

Study of Dynamic Mechanical Properties of Poly(vinyl Chloride)-Ethylene Vinyl Acetate Copolymer and Poly(vinyl Chloride)-Chlorinated Ethylene Vinyl Acetate Copolymer Mixtures

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Synopsis

The compatibility of the mixtures poly(vinyl chloride)-ethylene vinyl acetate copolymer and poly(vinyl chloride)-chlorinated ethylene vinyl acetate copolymer was studied by the method of dynamic mechanical testing. The character of G' and G'' was confronted with the Takayanagi model. In all cases a limited compatibility of the components was observed.

INTRODUCTION

Recently, Hard,¹ Hamer,² and Göbel³ were concerned with the study of the mixture of poly(vinyl chloride) (PVC) with ethylene vinyl acetate copolymer (EVAc). They found that compatibility with PVC could be obtained for arbitrary composition of the mixture provided the composition of EVAc varied within a limited region (from 60 to 75 weight-% of vinyl acetate). If the content of vinyl acetate in the copolymer is less than 50%, the mixture has the character of a two-phase system. In this study, the mixture of PVC with EVAc copolymer containing approximately 45 weight-% of vinyl acetate were investigated at varying PVC and EVAc proportions. In the same concentration range, mixtures of PVC with chlorinated EVAc were studied. The aim was to find the effect of component proportions and degree of EVAc chlorination on the properties of the mixture.

EXPERIMENTAL

Materials

The following materials were used: poly(vinyl chloride), trademark Sicon 548 FM; ethylene vinyl acetate copolymer, trademark Levapren 450 P, content of ethylene component ~45% by weight, $M_n = 4.73 \times 10^4$, $T_g = -30^\circ\text{C}$ (determined by dynamic mechanical method at 1 Hz).

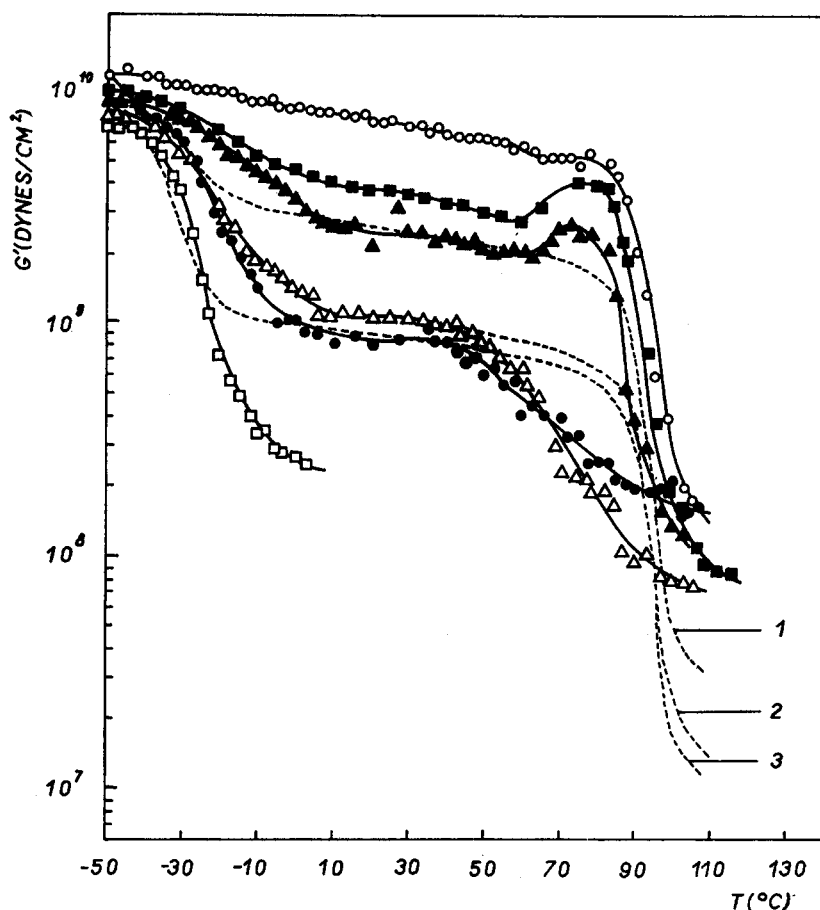


Fig. 1. Dependence of dynamic modulus G' on temperature for the mixture poly(vinyl chloride) and ethylene vinylacetate copolymer of the following composition: (O) EVAc + PVC, 0.1:0.9; (■) EVAc + PVC, 0.2:0.8; (▲) EVAc + PVC, 0.25:0.75; (Δ) EVAc + PVC, 0.4:0.6; (●) EVAc + PVC, 0.5:0.5; (□) EVAc + PVC, 0.75:0.25. Dashed lines show G' values according to Takayanagi's model for the mixtures EVAc-PVC in the ratios 0.25:0.75 (1), 0.4:0.6 (2), and 0.5:0.5 (3).

Methods

The mixtures were prepared from 1% chlorobenzene solution by precipitating into methanol and drying to constant weight at 60°C under vacuum.

The chlorination was carried out by bubbling chlorine through 1% chlorobenzene solution of EVAc and irradiating with ultraviolet light.

The chlorine content was determined by the modified Schöniger method.^{4,5}

Dynamic mechanical testing was performed by means of a torsion pendulum at the frequency of about 1 Hz.

RESULTS AND DISCUSSION

Figures 1 and 2 present the dependence of dynamic modulus G' and loss modulus G'' on temperature for different compositions of the PVC-EVAc mixture. The mixture shows two transition regions and may be characterized as a two-component system. The values of dynamic modulus G' in the region between T_g of the components decrease with increasing content of EVAc. The dashed lines in Figures 1 and 2 give the values of moduli G' and G'' calculated according to the Takayanagi model⁶ by using the relationship

$$G_{\text{mixt}}^* = \left[\frac{\varphi}{\lambda G_R^* + (1 - \lambda) G_P^*} + \frac{1 - \varphi}{G_P^*} \right]^{-1} \quad (1)$$

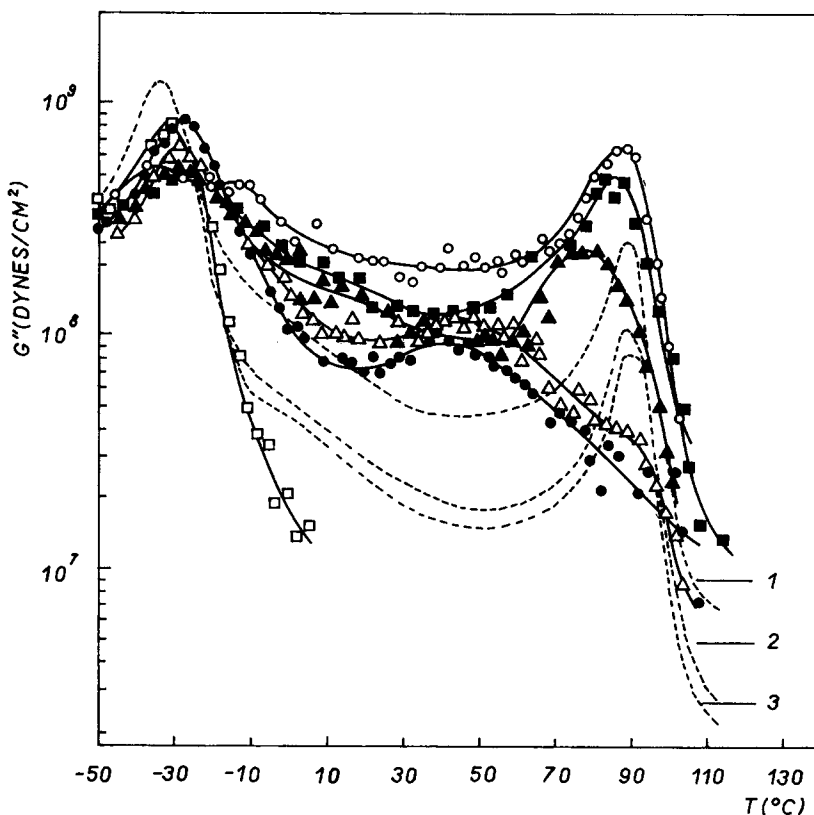


Fig. 2. Dependence of loss modulus G'' on temperature for the mixture poly(vinyl chloride) and ethylene vinyl acetate copolymer of the following composition: (O) EVAc + PVC, 0.1:0.9; (■) EVAc + PVC, 0.2:0.8; (▲) EVAc + PVC, 0.25:0.75; (Δ) EVAc + PVC, 0.4:0.6; (●) EVAc + PVC, 0.5:0.5; (□) EVAc + PVC, 0.75:0.25. Dashed lines show G'' values according to Takayanagi's model for the mixtures EVAc-PVC in the ratios 0.25:0.75 (1), 0.4:0.6 (2), and 0.5:0.5 (3).

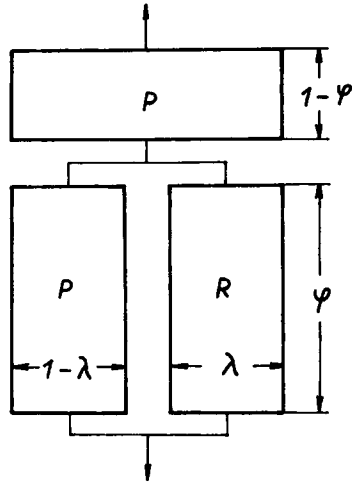


Fig. 3. Graphic representation of Takayanagi's model.

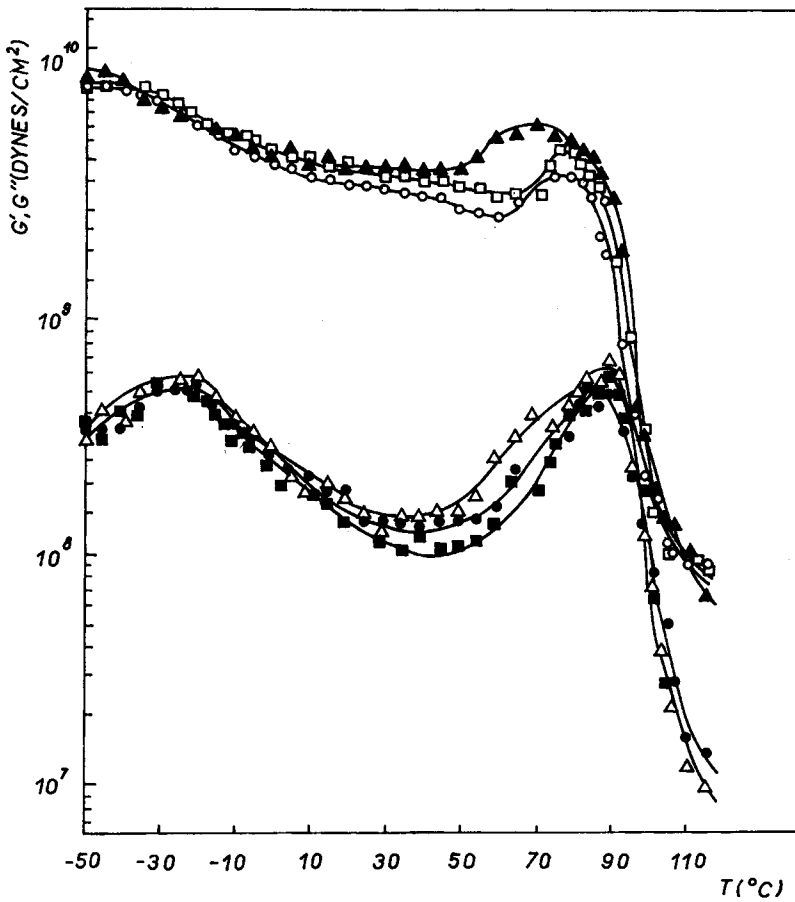


Fig. 4. Dependence of dynamic modulus G' and loss modulus G'' on temperature for the mixture poly(vinyl chloride) and ethylene vinyl acetate copolymer (0.8:0.2): (O) (●) sample pressed at 100°C; (▲) (Δ) sample kept at 100°C for 30 min; (□) (■) sample kept at 100°C for 60 min.

TABLE I
Values of Parameter λ According to Takayanagi's Model^a

Volume fraction of EVAc	λ_K	λ_E
0.1494	0.4896	0.6737
0.2182	0.5309	0.6411
0.2833	0.5700	0.8366
0.3452	0.6071	0.8923
0.5132	0.7079	0.9426
0.6126	0.7676	0.9437
0.7034	0.8220	0.9815
0.8259	0.8955	—

^a λ_K = values corresponding to the measured course of modulus G' ; λ_E = values calculated for spherical particles according to Kerner condition.

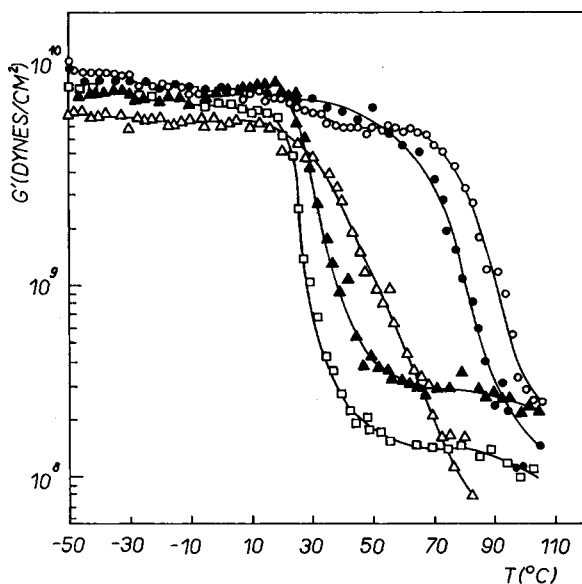


Fig. 5. Dependence of dynamic modulus G' on temperature for the mixtures poly(vinyl chloride) and chlorinated ethylene vinyl acetate copolymer (32% Cl) of the following composition: (O) Cl-EVAc + PVC, 0.2:0.8; (●) Cl-EVAc + PVC, 0.3:0.7; (Δ) Cl-EVAc + PVC, 0.5:0.5; (▲) Cl-EVAc + PVC, 0.7:0.3; (□) Cl-EVAc + PVC, 0.8:0.2.

where G_R^* and G_P^* denote the complex dynamic moduli of the components (rubberlike and glassy). The graphic representation of this model is given in Figure 3. The parameters φ and λ characterize the state of mixing, and their product expresses the volume fraction of the disperse phase v_r . Provided the disperse phase forms spherulites, it follows from a comparison of the Takayanagi model with the Kerner model^{6,7} that

$$\varphi = \frac{5v_r}{2 + 3v_r} \quad \lambda = \frac{2 + 3v_r}{5} \quad (2)$$

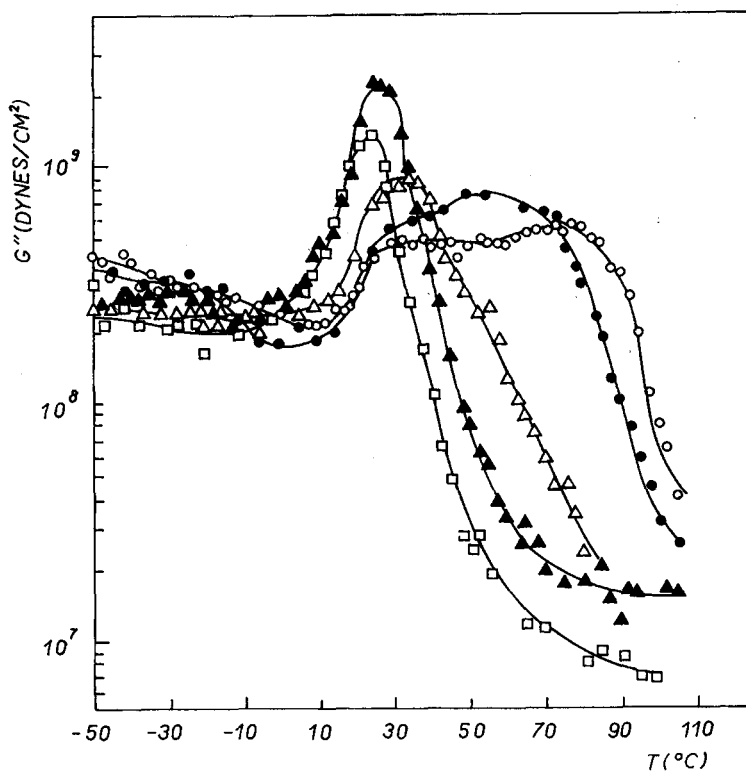


Fig. 6. Dependence of loss modulus G'' on temperature for the mixtures poly(vinyl chloride) and chlorinated ethylene vinyl acetate copolymer (32% Cl) of the following composition: (O) Cl-EVAc + PVC, 0.2:0.8; (●) Cl-EVAc + PVC, 0.3:0.7; (Δ) Cl-EVAc + PVC, 0.5:0.5; (\blacktriangle) Cl-EVAc + PVC, 0.7:0.3; (\square) Cl-EVAc + PVC, 0.8:0.2.

If the disperse phase forms aggregates, the parameter λ increases. To calculate the curves (dashed lines in Figs. 1 and 2), the values of λ were so chosen that the agreement with the experimentally found modulus G' could be reached at a temperature of 30°C. In Table I, the values of λ thus chosen are compared with the values calculated according to eq. (2). The values of λ calculated by using eq. (2) are smaller over the whole composition range. It would indicate some formation of aggregates from the particles dispersed. But it is obvious from the shift of transition regions (especially 80°C for the PVC transition) that the mixing of the components to a certain extent results in a molecular mixture formation. According to Hammer,² EVAc containing 60–75 weight-% of vinyl acetate forms a mixture compatible with PVC. EVAc used had a composition approximate to the above mentioned, and at the statistical distribution of monomer units it is not possible to exclude the existence of segments or longer sections of the EVAc macromolecules in which the vinyl acetate content exceeds 60%.

It follows from the course of the dependence of G' and G'' on temperature that there is no distinct interface between the phases, so that a continuous

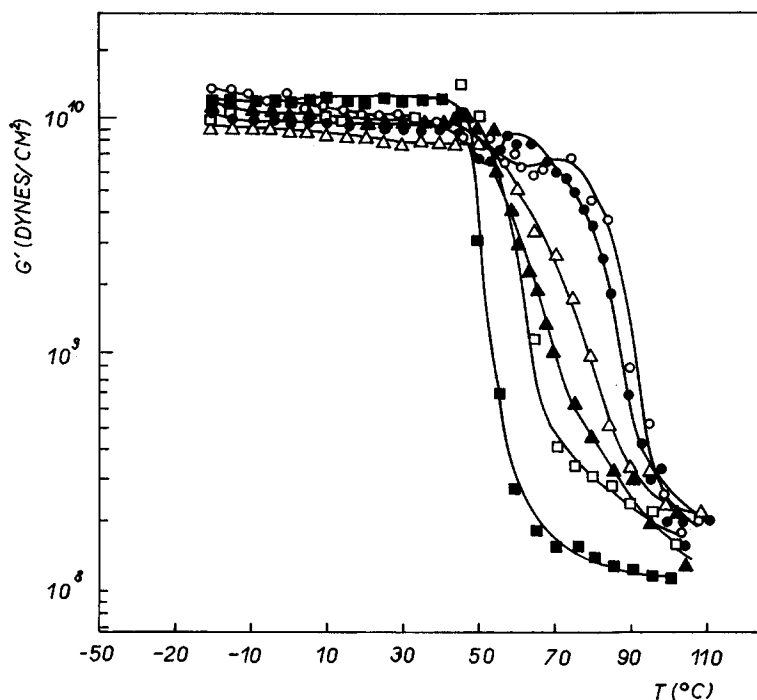


Fig. 7. Dependence of dynamic modulus G' on temperature for the mixtures poly(vinyl chloride) and chlorinated ethylene vinyl acetate copolymer (38% Cl) of the following composition: (○) Cl-EVAc + PVC, 0.2:0.8; (●) Cl-EVAc + PVC, 0.3:0.7; (Δ) Cl-EVAc + PVC, 0.4:0.6; (▲) Cl-EVAc + PVC, 0.5:0.5; (□) Cl-EVAc + PVC, 0.6:0.4; (■) Cl-EVAc + PVC, 0.8:0.2.

transition from molecular mixing to dispersed particles is more likely to exist. Such a state of mixing may also give rise to smaller λ values.

A remarkable difference between the measured and calculated values of G' occurs at temperatures ranging from 70° to 90°C if the ratio of PVC to EVAc in the mixture is 0.8:0.2 or 0.75:0.25. In this concentration region, the modulus G' rises again. A similar case occurs in the event of phase inversion. A suitable preparation of mixtures would permit the formation of a composite in which the component with the lower T_g forms a continuous phase and an irreversible inversion^{8,9} takes place during temperature rise. But for the mixtures of PVC with EVAc under consideration, the course of the modulus G' does not change even after keeping the mixture two times at 100°C for 30 min (Fig. 4). The phase inversion is also contradicted by the low EVAc content in the mixture. It is a well-known fact that, provided a component in a system represents less than 20–25% by volume, the formation of a continuous phase by this component is not probable.¹⁰

One of the possible explanations for the increase of the modulus in the temperature range from 70°C to 80°C may be based on the assumption that the motion of segments in EVAc is hindered when the motion of segments in

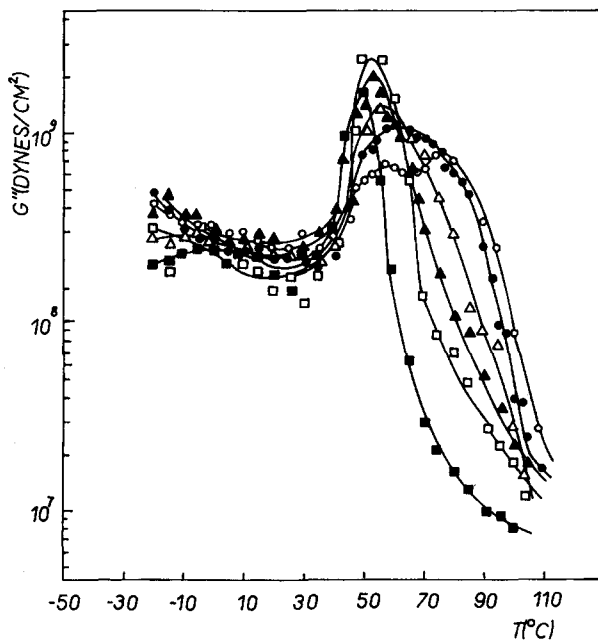


Fig. 8. Dependence of loss modulus G'' on temperature for the mixtures poly(vinyl chloride) and chlorinated ethylene vinyl acetate copolymer (38% Cl) of the following composition: (O) Cl-EVAc + PVC, 0.2:0.8; (●) Cl-EVAc + PVC 0.3:0.7; (Δ) Cl-EVAc + PVC, 0.4:0.6; (\blacktriangle) Cl-EVAc + PVC, 0.5:0.5; (\square) Cl-EVAc + PVC, 0.6:0.4; (\blacksquare) Cl-EVAc + PVC, 0.8:0.2.

PVC begins. If the temperature is above the T_g of PVC, the motion of segments in both components may affect each other to a higher degree than at lower temperatures. Assuming that such mixture is completely compatible above the T_g of PVC, it has still properties of glass in a narrow temperature interval at dynamic tests, and the value of modulus G' rises to the level corresponding to the glass state. An improved bonding between the phases as well as a release of the internal strain due to different thermal expansion of the phases may be assumed to be another possible cause of that phenomenon.

Figures 5 and 6 represent the variation of dynamic modulus G' and loss modulus G'' with temperature for the mixtures of PVC with chlorinated EVAc (Cl-EVAc). (The chlorine content was 32%, $T_g \sim 25^\circ\text{C}$.) The character of the curves indicates a two-phase system, which is obvious especially in the case of higher contents of PVC. The mixture PVC-Cl-EVAc (0.7:0.3) apparently shows only one, but a considerably extended, transition region. For a polymer mixture, such a wide transition region may represent an ensemble of adjoining regions (determined by the distribution of composition in this case). The PVC-Cl-EVAc mixture (0.5:0.5) shows a single maximum of loss modulus which occurs between the transition temperatures of both components. This would indicate a higher

degree of compatibility in comparison with nonchlorinated EVAc. For lower contents of PVC, it is difficult to draw any conclusion from dynamic mechanical measurements as to mutual compatibility of components. The shape of the curves is largely determined by the properties of C-EVAc (which forms a continuous phase); nevertheless a certain shift of transition regions to higher temperatures is apparent.

For chlorine contents of 38% in Cl-EVAc (T_g 45°C) (Figs. 7 and 8), further improvement of compatibility can be observed and only one transition region appears in the whole composition range of the mixture.

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Received March 20, 1972