The Effect of Surfactant and Copolymer Polarity on the Film-Formation Temperatures of Some Vinylidene Chloride Copolymers

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Synopsis

The minimum temperature required for a copolymer emulsion to form a continuous film, T_{mf}, and the glass transition temperature T_g of the copolymer were studied for vinylidene chloride–acrylate copolymers and vinylidene chloride–acrylonitrile copolymers. The T_{mf} and T_g were studied as a function of the nature of the surfactant used in the preparation of the emulsion. The T_{mf} was found to deviate markedly from the T_g for most compositions and the T_{mf}-composition curves were found to be similar in shape to the T_g-composition curves, exhibiting a maximum in the case of the acrylate copolymers. The quantity $T_{mf} - T_g$ changes from negative to positive with decreasing polar character of the methyl and ethyl acrylate copolymers. This is especially obvious in the ethyl acrylate copolymer. The high T_{mf} values for copolymers containing acrylonitrile is attributed to strong interchain forces, which orientate the neighboring segments in a latex particle unfavorably for interpenetration with other particles. The nature of the surfactant used in the preparation of the emulsion was found to affect the T_{mf}. Emulsions of nonpolar, hydrophobic copolymers containing a blend of anionic and nonionic surfactants have a higher T_{mf} than those containing only anionic surfactant; however, with an increase in the amount of hydrophilic units in the copolymer the converse is true, except in the case of the highly polar copolymers of vinylidene chloride–methyl acrylate, in which the T_{mf}'s for both surfactant systems are similar.

INTRODUCTION

The increasing use of copolymer emulsions as surface coatings for a variety of substrates makes a knowledge of such fundamental properties as the glass transition temperature T_g, the minimum film-formation temperature T_{mf}, and the relationship between the two of vital importance. The manner in which the nature of the surfactant in the emulsion and the composition or polarity of the copolymer modifies such relationships is also of importance to emulsion formulators and may also be useful in supporting some current theories on the mechanism of film formation.

There are several theories which purport to explain the process of film formation from an aqueous latex;[1,2,3] they have been reviewed in a paper by Brodnyan and Konen.[4] What little experimental data are on hand tend to favor the theory proposed by Brown.[2] This theory suggests that film

formation occurs by a process which involves the polymer's being pulled into the vacant spaces left as the water is transported to the surface under surface tension forces.   Recently Sheetz[5] suggested that flocculation, wet sintering, and capillarity may all be important phenomena in the early stages of drying, but diffusion of water vapor through the polymer becomes more important in the later stages.   The magnitude of the contribution of these factors is considered to depend upon the surface free energy of the polymer–water interface, the particle diameter, the water permeability of the polymer, the contact angle between the polymer and water, and the surface tension at the water–air interface.   Deformation of the polymer is necessary for the processes of drying and coalescence to take place.   Since deformation occurs, the T_{mf} ought to be equal to, or close to, the T_g. For a surface process, however, which involves surfactant, water and the polymer–water interface the polarity of the polymer, i.e., its hydrophilic-lyophobic character, and the nature of the surfactant would be expected to affect the temperature at which film formation occurs, and it may be considerably different from the T_g.   Voyutskii[6] has suggested that the nature of the surfactant should be an important factor in film formation. Hwa[7] has shown that the volume fraction of polymer at which flocculation occurs varies with the surfactant type present in the latex.

Brodnyan and Konen[4] studied some copolymers of different polarities, measuring the T_{mf} and calculating the T_g.   They found that two copolymers could have the same T_g, but because of differences in polarity the T_{mf} values were widely different.

In this paper we describe the measurements of T_g made from dried, purified copolymers and of T_{mf} made from copolymer emulsions.   The systems studied were vinylidene chloride–methyl acrylate, vinylidene chloride–ethyl acrylate and vinylidene chloride–acrylonitrile.   Two series of copolymers of varying composition were prepared for each system.   The two series differed only in the nature of the emulsifier used.   One contained a mixed anionic and nonionic surfactant, and the other was prepared with the anionic type alone.

Recently, Illers[8] demonstrated that many copolymer systems exhibit considerable deviation from the ideal type equations of Gordon and Taylor[9] and Wood,[10] and it was considered necessary to determine the T_g experimentally rather than to calculate it for particular copolymers from these equations.   Some of these T_g results were reported in an earlier communication.[11]

EXPERIMENTAL METHODS

Preparation of Copolymer Emulsions

Copolymer emulsions were prepared in a 700 ml. flanged flask fitted with a stirrer through a gland in the center neck.   One of the side necks held a reflux condenser fitted with a cold finger containing an ice–salt mixture to prevent loss of vinylidene chloride (b.p. 31.7°C.).   The monomers were

freed from inhibitor and distilled before use. All polymerizations were carried out under an atmosphere of purified nitrogen. The redox initiators used were ammonium persulfate and sodium metabisulfite, and the continuous addition method was employed, monomers being added continuously to an initial charge at 35°C. Sodium lauryl sulfate (B.D.H. special-purity grade) was used for the anionic type of emulsion and for those containing a mixed anionic and nonionic surfactant; sodium lauryl sulfate and a nonyl phenol–ethylene oxide condensate containing 20 moles of ethylene oxide was used in the ratio 1:3.

Copolymer Analysis

A sample of polymer from each emulsion was analyzed for chlorine content by the oxygen flask method.[12] The polymers were purified prior to analysis by repeated precipitation from tetrahydrofuran by the addition of methanol. The copolymer compositions were calculated from the chlorine contents and were found to agree well with expected values based on monomer feed compositions.

Glass Transition Temperatures

The glass transition temperatures of copolymers of vinylidene chloride–methyl acrylate and vinylidene chloride–ethyl acrylate, which form clear, transparent films, were measured by the refractive-index method described by Beevers et al.[13] The copolymers were precipitated from the emulsion by adding solid CO_2 and purified by repeated precipitation from tetrahydrofuran by the addition of methanol. Films were cast on glass from tetrahydrofuran solution and dried at 100°C. The refractive-index measurements were carried out with an Abbé refractometer, and the heating rate was 1°C. per 5 min.

The glass temperatures of the vinylidene chloride–acrylonitrile copolymers were determined in conventional glass dilatometers with mercury as containing fluid.

Minimum Film-Formation Temperatures

The minimum film-formation temperatures T_{mf} were determined by coating the emulsions on an aluminum temperature-gradient bar and determining the temperature at which a continuous strong film formed. This method has been described by Protzman and Brown[14] and Brodnyan and Konen.[4] We found it possible to reproduce T_{mf} with an accuracy of ±1°C. No difference was found in determining T_{mf} under different conditions of humidity, and the T_{mf} was found to be independent of the amount of emulsion used. This is in agreement with observations made by the workers cited above.

Experimental Results

Tables I–III give the results of T_g together with T_{mf} values for the three systems studied. Tables IV and V give the $T_{mf} - T_g$ values for vinyl-
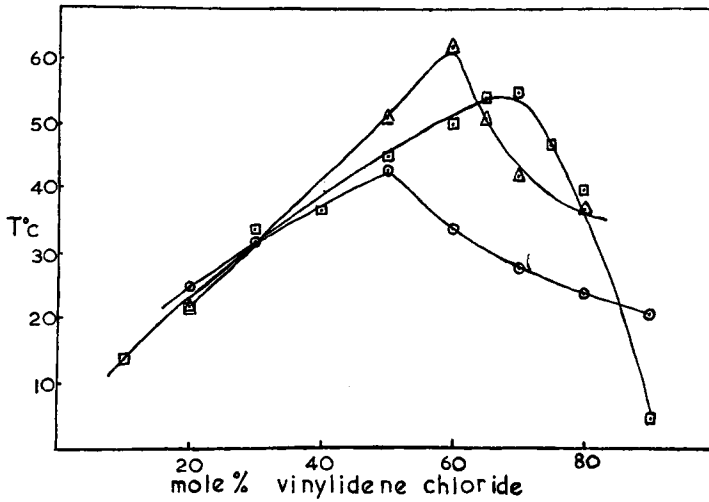
Fig. 1. Glass transition temperatures and minimum film-formation temperatures of vinylidene chloride–methyl acrylate copolymers: (⊙) T_g; (▣) T_{mf}, anionic–nonionic surfactant; (△) T_{mf}, anionic surfactant.
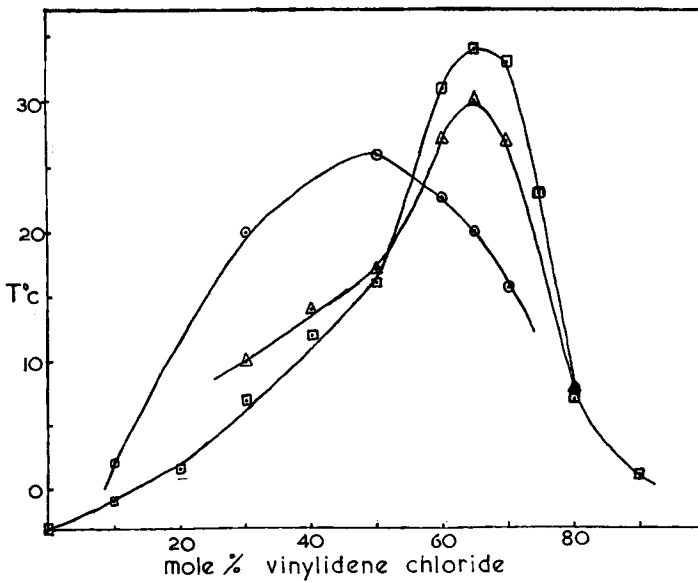

Fig. 2. Glass transition temperature and minimum film-formation temperatures of vinylidene chloride–ethyl acrylate copolymers: (⊙) T_g; (▣) T_{mf}, anionic–nonionic surfactant; (△) T_{mf}, anionic surfactant.
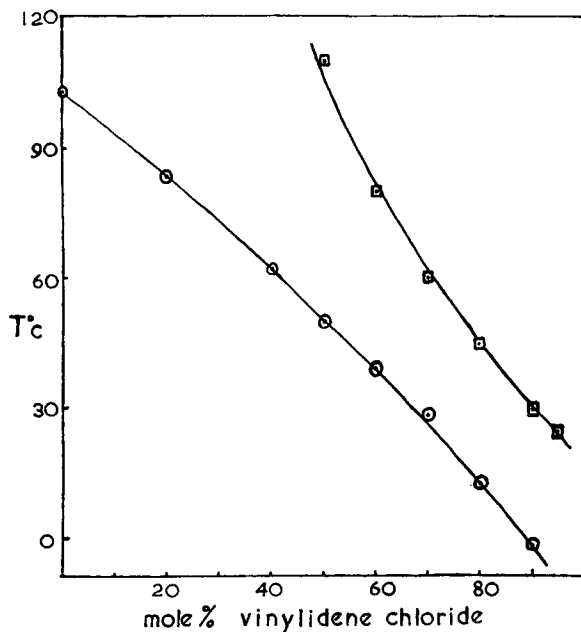
Fig. 3. Glass transition temperatures and minimum film-formation temperatures of vinylidene chloride–acrylonitrile copolymers: (⊙) T_g; (▫) T_{mf}, anionic–nonionic surfactant.

idene chloride–methyl acrylate and vinylidene chloride–ethyl acrylate copolymer systems, respectively, both in the presence of anionic surfactant alone and anionic–nonionic surfactant blends. The data in Tables I–III are plotted as graphs in Figures 1–3.

TABLE I
Minimum Film-Formation Temperatures and Glass Temperatures
of Vinylidene Chloride–Methyl Acrylate Copolymers

Vinylidene chloride, mole-%	Mixed surfactant T_{mf}, °C.	Anionic surfactant T_{mf}, °C.	T_g, °C.
10	14	—	—
20	22	22	25.5
30	34	—	32
40	37	—	—
50	45	51	43
60	50	62	34
65	54	51	—
70	55	42	28
75	47	—	—
80	40	37	24
90	5	—	21

TABLE II

Minimum Film-Formation Temperatures and Glass Temperatures of
Vinylidene Chloride–Ethyl Acrylate Copolymers

Vinylidene chloride, mole-%	Mixed surfactant T_{mf}, °C.	Anionic surfactant T_{mf}, °C.	T_g, °C.
0	−3	—	—
10	−1	—	2
20	1.6	—	—
30	7	10	20
40	12	14	—
50	16	17	26
60	31	27	22.6
65	34	30	20
70	33	27	15.7
75	23	—	—
80	7	7.8	—
90	1	—	—

TABLE III

Minimum Film-Formation Temperatures and Glass Temperatures of
Vinylidene Chloride–Acrylonitrile Copolymers

Vinylidene chloride, mole-%	Mixed surfactant, T_{mf}, °C.	Anionic surfactant, T_{mf}, °C.	T_g, °C.
0	—	—	105
20	>100	—	83
40	>100	—	61.8
50	110	—	49.8
60	80	—	39.3
70	60	>100	28.7
80	45	93	12.6
90	30	—	−1.5
95	25	—	—

TABLE IV

Minimum Film-Formation Temperatures Minus Glass Temperatures of Vinylidene
Chloride–Methyl Acrylate Copolymers with Anionic and Anionic–Nonionic
Mixed Surfactants

Vinylidene chloride, mole-%	Mixed surfactant $T_{mf} - T_g$	Anionic surfactant $T_{mf} - T_g$
20	−4	−4
30	2	—
50	2	8
60	16	28
65	23.5	20.5
70	27	14
80	16	13

TABLE V
Minimum Film-Formation Temperatures Minus Glass Temperatures of Vinylidene
Chloride–Ethyl Acrylate Copolymers with Anionic and
Aniohic–Nonionic Surfactants

Vinylidene chloride, mole-%	Mixed surfactant $T_{mf} - T_g$	Anionic surfactant $T_{mf} - T_g$
30	−13	−10
40	−12	−10
50	−10	−9
60	8.4	4.4
65	14.0	10
70	17.2	11.2
80	1.0	1.5

DISCUSSION

Figures 1 and 2 show that the T_g of copolymers of vinylidene chloride–methyl acrylate and vinylidene chloride–ethyl acrylate do not fall on a line joining the T_g's of the two homopolymers but, rather, pass through a maximum at 50 mole-% vinylidene chloride. This is due to the probable restriction of free rotation of the ester groups by adjacent chlorine atoms in neighboring vinylidene chloride units. This is likely to be at a maximum when there are equimolar amounts of the comonomers present, provided no long sequence of either unit occurs in the copolymer. The vinylidene chloride–acrylonitrile copolymer, on the other hand, shows a small, positive deviation from the linear variation of T_g with composition. The higher T_g's are a result of increased chain-stiffening caused by hindrance of rotation of the nitrile groups by the bulky chlorine groups.

The T_{mf} is found to differ quite considerably from the T_g and, in fact, only coincides with it at certain compositions (Figs. 1 and 2). It may lie several degrees above or below the T_g, depending upon the composition (polarity) of the copolymer. The T_{mf}–composition curve is of similar shape to the T_g–composition curve for the three systems studied. Both the systems containing acrylate monomers have T_{mf} curves exhibiting a maximum. The differences between T_{mf} and T_g appear to shift from negative to positive values as the hydrophilic, or polar, nature of the copolymer decreases. The acrylonitrile-containing copolymers have large positive values of $T_{mf} - T_g$ over the range of composition measured. The high temperatures required for film formation to occur may be due, as Barb[3] has pointed out, to hindrance to coagulation and coalescence arising from the strong interchain forces. These may cause the outermost layer of the latex particles to become orientated relative to its neighboring segments in such a way that interpenetration with other latex particles is prevented. Rochow and Rowe[15] have shown that polyacrylonitrile latex particles show little interpenetration after conventional molding. Recently determined mono-

mer reactivity ratios in emulsion[16] suggest that long sequences of acrylonitrile units are present in these copolymers.

Since deformation of polymer particles is required for film formation to take place, it might be expected that the T_{mf} should coincide with the T_g. The T_g of the copolymers studied were determined for carefully purified and dried copolymers. This T_g value may not truly represent the T_g of the polymer in the latex that actually forms the film. In the case of the more polar copolymers, for which the T_{mf} lies below the T_g, other factors could contribute to a significant lowering of the actual T_g of the polymer in the latex.

Plasticization by water is possible, although Brodnyan and Konen[4] have demonstrated from a study of the mechanical properties of copolymers of different polarity in the wet and dry state that preferential plasticization of the more hydrophilic copolymers by water is unlikely.

Plasticization by surfactant or traces of residual monomer are possible. The emulsifier may act as a plasticizer either externally or internally, if it becomes grafted onto the polymer chains by transfer reactions. After carefully purifying copolymers by repeated precipitation we were not able to detect any evidence spectroscopically of nonyl phenoxy groups in copolymers prepared with nonionic surfactant. However, such plasticization cannot be ruled out. During the reprecipitation steps the polymer may have been fractionated, which would produce an unrealistically high T_g. Traces of solvent which are very difficult to remove from solvent cast films would tend to lower the T_g by plasticization.

While it may be argued that all these factors, except the last mentioned, could explain the T_{mf} and T_g data on the more polar copolymers, they are equally applicable to the nonpolar copolymers; yet lattices of these have T_{mf}'s that are higher than the corresponding T_g's of the copolymers. Clearly, the temperature at which film formation occurs must be governed by other factors, such as copolymer polarity and the surfactant type.

The nature of the surfactant used appears to have a marked effect on the T_{mf}. The results for the acrylate-containing copolymers suggest that, when the copolymers are highly hydrophobic, i.e. contain only small amounts of acrylate monomer, the presence of anionic surfactant alone tends to give lower T_{mf}'s than when nonionic surfactant is present. With an increase in hydrophilic character the reverse is true, the anionic–nonionic emulsions having the low T_{mf}'s, except in the highly polar copolymer region of the vinylidene chloride–methyl acrylate system below ≈ 30 mole-% vinylidene chloride, where the T_{mf}'s for both surfactant systems coincide. It is unlikely that this results from a change in the particle size, since Brodnyan and Konen[4] have demonstrated that the T_{mf} is independent of the surface-to-volume ratio. The sensitivity of the T_{mf} to change in the nature of the surfactant is more likely to be a surface-active effect involving the polarity of the copolymer. Considering the hydrophile–lipophile balance (HLB) of the surfactant system used, the HLB for sodium lauryl sulfate is approximately 40, whereas that calculated for the mixed

surfactant is 22. It is known that the HLB required for optimum stability shifts from lower to higher values as the polarity or hydrophilicity of the disperse phase increases.[17] In this respect the anionic system is, therefore, a more effective surfactant for the more polar copolymers than the mixed surfactant. This may well cause film formation to take place at a relatively higher temperature, since the surface tension would be expected to be lower and Brown's theory predicts that the T_{mf} is a function of the surface tension, increasing as the surface tension decreases. Accordingly, emulsions of the less polar copolymers containing the nonionic surfactant would be expected to have higher T_{mf}'s than the anionic emulsions, as is observed.

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