PET polyester resins used in the wet end at neutral-alkaline papermaking conditions

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ABSTRACT: Two environmentally friendly, water-borne polyesters were used with rosin as internal sizes at the wet end in neutral-alkaline papermaking conditions. Two different furnishes were tested. We studied the effects of mixing two or more chemicals together before adding them to pulp or stock. The results show that the premixing process improved the polyester sizing efficiency. We also investigated the mechanism of the premixing process and describe a new wet-end process that shows improved physical properties.

Application: This study will help in developing new technologies for PET polyester resin or other anionic sizes to be used in neutral-alkaline papermaking systems.

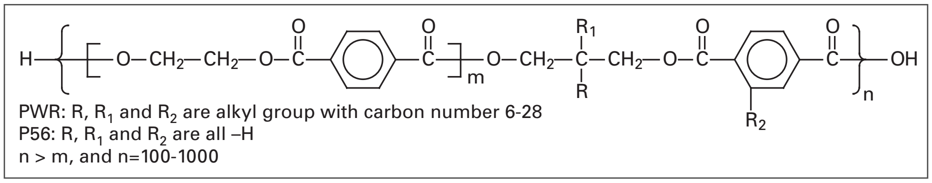
In papermaking, internal sizing is the process of providing paper and paperboard with moisture resistance to liquid wetting, penetration, and absorption by the use of sizing agents during paper formation. The sizing agents used in the paper industry cover a wide range of chemicals, including rosin size, synthetic resin, starch or cellulose derivatives, etc. Rosin size and synthetic resins are the two principal materials used for the internal sizing of paper and rosin size remains an important internal sizing agent.

Rosin is still widely used in the papermaking industry as a size under acid conditions. Unfortunately, acidic sizing has several drawbacks, such as yellowing and embritttlement of the paper, machine corrosion, and paper strength losses. In fact, mills have been shifting from acidic to neutral-alkaline papermaking. In these instances, synthetic sizes, such as alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA), are also used to satisfy the requirements of:

- higher paper strength
- the ability to use calcium carbonate fillers in the printing paper
- increased longevity of archival papers.

However, the traditional acid sizing agents, including acid rosin emulsion size and rosin soap size, are easy to prepare and inexpensive. That is why their application to the neutral-alkaline paper sizing is of interest and possibly attractive from a cost perspective [1, 2].

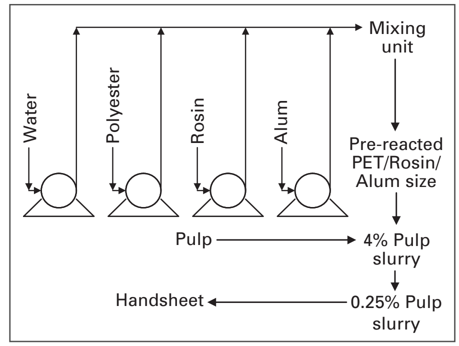
It is of our challenge as papermakers to determine how to maximize the efficiency of operations and make them increasingly economically and environmentally friendly. Recently, EvCo Research, LLC, has successfully developed a series of polyester resins from recycled polyethylene terephthalate (PET). The polyester resins have been successfully used as paper coatings,



1. Fundamental structures of PET resins studied (PWR and P56).

Sample	Chemical Premixing	Chemical Addition Order	Charge at Pulper	Initial Pulp pH
1	—	rosin+alum	-0.57	7.13
2	—	H_2SO_4+rosin+alum	-0.04	5.02
3	rosin+alum	Mixture	-0.68	7.13
4	—	PWR+rosin+alum	-0.47	7.13
5	—	H_2SO_4+PWR+rosin+alum	-0.07	5.02
6	rosin+alum	PWR+Mixture	-0.49	7.13
7	PWR+rosin+alum	Mixture	-0.50	7.13

I. Stock preparation procedures and furnish properties.



2. Proposed wet-end process.

Sample	Cobb No., g/m² (30 min)	Wicking, mm (30 min)
1	830.9	10
2	96.3	0
3	680.2	5
4	178.3	0
5	84.0	0
6	117.3	0
7	115.4	0

II. Sheet properties.

replacing non-recyclable wax coatings, and thereby changing the process from using a natural resource one time into being able to recycle and repulp the coated papers. This has the potential to save trees and energy, reduce land filling, and realize other environmental benefits [3].

Researchers have studied the use of polyester resins as internal size when applied at the wet end [4, 5]. The polyester is water-dispersible. When added to the pulp slurry with a cationic promoter, it is deposited on the fibers. As those fibers begin to form paper, the polyester resin bonds the fibers. With the polyester resin bonds, the paper has improved dry and wet strength, greater stiffness, improved water and high humidity resistance, lower porosity, and nonwicking properties.

The water-dispersible polyester resins are anionic polymers. When they are used at the wet end for internal sizing or for high humidity and wet strength, good results can be obtained under acid conditions. The acid can help to decrease the charge level in the system and increase PET/rosin retention. In these instances, a cationic promoter is still required to improve PET retention. When the polyester resins were used in neutral or slightly alkaline systems, they sometimes would work well by replacing alum with polyaluminum chloride (PAC) as a cationic promoter, but sometimes they did not, for unknown reasons.

The main objective of this study was to better understand the conditions under which PET can be effective as an internal size and to develop new technologies for the water-dispersible polyester resins as internal sizes when used with rosin under neutral-alkaline conditions.

EXPERIMENTAL

Materials

Two types of PET resins, EvCote® PWR and EvCote® P56, were obtained from EvCo Research, LLC. **Figure 1** shows their fundamental structures.

We evaluated the resins with two types of pulp: a recycled, high filler pulp used for molded products; and a kraft virgin pulp, used for packaging board, from an acid mill.

Preparation of handsheets

To prepare handsheets, we diluted the pulp to 4% solids slurry in a pulper. The chemicals, premixed or separately, were added into the pulp slurry. Following chemical addition, we diluted the pulp slurry to 0.25% solids for formation on an M/K automatic sheet former. We then formed 12-by-12 inch handsheets.

For the formation of the molding sheet (with PWR), the sheets were made from 4% solids stock by direct dewatering on a screen. These sheets were pressed at 50 psi and dried on a drum dryer that had a surface temperature of 120°C. Following a single pass around the drum dryer, the sheets were placed in a convection oven at 125°C for 10 min.

All sheets were conditioned at TAPPI standard conditions before property testing. **Figure 2** shows the procedure in detail.

Testing conditions

The charge and pH value of the 4% solids pulp slurry before and after chemical addition were determined using a Hemtrac ECA 2000P Electrokintic charge analyzer and a VWR Scientific Model 8005 pH meter.

The dispersion of the PET was made using a Ross-ME100LC mixer. The charge, particle size, and viscosity of the solution were measured with the Hemtrac charge analyzer; a Hemtrac HORIBA LA-910 laser scattering particle size analyzer, and a Brookfield Model-RVT viscosity meter, respectively.

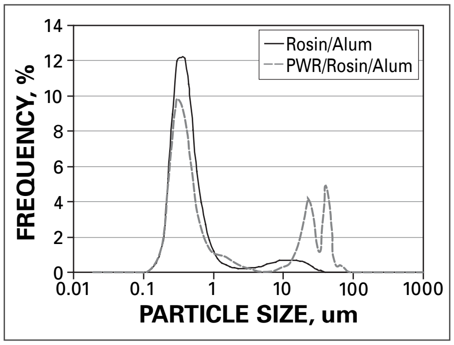
We tested tensile strength, ring crush, and short-span compression test (SCT) strength with, respectively, a QC-1000 tensile tester from Thwing-Albert Instrument Company; a Monitor/Compression Model No.17-71 from Testing Machine INC (TMI); and a short span compression tester, Model K455, from MESSMER BUCHEL. Wicking was measured by dipping one end of the paper in water and noting the distance water migrated up the strip after 30 min. Cobb (30 min) values were obtained according to TAPPI Standard T441-om-90. All test conditions were run under TAPPI Standard conditions.

RESULTS AND DISCUSSIONS

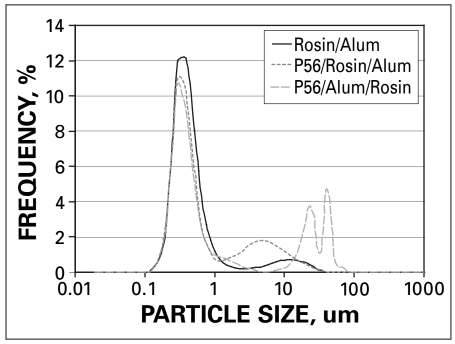
Several studies reported that pre-reacting alum and rosin either neat or in solution before introducing the mixture into the papermaking furnish could improve sizing efficiency [6-8]. The water-dispersible polyesters have the same negative charge as rosin. Could this pre-mixing process

Sample	Chemical Premixing	Charge of Mixture Solution	Viscosity of Mixture Solution
6	rosin+alum	+0.05	17
7	PWR+ rosin+alum	+0.045	110

III 1.0% Solids Mixture Properties (PWR).



3. Particle size distribution of 1% solids mixture (PWR).



4. Particle size distribution of 1% solids solution (P56).

Sample	Chemical Premixing	Chemical Addition Order	Charge at Pulper	Initial Pulp pH
8	—	H_2SO_4+P56+rosin+alum+PAE	-0.26	5.50
9	rosin+alum	P56+Mixture+PAE	-0.86	7.20
10	P56+alum+rosin	Mixture+PAE	-0.85	7.20
11	P56+rosin+alum	Mixture+PAE	-0.83	7.20

IV. Stock preparation procedures and furnish properties.

Sample	Ring Crush, lbs	STFI, lbs/inch	Tensile, kg	Wet Tear, gram-force	Cobb, g/m² (30 in)
8	60.1	19.9	19.4	258.0	85.5
9	74.8	21.6	19.9	239.0	71.0
10	75.4	23.2	22.4	253.0	72.4
11	72.3	22.9	22.6	277.0	75.3

V. Properties of sheet.

Sample	Chemical Premixing	Charge of Mixture Solution	Viscosity of Mixture Solution
9	rosin+alum	+0.05	17
10	P56+alum+rosin	+0.05	100
11	P56+rosin+alum	+0.045	150

VI. 1.0% solids mixture properties (P56).

increase their sizing efficiency or widen their application pH range?

We used two polyesters, an anionic, highly hydrophobic copolymer (PWR) and an anionic, slightly hydrophobic copolymer (P56). We also used two types of pulp for the systematic studies of the premixing technology. The first portion of the study, in which we used PWR with recycled pulp, concentrates on the sizing property. The second portion, in which we used P56 with virgin kraft, evaluates paper wet strength (specifically wet tear). Both show the widened pH range and premixing advantage for the polyesters when used in the wet end.

PWR

With the PWR, we used a recycled pulp that was very dirty and contained a large amount of calcium carbonate filler. The mill uses this pulp to make water-resistant, molded products at a pH of 5. It takes a significant amount of acid to reduce the pH from 7-8 and the molded product loses strength when this is done. To solve this problem, we tried a different approach: adding PET polymer and premixing the sizing components while operating under neutral-alkaline conditions. These results were compared with the results achieved with acid conditions.

Tables I and **II** list the stock preparation procedure and properties, and the results from testing Cobb and wicking, respectively.

Table II shows that PWR can greatly improve the molded paper water repellency (sizing), particularly at neutral-to-slightly alkaline conditions (compare sample 7 with 1 and 3). It affirms that PWR and rosin sizing under acid conditions are still the best (sample 5). Even so, using the new procedure (premixing rosin and PWR, then mixing with alum before adding to the pulp [sample 7]), the sizing efficiency has been greatly increased, and the results can almost compete with acid conditions.

The sizing results under acid condition (particularly pH 5) for rosin and PWR are better than under basic conditions, because alum has the structure $Al_8(OH)_{20}^{+4}$, which has a greater positive charge. The improvement in sizing efficiency is due to the rosin or PWR reacting with alum to form a carbonic-aluminum complex directly. The complex not only avoids the hydrolysis of alum, but also changes the rosin and/or PWR from anionic to cationic, as shown in **Table III**. This results in rosin and/or PWR being retained in the anionic fiber [2]. The size efficiency for the mixture of PWR, rosin, and alum (sample 7) is a little better than for PWR added to the rosin and alum mixed together first (sample 6). That is because the PWR is first reacted with rosin and then this complex is reacted with alum to form a new complex, which should have a higher molecular weight and be retained more easily. This effect is evident in **Fig. 3**, which shows the particle size distribution.

P56

For this part of the study, we obtained virgin kraft pulp from an acid mill used as a packaging board. The objective of the study has been to improve the product's wet tear strength. We evaluated EvCote® P56 with rosin and alum to accomplish that objective.

Tables IV and **V** list the stock preparation procedure and properties, and the product's main properties, respectively.

The results show that strength properties such as ring crush, STFI, and tensile are improved using PET and premixing on the wet end; but wet tear results are not significantly improved. The water repellency of the PET-treated sheets is also improved with premixing of rosin or P56 with alum, when added at slightly acidic conditions, compared to the conventional sizing process. **Table VI** shows the effects on charge and viscosity due to the PET forming the proposed new complex. **Figure 4** shows the particle size distribution.

Compared to the previous study, the situation is almost the same. The premixture of P56, rosin, and alum (in that order) becomes cationic, forming a new complex. However, when P56, alum, and rosin are premixed (in that order), the particle size distribution of this mixture is almost the same as rosin and alum by themselves and entirely different than the P56/rosin/alum premix (Fig. 4). This indicates that different complexes are being formed.

CONCLUSIONS

This detailed study evaluated new PET resins for use with rosin as a wet-end size under acid and neutral-alkaline conditions. The results showed that a highly hydrophobic copolymer and rosin are a good size for molded products, as shown by water repellency/resistance results. They also showed that, compared to the conventional sizing process for neutral-alkaline conditions, a premixing process improved sizing efficiency. This was evident from improved sizing for paper treated with PWR and improved physical properties when the paper was treated with the slightly hydrophobic copolymer. The sizing results are almost equivalent to those achieved under acid conditions. We believe this is due to the polyester or rosin reacting with alum to form a carbonic-aluminum complex. The complex not only delays the hydrolysis of alum, it converts the rosin and/or polyester from anionic to cationic. In addition, we found that the formation of paper under acid conditions is more favorable for the polyester, because the acid can help decrease the negative charge level in the system and increase the PET/rosin retention. **TJ**

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INSIGHTS FROM THE AUTHORS

We have been developing anionic resin and rosin with other sizes, such as AKD, to be used in neutral-alkaline papermaking conditions.

This study explored the mechanism of the premixing process for anionic resin, rosin, and alum. It confirmed that the premixing process greatly improved anionic resin and rosin efficiency under neutral-alkaline papermaking conditions.

The challenging aspect of this study was to determine how to completely understand the mechanism of the premixing process. We focused on the mixture solution particle size, charge, and the product's physical properties.

Through this work, we found that the alum with rosin/anionic rosin became cationic from anionic rosin and that the order of premixing process affected size efficiency.

Mills can directly use the premixing process as the paper designed. Particularly, the anionic resin can make the paper repulpable and recyclable.

Through further study, we hope to understand the properties more deeply and best uses of polyester-anionic resin and blends with other paper additives, such as AKD, wet strength agents, starch, etc., for use in neutral-alkaline papermaking systems.

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