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Synthesis and Characterization of Poly Methyl Acrylate-Poly Ethyl Acrylate Copolymer

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Polymethyl acrylate-polyethyl acrylate copolymers were synthesized through emulsion polymerization at different chemical compositions. Samples in the whole range of compositions were studied to obtain empirical correlations between the physical properties of the samples and the composition of the copolymer. A complete characterization of the samples aimed to gather information on the corresponding microstructure and physical and chemical properties. The samples were characterized by TEM, FTIR, Raman, Viscosimetry, Thermal Analysis, Light Scattering, UV-Vis spectroscopy, Mechanical Testing, etc.

Keywords: Poly methyl acrylate-poly ethyl acrylate copolymers; synthesis; emulsion polymerization structure; mechanical properties

INTRODUCTION

Acrylic materials were originally developed approximately six decades ago. However, in the middle of fifties, the scientific and technological interest in this kind of materials grew significantly due to their applications in preparing paints and coatings, due to their high resistance for outdoor applications. This type of materials is very resistant to UV

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radiation and are hardly hydrolyzed. Additionally, they present good transparency and good compatibility with additives and plastifiers. For these reasons, the fields of application became wider in the sixties when several acrylic monomers were developed. Today, acrylic polymers are routinely used for indoor and outdoor paints, adhesives, paper applications, fabrics, waxes, elastomers, automotive parts, etc. [1–3].

In this paper, the synthesis and characterization of poly methyl acrylate-poly ethyl acrylate copolymers produced by emulsion polymerization [2, 4–7], are reported. Six different copolymer samples at different chemical compositions were prepared, covering the whole range of concentrations.

COPOLYMERS PREPARATION

Several samples of poly methyl acrylate-poly ethyl acrylate copolymer were prepared at different chemical compositions. The methyl acrylate (MA) and ethyl acrylate (EA) monomers (Celanese Mexicana S.A.) were used as received; the EA/MA weight ratio was varied from 0 to 100% with four intermediate concentrations equally spaced. The surfactant used was a sodic salt of octiphenyl sulfated and etoxilated with 25 mol of ethylene oxide ($C_8H_{17}-C_6H_4-O-(CH_2-CH_2-O)_{25}-OSO_3Na$) (Henkel Mexicana, S.A.) while the initiator used was ammonium persulfate (Quimica Argostal, S.A.). The concentrations of the surfactant and the initiator in monomers were set to 0.99% and 0.26% by weight, respectively.

The emulsion polymerization procedure is similar to that reported elsewhere [4, 7–11]. It consists of a batch process to form the seed, followed by a semi-continuous process. The polymerization reaction was carried out in a 2 litres reactor with temperature control, stirring at 60 rpm, with two addition tanks (one with stirring and the other without it) and nitrogen inlet to control the atmosphere.

Initially, the reactor was fed with 35% of the water and 10% of the surfactant. In the unstirred tank, 15% of the water is mixed with the initiator until to obtain a solution, while the other tank contains the rest of the water, the EA and MA monomers and the rest of surfactant, all emulsified.

The polymerization begins when 4% of the stirred tank and 4% of the unstirred tank were added to the reactor and the temperature has raised to 85°C. Periodic additions of both tanks were performed in such a way that the whole procedure took 3.5 hours. This polymerization was carried out under nitrogen atmosphere and in reflux condition. Once the whole amount of monomers were added, the reactor temperature was increased to 90°C and held for 4 hours. Table I contains a summary of the compositions of the six families of specimens prepared.

RESULTS AND DISCUSSION

The density of the latex samples were determined by using an analytical balance and a picnometer and the results are reported in Figure 1. Here, it is possible to observe that the density of the samples is linearly reduced as the content of ethyl acrylate is increased; this is because the density of the EA monomer is lower than the MA monomer. The lateral group for EA is larger than in the case of MA; consequently, poly methyl acrylate (PMA) polymers are more compact than poly ethyl acrylate (PEA) polymers, producing a reduction in the density of the copolymer as the EA content is increased.

The spectroscopic studies of the samples [12, 13] were carry out in a FTIR Perkin Elmer machine. Two different spectra of the samples were obtained: the transmittance spectrum was obtained by applying the Attenuated Total Reflection technique to the wet samples, and the absorption spectrum was obtained for samples dried at 40°C for several days. In Figure 2 it is possible to see both spectra for sample No. 2, containing 20% of EA.

TABLE I Intrinsic Viscosity and the molecular compositions of the copolymers

Sample	Composition (EA/MA)	$[\eta]$ (ml/g)	M
1	0	130.71	481,994
2	0.2	109.98	397,575
3	0.4	108.79	403,455
4	0.6	105.67	396,945
5	0.8	108.01	422,147
6	1.0	104.75	411,653

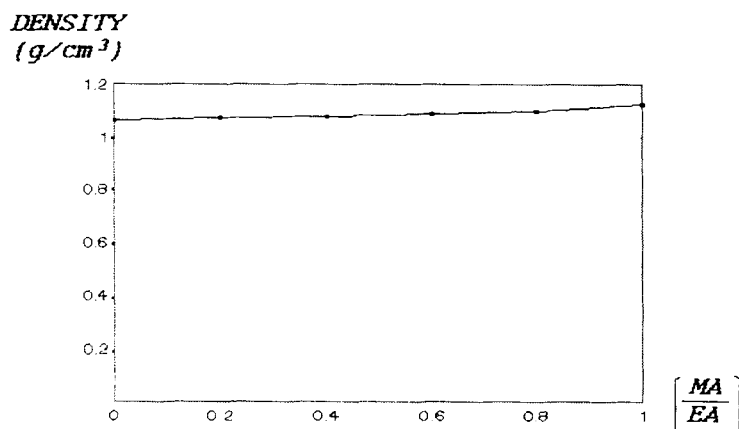


FIGURE 1 In this figure the mass density is plotted as a function of the copolymer composition.

The FTIR absorbance spectra of PEA and PMA, have characteristic peaks in 1298.15 cm^{-1} and 970.14 cm^{-1} respectively. These can be used to quantify the composition of the copolymer. In Figure 3 we are plotting the height of the absorbance peak for EA and for ME as a function of the mass composition of the copolymer. As can be noticed, these plots can be used as a calibration curves for evaluation of the monomers concentrations in the copolymer.

Raman spectroscopy was also performed to all samples; however, the Raman spectra are similar to each other. Figure 4 shows a typical Raman spectrum of the sample No. 4, containing 60% of EA.

The mean diameter of the latex spheres was determined by using a dynamic light scattering apparatus (Malvern). Also the average number of particles per gram of the emulsion was obtained, since the chemical composition and the particle size of the samples were already known. These data are shown in Figure 5 where it can be noticed that, for almost all samples, both the particle size and the number of particles per unit mass, are independent from the chemical composition of the latex spheres.

It is worth mentioning that sample No. 1, corresponding to pure MA latex spheres has a different behavior respect to the other samples. As can be noticed from Figure 5, for sample No. 1, the particle size is lower than the other samples, but the number of par-

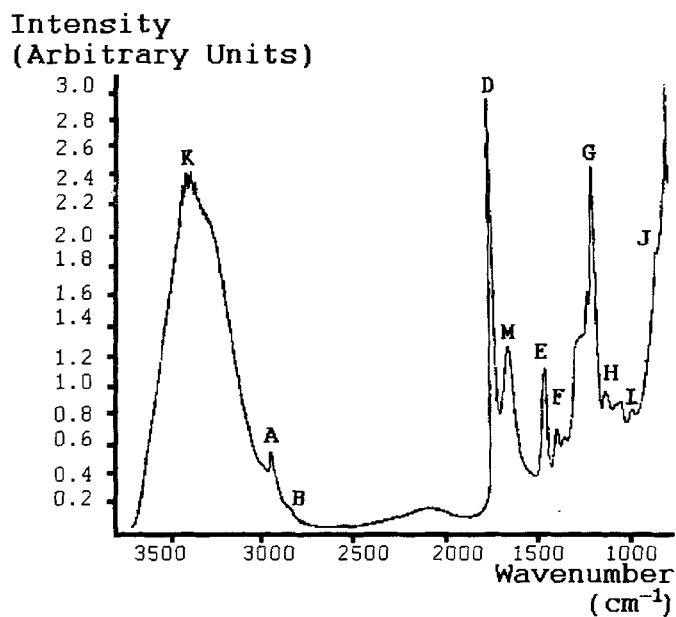
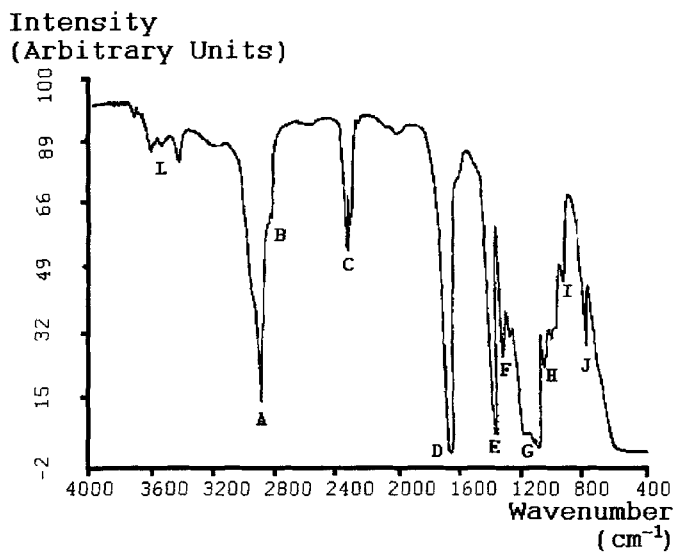


FIGURE 2 Typical FTIR spectra through Absorption (Attenuated Total Reflectance) [top] and Transmittance techniques [bottom] of sample No. 2, corresponding to 20% EA.

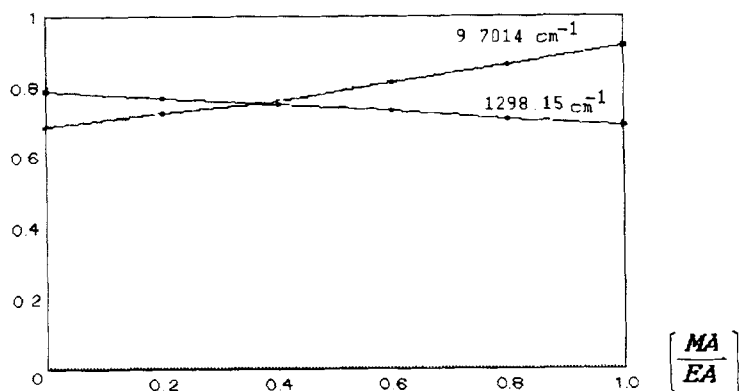
**RELATIVE
INTENSITY**

FIGURE 3 The intensities of the FTIR Absorption peaks at 970.14 and 1298.15 cm^{-1} are plotted as a function of the copolymer composition.

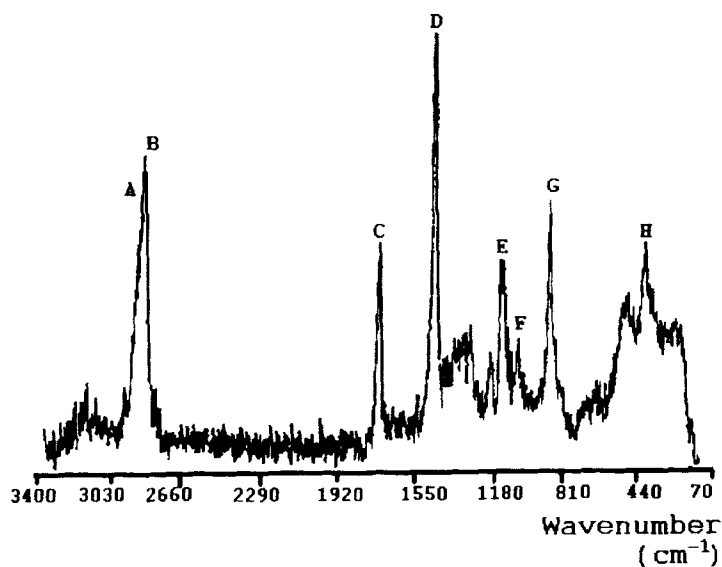


FIGURE 4 Typical Raman spectrum of the sample No. 4 corresponding to 60% of EA.

ticles per gram is larger than in the other cases. For this sample, the number of initiation centres during polymerization is substantially larger than in the other cases; this means that the monomer has to be

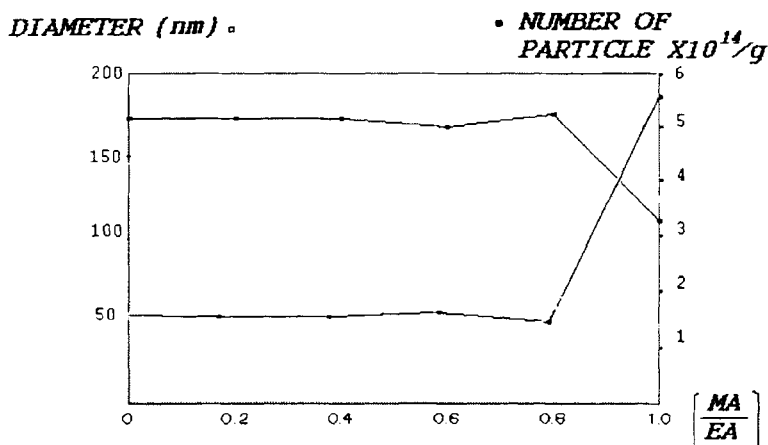


FIGURE 5 Particle size profile of the latex particles as a function of the composition. Also, the number of particles per unit of mass is shown.

distributed among more centers, reducing the size of the particles. The reason for this behavior is the low molecular weight of the methyl acrylate and the high density of this sample; additionally, the molecular weight of sample No. 1 is the largest of all samples.

The above curves mean that the emulsion polymerization produces a homogeneous growth of the particles until they reach the equilibrium size; additionally, once the polymerization starts, the number of initiation centers remain practically constant during the process; this is due to the fact that the amount of initiator and the surfactant was kept constant for all samples.

Due the solubility of the monomers in water, the polymerization process can be carried out into the seed by homogeneous nucleation, but once the sequential additions begin, the polymerization is pursued by micellar nucleation until the whole process is completed.

The molecular weights of the polymers were obtained by using a capillary Ubbelohde viscosimeter and acetone as solvent. The corresponding Mark-Howinks parameters for EA and MA at 25°C are [14]:

$$k(\text{EA}) = 51 \times 10^{-3}, \quad a(\text{EA}) = 0.59$$

$$k(\text{MA}) = 5.5 \times 10^{-3}, \quad a(\text{MA}) = 0.77$$

Table I contains the intrinsic viscosity $[\eta]$ and the molecular weight of the sample evaluated by using the expression:

$$\frac{1}{M} = \frac{w_{EA}}{\left[\frac{[\eta]}{k_{EA}}\right]^{1/a_{EA}}} + \frac{1-w_{EA}}{\left[\frac{[\eta]}{k_{EA}}\right]^{1/a_{EA}}}$$

where w_{EA} and w_{MA} are the weight fraction of EA and MA in the copolymer, M the copolymer molecular weight and we are using the Mark-Houwinks relationship $[\eta] = kM^a$.

The glass transition temperature T_g of the samples were obtained by using a DSC calorimeter Du Pont 2100. Figure 6 graphically shows the dependence of the inverse of the glass transition temperature T_g^{-1} as a function of the composition of the copolymer. The continuous line corresponds to the equation:

$$\frac{1}{T_g} = w_{EA} \left[\frac{1}{T_g} \right]_{EA} + w_{MA} \left[\frac{1}{T_g} \right]_{MA}$$

where, as before, w_i corresponds to the weight fraction of one component of the copolymer.

The latex samples were also studied by Transmission Electron Microscopy (TEM) using a JEOL 100CX machine; the samples were

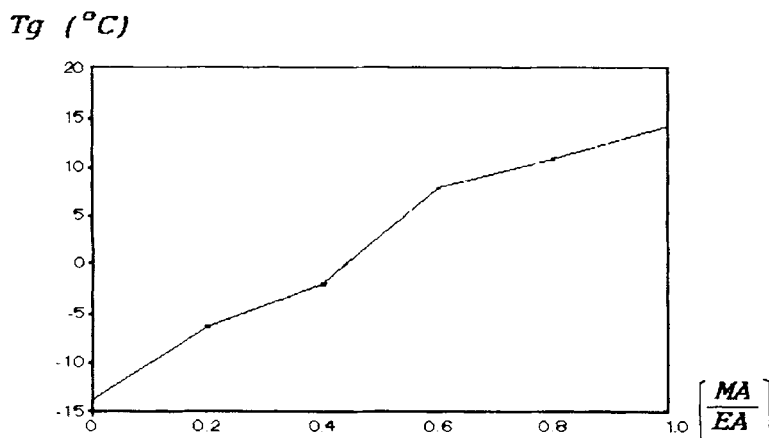


FIGURE 6 The inverse of the T_g follows a linear relationship with mass composition.

diluted and dried at room temperature and phosphotungstic acid was used as staining agent; the samples were supported in carbon-coated grids. The mean diameter of all samples obtained from TEM is about 122 nm; this value is smaller than that reported by dynamic light scattering (DLS), which is so because with TEM the number average is obtained, while with DLS the z-average is provided.

Mechanical tests were performed in an Instron machine model 1125. The films were obtained by evaporation of the latex samples for 5 days at 40°C [15–19]. From the stress-strain plots it was possible to obtain the Young modulus as a function of copolymer concentration. As observed in Figure 7, the Young modulus goes to zero as the EA content in the copolymer increases; this dependence can be mathematically expressed as:

$$Y([c]) = 1.748 e^{-5.35[c]}$$

where $[c]$ is the EA concentration in the copolymer; this is shown in this figure with continuous line. As can be noticed, the fitting to the experimental data is excellent.

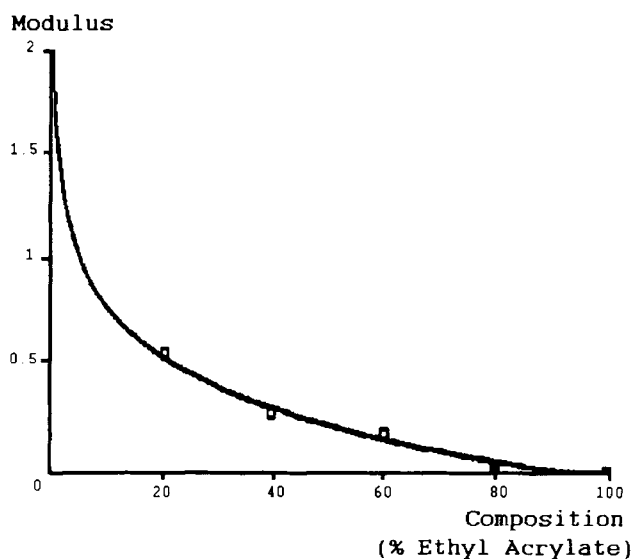


FIGURE 7 The Young Modulus of the EA-MA copolymer films plotted as a function of the composition.

CONCLUSION

A complete study of the copolymer samples prepared at different monomer concentrations is shown. The polymerization procedure produces a reproducible set of samples.

Acknowledgement

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