Eu/PMMA blend, a narrow and intense peak was observed at $2\theta = 18.35^\circ$.
4. For all the blends, there were two broad and low-intensity peaks at 2θ values of approximately 30 and 43° .

From the diffraction patterns of the various polyblends, the interplanar distance (d), C_s , and C_r values were computed for different peaks.

d

Bragg's equation was used to determine the distance between two successive planes from which the X-rays were diffracted:

TABLE I
Parameters of Eu/PMMA Blends from X-ray Diffraction

Sample	Eu/PMMA ratio	Peaks at 2θ ($^\circ$)	Intensity (cps)	d (\AA)	C_s (\AA)	C_r (%)
1	100:0	6.5	235	13.6	166	86
		23	230	3.86	143	90
2	70:30	14	270	6.3	27.8	43.7
		18.35	390	4.8	186	96
3	50:50	14	290	6.3	17.5	16.9
4	30:70	14	290	6.3	19.6	17.5
5	0:100	14	330	6.3	16.7	33.5

$$2d\sin\theta = n\lambda$$

where λ is the X-ray wavelength, θ is Bragg's angle, and n is the order of diffraction. d was calculated from the first order for various peaks obtained in the diffraction patterns:

$$d = \frac{\lambda}{2\sin\theta}$$

C_s

The three-dimensional crystal lattice diffracts X-rays in a manner analogous to the reflection of visible light from a ruled grating. The diffracted beams become diffused when the crystal size is nearly the same as the wavelength of the incident beam. As crystals decrease in size, the diffracted beam becomes more diffused until it is lost in the general background. Thus, the divergence of the X-ray beam is able to give C_s . The relationship between C_s and diffracted-ray line broadening was given by Scherrer as follows:¹⁰

$$C_s = \frac{k\lambda}{\beta\cos\theta}$$

where β is the pure diffraction broadening and k is a constant depending on the crystalline shape (usually taken as unity). C_s , or the distance up to which a regular arrangement of layers exists in a particular direction, was calculated from the diffraction broadening of the lines.

C_r

C_r is a measure of the regularity in the arrangement of structural elements. The diffraction intensity scan can be separated into contributions from the sharp diffractions and diffused halo. A comparison of the relative areas under the resolved curves yields C_r :

C_r

$$C_r = \frac{\text{Area of crystalline fraction (under peak)}}{\text{Area of crystalline fraction} + \text{Area of amorphous fraction}}$$

Various methods have been developed for measuring the areas under various fractions. Here C_r was measured on the premise that increasing amorphousness tended to broaden the line width, whereas increasing crystalline fraction increased the intensity. The height (CrH) of the main peak above its adjacent minimum represents the crystalline fraction of the sample, and the width of the peak at this adjacent minimum (AmW) is considered to represent the amorphousness of the sample.¹¹ C_r was calculated as follows:

$$C_r = 1 + t \left[\frac{\text{AmW}}{\text{CrH}} \right]$$

where t is a scale factor relating CrH to the full scale (total blackness). The C_r values of the polyblends were computed from the diffraction patterns.

The d , C_s , and C_r values computed for peaks with an intensity greater than 200 cps are given in Table I. The calculations revealed high C_r values for three peaks only:

1. In 70:30 Eu/PMMA blends, the peak at $2\theta = 18.35^\circ$.
2. In pure Eu, the peak at $2\theta = 6.5^\circ$.
3. In pure Eu, the peak at $2\theta = 23^\circ$.

In all the samples, broad peaks were observed at $2\theta = 14^\circ$, which yielded C_r values of less than 50%. Also, broad and less intense peaks were obtained at $2\theta = 30^\circ$ and $2\theta = 43^\circ$, which produced negative values of C_r . These were probably second- and third-order diffractions from the same planes, whose first order was at $2\theta = 14^\circ$.

The first-order diffraction peak at $2\theta = 14$ yielded $C_r = 33.5\%$ for pure PMMA. Blending with Eudragit reduced the orderliness and hence crystallinity of the substance. At 70% Eudragit, the structure of the blend

took such a form that a sharp and narrow peak was obtained at $2\theta = 18.35^\circ$, which yielded $C_r = 96\%$, $C_s = 186 \text{ \AA}$, and $d = 4.8 \text{ \AA}$. This revealed a regular arrangement up to 40 layers.

In pure Eudragit, two low-intensity sharp peaks at $2\theta = 6.5^\circ$ and $2\theta = 23^\circ$ also showed high C_r values (86 and 90%) with $d = 13.6$ or 3.86 \AA and $C_s = 166$ or 143 \AA ; this showed about 12 or 37 regularly arranged layers, respectively. Other peaks of pure Eu at 2θ values of 14 , 20 , 30 , and 43° were broad and less intense and yielded negative values of C_r . The regularity of the Eu structure was very much reduced by the presence of PMMA in the blends and totally disappeared with 50% PMMA or more. These blends produced only the PMMA structure.

CONCLUSIONS

Miscible blends of Eudragit and PMMA were formed in the melt state. The addition of PMMA to Eudragit RL increased the crystalline phase. Especially at 30 wt %, there was high regularity. The same polyblend had the highest values of the yield strength and toughness, a high hardness value, and a low brittleness index.² This revealed a correlation between the crystallinity and mechanical strength of the polyblends.

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