Comparison of the Kraft Paper Crosslinked by Polymeric Carboxylic Acids of Large and Small Molecular Sizes: Dry and Wet Performance

GORDON GUOZHONG XU, CHARLES QI-XIANG YANG

Department of Textiles, Merchandising and Interiors, The University of Georgia, Athens, Georgia 30602

Received 10 December 1998; accepted 6 February 1999

ABSTRACT: Polycarboxylic acids have been used as crosslinking agents for wood pulp cellulose for improving paper wet strength. Our previous research showed that low-molecular-weight polymeric carboxylic acids are effective in improving paper wet strength retention and reducing its flexibility. In this research, we compared two polymeric carboxylic acids, that is, poly(maleic acid) (PMA) with M_n of 800 and poly(methyl vinyl ether-*co*-maleic acid) (PMMA) with M_n of 1,130,000 for improving paper wet strength. The kraft paper sheets were treated at a 2% acid level and cured at different temperatures. The dry strength, wet strength, and folding endurance of the treated sheets were measured. We found that PMA and PMMA have comparable effectiveness in improving paper wet strength and wet stiffness. However, the treatment with PMA increases paper brittleness and severely diminishes paper folding endurance, whereas the treatment with PMMA increases both the dry strength and folding endurance by enhancing the paper's toughness. This striking difference in the performance of the treated paper is attributed to the different nature of the crosslinkages formed on the sheets. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 907–912, 1999

Key words: carboxylic acids; cellulose; crosslinking; esterification; paper; polymeric acids; strength; wet strength resins; folding endurance; wood pulp

INTRODUCTION

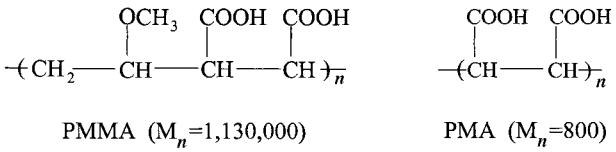
Polycarboxylic acids were originally developed as nonformaldehyde crosslinking agents for cotton.[1] Previous studies have shown that multifunctional carboxylic acids have the potential to become environment-friendly wet strength agents of paper. Horie and Biermann reported that the bleached kraft handsheets treated with 1,2,3,4-butanetetracarboxylic acids (BTCA) show significantly improved wet strength.[2] Caulifield studied the dry and wet performance of unbleached kraft board treated with BTCA and citric acid.[3] Zhou et al. investigated the treatment of paper with BTCA, tricarballylic acid, and succinic acid, and found that BTCA is the most effective crosslinking agent for wood pulp cellulose.[4,5] To overcome the high cost of BTCA, we applied cost-effective poly(maleic acid) (PMA) as a wet strength agent and found that PMA is equally efficient as BTCA for improving wet performance of paper.[6–8] We also found that linear relationships exist between the amount of ester formed on the paper and wet strength retention, dimensional stability, and wet stiffness of the treated paper, indicating that the improvement of wet performance of the treated paper is directly attributed to the ester crosslinking of cellulose.[7] The treatment using BTCA, PMA, and other polycarboxylic acids with relatively small molecular sizes causes severe fiber

Correspondence to: C. Q.-X. Yang.

Journal of Applied Polymer Science, Vol. 74, 907–912 (1999)
 CCC 0021-8995/99/040907-06

embrittlement and consequently reduces folding endurance of paper.[7,8]

In this research, we compare the effects of two polymeric carboxylic acids, that is, PMA with a number-average molecular weight (M_n) of 800 and poly(methyl vinyl ether-*co*-maleic acid) (PMMA) with a M_n of 1,130,000 on dry/wet strength and other mechanical properties of the treated paper.



PMMA (M_n=1,130,000) PMA (M_n=800)

EXPERIMENTAL

Materials

The unbleached kraft paper used in this research was a commercial product with 65 g/m^2 manufactured by Southwest Paper, Georgia. PMA with a M_n of 800 was a 50% aqueous solution made by FMC. Sodium hypophosphite (NaH_2PO_2) and PMMA with a M_n of 1,130,000 were supplied by Aldrich. The solutions used to treat the paper sheets consisted of 2% PMA or PMMA in combination with 1% sodium hypophosphite as a catalyst.

Paper Treatment

The kraft paper sheets with a size of 25 × 25 cm^2 were immersed in a solution for 30 s, then pressed between squeezing rolls to remove excess liquid to reach about 95% wet pick-up. The impregnated sheets were dried on a hot plate dryer at 85°C to prevent curling. Each sheet was cured in a force draft oven at specified temperatures ranging from 140 to 180°C for 1.5 min. The cured sheets were rinsed in running water for 15 min to remove unreacted chemicals and then dried. Five specimens were treated under each condition.

Paper Performance Testing

Dry tensile properties, wet tensile properties, and folding endurance of the paper sheets were evaluated according to TAPPI standard test methods T 494 om-88, T 456 om-87, and T 511 om-96, respectively. The tensile properties measured included tensile strength, stretch, tensile energy absorption, energy absorption to a 0.2% yield point, and Young's modulus. For wet tensile test, the specimens were first immersed in distilled water for 24 h. Ten measurements were performed for each testing procedure.

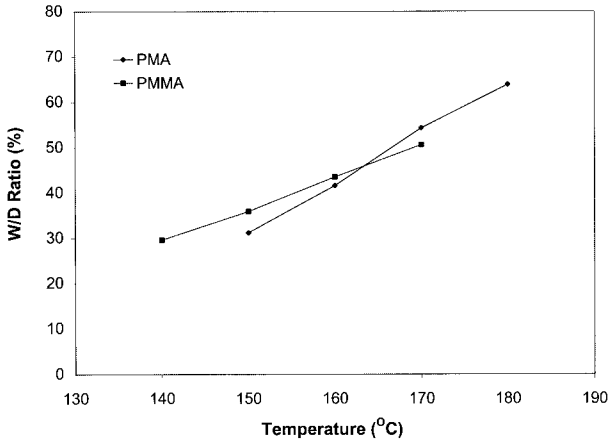


Figure 1 Wet strength (*W/D* ratio) of the kraft paper treated with 2% PMA and 2% PMMA and cured at different temperatures.

RESULTS AND DISCUSSION

The Wet Properties of the Treated Paper

The kraft paper treated with 2% PMA and 2% PMMA in the presence of 1% NaH_2PO_2 as a catalyst was cured at temperatures ranging from 140 to 180°C for 1.5 min. The wet/dry strength ratios of the paper sheets cured at different temperatures are presented in Figure 1. Because PMMA increases dry strength, whereas PMA has little effect on dry strength of treated paper, we use ratio of the wet strength of treated paper to the dry strength of control sample (*W/D*) as the basis to compare the wet strength of treated paper. The data show that the wet strength increases as the curing temperature increases. It is evident that the wet strength of the PMA-treated and PMMA-treated sheets demonstrates similar temperature dependence and that the effectiveness of PMA and PMMA for improving wet strength of paper is comparable. The increase in wet Young's modulus of the treated paper sheets is shown as a function of curing temperatures in Figure 2. The similarity between the PMA and PMMA treatments, as illustrated in Figure 2, indicates that PMA and PMMA are equally effective in improving the paper wet stiffness.

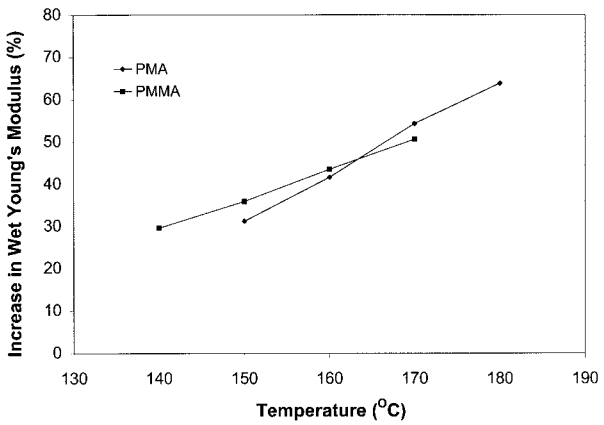


Figure 2 Increase in the wet Young's modulus of the kraft paper treated with 2% PMA and 2% PMMA and cured at different temperatures.

The wet strength retention of paper is determined to a large extent by the fiber–fiber bonds on paper.[9] The diminished tensile strength and stiffness of paper under wet conditions is a result of water penetration into the paper and the swelling of the cellulose fiber, and consequently, the destruction of the hydrogen bonds which hold the fibers together. It is believed that the amount of surviving hydrogen bonds is the overriding factor in retaining wet strength of paper.[10] Therefore, the effectiveness of a crosslinking agent depends on its ability to create a crosslinking network to restrain the cellulose structure and to protect the existing hydrogen bonds from the disruption of water. For a crosslinking agent of high molecular weight, such as PMMA, the large molecular size prohibits it from passing through fiber wall into the interior.[11] Therefore, the predominant bonding formed by PMMA on paper is interfiber crosslinking.

Our previous studies show that the improvement of wet strength of the paper treated with low-molecular-weight crosslinking agents, such as BTCA and PMA, is directly attributed to ester crosslinking of wood cellulose.[7] A crosslinking agent of small molecular size is able to penetrate easily through pores on cell wall into the bulk of wood cellulose fibers. Therefore, the predominant bonding formed by PMA is intrafiber crosslinking between cellulose molecules. The intrafiber crosslinking formed by a small size crosslinking agent prevents the swelling of the fibers, preserves the hydrogen bonding among the fibers, and, thus, improves the wet strength of the treated paper.

In this research, the paper sheets were treated with PMA and PMMA of equal concentration (2% *w*/*w*). However, the mole concentration of carboxylic acid groups for PMA is approximately 50% higher than that for PMMA because the methyl vinyl ether repeating unit in PMMA is inactive for crosslinking cellulose. Secondly, the carboxylic acid groups of PMMA have less mobility to access cellulose hydroxyl groups of cellulose for esterification. Therefore, PMMA produced far less ester linkages with cellulose than PMA, even if the PMMA and PMA solutions used to treat the paper have equal carboxylic acid mole concentrations. The data presented above indicate that PMMA and PMA with the same weight concentrations are equally effective in enhancing the wet strength and wet stiffness. Obviously, the crosslinking formed by PMMA has higher effectiveness than that by PMA in enhancing wet strength of paper. We believe that different mechanisms exist for the improvement of wet performance of paper by crosslinking agents of different molecular sizes.

The wet strength agents must locate at weak links of the fiber network that are vulnerable to the attack by water, if they are to be effective. The individual fiber has a diameter in the range of 10 to 50 μm, macrofibrils have a width around 0.5 μm, and microfibrils have a diameter about 25 nm.[12] The distribution of pore sizes on fiber wall depends on the particular choice of wood species and control of pulping process. For unbleached kraft paper, the pore sizes distribute with a modal radius of about 1 μm, depending on the beating degree.[13] PMA with a M_n of 800 has a mean extended molecular length around 1.7 nm. With a dimension much smaller than pore sizes, PMA molecules are able to enter the fiber interior freely. In contrary, the high-molecular-weight polymers, such as PMMA with a M_n of 1,130,000, cannot penetrate fiber wall.[14] Driven by capillary and surface tension forces during drying process, however, they move towards the fiber crossover areas, where they produce interfiber crosslinking. Due to the same reason, polyacrylamide resins, with molecular weights between 100,000 and 500,000, are very effective in strengthening fiber-to-fiber bonding and are widely used as dry strength additives of paper. Apparently, the long molecule chains of PMMA tend to form interfiber bonding, whereas the PMA molecules may only attach to the same fiber lamella and form intrafiber bonding. Therefore, even though fewer ester links are formed between PMMA and cellulose, the treated paper is still able to achieve the same level of wet strength and wet stiffness as that

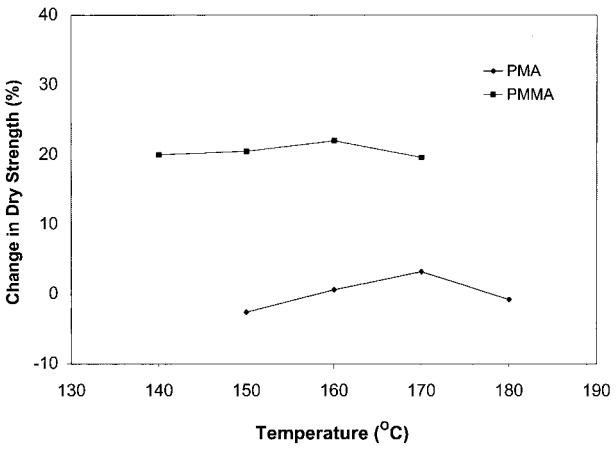


Figure 3 Change in the dry strength of the kraft paper treated with 2% PMA and 2% PMMA and cured at different temperatures.

treated with PMA. When temperature is below 160°C, PMMA appears to be slightly more efficient than PMA (Figs. 1 and 2).

The Dry Properties of the Treated Paper

Presented in Figure 3 is the change in dry tensile strength of the treated paper. A striking difference between PMMA and PMA is found in their impact on the dry strength of treated paper. The PMMA-treated paper shows an approximate 20% increase in dry tensile strength over the control sample, whereas the PMA-treated paper has little change in its dry strength after treatment. This significant difference is attributed to the different nature of the crosslinking formed by low- and high-molecular-weight crosslinking agents.

The tensile strength of paper is determined by the intrinsic fiber strength as well as the amount and strength of fiber-to-fiber bonds.[12] Crosslinking agents of small sizes can penetrate into pore structure of cellulose cell wall and form intrafiber crosslinks. This is the reason why small multifunctional hydroxyl-reactive compounds have been used to crosslink individual pulp fibers for producing resilient fibers.[15,16] The intrafiber crosslinking formed by these small molecular compounds has little effect on the dry tensile strength of the treated paper. The small size crosslinking agents, such as BTCA and PMA, form few interfiber crosslinks; thus, they essentially have no effects on the dry strength of the treated paper. Xu and his coworkers found that the kraft paper treated with BTCA of different concentrations showed little change in its dry strength.[8] For large size crosslinking agents, such as PMMA, the interfiber crosslinking reinforces the fiber-to-fiber bonds, thus resulting in a significant increase in the dry strength of the treated paper, as shown in Figure 3.

Xu and his coworkers also studied the z-direction tensile strength of paper treated by poly(ethene-maleic acid) (PEMA) (M_n = 100,000) and BTCA and found that the z-direction tensile strength of paper treated with PEMA was significantly higher than that treated with BTCA at the same levels of crosslinking.[17] This finding provides a direct evidence that high-molecular-weight polymeric carboxylic acids favor the formation of interfiber crosslinking, thus reinforcing fiber–fiber bonding on the treated paper.

The extensibility and toughness of treated paper, expressed as stretch and tensile energy absorption (TEA), respectively, were shown in Figures 4 and 5. The PMMA-treated paper increases its stretch by 3–5%, whereas the PMA-treated paper decreases it by 15–30% (Fig. 4). The PMMA-treated paper increases its tensile energy absorption by 22%, whereas the PMA-treated paper decreases by 13–30% (Fig. 5). Apparently, PMMA treatment improves toughness of the dry paper, whereas PMA treatment causes embrittlement and diminishes the toughness of paper.

The paper extensibility depends on not only the extensibility potential of the individual fibers, but also the nature of the fiber network.[18] The paper stretch increases as its tensile strength increases because higher tensile strength reduces the possibility of premature fracture. The intrafiber crosslinking induced by PMA limits the relative

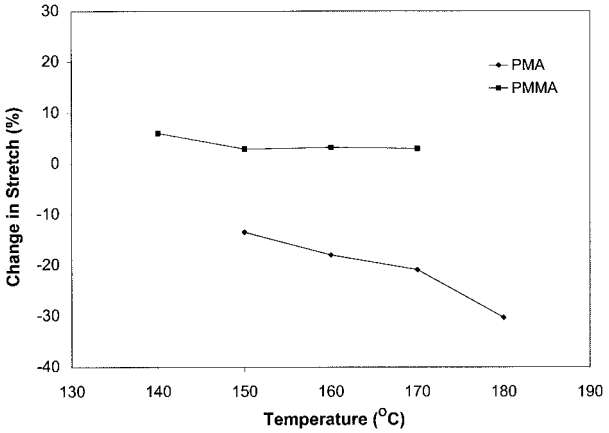


Figure 4 Change in the stretch of the kraft paper treated with 2% PMA and 2% PMMA and cured at different temperatures.

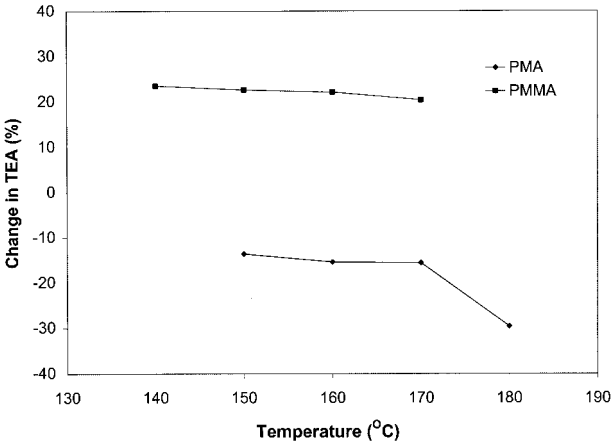


Figure 5 Change in the tensile energy absorption of the kraft paper treated with 2% PMA and 2% PMMA and cured at different temperatures.

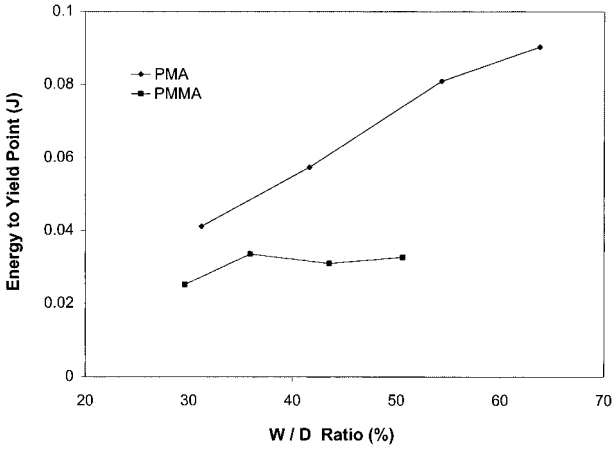


Figure 6 Energy to a 0.2% yield point of the kraft paper treated with 2% PMA and 2% PMMA as a function of wet strength retention.

movement between adjacent cellulosic chains, thus reduces the extensibility of fibers. The interfiber crosslinking formed by PMMA increases tensile strength of the paper, thus improving the extensibility of the treated paper.

PMMA treatment significantly improves TEA, whereas PMA treatment reduces TEA, as shown in Figure 5. TEA is the area under the stress–strain curve as the paper is stretched to rupture. TEA increases with increasing tensile strength, increasing stretch, or both. Stretch and TEA are two important factors for paper products that are frequently folded or exposed to stress during use. Low stretch causes localized buildup of high stress and rupture takes place under a small load. Paper with high extensibility and high TEA can absorb stress and withstand heavy impact without breaking.

The energy to a 0.2% yield point for the paper treated with PMMA and PMA is plotted as a function of the *W*/*D* ratio in Figure 6. One observes that the energy to a 0.2% yield point is much lower for paper sheets treated by PMMA than for those treated by PMA at the same wet strength level. This indicates that the PMMA-treated paper demonstrates better sensitivity to stress and, thus, faster stress relaxation. Rapid stress relaxation facilitates distribution of stress on the paper to a much wider area, thus increasing tensile strength and tensile energy absorption.

Folding endurance is another important parameter for wet strengthened paper. In our previous research, we found that paper treated by crosslinking agents of small sizes show drastically reduced folding endurance.[7] The folding endurance of the paper treated with 2% PMMA and 2% PMA is presented as function of *W*/*D* ratio in Figure 7. Folding endurance of the PMA-treated paper is lower than the untreated; meanwhile, it also decreases with increasing wet strength. For the PMA-treated paper, the benefit of higher wet strength achieved by higher curing temperatures is offset by the loss of flexibility and reduction in folding endurance. For the PMMA-treated paper, the folding endurance is better than that of the control, and it remains at a high level as the wet strength increases. The change of folding endurance is consistent with the TEA and energy-to-yield-point data presented in Figures 5 and 6, respectively.

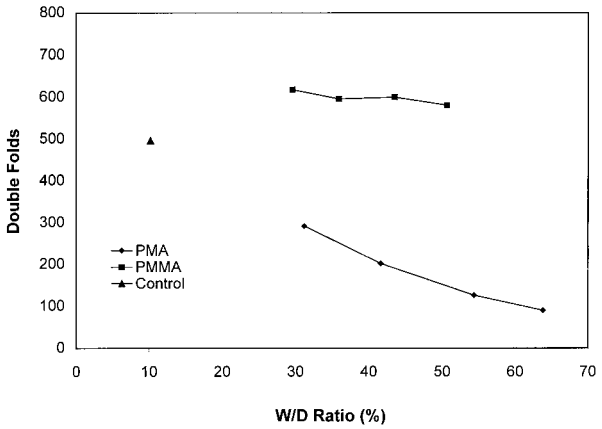


Figure 7 Folding endurance of the kraft paper treated with 2% PMA and 2% PMMA as a function of wet strength retention.

CONCLUSIONS

High-molecular-weight PMMA and low-molecular-weight PMA demonstrate comparable effectiveness in improving the wet strength and wet stiffness of paper. PMMA treatment provides significant improvement in dry strength, tensile energy absorption, and folding endurance of the treated paper, and it also increases stretch to a less degree. In contrast, PMA treatment causes severe reduction in stretch, tensile energy absorption, and folding endurance. Paper treated with PMMA shows lower energy-to-yield-point than that with PMA. The difference in the properties of the paper treated with these two polymeric carboxylic acids is attributed to the difference in their molecular sizes. High-molecular-weight PMMA favors formation of interfiber crosslinking, thus improving dry strength and toughness. Low-molecular-weight PMA predominately produces intrafiber crosslinking. This causes embrittlement of fibers and diminishes flexibility of the treated paper.

REFERENCES

1. Welch, C. M. Rev Prog Color 1992, 22, 32–41.
2. Horie, D.; Biermann, C. J. TAPPI J 1994, 77(8), 135–140.
3. Caulifield, D. F. TAPPI J 1994, 77(3), 205–212.
4. Zhou, Y. J.; Luner, P.; Caluwe, P.; Tekin, B. Prod Papermaking 1993, 2, 1045–1072.
5. Zhou, Y. J.; Luner, P.; Caluwe, P. J Appl Polym Sci 1995, 58, 1523–1534.
6. Yang, C. Q.; Xu, Y.; Wang, D. Ind Eng Chem Res 1996, 35, 4037–4042.
7. Yang, C. Q.; Xu, Y. J Appl Polym Sci 1998, 67, 649–658.
8. Xu, Y.; Chen, C.; Yang, C. Q. TAPPI J 1998, 81(11), 159–164.
9. Casey, J. P. Pulp and Paper Chemistry and Chemical Technology; 3rd ed.; John Wiley & Sons: New York, 1981; p. 1788.
10. Caulfield, D. F.; Weatherwax, R. C. TAPPI J 1976, 59(7), 114–118.
11. Stone, J. E.; Scallan, A. M. Pulp Paper Mag Canada 1968, 69, 69–74.
12. Roberts, J. C. The Chemistry of Paper; The Royal Society of Chemistry: Cambridge, 1996; pp. 19 and 52.
13. Corte, H. in Transactions of the Symposium for Fundamental Paper-making Fibers, 1957; British Paper Board Makers' Assoc.: London, UK, 1958; pp. 301–331.
14. Roberts, J. C. Paper Chemistry, Chapman and Hall: New York, 1991; pp. 63–75.
15. Herron, C. M.; Cooper, D. J. U.S. Pat. 5,137,537, 1995.
16. Kokko, B. J. U.S. Pat. 5,543,456, 1991.
17. Xu, Y.; Chen, C.; Yang, C. Q. TAPPI J, to appear.
18. Seth, R. S. TAPPI J 1996, 79(1), 170–178.