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Investigation of the Influence of Fillers on the Properties of Poly(vinyl acetate) Adhesives*

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The properties of poly(vinyl acetate) compositions prepared as potential wood adhesives were investigated. The paper presents the results of the influence of various kinds of inorganic fillers based on calcium carbonate and alumino-silicate and an organic filler, starch, on the adhesive composition properties. The comparison among rheological behavior of the adhesive dispersions concerning the specific role of fillers were made. Mechanical and relaxation properties of the adhesive films could reveal the effect of filler characteristics on the polymer matrix. The significant influences of particle size distribution and specific surface area on the poly(vinyl acetate) adhesive composition were determined, along with other filler characteristics.

KEY WORDS poly(vinyl acetate) adhesives; fillers; calcite; alumino-silicates; starch; wood adhesive joint.

INTRODUCTION

Adhesive compositions frequently include a number of additives or modifiers such as plasticizers, tackifiers, viscosity/rheology modifiers, extenders, solvents and various fillers in their formulation.^{1,2} Many poly(vinyl acetate) emulsions can be used without further modification; however, in adhesives they should usually be compounded in order to tailor the product for particular applications.²

The properties of adhesive compositions of poly(vinyl acetate) are strongly dependent on molecular structure, molecular weight distribution and on the specific characteristics of additives.³

The influence of fillers on the properties of adhesive compositions has been the subject of many investigations.²

In poly(vinyl acetate) adhesives the fillers may exert a quite specific influence on adhesive properties.⁴ The selection of fillers is primarily determined by the

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particle size distribution, the particle shape and how the particles are packed together.⁵ The adhesion of filler to polymer matrix was found to depend strongly on the diameter of the particles.⁶ Many effects of fillers are dependent on specific surface area, as well as the shape factors and chemical constitution of the fillers. Differences in particle size distribution are expected to reflect the rheological effects, particle packing relationships, dispersibility, chemical resistance and tensile properties of the adhesive composition.

The aim of the present work was to investigate the correlation between filler characteristics and adhesive properties. A good understanding of rheological and mechanical properties is of great importance for successful practical application of adhesives.

EXPERIMENTAL

Materials

Materials used in the work were all of commercial grade, obtained from the producers (Karbon, PVAC-Vinapol A, produced by Karbon, Zagreb) without further purification. A suspension type of PVAC (Vinapol A) was used for the preparation of all adhesive compositions investigated in the work. A detailed morphological and chemical characterization of various types of calcite, aluminum-silicate and starch was performed. The samples of poly(vinyl acetate) adhesives were prepared by mixing the PVAC suspension and other components with a previously-prepared paste of filler and thickener (Table I).

Other components used were dibutylphtalate as plasticizer, butyldiglycol acetate as extender/coalescent and carboxymethylcellulose (Mavibond CPA 2000) as thickener.

TABLE I
Composition of poly(vinyl acetate) adhesives

Component	Mass content (%)
PVAC ¹ emulsion	77.0
Plasticizer	3.0
Extender/coalescent	1.0
Thickener	4.1
Water	4.1
Filler ²	10.5

¹Commercial sample (DSC characteristic of film: $T_g = 47.5^\circ\text{C}$)

²Various fillers (Table II)

Samples of poly(vinyl acetate) adhesives were also prepared in the form of films by peeling from the glass plates and drying in air.

Testing Techniques

Characterization of the components in the adhesive composition The commercial sample of PVAC was used as received. Differential scanning calorimetric measurements (DSC) were made to determine the thermal profile of the initial PVAC component, using a Perkin-Elmer DSC-1B at a heating rate of 8°C/min with a sample size of 15 mg. The only distinctive feature of the DSC thermograms was the glass transition temperature, which was taken as the temperature at which the midpoint of heat capacity was achieved.

Wide angle X-ray diffraction experiments (WAXD) were made on a Philips diffractometer with monochromatic $\text{CuK}\alpha$ radiation in the range of Bragg's angle $\Theta=2\text{--}26^\circ$. Quantitative chemical composition and the degree of crystallinity of fillers were calculated.^{7,8}

Particle size distributions of fillers were determined by using the Electrical Sensing Zone method with a Coulter Counter Z_B . Particle size distribution, measured as volume characteristics of particles ($r=3$), was approximated by a log-normal (LN) distribution function.⁹ The measure of central tendency ($x_{50,3}$, median of distribution—50% of particles in the system are smaller than this value), and the parameter of spreading—standard deviation of log variable $x(\sigma_L)$ —were determined.⁹

Specific surface area (S_{BET}) and the specific pore volume (V_p) of fillers were measured on an ASAP 2000, Micromeritics, using a gas adsorption (B.E.T.) method.¹⁰

Effective permeability mass specific surface (S_m) was obtained from permeability measurements.¹¹ Scanning electron microscope (SEM) analysis of fillers, and also adhesive compositions in the form of films, were made on a Cambridge S600 Stereoscan scanning electron microscope.

Characterization of Adhesive Compositions Rheological behavior of poly(vinyl acetate) adhesive compositions with various fillers was tested using a Haake Rotovisco RV3 rotational viscometer with coaxial cylinders with measuring head 50 and sensor system SVII. The results were compared with rheological models proposed by Ostwald¹² ($\tau=k\bullet D^n$), and Trippy-Ory¹³ ($D=a\tau^3+c\tau$), where τ =shear stress (Pa); D =shear rate (s^{-1}); $k, n, a, c,$ =coefficients. Comparisons between measured and calculated values were made to reach conclusions about the proposed models. Experimental data were handled by a personal computer using linear regression by the least squares method. Correlation coefficients were calculated and relative deviation (S) of the calculated and experimentally-measured values was determined.¹⁴ Tensile properties of adhesive compositions in the form of films were determined using a Zwick 1445 Universal testing machine at a crosshead speed of 100 mm/min by a standard procedure (DIN 53455). Molecular relaxation processes as a function of time were measured by relaxation tests ($\epsilon_0=130\%$, test speed 400 mm/min) by a standard procedure (DIN 53441).

Hysteresis curves after the first and tenth cycles ($\epsilon_0=130\%$) using a 100 mm/min test rate were determined using the Zwick PC Software system 7047.7a, "Hysteresis, relaxation and retardation testing."

Adhesive compositions were characterized by determining their lap shear strengths with standard wood test specimens (DIN 53254).

RESULTS AND DISCUSSION

The commercial PVAC used in this work was insoluble in conventional organic solvents, thus limiting the application of standard characterization methods. The insolubility of PVAC can be attributed to high branching or partial cross-linking. This assumption is in agreement with the relative high T_g of the tested specimen ($T_g=47.5^\circ\text{C}$) compared with the T_g of linear PVAC ($T_g=28\text{--}31^\circ\text{C}$).³ Various types of calcite, alumino-silicate and starch were added in order to study the specific role of individual components and their influence on the adhesive properties. The influence of chemical structure, the degree of crystallinity and other morphological characteristics on the adhesive properties have been investigated.

X-ray analysis shown in Table II and Figure 1 gives the results of quantitative chemical composition of fillers and the degree of crystallinity. Katz and Milewski⁵ have shown that various types of calcium carbonates as fillers, due to their polar, highly water soluble characteristics, could react with a great variety of chemical reagents. Similar effects were also described by Skeist² for magnesium carbonate. Due to the highly reactive characteristics of alumino-silicate it could be expected that it will cause a variety of surface activities and other effects as filler.

As mentioned above, various types of calcium carbonate, as fillers, are polar substances of fairly high water solubility making them reactive with a great variety of chemical reagents.⁵ It could be also expected that the presence of magnesium carbonate would cause some higher reactivity and a thickening effect.² Complex chemical composition of the investigated aluminum silicate fillers was highly reactive and could also lead to a variety of surface activities and effects.

Fillers of the same or similar chemical composition could cause different properties of adhesives, mostly as a consequence of the difference in crystallinity, although some other characteristics could be of more importance in special applications.¹⁶

Many effects of fillers are dependent on specific surface area, but it is also known that besides the particle size distribution, the shape of particles must also be taken into consideration. The measured characteristics of particle size distribution are given in Table III.

A median particle size value indicates coarse or fine particles while higher standard deviation is an indication of narrow or broad particle size distribution. The observed differences in specific surface area, S_{BET} , between the fillers with quite similar particle size and chemical characteristics (samples A1 and A2; B and C, in Table III) have to be explained. Comparative results of permeability mass specific surface S_m , which is the measure of effective surfaces but does not include porosity¹⁰ did not show such differences. Higher values of S_{BET} , detected by isothermal adsorption of nitrogen gas into pores, could be the consequence of larger porosity. This was also confirmed by the higher values of specific pore volume. The conclusion was drawn that the comparison between the same types of fillers with similar particle size distribution could also be based on direct surface area measurements which includes the porosity of the specimens.

From the results of morphological characteristics it can be concluded that specific shape, particle size and their distribution and special porosity, would have specific influences on poly(vinyl acetate) adhesive properties.

TABLE II
X-ray analysis of fillers

Filler	Interplanar spacings d(Å)	Assignment structure ¹	Composition (%)	Degree of crystallinity (%)
A1,A2,A4*	3.850,3.030,2.845,2.496 2.285,2.090,1.928,1.909 1.872,1.622,1.602,1.583 1.524,1.505,1.473,1.440	Calcite ²	100	100
A3	d, Calcite 2.690,2.885,2.665,2.405 2.190,2.015,1.802,1.786 1.598	Calcite Dolomite Ferroan ³	79.0 21.0	100
B	4.260,3.350,2.456,2.285 2.236,2.130,1.980,1.819 1.670,1.543,1.452,1.383 1.372 7.190,4.470,4.130,3.880 3.730,3.580,3.340,2.560 2.497,2.382,2.340,2.190 1.996,1.688,1.649,1.630 10.070,4.980,4.470,3.880 3.730,3.340,3.250,3.190 2.986,2.885,2.789,2.560 2.456 11.900	α -Quartz ⁴ Kaolinite ⁵ Illite ⁶ Rectorite ⁷	80.0 9.4 8.6 2.0	100
C	d, α -Quartz 9.160,4.610,4.410,4.190 3.060,2.568,2.540,2.456 2.296,2.088,2.060,1.840 1.646,1.543,1.490 d, Dolomite Ferroan	α -Quartz Pyrophyllite ⁸ Dolomite Ferroan	42.0 35.1 12.5	100
	d, Kaolinite d, Calcite 4.980,3.350,2.568,2.000	Kaolinite Calcite Muskovite ⁹	4.2 3.5 2.7	
D	5.880,5.150,4.940,4.550 4.390,4.170,4.020,3.860 2.510,3.400,3.340,2.345	Starch ¹⁰	100	24.3

¹Reference d-values¹⁵

²CaCO₃

³Ca(Mg_{0.65}Fe_{0.33})(CO₃)₂

⁴ α -SiO₂

⁵Al₈(OH)₄Si₂O₅

*Commercially surface modified with stearic acid

⁶(K,H₃O)Al₂Si₃AlO₁₀(OH)₂

⁷(Na,Ca)Al₄(Al_{1,7}Si_{6,3})O₂(OH)₄•2H₂O

⁸Al₂Si₄O₁₀(OH)₂

⁹(K,Na)(Al,Mg,Fe)₂(Si_{2,1}Al_{10,9})O₁₀(OH)₂

¹⁰d-Melibiose Hydrate C₁₂H₂₂O₁₁•H₂O

Comparative scanning electron micrographs of filler particles and films of adhesive compositions without and with fillers are shown in Figure 2. It is visible from this illustration that the tested fillers are generally of quite irregular shapes.

It seems that, for calcite fillers characterized by fine particles and narrow particle size distribution (samples A1 and A2, in Table III), the higher specific surface area in sample A1 could be the consequence of larger porosity, but on the microporous level. Adhesive film with calcite filler was quite continuous except for the few visible agglomerates, which are also seen in the film without filler

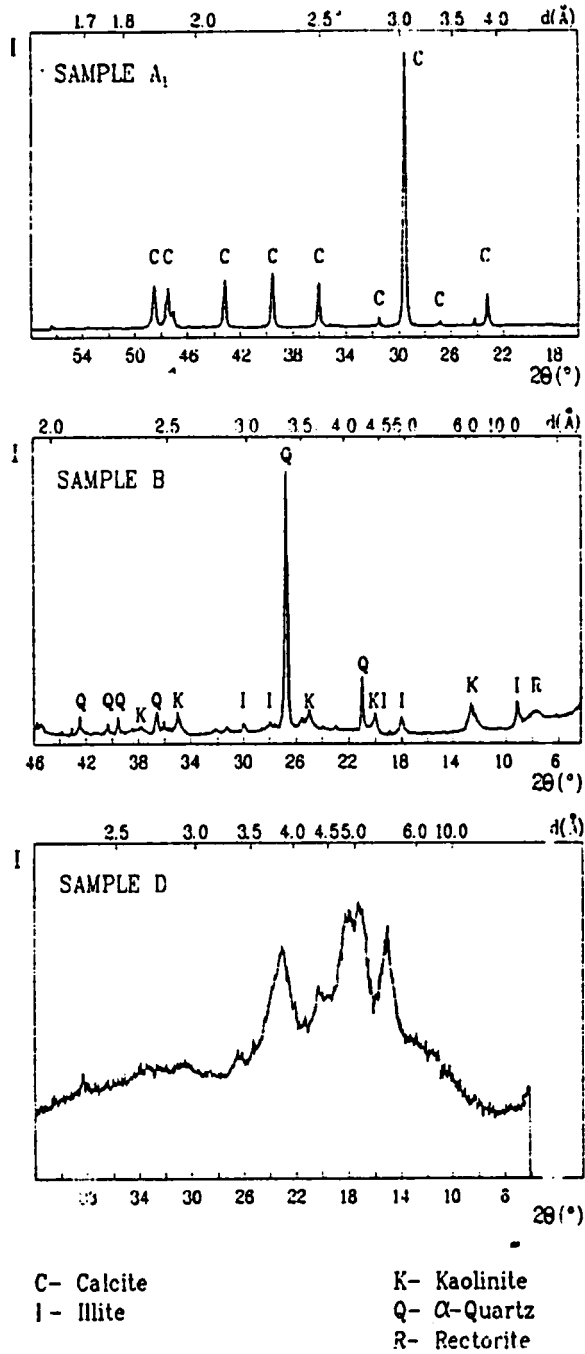


FIGURE 1 X-ray patterns of fillers; calcite (A₁), alumino-silicate (B) and starch (D).

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TABLE III
Particulate characteristics of fillers

Filler	Median $x_{50.3}^1$ (μm)	Standard deviation ² σ_L	Specific surface		Specific pore volume ⁵ V_p (cm^3g^{-1})
			S_{BET}^3 (m^2g^{-1})	S_m^4 (m^2g^{-1})	
A1	6.5	0.202	4.210	0.782	0.0136
A2	5.5	0.240	0.914	0.461	0.0031
A3	33.2	0.556	1.152	0.284	0.0040
A4	9.3	0.300	0.743	0.319	0.0026
B	7.8	0.359	25.276	1.282	0.0676
C	10.5	0.366	6.275	0.872	0.0193
D	15.0	0.170	0.632	0.360	0.0014

¹Median of distribution (50% of particles are smaller than this value)

²Parameter of spreading (standard deviation of log variable x)

³Specific surface area (nitrogen gas adsorption method)

⁴Effective permeability mass specific surface (air permeability measurements)

⁵Relevant only for pore diameter $<0.2\mu\text{m}$

(Figure 2). On the contrary, very coarse particles of calcite filler with visible agglomerates of about $33\mu\text{m}$, and particle size analysis (A3 in Table III) have an influence on the discontinuity of the adhesive film probably due to a lower amount of intermolecular contacts. Katz and Milewski⁵ have shown that the adhesion of filler to polymer matrix strongly depends on the diameter of particles. It was noticed that surface treatment with stearic acid in one of the used calcites (A4 in Figure 2) reduced the particle-particle interactions resulting in the decrease of particle agglomeration. Calcite filler treated with stearic acid showed higher compatibility with the polymer matrix in the adhesive film because of chemical changes on the surface and the more spherical shape of the particles. It could also be expected that more or less spherical shape of filler in contact with polymer matrix would lower residual stresses in the system. Alumino-silicate fillers were characterized by larger average particle sizes and consisted of mixtures of "blocky" and "platy" particles and agglomerates. They were better incorporated into the adhesive film, because of their chemical reactivity, but nonregular agglomerates were still visible. Very good dispersion and rather large but spherical and compatible particles were obtained for adhesive film filled with starch (sample OD in Figure 2).

Dispersion of particles and the level of interaction in the liquid adhesive composition is related to many factors such as particle content, particle-matrix interactions and to their intrinsic characteristics including kind, shape, surface and size of fillers particles. The results of rheological behavior of the investigated poly(vinyl acetate) adhesives are given in the Table IV and Figures 3, 4 and 5.

The position of rheological curves in all investigated adhesive systems indicated the same trend to pseudoplasticity and low thixotropy. Values based on the experimental data, and data calculated on the basis of the rheological models, indicate pseudoplastic behavior (coefficient $c>0$ in Table IV). Relatively higher k -values in some tested systems indicate the presence of higher structuration in the adhesive systems.¹² However, the higher a -coefficients indicate better fluidity of the sys-

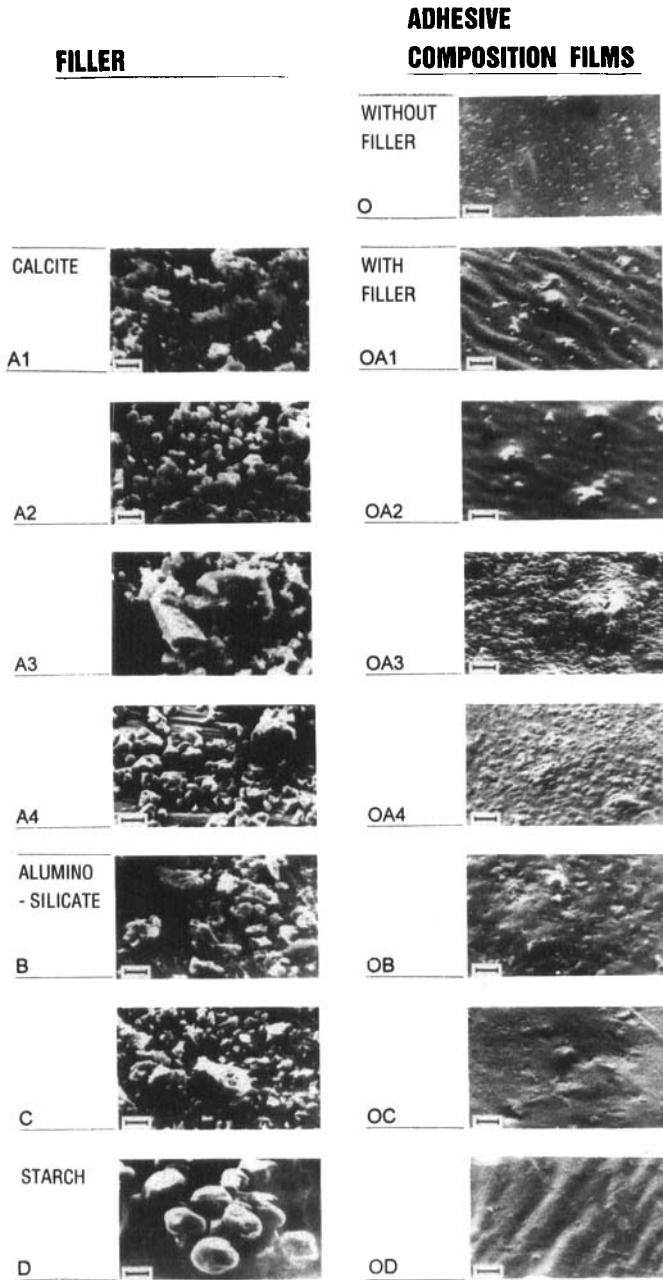


FIGURE 2 Comparative scanning electron micrographs of fillers; calcite (A1, A2, A3), surface modified calcite (A4), aluminum-silicate (B,C), starch (D) and films adhesive compositions; without filler (O) and with filler (OA1, OA2, OA3, OB, OC, and OD) (— = 10 μm).

TABLE IV
Rheological coefficients of poly(vinyl acetate) adhesive composition without (O) and with fillers

PVAC adhesive	Rheological model				Relative deviation ¹ S (%)
	Ostwald n	k	Trippy-Ory a-10 ⁶	c	
O	0.779	11.073	2.005	0.141	2.03
OA1	0.765	12.825	1.594	0.123	2.29
OA2	0.829	10.213	1.569	0.133	4.31
OA3	0.838	7.457	3.339	0.182	3.20
OA4	0.856	7.572	2.672	0.170	3.23
OB	0.761	14.156	0.947	0.120	4.81
OC	0.882	5.644	3.008	0.227	3.71
OD	0.815	10.161	1.711	0.140	2.79

¹Differences between calculated and experimental τ values (Ostwald model)

tem.¹³ It shows that the proposed rheological models are useful in the characterization of viscous behavior of the non-Newtonian, shear-thinning adhesive systems.¹³ Relative deviation (*ca.* 4%) confirms good correlation with the proposed rheological model. The comparably higher level of viscosity curves for adhesive systems with similar filler characteristics could be explained by higher specific surface area and higher porosity of filler particles (samples OA1, OB in Figures 3 and 4). At the same time, fine calcite particles contribute to the higher viscosity of the adhesive dispersions, especially at lower shear rates. A quite opposite effect was noticed when coarse calcite particles were added (sample

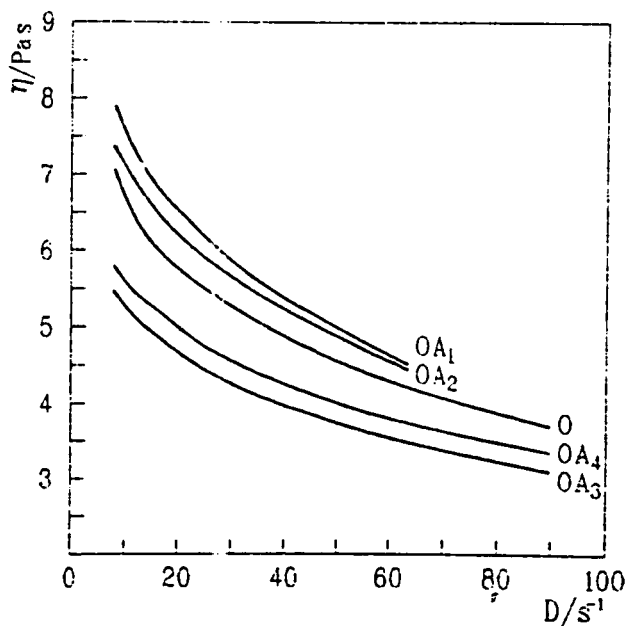


FIGURE 3 Rheological behavior of poly(vinyl acetate) adhesives without (O) and with various calcite fillers (OA1–OA4).

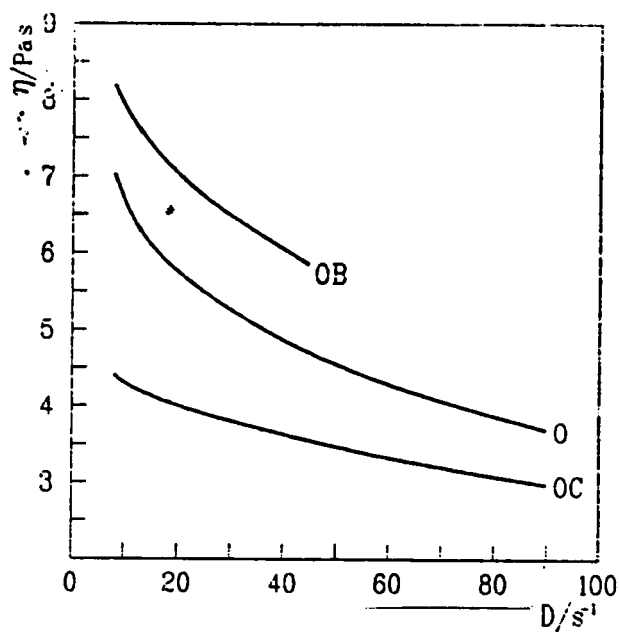


FIGURE 4 Rheological behavior of poly(vinyl acetate) adhesives with aluminosilicate fillers of various surface area.

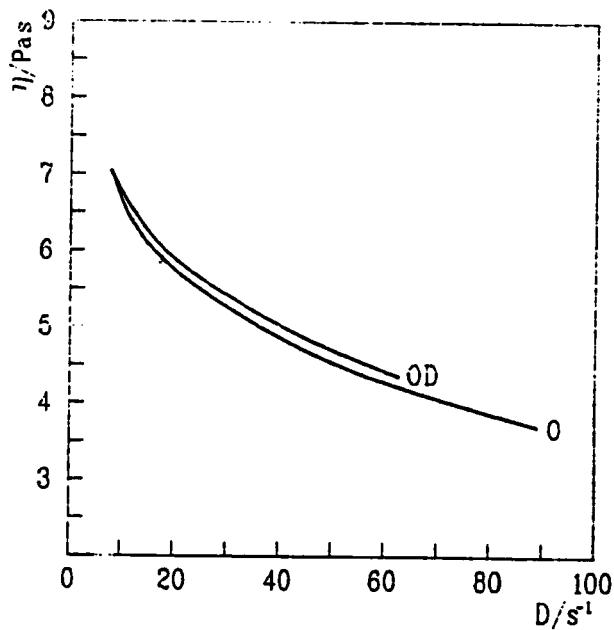


FIGURE 5 Rheological behavior of adhesive composition without (O) and with (OD) starch filler.

OA3 in Figure 3). Fillers having the quasispherical shape of surface-modified calcite or starch did not change the viscosity of poly(vinyl acetate) adhesives significantly.

It is obvious that many factors, especially the characteristics of fillers, have an influence on the flow behavior of adhesives. The observed effect of lowering of the viscosity of the adhesive compositions by coarse particles was not the consequence of better dispersion but was the result of the lack of contacts with the polymer matrix. More reactive aluminium silicate filler, although with lower specific surface area, could improve the flow properties. The reason could be better intermolecular interaction with polymer matrix, as confirmed by the relative continuity of the adhesive film observed in the scanning electron micrographs (Figure 2). However, it has to be emphasized that the increase of intermolecular bonds could lower the elasticity and produce rigid adhesive films.

Tensile properties of poly(vinyl acetate) adhesives in the form of films are shown in Table V and Figures 6–8.

TABLE V
Mechanical properties of poly(vinyl acetate) adhesive films

Adhesive film (filler)	Tensile characteristics		
	σ^1 (Nmm ⁻¹)	ϵ^2 (%)	W ³ (Nm)
O (without)	4.77	538.26	0.83
OA1 (calcite)	5.38	484.50	1.13
OA2 (calcite)	5.28	538.20	1.33
OA3 (calcite)	5.28	356.62	1.59
OA4 (calcite)	4.86	537.20	1.02
OB (alumino-silicate)	4.67	286.10	1.13
OC (alumino-silicate)	6.43	437.58	1.42
OD (starch)	3.86	494.62	1.35

¹Stress at Fracture

²Strain at Fracture

³Work to Break

Tensile properties of the films depend on the packing characteristics, size and interfacial bonding of the fillers. The differences in mechanical curves with various calcite fillers in Figure 6 indicate that fine particles, due to lower amount of stress points in the polymer matrix, cause higher strength and toughness, but still retain elastoplastic behavior. As expected, the high specific surface area of similar calcite particles (sample OA1 in Figure 6) decreases the elasticity of adhesive films, which is not a desirable property in adhesive compositions. The same effect was noticed in the composition with alumino-silicate particles (sample OB in Figure 7). Relatively large elasticity of the adhesive film without filler was obtained, and the elasticity did not change appreciably with addition of a filler with spherical shape or with fillers compatibilized with stearic acid. The addition of starch has a similar effect.

The change in the stress-strain curve of film filled with coarse calcite particles (sample OA3 in Figure 6) is in agreement with the change of apparent decrease of viscosity due to the low level of interaction between coarse particles and the polymer matrix.

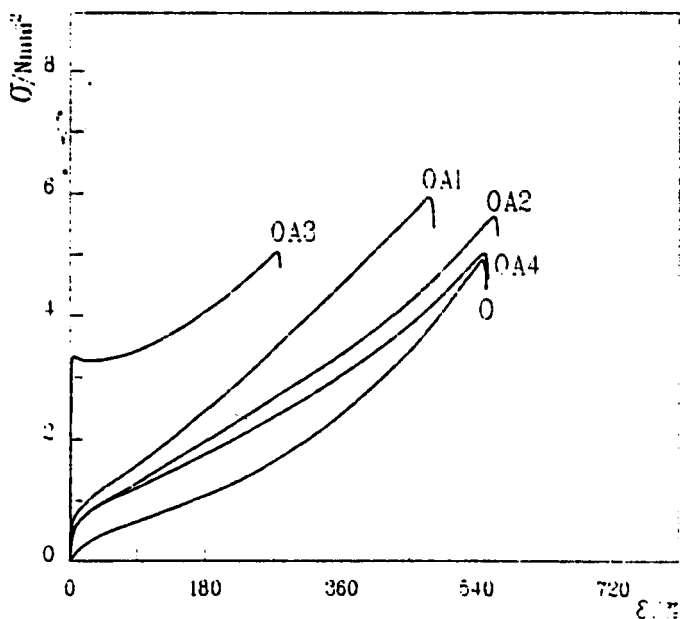


FIGURE 6 Stress-strain relationship for adhesive films without (O) and with various calcite fillers (OA1-OA4).

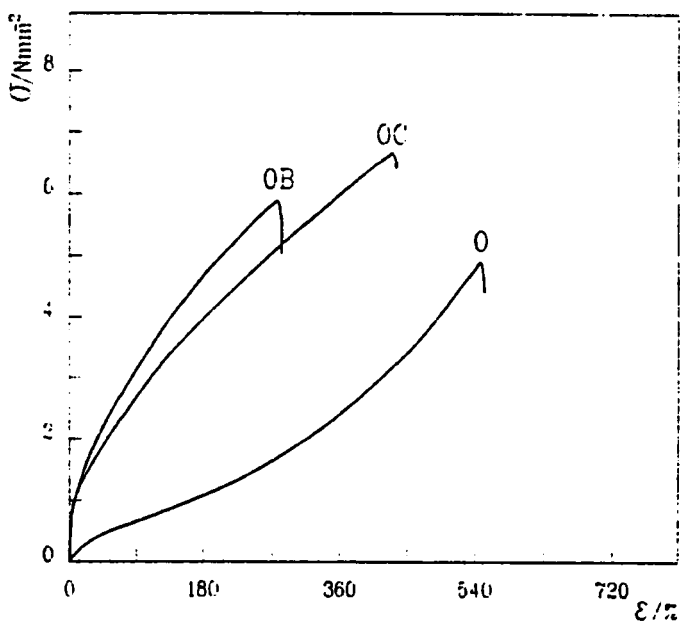


FIGURE 7 Stress-strain relationship for adhesive films without (O) and with (OB and OC) addition of aluminosilicate filler.

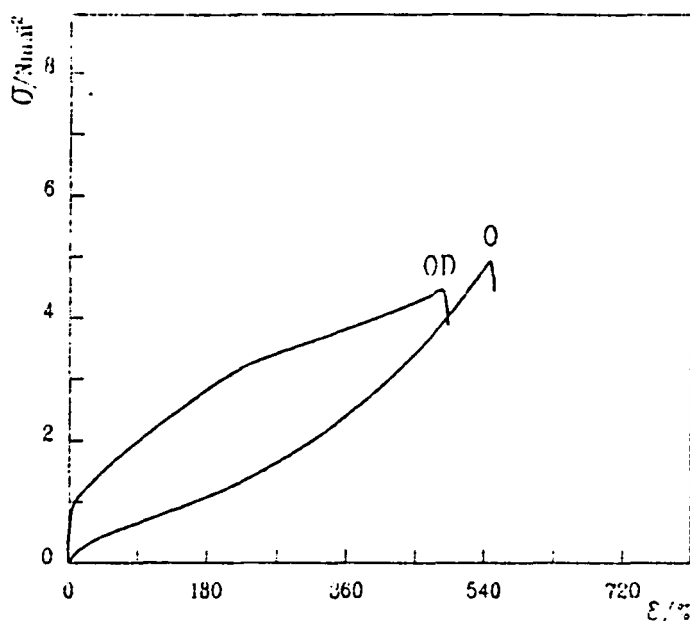


FIGURE 8 Stress-strain relationship for adhesive films without (O) and with (OD) starch filler.

A large number of intermolecular bonds between the polymer matrix and aluminosilicate fillers leads to the decreased elasticity and a more rigid cross-linked adhesive film. This effect is more pronounced for fillers with higher active surface area (sample OB in Figure 7).

The results of strength tests of standard wood adhesive joints presented in Table VI generally show the increase of strength with filler addition, and also the weakening of the adhesive layer when aluminosilicate, starch or calcite surface-modified fillers were used.

TABLE VI
Mechanical properties of adhesive joint

Adhesive composition (filler)	Adhesive joint strength τ (Nmm ⁻²) ¹	Surface appearance ²
O (without)	9.93	100 b
OA1 (calcite)	12.35	100 a
OA2 (calcite)	12.50	100 a
OA3 (calcite)	12.50	100 a
OA4 (calcite)	10.70	28 a/72 b
OB (aluminosilicate)	11.12	20 a/80 b
OC (aluminosilicate)	10.28	42 a/58 b
OD (starch)	10.90	32 a/68 b

¹Lap shear measurement with standard wood samples

²a (% wood), b (% adhesive)

The conclusion could be drawn that neither compatibility nor too many interactions of filler particles with the polymer matrix were recommendable for poly(vinyl acetate) adhesive applications.

Relaxation tests were also performed for adhesive films with various fillers (Table VII).

TABLE VII
Relaxation properties of poly(vinyl acetate) adhesive films

Adhesive composition (filler)	$F_{(0)1}^1$ (N)	$F_{(0)2}^2$ (N)	$\Delta F/\Delta t$ (N_s^{-1})	W_1^3 (Nm)	S_d^4 (mm)
O (without)	2.84	0.04	0.0277	0.1329	28.45
OA1 (calcite)	3.43	0.37	0.0091	0.1977	29.51
OA2 (calcite)	3.16	0.27	0.0091	0.1566	28.47
OA3 (calcite)	13.08	0.39	0.0163	0.5731	47.37
OA4 (calcite)	3.14	0.16	0.0072	0.1726	26.19
OB (alumino-silicate)	8.54	0.97	0.0117	0.3592	37.14
OC (alumino-silicate)	7.50	0.66	0.0105	0.2940	32.35
OD (starch)	5.84	0.59	0.0112	0.2451	41.52

¹Initial stress value

²Equilibrium stress after relaxation time, $\Delta t=5$ s, when $\Delta F_{(0)2}<0.02$ N

³Work (hysteresis curve) after 1st cycle

⁴Seating-in distance (residual deformation after 10 cycles)

The lower residual stress with calcite fillers, especially for samples treated with stearic acid, and for fillers with lower active surface area, could be explained by optimal intermolecular contacts with the polymer matrix. This is in agreement with other mechanical and rheological results. A large hysteresis area, after 10 cycles, for adhesive compositions with alumino-silicate fillers could be explained by intermolecular interaction and by crosslinked structure. They result in a decrease in extension of the adhesive film, in a higher k-coefficient, and in increased structuring of the dispersion in such an adhesive system. It is concluded that the mechanical properties of the adhesive joint could be explained and predicted by knowing the behavior of the adhesive film and the dispersion of the filler. Weak points in the adhesive joint with alumino-silicate filler were observed in the adhesive layer (Table VI). From the results of high residual stresses in the adhesive film with coarse calcite particles (sample OA3 in Table VII) it is obvious that the apparently low viscosity of the dispersion was only the consequence of agglomeration.

CONCLUSIONS

The characteristics of fillers influence, in a specific way, the behavior of a poly(vinyl acetate) adhesive. Coarse and agglomerated particles lowered the viscosity and flow characteristics, apparently because of the lack of interaction with the polymer matrix, which resulted in a lower elasticity and higher residual stress in the adhesive film.

A filler with a large, active surface area is not recommended for adhesive applications because of the resulting increase in stiffness of the adhesive film and the greater structuring and higher viscosity in the adhesive dispersion, especially for aluminosilicate filler. Strengths of wood joints with poly(vinyl acetate) adhesives are generally increased by the addition of fillers. Characteristics of fillers such as particle size, particle size distribution, active surface area and porosity, particle shape and chemical constitution have specific influences. Fine calcite particles, with narrow particle size distribution and low active surface area improved the strength, toughness and elasticity, but did not change the elastoplastic behavior of poly(vinyl acetate) adhesives. It can also be concluded that reactive aluminosilicate fillers, because of large interactions with the polymer matrix, decrease the elongation and affect the rearrangement of macromolecular structure as well as the possibility of stress transfer by large particles, or by particles with high active surface area.

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