Polyvinylbutyral, More Than Just a Binder

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Various properties of polyvinylbutyral (PVB), the most widely used polymer binder in photothermographic imaging materials, have been identified and characterized. These properties, including its solution and coating behavior, its ability to disperse silver behenate, as well as being a reducing agent for it, and its compatibility with behenic acid can all be credited for its widespread use as a binder for photothermographic recording materials. The reducing character of PVB is particularly important, although it was not found to be a property common to all sources of PVB, and is strongly dependent upon manufacturing method and purity. It is concluded that it is the combination of reducing character of PVB, together with its strong affinity for behenic acid, plasticizing the matrix, that makes PVB the binder of choice for photothermographic recording materials. This model enables targeted screening of alternative polymers to be carried out for future generations of photothermographic recording materials.

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Introduction

Polyvinylbutyral (PVB), having the structure shown in Fig. 1, is widely used as a binder for photothermographic materials. Its suitability is based on its very particular mix of properties. Its ability to disperse silver behenate and its chemical compatibility with a variety of other polymers and compounds are welcome attributes to product designers. Its role as a reducing agent for silver behenate is quite intriguing. Furthermore, its ability to partially dissolve the behenic acid formed upon reduction of silver behenate provides a driving force for image formation, by promoting the formation of silver nuclei and increasing the diffusion mobility of active components such as tone modifier and reducing agent. Although a difficult polymer in terms of quality control, it exhibits interesting behavior in the two-component system with behenic acid. In the search for alternative binders in photothermography, polyvinylbutyral is a worthy model.

Polyvinylbutyral is not a very well-defined material and has rather broad product specifications that are seldom completely met. This is due to the fact that most applications are found in the automotive industry or in adhesives.[1] On the other hand, in the patent literature polyvinylbutyral is overwhelmingly to be found as the binder of choice and this is borne out in commercially available photothermographic recording materials, such as Dry Star™, Dry View™ films and Dry Silver™ papers. At the beginning of this research the question was posed: why polyvinylbutyral? What makes it unique? The role of this polymer in a solvent-based photothermographic material was first investigated with respect to solution behavior, pigment stabilization, coating behavior and, of course, thermographic response.

Experimental

Commercial polyvinylbutyral (PVB) was purchased from Monsanto (Butvar), Wacker (Pioloform) and Sekisui (S-lec). The copolymer consists about of 80 wt% acetal, 20% alcohol and a minor portion of acetate units, unless stated otherwise in the text. The polymer was dried in a vacuum oven at 50°C for several days prior to use and stored in a desiccator. The solvents were MCB reagent grade. The polymer was dissolved at room temperature with the aid of a small magnetic bar and allowed to stand for 24 h before use. The polymer solutions were examined as a function of time and as a function of solvent composition using viscosimetric and light scattering techniques. Adsorption isotherms were obtained after dispersion (ball mill) of the pigment in diluted polymer solutions (ranging from 0 to 1% w/w) and after sedimentation and subsequent thermogravimetric analysis of the supernatant. Silver behenate was commercially available. Rheological and thermal analysis were performed on TA Instruments™ apparatus under air at a heating rate of 10/min. Static light scattering experiments were performed on PVB solutions in 2-butanone (MEK), ei-

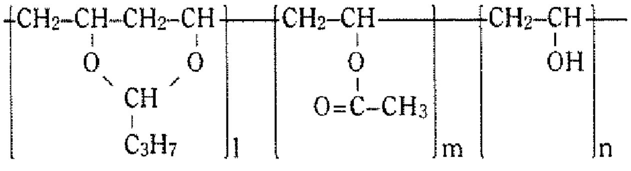

Figure 1. General structure of polyvinylbutyral.

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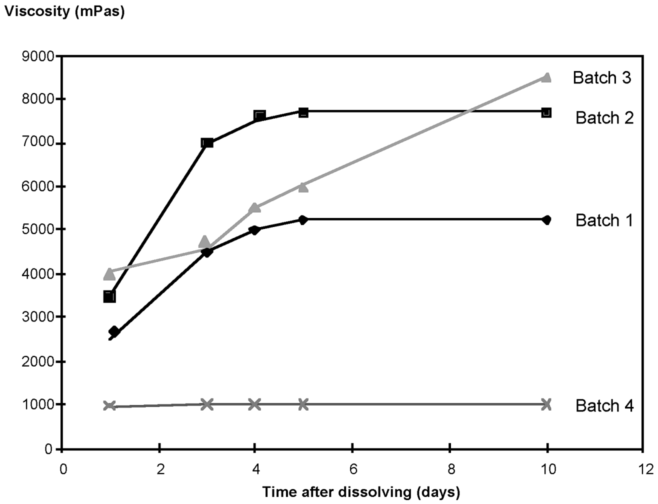


Figure 2. Newtonian viscosity of a 22% solution of PVB in MEK as a function of time after dissolving. Different batches of the same manufacturer/brand are compared.

TABLE I. Data from rheological and light scattering experiments on Butvar B79 (Monsanto) indicating the presence of H-bonded aggregates in pure MEK.

Solvent	Intrinsic viscocity ([η] in dl/g)	Huggins coefficient (kH)	Radius of gyration (Rg in nm)	Calculated molar mass of associated PVB
MEK	0.618	0.49	40	54,000
MEK (reflux)	0.66	0.41	23	10,400
MEK/MeOH (90/10)	0.655	0.412	29	12,600

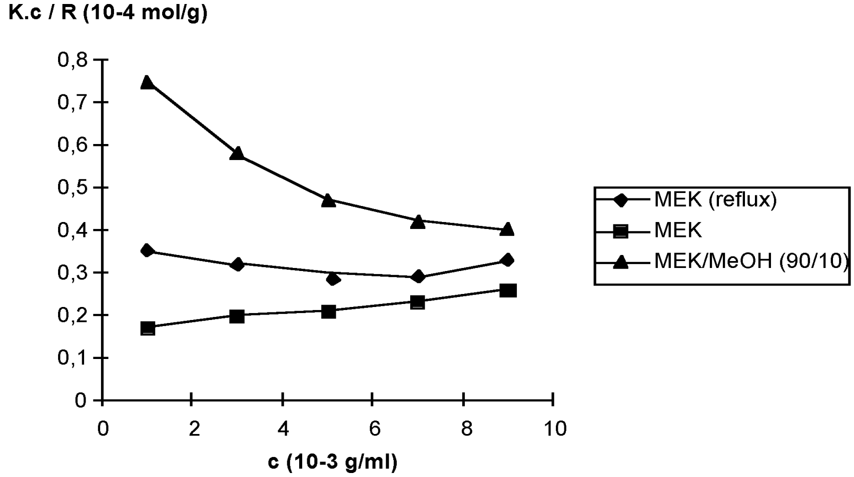


Figure 3. Light scattering experiment (Debye Plot) for PVB (Butvar B79, Monsanto) in MEK at 25°C. K is an optical constant, c is polymer concentration, R is the Rayleigh ratio.

ther dissolved at room temperature or after refluxing for 3 h, and in in mixtures of MEK/methanol (90/10).

Results and Discussion

Solution Behavior. One of the most striking features of PVB is its distinctive solution behavior in 2-butanone (MEK). Considerable fluctuations in solution viscosity were observed between different batches of a given brand. Not only did they differ in solution viscosity at a given time after dissolving, but the evolution of viscosity with time was different for each batch as shown in Fig. 2. Aging of the PVB-powder in ambient conditions made things even more complicated when it became clear that, while solutions of fresh samples took almost 14 days to reach a constant viscosity, solutions of one-year-old samples reached a lower constant viscosity value almost immediately after dissolving. These phenomena make optimization of production processes complex and problematical. Therefore the solution behavior of PVB in different solvents was investigated and different PVB manufacturers were consulted. It emerged that hydrolysis as a result of traces of acid catalyst and OH-content play a key role in solution behavior of the polymer.

In the Debye plot (Fig. 3) K.c/R is reciprocal to an apparent molecular weight, strongly indicating the presence of H-bonded aggregation in MEK.[2] After refluxing the solution, or after addition of 10% MeOH, aggregation diminishes.

Rheological data on the same diluted polymer solutions confirm the above interpretation. Intrinsic viscosity increases according to MEK < MEK (reflux) < MEK/MeOH (90/10), indicating a better solvent compatibility in this series.[3] The Huggins coefficient accordingly decreases. The values may be illustratively compared with the radius of gyration (obtained in the light scattering experiment), being very sensitive to inter- and intra-molecular aggregation. Combination of data from rheological and light scattering experiments results in a calculated molecular mass of PVB, that again indicate polymer association as shown in Table I.

Coating Behavior. In shear rheometry a structural viscosity due to inter- and intramolecular entanglements is observed at lower oscillation frequencies, indicative for the low shear region. Entanglements of PVB chains were found to occur at fairly low PVB concentrations. The effect is far more pronounced when the temperature of the solution is increased from 30°C to 40°C. These

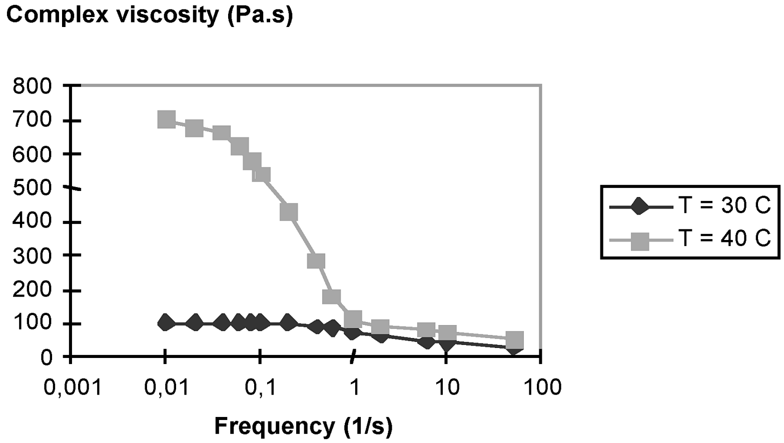


Figure 4. Complex viscosity from oscillation experiments on a 30% solution of PVB (Butvar B79, Monsanto) in MEK.

TABLE II. Miscibility parameters (MP) of the constituent monomers of PVB (vinylbutyrate, vinylalcohol, vinylacetate) and of the complete polymer as well as a function of temperature.

T (°C)	20	25	35	40	45	50
MP (But)	0.026	0.017	0.004	0.001	0.001	0.003
MP (VOH)	43.5	43.7	43.8	43.9	44.1	44.2
MP (VOAc)	5.1	5.2	5.4	5.62	5.71	5.86
MP (PVB)	3.8	3.7	3.5	2.8	2.9	2.1

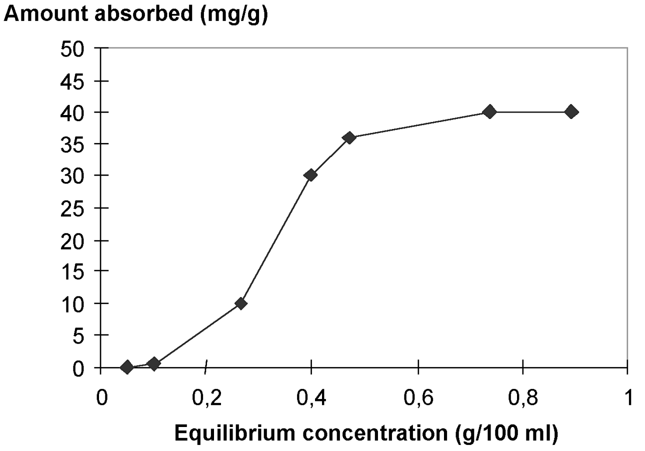


Figure 5. Adsorption isotherm of PVB (Butvar B79, Monsanto) on silver behenate from MEK at 25°C.

rheological characteristics are fundamental to the coating of PVB-based dispersions. The high zero-shear viscosity prevents the settling and sedimentation of pigments in the coating solution. The shear thinning behavior is essential to high shear coating processes.

Especially noteworthy is the effect of temperature on the rheology of PVB/MEK solutions. From Fig. 4 it is clear that increasing the temperature from 30°C to 40°C, gives rise to an increase in low-shear viscosity. This effect results from changing solvency of the constituent PVB monomers, as is indicated by theoretical calculations: the miscibility parameter (MP), as shown in Table II, was calculated for the overall polymer and for the constituent monomers.[3,4] The smaller the value of the miscibility parameter, the better the compatibility of polymer (groups) with MEK. MP should go to 0 in an ideal solvent compatibility. The solubility of vinylalcohol and vinylacetate decreases upon increasing the temperature, that of vinylbutyral groups increases. It is evident that a decrease in solvency of vinyl alcohol groups promotes the formation of entanglements. The overall solvent compatibility on the other hand is higher with higher temperature. Moreover, the changing solvent compatibility suggests major changes in the colloidal stabilization mechanism of the pigment dispersion.

The influence of temperature on the solution behavior of PVB in MEK was also examined experimentally. Viscosimetric data on diluted polymer solutions revealed an increase in intrinsic viscosity with increasing temperature, indicating an overall increase in solvent compatibility, and a decrease in Huggins coefficient, indicating the same.

Pigment Stabilization. PVB sterically stabilizes silver behenate crystals and particles in methylethylketone. The adsorption of PVB on silver behenate was studied as a function of batch and PVB-type.[5] A monolayer capacity of about 40 mg/g was calculated for a typical batch of pigment and polymer. The adsorption was found to correlate strongly with the OH-content of PVB and to be strongly influenced by temperature. A minimum of 20% vinylalcohol in PVB is required to obtain optimal dispersion quality, as indicated by gloss and haze parameters.

Photothermographic Response. Silver behenate, as a dry powder, decomposes if kept at a temperature of 150°C for 1 h,[6] but a humid atmosphere must be present for behenic acid to be formed. A characteristic double endotherm is indicative for the presence of silver behenate. Embedded in a PVB-matrix, however, the silver behenate is observed to partially decompose in more moderate conditions (120°C for 10 min). A new melting endotherm of behenic acid appears at 70°C – 80°C, as can be seen from the following thermograms, Fig. 7, and metallic silver can be visually observed in the cooled solid.

Differential scanning calorimetry (DSC) revealed that in a PVB matrix, only part of the behenic acid formed is crystalline and that the glass transition temperature (Tg) of the PVB-matrix decreased as the degree of decomposition increased due to plasticization with the behenic acid released. It was calculated that up to 9% of the behenic acid formed was dissolved in the matrix, and that the Tg of PVB could decrease from 56°C to 38°C. A phase diagram was constructed to describe the observations made (Fig. 8).

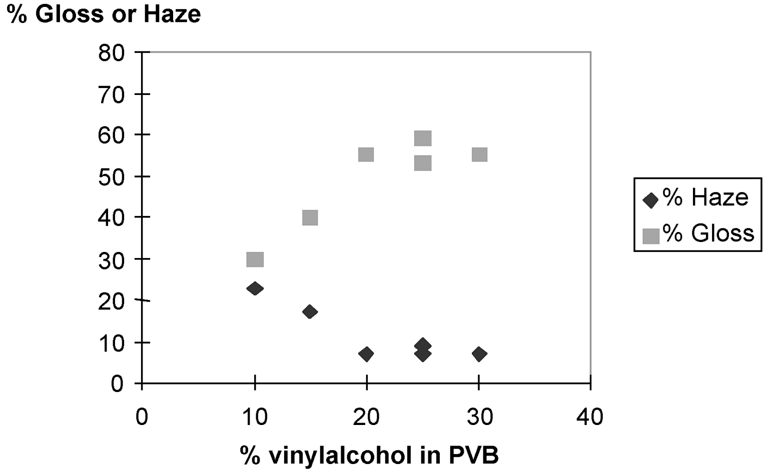
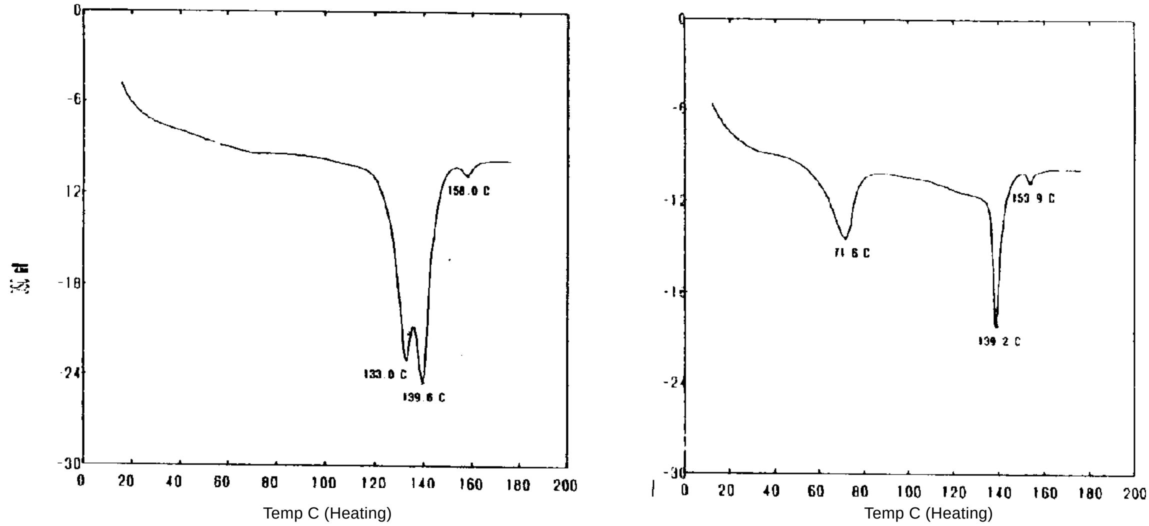


Figure 6. Gloss or Haze of dried coating dispersions of silver behenate, relative to vinylalcohol content of PVB (Butvar (Monsanto), Pioloform (Wacker) and S-lec (Sekisui).



a

b

Figure 7. DSC experiments on silver behenate : (a) as a powder after 1 h at 150, (b) embedded in a PVB (Butvar B79, Monsanto) matrix with 20% vinylalcohol content.

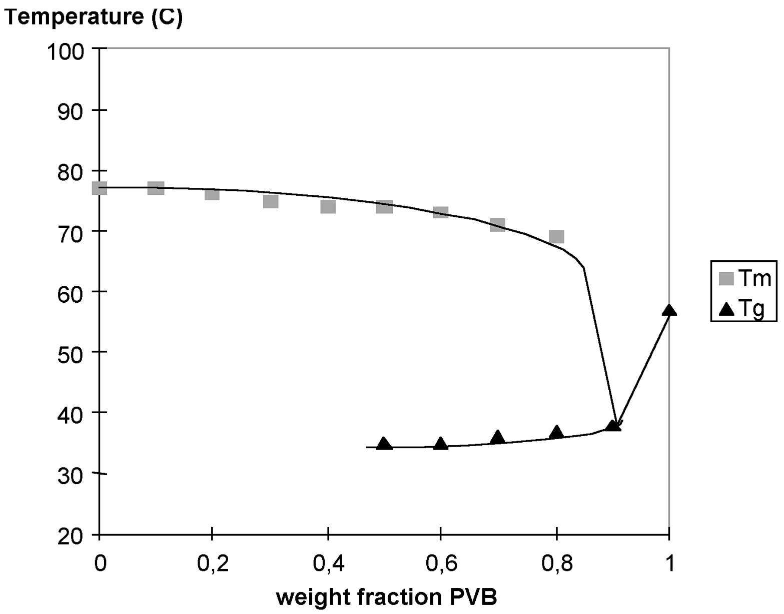


Figure 8. Phase diagram of the behenic acid / PVB (Butvar B79) system

It became clear that two major characteristics of PVB affect the performance of photothermographic materials: its role as a reducing agent and its ability to dissolve behenic acid thereby facilitating the decomposition of silver behenate. Diffusion controlled processes are, moreover, facilitated in the behenic acid plasticized matrix which strongly influences the mechanism of image formation.[7–9]

Prolonged storage at temperatures well above the Tg of the behenic acid plasticized matrix might be expected to promote crystallization and phase separation of behenic acid. XRD-data on the other hand suggest that upon thermal processing part of the behenic acid reacts with the butyral units in PVB, giving rise to more vicinal vinylalcohol groups and hence to an increase in crystallinity of the polymer. Comparison of PVB brands obtained from different manufacturers shows that large differences exist in the ability of the polymer matrix to promote behenic acid formation. A correlation is found with manufacturing method, which implies a given synthesis type and, as a consequence, a given quantity of impurities (traces of acid, stabilizers, antioxidants etc.).

Conclusions

Various properties of polyvinylbutyral, such as its solution behavior, its coating behavior, its dispersing properties, its reducing character for silver behenate and its compatibility with behenic acid have been identified. Although all of these properties may explain its widespread use as a binder for photothermographic recording materials, it is the reducing character of PVB that remains most fascinating. However, this ability to reduce silver behenate is not standard to PVB, but is strongly dependent upon manufacturing method and purity. Moreover, as other ingredients in photothermographic materials were also found to influence the behenic acid formation, other polymers might be more or less strong reducing agents for silver behenate as well. We believe that it is the combination of reducing character of PVB together with its strong affinity for behenic acid, plasticizing the matrix, that makes PVB the binder of choice for photothermographic recording materials. This model enables targeted screening of alternative polymers to be carried out for future generations of photothermographic recording materials.

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