

Effect of Colophony Emulsion on the Adhesive Properties of Vinyl Acetate/*n*-Butyl Acrylate Copolymeric Latex

Ai-Ping Zhu, Rui Chen, Lan-Hua Yuan

College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, People's Republic of China

Received 6 November 2006; accepted 26 June 2007

DOI 10.1002/app.27125

Published online 24 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We prepared a novel copolymeric latex of vinyl acetate and *n*-butyl acrylate (V-B) using a semibatch emulsion polymerization process. The glass-transition temperature (T_g), steady viscosity, flow activation energy (E_f), dynamic moduli, and amphiphilic properties of the V-B latex in the presence of colophony were systematically investigated. The experimental results demonstrate that excellent adhesive behaviors were achieved for the V-B latex blended with 20 wt % colophony, whereas good adhesive performance was

related to the moderate T_g , viscosity, E_f , storage modulus, and low contact angle on the adherent. The debonding mechanisms for V-B and its colophony-modified latexes were analyzed. A possible mechanism for the V-B latex blended with colophony emulsion was determined. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 629–635, 2008

Key words: additives; copolymerization; poly(vinyl ethers); rheology; viscoelastic properties

INTRODUCTION

Macromolecular adhesive products have the usual characteristics of polymers, but some of them are more significant with respect to their adhesive properties,^{1–4} such as chemical composition, molecular weight, polarity, glass-transition temperature (T_g), and rheological properties. These fundamental characteristics can be correlated with the adhesion and cohesion capacities and the adherence of the copolymers to different substrates. After analytical characterization and evaluation of the physical properties of the polymer, it is possible to choose a field for application.^{5–7}

Acrylic polymers have been widely applied in the modern adhesive industry because they have an ensemble of characteristics, including easy control of their T_g , molecular architecture, crosslinking density, and competitive cost.^{8,9} Therefore, both academia and industry have a great interest in the investigation of the relationship between the molecular structure of adhesive systems and the adhesive properties of acrylic polymers. Focusing on water-based acrylic adhesives, a number of studies have related polymer structure and rheological properties to adhesive performance. The first information on the role of molecular structure in the adhesive properties of acrylic

polymers was reported by Zosel.^{10,11} To achieve high fracture energy during separation of the adhesive bond, the acrylic adhesives (made from the homopolymer of 2-ethylhexyl acrylate) had to form bridging fibrils, produced only when the elastic modulus (G') was below a certain value. Lakrout and coworkers^{12,13} reported that the fibrils were actually the walls between cavities and expanded from defects at the interface between the adhesive and the rigid surface.

A second category of studies, generally from more chemistry-inclined groups, focused on the role played by some of the additional synthesis parameters specific to emulsion polymerization techniques, such as the composition profile of the particle (e.g., core-shell particles);^{14,15} selection of an adequate component as a crosslinking comonomer;^{16,17} application vegetable extract (a kind of special functional monomer) during the synthesis of the acrylovinyl macromolecular compound;¹⁸ and composition profile of the latex particles (with two comonomers).¹⁹ Their results demonstrate that the structure of acrylics could be varied in a great range and the most important properties of an adhesive, which are a balanced relationship of tack, cohesion, and adhesion, can be readily adapted to the requirements imposed.²⁰

A third kind of study reported by Amaral et al.,²¹ revealed that both rheological and adhesive properties were strongly dependent on the initial latex particle size distribution. The blends of small- and large-model pressure-sensitive adhesives had a synergistic effect, and the optimum adhesive properties could be attained for a proportion of small particles close to 60 wt %.

Correspondence to: A.-P. Zhu (apzhu@yzu.edu.cn).

Contract grant sponsor: Natural & Scientific Grant of Jiangsu Province; contract grant numbers: 05KJB430149, BK2006072.

Different thickening agents have been used to obtain a desired degree of tackiness of the polymeric latex. To obtain good adhesive properties, the polymer must contain an effective amount of a suitable thickening agent.^{22,23} As it is well known, the additives to nonpolar polymers need to have a nonpolar part for solubility and a polar part for strong intermolecular forces. Representative materials useful as tackifying agents include hydrocarbon resins such as terpene resins, hydrogenated resins, and esters resins.

Poly(vinyl acetate-butyl acrylate) latex is used for interior architectural coatings in North America. These copolymers are characterized by extensive branching because of side reactions during particle synthesis.²⁴ Branching is accompanied by gel formation within individual latex particles. In semicontinuous emulsion polymerization under monomer-starved conditions, the use of a chain-transfer agent can substantially reduce the formation of gel and also lowers the mean molar mass of the polymer.

In this study, the synthesis of a V-B latex and the effect of a tackifying agent, colophony, on T_g , viscosity, flow activation energy (E_f), dynamic moduli, and the amphiphilic properties of V-B latexes and adhesive behaviors were investigated. The relationship between the physicochemical properties of the latex and the adhesive strength were determined.

EXPERIMENTAL

Materials

Monomers of *n*-butyl acrylate and vinyl acetate were distilled under reduced pressure to remove trace amounts of hydroquinone monomethyl ether and stored in a refrigerator under a N_2 atmosphere. Acrylic acid (AA; 99% pure) was used without purification. Colophony emulsion (the colophony content of the emulsion was 50%), di-*n*-butylphthalate (DBP), glycol, and poly(vinyl alcohol) (PVA or PVA-1788) were purchased from Guangzhou Langri Chemical Co., Ltd. (Guangdong, China) and used directly without further purification. A water-soluble initiator, potassium persulfate; an emulsifier, nonyl phenol poly(oxyethylene ether) (OP-10); sodium bicarbonate ($NaHCO_3$); and aluminum nitrate [$Al(NO_3)_3$] were used as received. The water used throughout the work was double-distilled deionized water.

Synthesis of V-B latexes

Semibatch emulsion polymerizations were carried out in a 500-mL jacketed glass reactor equipped with a reflux condenser, a thermocouple, a stainless steel stirrer operated at 250 rpm, a nitrogen inlet, and three inlet tubes. The initial composition of the monomer mixture is given in Table I. PVA was pre-

TABLE I
Initial Chemical Composition

Component	Initial composition of the copolymer variant (%)
PVA-1788	5
<i>n</i> -Butyl acrylate	22
Vinyl acetate	6.75
AA	0.25
OP-10	1.8% of mixed monomer
$NaHCO_3$	0.5
$K_2S_2O_8$	0.4% of mixed monomer
Glycol	0.7
$Al(NO_3)_3$	0.01
DBP	2.2
Distilled water	65

dissolved in 90°C water for at least 1 h. PVA solution, OP-10, 15% mixed monomers, $\frac{1}{3}$ DBP, and 40% potassium persulfate were added to the reactor and stirred to emulsify for 30 min. The reactor was heated to 70–80°C, where the polymerization started, and the temperature of the reactor rose to around 85°C. After the temperature returned to 75–80°C, the remaining mixed monomers and initiator solution were continuously added to the reactor through inlets at the same time. After 6 h of addition of the initiator solution, $Al(NO_3)_3$ (a 5% aqueous solution) was added. The reactor was heated to 90–95°C and left for 30 min to allow for complete conversion; then, $NaHCO_3$ (a 5% aqueous solution) was added to adjust the pH to 6–7, and the remaining DBP was added. The reaction system was stirred for another 20 min. Finally, the glycol was added to the reactor and mixed. The reactor was cooled to 50°C. No coagulum was found on the reactor walls or on the surface of the stirrer. The solid content was determined to be 33.5 wt % by gravimetric analysis. The aim of the addition of $Al(NO_3)_3$ was to endow some cross-linking structure and, thus, increase the viscosity of the V-B latex. Glycol was added to improve the plastic properties of the resulting V-B latex.

Colophony-modified V-B latexes

To keep the solid content the same as that of the V-B latex, the designed amount of colophony emulsions were blended with the V-B latex to prepare the colophony-modified V-B latexes, which were named V-B-1 (V-B latex blended with 20% colophony) and V-B-2 (V-B latex blended with 40% colophony). The mixtures were stirred in a flask at room temperature for 30 min at 150 rpm.

Characterization

The T_g values of V-B, V-B-1, and V-B-2 films were determined by differential scanning calorimetry

(DSC) at a heating rate of 10°C/min under a N₂ flow. A 204 F1 modulated differential scanning calorimeter from Netzsch Geratebau GmbH Instruments (Netzsch, Germany) was used. The DSC sample we used was in a dried state to avoid the disturbance of crystal water. The flow properties of V-B and its modified latexes were measured with a control-stress rheometer equipped with parallel-plate geometry at stresses between 0.1 and 100 Pa at 25°C (RS600, Rheometrics, Karlsruhe, Germany). Static contact angles were measured with a contact angle analyzer (OCA40, Hamburg, Germany). Water contact angle measurements were carried out at room temperature in air to evaluate the latex spread on the thick paper with a surface coated with a UV photosolidified acrylic polymeric coating. Diluted latex droplets (25 μ L; with too-viscous latex, it was difficult to control the size and volume of the droplets) were deposited onto the sample surface through a gauge 22 sized dispensing needle at a rate of 5 μ L/s. Each contact angle reported here is an average of at least five measurements. The substrate for water contact angle was a thick paper with a surface coated with a UV photosolidified acrylic polymeric coating. Adhesive strengths were measured by 90° peel strength. The interested adherent was the thick paper with a surface coated with UV photosolidified acrylic polymeric coating.

RESULTS AND DISCUSSION

T_g

Figure 1 shows DSC curves of dried V-B, V-B-1, and V-B-2 latexes. As shown in Figure 1, the T_g values observed for V-B, V-B-1, and V-B-2 were 5.9, 8.0, and 13.3°C, respectively. An increase of T_g was clear for the colophony-modified latexes, which suggested

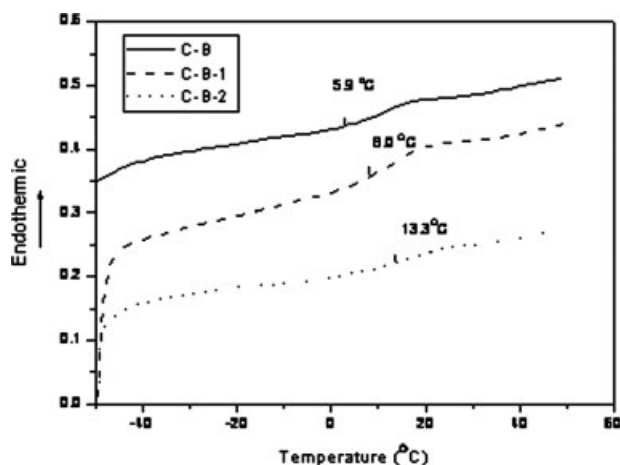


Figure 1 DSC thermograms of V-B, V-B-1, and V-B-2. C-B, latex of vinyl acetate and n-butyl acrylate (V-B); C-B-1, V-B latex blended with 20% colophony; and C-B-2, V-B latex blended with 40% colophony.

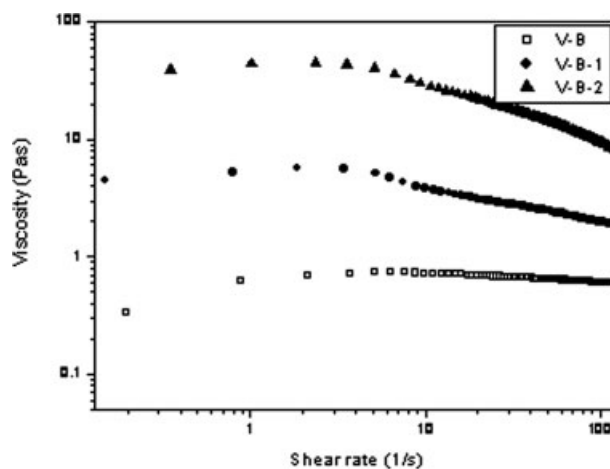


Figure 2 Dependence of viscosity on the shear rate for V-B, V-B-1, and V-B-2.

that the colophony molecules effectively affected the chain motion of the V-B latex. Although the total solid content was the same for V-B, V-B-1, and V-B-2, T_g increased with the blending of colophony. Moreover, as a high percentage of colophony was blended with the V-B latex, the T_g transition from the DSC curve became less obvious as observed for V-B-2. This result may be attributed to the formation of physical crosslinking inside the V-B latex. In industrial formulations, T_g plays an important role in the determination of the degree of interdiffusion for an adhesive across the interface. The interdiffusion across interfaces should be fast and complete for the polymeric latex with a low T_g . According to the literature,²⁵ it seems that only mobile chains can diffuse across the interface, whereas gelation chains remain essentially immobile.

Steady-state flow properties

Figure 2 compares the flow curves for the V-B, V-B-1, and V-B-2 latexes at 25°C. All of the latexes revealed Newtonian behavior at a low shear rate but shear thinning under high shear. In addition, the presence of colophony significantly affected the low shear viscosity. The latex viscosity of V-B blended with 20% colophony increased nearly 8 times, whereas the introduction of 40% colophony led to a 65 times greater improvement in the low shear viscosity compared to the V-B latex. Generally, a latex with a low viscosity diffuses easily across an interface, whereas a latex with a high viscosity has difficulty diffusing across an interface. Viscosity is an important factor for controlling industrial formulations. The viscosity of the V-B latex was not high enough for brushing coating. This result suggests that colophony was a good thickening agent for the V-B latex because of its ability to increase the viscosity of the V-B latex.

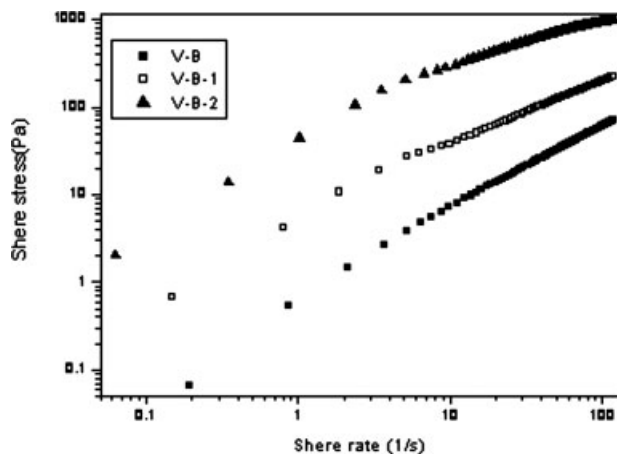


Figure 3 Dependence of the shear stress on the shear rate for V-B, V-B-1, and V-B-2.

The shear stress versus shear rate for V-B, V-B-1, and V-B-2 is shown in Figure 3. On the basis of the scaling law

$$\sigma = K(\dot{\gamma})^n \quad (1)$$

where σ is shear stress, $\dot{\gamma}$ is shear rate, K is consistency coefficient, and n is flow exponent. In Figure 4, the value of K and n in the exponential formula can be observed and are shown in Table II. For V-B latex, the n value was close to 1, which indicated that the V-B latex showed Newtonian behavior, whereas the solution viscosity did not vary much throughout shear rate range. However, the n values for V-B-1 and V-B-2 were 0.87 and 0.82, respectively. The colophony-modified V-B latexes revealed obvious pseudoplastic characteristics. Such a transition from Newtonian to pseudoplastic behavior after blending with colophony may have been caused by the deformation or disaggregation of particles in the V-B-1 and V-B-2 latexes.

E_f was determined from the temperature dependence of the solution viscosity through the setup of the Arrhenius relationship. Figure 4 shows the $\ln \eta$ (viscosity) dependence on $1/T$ (temperature) for V-B, V-B-1, and V-B-2. E_f was calculated from the slope in Figure 4, and the E_f values are listed in Table II. The E_f values for V-B, V-B-1, and V-B-2 were 14.9, 34.2, and 84.8 kJ/mol, respectively. Possible factors causing the increase in E_f were the increase in T_g and the structural changes of the particles inside the latex because when the T_g of an adhesive enhances or the crosslinking structure forms in the latex system, E_f will increase. The high E_f will result in a high cohesion capacity of an adhesive.

Dynamic oscillation

Figure 5 shows shear stress dependence of G' and G'' (G , loss modulus) for the V-B, V-B-1, and V-B-2.

It shows that the linear viscoelastic range enlarged with increasing colophony content. In addition, both G' and G'' for the colophony-modified latexes increased greatly. G' of V-B-2 was highest and was constant in a large range of stresses, which indicated that V-B-2 was difficult to deform. This result suggests that there should have been an aggregate structure formed. G' for V-B latex was lowest and decreased even at very low stress, indicating that the small amplitude of stress could break down the interaction inside the V-B latex because that was too weak. The plateau G' values for V-B, V-B-1, and

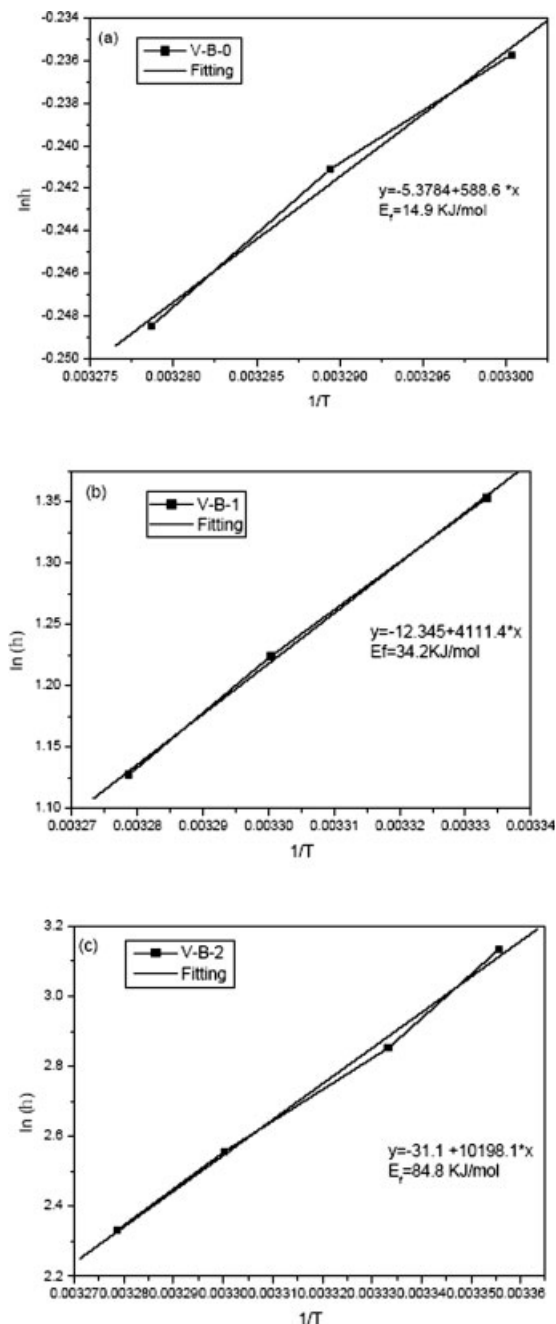


Figure 4 E_f for V-B, V-B-1, and V-B-2.

TABLE II
Viscosity and E_f of V-B and the Colophony-Modified Latexes

Sample	Viscosity (Pa s)	K	n	Correlation factor	E_f (kJ/mol)	Peel strength (N/cm)
V-B	0.7	0.40	1.08	0.9969	14.9	4.5
V-B-1	5.7	3.5	0.87	0.9978	34.2	7.8
V-B-2	45.2	19.2	0.82	0.9989	84.8	6.2

V-B-2 latexes were determined to be 0.21, 2.65, and 44.9 Pa, respectively. These results demonstrated that colophony increased the storage modulus of the V-B latex effectively.

Figure 6 demonstrates the viscoelastic behavior under different shear stresses for the V-B, V-B-1, and V-B-2 latexes, respectively. As shown in Figure 6(a), G'' was much higher than G' at low stress for the V-B latex, which indicated that the flow properties dominated compared with the elastic properties. In the case of V-B-1, the values of G' and G'' were com-

parable, indicating that V-B-1 showed more elasticity than flow [Fig. 6(b)]. It was interesting that the G' value was higher than that of G'' at low stresses and

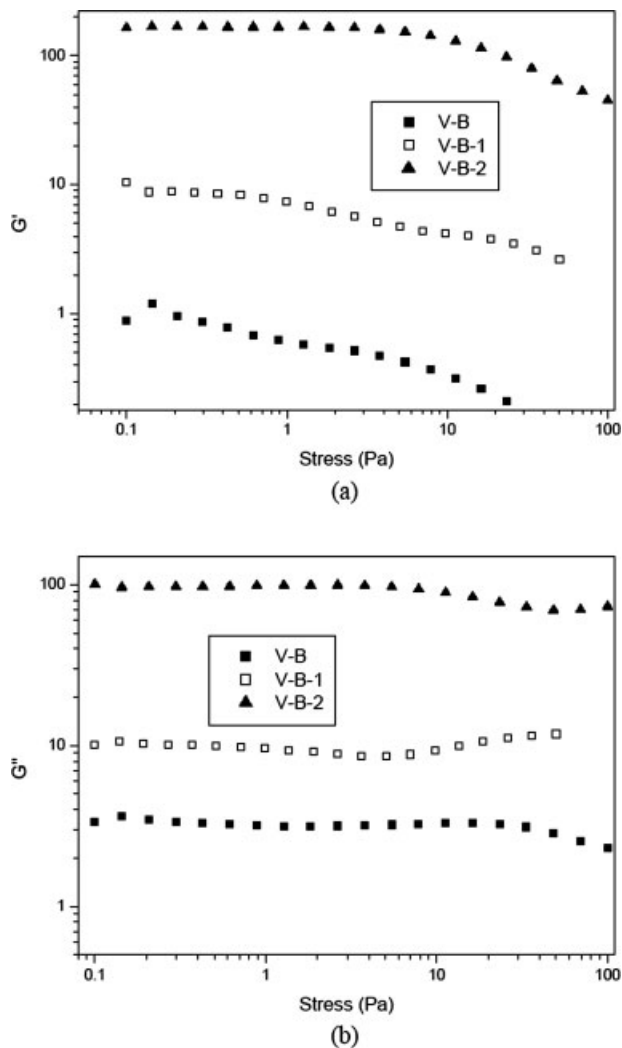


Figure 5 Dependence of (a) G' and (b) G'' on the shear stress.

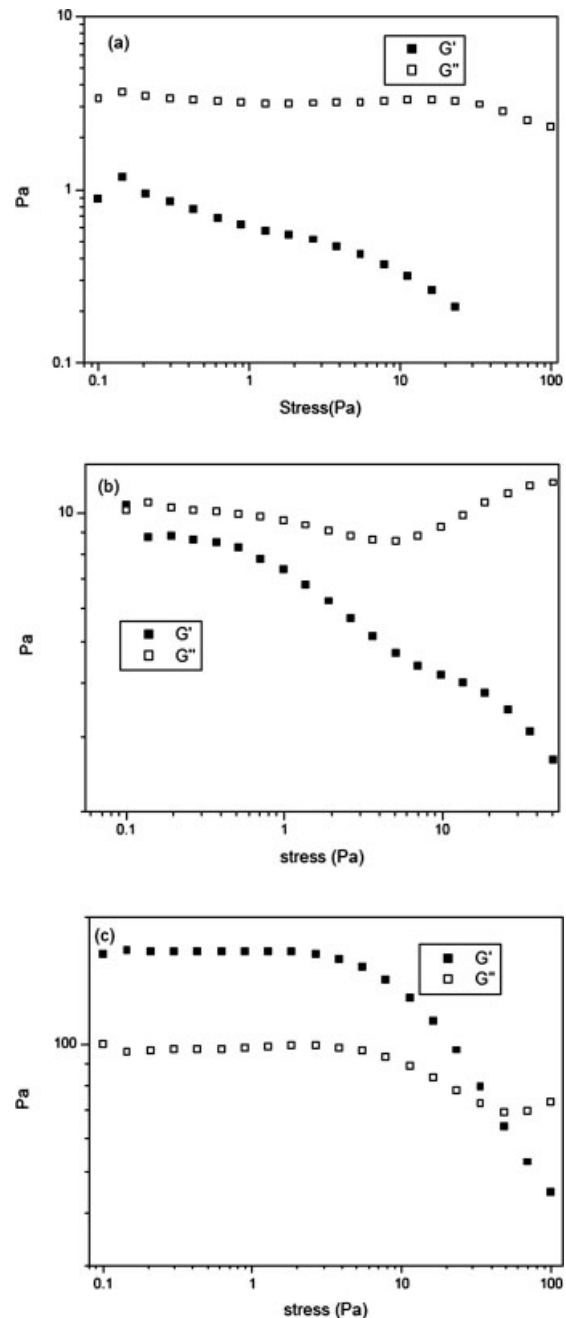
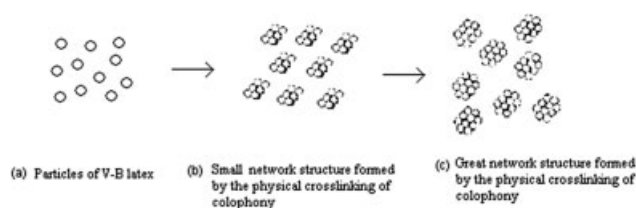


Figure 6 Dependence of G' and G'' on the shear stress for (a) V-B, (b) V-B-1, and (c) V-B-2.



Scheme 1 Interactions between the V-B latex and colophony.

that G'' became higher than G' at high stresses. There is a point of intersection appearing in Figure 6(c), which indicates the strength of V-B-2 was higher than the other two. This result verifies that the aggregates formed were driven by the physical crosslinking of colophony in the V-B-2 latex.

According to the thermal and rheological properties of V-B, V-B-1, and V-B-2, a possible scheme to represent the interaction when colophony was blended into V-B latex was determined and is shown in Scheme 1. When blended with 20% colophony, a small network structure formed [Scheme 1(b)], and the colophony molecules acted as the physical crosslinking point. At higher concentrations of colophony, a greater network structure formed [Scheme 1(c)]. The networks formed were driven by the physical crosslinking of colophony, which limited the chain motion of the V-B latex and led to an increase in T_g , E_f , viscosity, and dynamic moduli. As a result, the T_g peak in the DSC curve of V-B-2 became less obvious because large amounts of physical crosslinking points hampered the chain motion.

Contact angle

The spreading of latex on the adherent was characterized by contact angle measurement. The contact angle was correlated to the free surface energy of the adhesive and the adherent, the degree of roughness, and the diffusion of latex across the interface. Table III shows the diluted latex contact angles on the adherent (a thick paper with a surface coated with a UV photosolidified acrylic polymeric coating). Before measurement, the latexes were first diluted to a predetermined viscosity to control the size and volume of the droplets. As shown in Table III, we generally found that with the addition of colophony, the contact angle decreased, which suggested that the colophony blending facilitated the spreading of the latex on the aimed adherent.

Adhesive strength

The peel strengths of the V-B, V-B-1, and V-B-2 latexes are listed in Table II. As shown in this table, we found that the peel strengths for V-B, V-B-1, and V-B-2 were 4.5, 7.8, and 6.2 N/cm, respectively,

which indicated that the latex blended with 20% colophony achieved the maximum adhesive strength.

Discussion

The term *debonding mechanisms* refers to cavities that have propagated at the interface rather rapidly under low stresses. During the debonding process, two main mechanisms compete with each other: the propagation of cavities along the interface as cracks (normal to the tensile direction) and the bulk expansion of the same cavities parallel to the tensile direction. The balance of competition determines to a large extent the final properties of the adhesive.

Interfacial propagation is limited by the interfacial critical energy release rate (G_c), which characterizes the amount of energy dissipated by a propagating crack at the interface between the adhesive and the surface.²⁶ It depends mainly on the adherent's surface and the dissipative properties of the adhesive. Bulk expansion is limited chiefly^{27,28} by the elastic properties of the adhesive, that is, by its G' . When the experimental geometry is fixed, the key parameter controlling the behavior of the adhesive is the ratio of the energy release rate to G' , G_c/G' . Three different cases can be observed.²⁹ For high G_c/G' values, the initial mechanism of failure is cavitation and fibrillation. The maximum extension of the fibrils is not controlled by the surface but rather by the rheological properties of the adhesive.³⁰ For very low values of G_c/G' , failure occurs by crack propagation without any pre-existing cavitation in the bulk.^{26,31} This mechanism is observed only when the adhesion is very weak. For intermediate values of G_c/G' the initial failure mechanism can still be cavitation; however, the maximum extension of the fibrils is controlled by the surface of the adhesive.²⁹

G_c should be related to permeability and diffusion of the latex across the interface of the adherent, which is dependant on the viscosity, T_g of the latex, and the contact angle of latex on the adherent. The V-B latex should have had the highest value of G_c/G' because of the high G_c and low G' . High G_c is caused by low viscosity and T_g , which leads to a good permeability and diffusion across the interface. However, the V-B-2 latex should have had the lowest value of G_c/G' because of the poor permeability and diffusion across the interface and the highest value of G' . The V-B-1 latex had an intermediate

TABLE III
Contact Angles of the Diluted Latex on the Substrate

Sample	Dilution (\times)	Water contact angle ($^\circ$)
V-B	2	25.6 \pm 1.44
V-B-1	2	22.5 \pm 1.91
V-B-2	3	22.8 \pm 1.43

value of G_c/G' due to its mediate viscosity, $T_{g'}$, and G' . For the V-B latex, the initial mechanisms of failure were cavitation and fibrillation. The adhesive strength was not controlled by the surface but rather by the rheological properties. For the V-B-2 latex, failure occurred by crack propagation without any preexisting cavitation in the bulk. For the V-B-1, the debonding was controlled by both cavitation and the surface of the adhesive. It was the balance of G_c/G' that made V-B-1 have excellent adhesive strength against adherent surfaces. Moreover, in the view of operative techniques, the viscosity of V-B-1 was most suitable for brushing coating than that of V-B and V-B-2.

CONCLUSIONS

The copolymeric latex composed from vinyl acetate and *n*-butyl acrylate (V-B) was prepared with an emulsion polymerization process. $T_{g'}$, viscosity, $E_{f'}$, G' , and polar properties of the V-B latex were effectively modulated by blending with a colophony emulsion. The particle aggregates formed were driven by the physical crosslinking of colophony molecules, which resulted in a significant change in the rheological and other physicochemical properties of the V-B latex. The experimental results demonstrate that the V-B latex blended with 20% colophony (V-B-1) showed excellent adhesive performance, which was due to V-B-1 with its moderate $T_{g'}$, viscosity, $E_{f'}$, G' , and low contact angle against the adherent.

References

1. Clearfield, H. M. *Fundamentals of Adhesive Bonding*; Plenum: New York, 1990.
2. Caucheteaux, T. *New Trends in Physics and Physical Chemistry of Polymers*; Plenum: New York, 1989.
3. Allen, K. W. *Proceedings of the 16th Annual Meeting International Symposium Interphase of the Adhesive Society*; Williamsburg, Virginia; 1993, p 238.
4. Fourche, G. *Polym Eng Sci* 1995, 35, 957.
5. Fourche, G. *Polym Eng Sci* 1995, 35, 968.
6. Pang, S. S. *Selected Papers Presented at the International Conference for Composites Engineering New Orleans, LA, Aug 1994*; Pergamon: Oxford, 1994.
7. Friederich, J. *Macromol Symp* 1995, 111, 1994.
8. Creton, C. In *Materials Science and Pressure-Sensitive Adhesives*; Meijer, H. E. H., Ed.; VCH: Weinheim, 1997; Vol. 18.
9. Satas, D. *Handbook of Pressure Sensitive Adhesive Technology*, 2nd ed.; Van Nostrand-Reinhold: Melbourne, 1989; Vol. 1.
10. Zosel, A. *Colloid Polym Sci* 1985, 263, 541.
11. Zosel, A. *Int J Adhes Adhes* 1998, 18, 265.
12. Lakrou, H.; Sergot, P.; Creton, C. *J Adhes* 1999, 69, 307.
13. Lakrou, H. Ph.D. Dissertation, Université Paris 7, France, 1998.
14. Laureau, C.; Vicente, M.; Barandiaran, M. J.; Leiza, J. R.; Asua, J. M. *J Appl Polym Sci* 2001, 81, 1258.
15. Aymonier-Marçais, A.; Papon, E.; Villenave, J. J.; Tordjeman, P. H.; Pirri, R.; Gerard, P. *Macromol Symp* 2000, 151, 497.
16. Simionescu, C. I.; Chiriac, A. P. *Mater Plast* 1996, 33, 12.
17. Neamtu, I.; Chiriac, A. P.; Ioanid, G. E.; Simionescu, C. I. *Polym Test* 1999, 18, 415.
18. Chiriac, A. P. *Polym Test* 2001, 20, 873.
19. Mayer, A.; Pith, T.; Hu, G. H.; Lambla, M. *J Polym Sci Part B: Polym Phys* 1995, 33, 1781.
20. Chiriac, A. P.; Simionescu, C. I. *Polym Test* 1997, 16, 185.
21. Amaral, M.; Roos, A.; Asua, J. M.; Creton, C. *J Colloid Interface Sci* 2005, 281, 325.
22. Romanov, A.; Novak, I.; Ambrusova, M.; Brenner, R.; Florian, S.; Lath, D. *Czech. Pat.* 261,667 (1989).
23. Novak, I.; Romanov, A.; Ambrusova, M.; Brenner, R.; Florian, S.; Lath, D. *Czech. Pat.* 261,666 (1989).
24. Lovell, P. A.; Shah, T. H.; Heatley, F. In *Polymer Latexes; Preparation, Characterization and Application*; Daniels, E. S.; Sudol, E. D.; El-Aasser, M. S., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1992; 492, Chapter 12, p 493.
25. Wu, J.; Tomba, J. P.; Winnik, M. A. Farwaha, R.; Rademacher, J. *Macromolecules* 2004, 37, 4247.
26. Josse, G.; Sergot, P.; Dorget, M.; Creton, C. *J Adhes* 2004, 80, 4948.
27. Gent, A. N.; Lundley, P. B. *Proc R Soc London Ser A* 1958, 249, 195.
28. Dollhofer, J.; Chiche, A.; Muralidharan, V.; Creton, C.; Hui, C. Y. *Int J Sol Struct* 2004, 41, 6111.
29. Shull, K. R.; Creton, C. *J Polym Sci Part B: Polym Phys* 2004, 42, 4023.
30. Brown, K.; Hooker, J. C.; Creton, C. *Macromol Mater Eng* 2002, 287, 163.
31. Creton, C.; Hooker, J. C.; Shull, K. R. *Langmuir* 2001, 17, 4948.