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Effects of colloidal stabilizer on vinyl acetate-ethylene copolymer emulsions and films

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SUMMARY: For vinyl acetate-ethylene (VAE) emulsion polymerization, a comparison of stabilization mechanisms and their effect upon latex and film properties was made in which the different stabilizers were poly(vinyl alcohol) (PVOH), alkylphenol ethoxylate (APE) surfactants, and a urethane linked poly(ethylene glycol) (PEG) based polymer. PVOH stabilized VAE emulsions possessed high viscosity and no freeze-thaw stability while the films were actually continuous in PVOH, much of which was due to the high content of PVOH in the continuous aqueous phase. APE stabilized VAE latexes were also of higher viscosity and the surfactants were miscible in the VAE continuous films. PEG-based stabilization resulted in emulsions and films which were largely affected by the hydrophobicity of the latex (amount of ethylene incorporated into the copolymer).

Introduction

Current emulsion stabilization mechanisms for the industrially important vinyl acetate - ethylene (VAE) copolymer family are via colloidal stabilizer [e.g. poly(vinyl alcohol) (PVOH)], a surfactant mixture (typically containing a blend of nonionic surfactants) or a combination of surfactant and PVOH[1)]. Several other materials have also been used as colloidal type stabilizers in the emulsion polymerization of VAE[2)]. Recently, a new family of emulsion stabilizers were reported to be useful for emulsion polymerization; these were polymeric stabilizers based on diisocyanate chain extended poly(ethylene glycol)[3)]. This paper examines the resulting emulsions from these products in comparison to more traditional VAE emulsion stabilizers; additionally, the comparison of stabilizers effects on emulsion characteristics, film properties and applications behavior is examined. The use of higher molecular weight PEG-containing stabilizers in VAE polymerization should be differentiated from standard surfactants by providing a less mobile stabilizer with multiple contact points available for the stabilization of a polymer particle in an emulsion.

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Experimental

All of the VAE emulsion polymers reported herein were prepared by batch polymerization techniques, except where noted, similar to examples described in patent literature[1)]. The PVOH used in this study was partially hydrolyzed (87-89% hydrolyzed) and possessed a low to medium molecular weight (Mn = 15,000 to 65,000 g/mole); more details about PVOH effects in the emulsion polymerization of vinyl acetate polymers can be found in the literature[1,5)]. PEG-based stabilizers were obtained from Henkel Corporation as Disponil® PC-series (abbreviated PUR in this paper). Final solids content of the emulsions was 55 weight%. Polymerization was initiated by redox methods as summarized in the references above. All glass transition temperatures quoted are the onset of T_g as determined by differential scanning calorimetry. Tensile dynamic mechanical data of films cast from the emulsions were obtained on a Rheometrics Solids Analyzer. The films were cast and dried at ambient conditions for about two weeks prior to testing. Data were obtained every 6°C over the -100 to 150°C range using a deformation frequency of 6.28 rad/sec. A soak time of one minute was used at each temperature to ensure isothermal conditions.

Results and Discussion

One of the most important variables in the emulsion polymerization of vinyl acetate and ethylene (VAE) is the stabilization mechanism chosen, for it is the mechanism of stabilization which, after the polymer composition itself, defines to a large extent the material properties of the resulting product. Thus, a PVOH colloidally stabilized VAE with identical particle size characteristics to a surfactant stabilized VAE emulsion will inherently possess different advantages and disadvantages when compared, since the resulting products will have drastically different degrees of water-soluble and particle-soluble species. The partitioning of water-soluble species will ultimately translate to various degrees of solubility of stabilizing species in the film of latex. PVOH fragments remaining in and extending into the aqueous phase for PVOH-stabilized VAE emulsions not only play a large part in determining the final viscosity and stability of the product, but also play a large role in film formation and application physical properties. An example of this is illustrated by the dynamic mechanical data of a VAE (18 wt.% ethylene) stabilized solely by PVOH shown in Fig. 1. This sample displays two separate thermal transitions: the primary modulus loss around 0°C corresponding to the VAE T_g and the higher temperature transition around 80-100°C corresponding to the glass transition for the phase separated PVOH fragments not miscible with the VAE particles, thus remaining as a separate continuous phase.

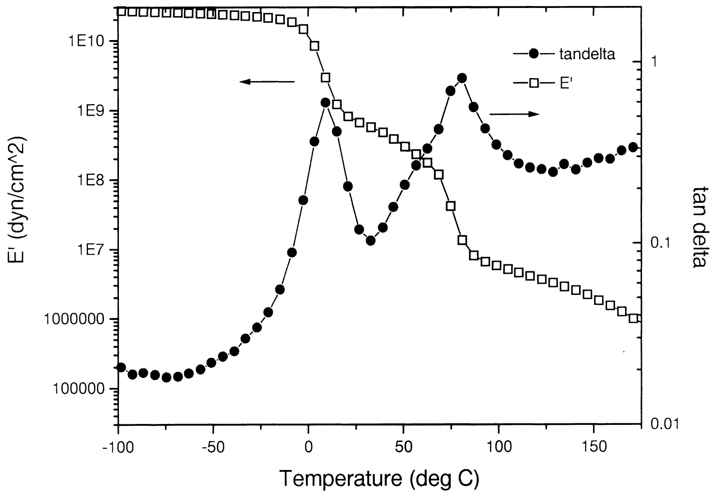

Fig. 1: Dynamic Mechanical Data of PVOH Stabilized VAE Film

It is interesting to contrast the PVOH-stabilized latex with a surfactant stabilized latex in terms of stabilizer location in the final film. Shown in Fig. 2 are the DMA data for a VAE (13 wt.% ethylene) stabilized almost solely by nonionic surfactants prepared by a semi-continuous method. The glass transition temperature of this sample is almost the same as the T_g of the VAE phase in the PVOH-stabilized VAE described above. Clearly, the VAE material stabilized solely by surfactant is dominated by a single VAE T_g. Note that the plasticization of the VAE by the surfactant mixture results in an equivalent T_g at lower ethylene content when compared to a VAE stabilized by PVOH. The rubbery plateau is less dominant in the surfactant stabilized material, due to its linear nature as compared to the PVOH-stabilized latex film, which is significantly grafted/branched/crosslinked5).

A new class of polymeric colloidal stabilizer for vinyl acetate based emulsions has been reported in the patent literature3) consisting of condensates of PEG oligomers with diisocyanates. These materials may indeed be utilized as sole stabilizers in VAE batch emulsion polymerization, to yield materials which are hybrid between surfactant stabilized latices and colloidal stabilized systems. For comparison to the materials prepared above, the

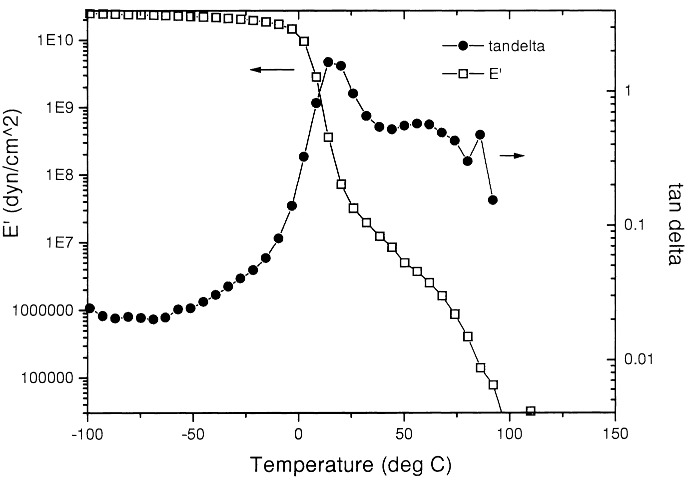

Fig. 2: Dynamic Mechanical Data of Surfactant Stabilized VAE Film

DMA data of this alternatively stabilized VAE are displayed in Fig. 3. Since the final stabilizer is predominately miscible with the VAE at this ethylene composition (18.7 wt. %), a single transition is observed for this film, similar to the surfactant stabilized latex. However, a pronounced high temperature plateau modulus was observed for the PUR stabilized material, similar to that observed for PVOH, indicative of branching/grafting reactions occurring during the emulsion polymerization.

A series of VAEs stabilized by the PUR material were prepared in which the ethylene content was varied. In these experiments, the batch polymerization procedure remained the same while the ratio of vinyl acetate to ethylene was varied. The effects of stabilizer plasticization on T_g are displayed in Fig. 4. The Fox equation was used with a T_g of polyethylene of - 90°C and a T_g of poly(vinyl acetate) of 35°C to yield the theoretical composition dependence straight line. Note that PVOH-stabilized VAEs fall almost directly on the calculated Fox equation line, while those of the PUR stabilized VAEs fall significantly below the line at low ethylene concentrations. This plasticization of VAE is similar to that observed in surfactant stabilized VAE. At higher ethylene contents, the T_g begins to track with the Fox equation once again, indicating that the stabilizer no longer plasticizes the high ethylene content VAE, but rather is phase separating from the VAE bulk phase. This behavior can be rationalized by the immiscibility of the relatively hydrophobic high ethylene VAE with the hydrophilic PUR stabilizer.

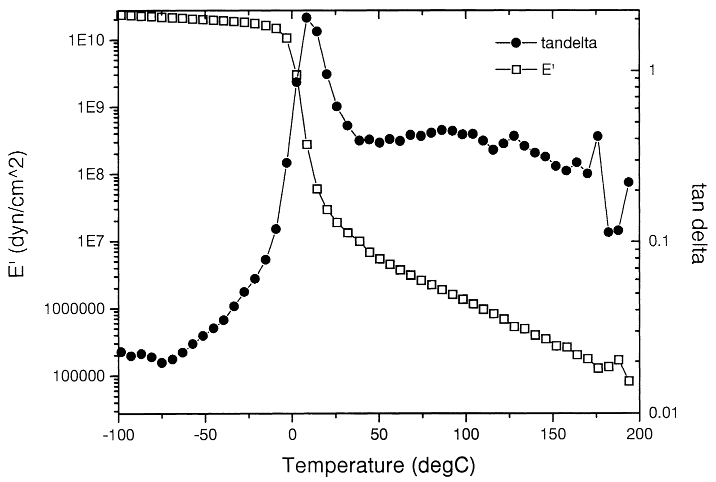

Fig. 3. Dynamic Mechanical Data of PUR-Stabilized VAE Film

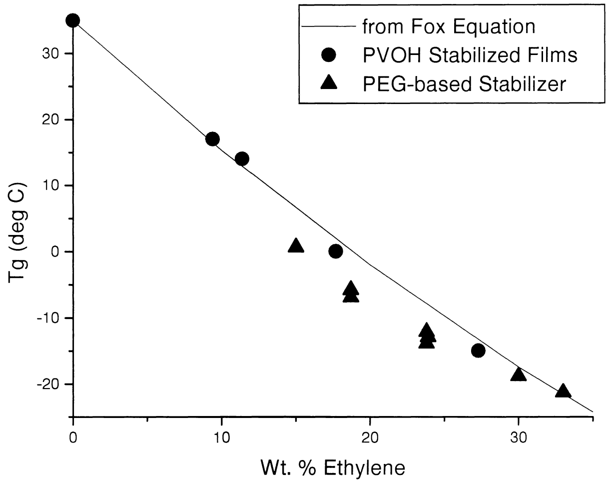

Fig. 4. Glass Transition Temperature for VAE as a Function of Ethylene Content for Various Stabilization Systems.

It is interesting to compare the data regarding freeze-thaw stability, viscosity and adhesive wet strength for these materials. Above 24% ethylene, the latices stabilized by PUR are freeze-thaw stable. Also, the viscosities of these higher ethylene samples are higher than the lower ethylene content VAEs (see Tab. 1), indicating that more of the stabilizer is excluded from the latex particle and driven into the aqueous phase, therefore yielding higher viscosity at equivalent particle size and particle size polydispersity.

Tab. 1: Effects of Stabilization on VAE Emulsion and Film Properties

Latex Stabilizer	% Ethylene	Dn (μm)	PD^	η* (cps)	T_g (°C)	T_m (°C)	ΔH_f (J/g)	WS (pli)**
PVOH	18.7	0.67	1.6	1670	2.4	none	n/a	1.4
Disponil ®PC-15	15	0.61	2.2	60	0.7	none	n/a	3.3
Disponil ®PC-15	18.7	0.67	1.6	80	-5.8	47.1	0.19	4.5
Disponil ®PC-15	23.9	0.66	1.8	115	-12.9	48.2	0.84	3.4
Disponil ®PC-15	30	---	---	580	-18.8	49.5	1.91	1.2
Disponil ®PC-15	33	---	---	1100	-21.3	49.2	2.86	0.04

^ Particle size polydispersity (Dw/Dn)

* Brookfield viscosity at 60 RPM with # 4 spindle

** Wet adhesive peel strength measured as cloth to cloth adhesion after one hour water immersion

It is assumed that this stabilizer exclusion from the particles into the aqueous phase contributes to or is the primary reason for freeze-thaw stability. Thus, the solid state character of these stabilizers (in terms of the PUR miscibility with the VAE and subsequent T_g depression by plasticization) may be linked to the solution state of these stabilizers (in terms of viscosity increases when stabilizer is not compatible with polymer particles). As solely PVOH stabilized VAE latices are not freeze-thaw stable at lower T_g, yet large amounts of PVOH partitioned into the aqueous phase, it is necessary to quantify both the amount and molecular weight of PUR or PVOH components in the aqueous phase of these emulsions prior to concluding the mechanism of freeze-thaw stability.

Also, it was discovered that wet peel adhesive strength for these latex adhesives goes through a maximum at ethylene contents where the PEG based stabilizer and the VAE are miscible. At higher ethylene contents, these materials possessed lower wet strength, similar to PVOH-stabilized VAE latex films (see Tab. 1). The phase separation of the PEG-based stabilizers may also be followed from the ΔHf of the resulting films. As the ethylene content increased from 15% to 33% by weight, the ΔHf of the phase separated PUR in the film increased from 0 to 2.9 J/g. Some literature precedent exists for this type of behavior with solution prepared 30% ethylene VAE blends with PEO in which melting points were exhibited as well as T_g depression(4). The morphology dependence of the PUR stabilized VAE films on VAE copolymer hydrophobic character is in contrast to PVOH stabilized VAE latex films.

References

(1) M.K. Lindemann, J.G. Iacoviello, U.S. Patent 3,708,388 (1973); M.L. Hausman, W.E. Lenney, U.S. Patent 4,521,561 (1985); W.E. Lenney, J.G. Iavociello, U.S. Patent 4,921,898 (1990); J.G. Iacoviello, U.S. Patent 5,084,503 (1992) all to Air Products and Chemicals, Inc.

(2) A. Beresniewicz, H.K. Inskip, U.S. Patent 4,043,961 (1977) to E.I. Du Pont de Nemours and Co.; W.E. Lenney, U.S. 5,124,394 (1992) to Air Products and Chemicals, Inc.

(3) C. Baumann, D. Feustel, N. Hübner, DE 195 08 856 A1 (1996); H. Fisher, W. Emmerling, T. Möller, H. Onusseit, B. Schöttmer, B. Herlfterkamp, D. Feustel, K. Friedrich, H. Büsching, N. Hübner, WO 94/13726 (1994) both to Henkel KGaA.

(4) R.H. Bott, J.A. Kuphal, L.M. Robeson, D.J. Sagl, *J. Appl. Polym. Sci.* **58**, 1593 (1995)

(5) G.S. Magallanes Gonzalez, V.L. Dimonie, E.D. Sudol, H.J. Yue, A.J. Klein, M.S. El-Aasser, *J. Polym. Sci.: Pt. A: Polym. Chem.* **34**, 849(1996)