

Hydrophobic Polymers as Barrier Dispersion Coatings

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ABSTRACT: The aim of this study was to evaluate the properties of polymer dispersions prepared from hydrophobic monomers as barrier coatings. These dispersions were produced using a new emulsion polymerization process involving cyclodextrin as a phase-transport catalyst. Conventional emulsion polymerization techniques are not applicable due to the low water solubility of the monomers, such as lauryl and stearyl (meth)-acrylates. The experimental polymers showed improvements in water and water vapor barriers, as a result of the incorporation of hydropho-

bic monomers. The barrier properties could be further improved with functional groups, crosslinking, and chain-regulating agents, as well as fillers. Grease and water barriers were strongly affected by pinholes, and functional monomers appeared to be effective in enhancing the grease barrier property. Particle morphology, glass transition temperature, and drying affected the performance of these dispersions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1958–1962, 2006

Key words: barrier; coatings; dispersions

INTRODUCTION

Barrier dispersion coatings are intended to provide paper or paperboard with a barrier against water vapor, water, grease and oil, various gases, and impurities, i.e., properties required in packaging applications. In addition, the coating must have suitable creasing and folding, nonblocking, as well as heat sealing or gluing properties.

The common dispersions prepared by emulsion polymerization are styrene-butadienes and (meth)-acrylics. The conventional emulsion polymerization process is suitable for monomers having slight water solubility, which allows the diffusion between the droplets and polymer particles during the polymerization. Consequently, hydrophobic monomers, such as lauryl and stearyl (meth)-acrylates (LMA and SMA), which have very low-water solubility, cannot be used in emulsion polymerization. Without effective diffusion between monomer droplets and polymer particles during the polymerization, poor incorporation of the hydrophobic monomers will lead to monomer pooling, large suspension particles, heterogeneous compositions, and low-monomer conversion.¹

The discovery of cyclodextrin (CD) as a phase-transport catalyst made it possible to polymerize monomers of low-water solubility (e.g., lauryl and stearyl (meth)-acrylates) by emulsion polymerization. Cyclo-

dextrins are cyclic polyglucoses whose physical structures resemble a truncated cone. The interior of the cavity is hydrophobic and the exterior is hydrophilic. These unique features make it possible for the water soluble CD to act as a host, enveloping less polar guest molecules, and rendering them more water soluble as a complex. The complexation of the hydrophobic guest is reversible, allowing the release of the guest molecule under suitable conditions. The use of a catalytic level of CD allows the use of very hydrophobic monomers in emulsion polymerization. The mechanism of the process is believed to involve a catalytic cycle in which CD acts as a "Phase Transport Catalyst," continuously complexing and solubilizing the hydrophobic monomers and releasing them to the polymer particles.^{1,2}

The incorporation of hydrophobic monomers has a strong effect on the polymer characteristics indicated by the increase in the contact angle with water from around 80–85° (conventional monomers) to 90–95°. As the length of the carbon chain and the percentage of hydrophobic monomer used increases, so does the contact angle and the hydrophobicity of the polymer. This new class of latex polymers was expected to have good water barrier properties as barrier coatings. To substantiate the attributes of the hydrophobic polymers, several compositions were tested at the laboratory scale with drawdowns, and polymers having the best properties were also tried on the pilot line.

MATERIALS AND PROCEDURES

Materials and coating

Coating was applied to the uncoated side of folding boxboard. The results presented include polymers

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TABLE I
Composition of Experimental and Reference Polymers

	Butyl acrylate	Styrene	MMA	Functional monomer	Chain- regulating agent	Crosslinker 1	Crosslinker 2	LMA	SMA	T_g	
Experimental hydrophobic polymers											
S-A			x						x	27	
S-B			x					x	x	-1	
S-C	x	x	x						x	15	
S-D	x	x	x			x			x	9	
S-E		x	x			x			x	50	
S-F		x	x			x			x	23	
S-G		x	x		x	x			x	25	
S-H		x	x		x				x	25	
S-I		x	x					x	x	28	
S-J		x	x	x				x	x	19	
S-L	x		x	x		x			x	19	
S-M			Special version of S-J, functional monomer at end of pol.								15
S-N			Special version of S-I, core-shell with styrene in shell								26
S-O			Special version of S-I, core-shell with MMA in shell								23
Reference polymers											
B-A	x	x	x							24	
B-B	x	x	x			x				21	
B-D	x		x	x		x				14	
B-E	x	x	x					x		24	

T_g , Glass transition temperature; MMA, methyl (meth)-acrylate; LMA, lauryl (meth)-acrylate; SMA, stearyl (meth)-acrylate.

with stearyl (meth)-acrylate (S-A . . . S-O) and the reference acrylate polymers (B-A . . . B-E). Table I provides more detailed information. Fillers (talc and clay) and functional monomers were also tested in addition to crosslinking and chain-regulating agents. The talc grade had 45–46% of the solids smaller than 2 μm . Clay had particles 50% smaller than 2 μm . An alkali soluble thickener was used in the pilot trials.

Coating was first applied in laboratory scale with grooved rods. The effect of drying temperature was evaluated, and drying at 150–160°C for 20 s was used when preparing coated samples for further tests. Pilot scale application was carried out at the paper converting laboratory, Tampere University of Technology, to observe the effect of coating parameters (drying, metering) on the barrier performance. This line has IR and air driers. The temperature in the air dryers was 160°C. Coating thickness target was 10 μm , i.e., rather low for uncoated paperboard surface.

Tests

Pinholes were tested with a dyed solution (ethanol, detergent, and Sudan red). Liquid was spread on the coated paper and allowed to penetrate for 5 min. The excess solution was then removed and the number of pinholes on the uncoated side was counted.

Water absorption was determined with the Cobb test (SCAN P 12 : 64). The amount of water penetrat-

ing into the sample during a 30 min (1800 s) time period was measured. Water vapor transmission rate, WVTR, was measured from flat samples (modified SCAN P 22 : 68). Water vapor transmission is expressed as $\text{g}/(\text{m}^2, \text{d})$, and normalized to a coating thickness of 25 μm . The test was carried out at 25°C and 75% relative humidity with the dispersion coated side facing the higher humidity level.

Grease resistance was estimated with colored turnip oil. Cups were formed from the samples with both flat surfaces and creases. Oil was poured into the cups, and the grease resistance was evaluated visually. The evaluation points were crease and 30° fold, crease and 180° fold, as well as the flat surface (Fig. 1).

Blocking test was performed at a temperature of 40°C and under a pressure of 15 MPa. Strips of samples were placed on top of the base paper, so that the coating faced the back-side of the base paper. Pressure was then applied with a hydraulic press in an oven. After 6 h, the samples were removed from the oven and detached after cooling.

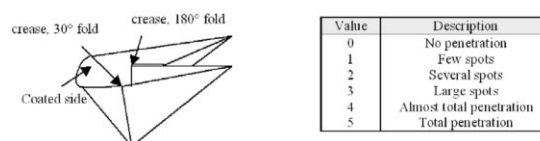


Figure 1 Grease resistance evaluation cup and scale used.

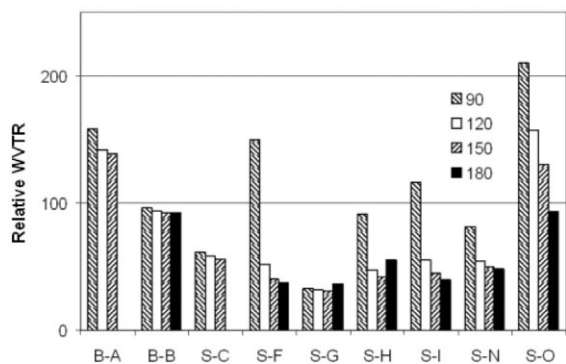


Figure 2 Relative WVTR values for dispersions as function of drying temperature (°C).

RESULTS

Laboratory scale trials

Figure 2 presents the relative WVTR of dispersion coatings dried at different temperatures, and Figure 3 shows the water absorption and WVTR after drying at 150°C. Stearyl (meth)acrylate improved water and water vapor barriers, as indicated by S-B, S-C, S-D, S-F, S-G, S-H, and S-I versus the reference dispersions. Crosslinking enhanced the barrier performance of both the reference and the SMA dispersions (B-A versus B-B/B-E and S-D versus S-C). Crosslinking agent 2 provided slightly better barrier than crosslinking agent 1 with the experimental dispersions in spite of a higher number of pinholes (S-I versus S-F). This is probably due to the different polymer structure. However, addition of SMA improved water and water vapor barriers more than crosslinking of the reference dispersion (S-C versus B-B and B-E). Polymers with high T_g demonstrated a high number of pinholes due to poor film formation, as indicated by S-E in Figure 3. The purpose of using a chain-regulating agent was to adjust the molecular weight of the polymer. The chain-regulating agent together with crosslinking did indeed provide the best WVTR values (S-G). Comparison of S-I, S-N and S-O indicated that changing the particle morphology to core-shell structures has an effect on barrier properties—particle shell containing

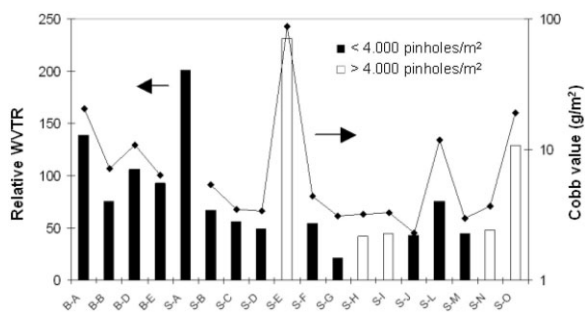


Figure 3 Water absorption and relative WVTR. White bars indicate over 4.000 pinholes/m².

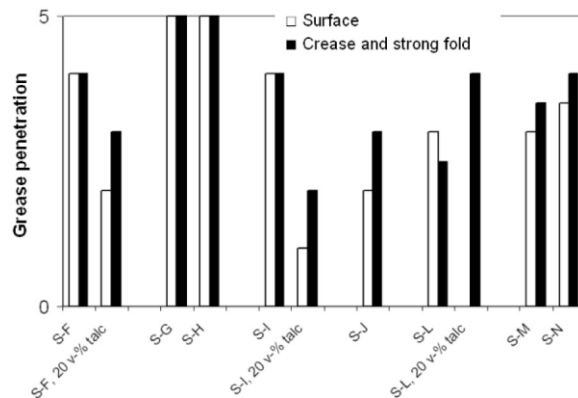


Figure 4 Grease barrier of some unfilled and talc-filled experimental dispersions after 24 h.

more hydrophobic and soft styrene allowed better film formation than methyl (meth)acrylate.

An increase in the glass transition temperature (T_g) led to a lower blocking tendency of unfilled dispersion coatings similar to the core-shell particles with a shell of high glass transition temperature (S-E and S-O). Grease penetration was reduced by functional monomers, e.g., S-J and S-L (Fig. 4). This can be explained by the effect on the surface energy and on the film formation. A high number of pinholes generally caused poor grease barrier, but not necessarily poor water and water vapor barrier (S-H and S-I). Chain-regulating agent impaired the grease barrier slightly compared to crosslinking, as indicated by S-G and S-H versus S-F and S-I. However, crosslinking had no clear effect on blocking.

Talc was tested as a filler for S-F, S-I, S-J, and S-L. Water vapor barrier of flat coatings was improved up to a pigment volume concentration of 40% (Fig. 5). Talc had little effect on an already low water absorption level. Small amount of talc improved the grease barrier. However, when the talc addition approached the optimum level for water vapor barrier, the flexibility of the coatings decreased, as indicated by a faster penetration of grease, especially through the

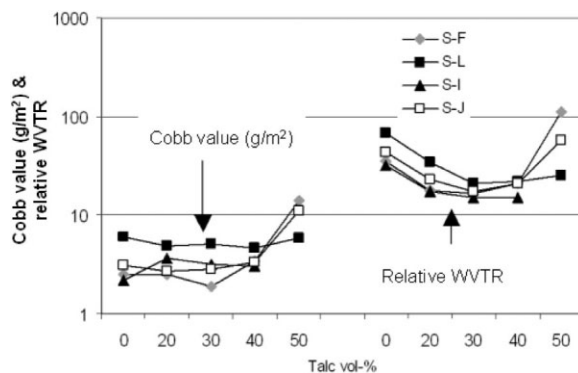


Figure 5 Effect of talc addition on water vapor transmission and water absorption.

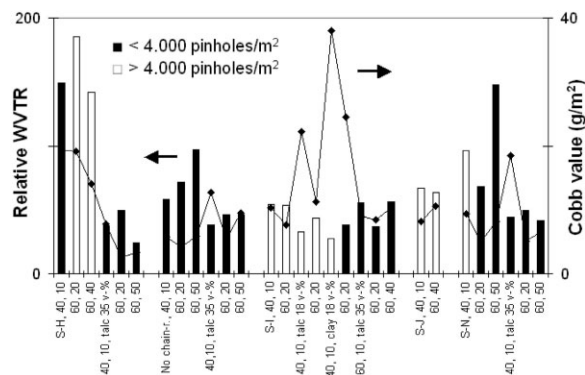


Figure 6 Results from the pilot trials. White bars indicate significant number of pinholes. First number in 40, 60 is coating speed (m/min), and second number to IR setting (Hz).

creased and folded samples. The experimental dispersions were also used as an additive in other dispersions. This mixture provided, in most cases, improved barrier properties compared to the base dispersions alone.

Pilot trials

The experimental dispersions tried at the pilot line as such and filled with talc/clay included S-H, S-H without chain-regulating agent, S-I, S-J, and S-N. The coating thickness in the pilot trials varied slightly and was low, partly explaining the differences, compared to the results obtained from the laboratory scale trials. Rod metering was used in the pilot trials, as it proved to be better than blade considering the coating weight. The line speed was not high enough to achieve adequate coating weights for the barrier applications with blade.

Figure 6 presents water and water vapor barrier of the experimental dispersions. Barrier properties, in general, depend both on the coating uniformity affected by coating method and drying, and the polymer properties. For example, pinholes are caused by poor coverage, high-temperature drying, and poor film formation. The negative effect of a too intensive drying has also been observed in a study with talc-filled dispersions.³ Although not shown here in detail, the number of pinholes decreased in most cases (e.g., S-H without chain-regulating agent, S-I and S-N) as the line speed increased, e.g., due to lower penetration into the substrate and more optimal drying. However, there were also samples with an increased number of pinholes. Unfilled S-H may have been sensitive to the water evaporation rate. On the other hand, the film thickness and the solids of S-J were lower than with the other coatings. Coating sustained water evaporation better when it was crosslinked and/or contained fillers (S-H, S-H without chain-regulating agent, S-I and S-N).

Chain-regulating agent increased the number of pinholes and thus water absorption of unfilled coatings (S-H; Fig. 6). Water absorption remained approximately constant or was lowered at higher coating speed due to fewer pinholes—S-J was again an exception. Water barrier of the core-shell dispersion S-N was slightly lower than with S-I probably due to a higher coating thickness. Water absorption of coatings filled with 35% of talc was almost equal to that of the unfilled coatings, except of S-H, and an intensive pre-IR heating decreased the water barrier. Clay as a hydrophilic filler provided poorer water barrier than talc (S-I). S-H with 35% talc had no pinholes and the best water barrier.

WVTR usually increased slightly as the coating speed increased (Fig. 6)—the opposite was the case with the grease and water barriers (e.g., S-H without chain-regulating agent and S-I), where a pinhole-free film is essential. Both talc and clay improved the water vapor barrier of the experimental dispersions. The platy clay and talc particles should be oriented better at higher speeds leading to a further improvement in the water vapor barrier. The drying conditions have also to be optimized. WVTR and the grease barrier of dispersions with core-shell particles were slightly worse than with the dispersions having a uniform composition (S-N versus S-I). The functional monomer had no effect on these barrier properties probably due to the low coating thickness (S-J versus S-I), while the dispersion with the chain-regulating agent (S-H; Fig. 7) provided poorer grease barrier of flat and creased/slightly folded samples than crosslinking or the dispersion without this chain-regulating agent.

The composition of the unfilled polymer dispersions did not affect the blocking tendency significantly. All dispersions demonstrated strong blocking, except of the core-shell dispersion (S-N) probably due to harder polymer particles. Fillers decreased blocking tendency. Talc-filled dispersion with the chain-regulating agent (S-H) indicated a stronger blocking tendency than the other filled dispersions due to more deformable particles.

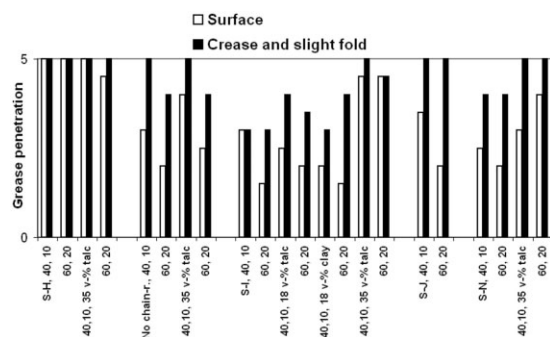


Figure 7 Grease barrier of unfilled and filled samples from pilot trials after 24 h.

SUMMARY

The experimental dispersions containing hydrophobic monomers provided better water and water vapor barriers than the reference dispersion. The best barrier in the laboratory scale trials was achieved with the use of stearyl (meth)-acrylate monomer, and crosslinking and chain-regulating agents. Also, particle morphology and T_g affected the performance of these dispersions. The grease barrier was affected by pinholes, but this barrier could be improved with a functional monomer. These dispersions were also successfully filled with for instance talc to improve the barrier performance.

The pilot trials mainly supported the conclusions obtained from the laboratory scale trials. However, the drying behavior of some dispersion seemed to affect

the barrier performance. Too intensive drying can cause pinholing and thus can be detrimental to the film quality. Using crosslinking agents and/or fillers improved the properties, but a chain-regulating agent increased the number of pinholes, and thus water absorption and grease penetration of unfilled coatings. The effect of coating speed and drying efficiency on the barrier properties depends on dispersion composition, coating formulation, and the penetrant.

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