Papermaking additives

Rosin sizing under neutral-alkaline papermaking conditions

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ABSTRACT: This paper examines the technology for rosin size used with neutral-alkaline papermaking systems. The technologies discussed include physical approaches, such as addition points, and alternative chemical retention aids, such as polyaluminium compounds and polyamine, metal ions/polyamine, and polyamine-epichlorohydrin resin. Potential significant research areas are suggested, also.
Application: This study may help in developing new technologies for using rosin size or anionic polymer size in neutral-alkaline papermaking systems.

The paper industry uses sizing agents to give paper and paperboard some degree of resistance to wetting and penetration by aqueous liquids. This is necessary because paper fiber consists of cellulose and hemicellulose, which have a strong, natural tendency to interact with water. There are two basic categories of sizing agents: acid and alkaline. Acid sizing agents are intended for use in acid papermaking systems, traditionally less than pH 5. Analogously, alkaline sizing agents are intended for use in alkaline papermaking systems, typically at a pH greater than 6.5 [1-2].

Most acid sizing agents are based on rosin; sizing agents for papermaking systems above pH 6.5 are generally based on alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Rosin size under acid conditions has been the most widely used sizing agent since sizing technology was developed in 1807. Unfortunately, acidic sizing has several drawbacks, such as yellowing and embrittlement of paper, machine corrosion, and paper strength losses. In fact, many mills have shifted their papermaking conditions from acidic to the neutral-alkaline region to satisfy the requirements of higher strength and increased longevity of archival papers. It also allows mills to use calcium carbonate fillers in making printing paper.

Traditional sizing agents, including acid emulsion rosin size and rosin soap size, are fairly inexpensive, abundant, and easy to use. Their sizing response curve is gradual, not steep and they are compatible with other wet end additives. Rosin-based size does not depend on covalent bond formation; and traditional sizing agents do not have on-machine size development problems. Therefore, it is very interesting and valuable to explore high efficiency technologies for rosin size used under neutral-alkaline papermaking conditions.

This report reviews current literature on rosin sizing at neutral-alkaline papermaking systems, focusing on modified rosin sizing systems used for these conditions. A closing section draws from that overview to suggest future research efforts in rosin sizing at neutral-alkaline papermaking conditions.

STATE OF THE ART

Conventional acid rosin size cannot be used to give papers good sizing at neutral-alkaline papermaking systems. Therefore, research has focused on a series of modified rosin sizes, in addition to exploring new types of rosin sizes. The modifications to the sizing process are divided into two categories: physical and chemical, which are reviewed below.

Physical technology

Hisken, et al [3] and Katz, et al [4-5] studied the effects of addition points on paper sizing based on polyaluminum chloride (PAC)/rosin and alum/rosin systems. They found that the sizing efficiency is greatly increased by using a premixing sizing procedure. **Tables I-IV** and **Fig. 1** highlight results from those studies.

Table I. Addition points effect on the paper sizing based on PAC/rosin system.

Rosin (%)	PAC (%)	pH	Cobb (g/m^2, 1 min)
Conventional sizing procedure			
1.0	0.5	7.4	146
1.0	1.0	7.2	156
1.0	1.5	7.3	154
Premixing sizing procedure			
1.0	0.5	7.8	68
1.0	1.0	7.6	29
1.0	1.5	7.6	29

Table II. Addition points effect on the paper sizing based on alum/rosin system.

Addition points	STAFOR 50 Rosin	Alum/Rosin	Cobb (water g/m^2)	HST (sec)
Conventional sizing	1.0%	3	166	16
Reverse sizing	1.0%	3	150	23
Premixing	1.0%	3	77	49

Table III. Effect of premixing concentration and temperature based on alum/rosin system.

Temperature (°C)	Concentration (%)	Cobb (g/m^2)	HST (sec)
25	0.1	38	173
25	1.0	77	49
25	10	144	13
50	0.1	42	112
50	1.0	132	32
50	10	150	13

Table IV. Effect of solution hardness at rosin (1%) and alum/rosin ratio of 3.0:1.0

Hardness ($CaCO_3$) (ppm)	Reverse Sizing Triton Cobb (g/m^2)	Premixing Sizing Triton Cobb (g/m^2)
0	66	60
75	79	57
225	101	67
450	136	109
750	167	100

From the above results, physical changes for rosin sizing additions under neutral-alkaline papermaking conditions can be summarized as follows:

- For both PAC/rosin and alum/rosin sizing systems, a premixing sizing procedure is much more efficient; the optimal ratio of PAC to rosin is 1.0:1.0 and alum to rosin is 1.5:1.0
- When premixing alum/rosin size, the lower the premixing concentration and the lower the temperature during premixing, the greater the paper sizing. With the reversed sizing procedure, the higher the solution hardness is, the more benefits the premixing sizing is, which is very attractive because more and more mills use inexpensive calcium carbonate as a filler.

Chemical technology

A number of researchers have attempted to substitute other chemicals for alum or to combine other chemicals with alum as retention aids to improve the neutral–alkaline sizing of traditional acid/rosin size. Of these chemicals, new polyaluminum compounds and polyamines are the most promising classes.

Polyaluminum compound

Several studies [6-8] found that replacing alum with PAC increased the efficiency of rosin sizing significantly at pH above 5.5. Actually, PAC has been used in the paper industry for some time. Gillberg, et al. [9] developed a new polyaluminum compound, which is very efficient for rosin sizing at neutral-alkaline papermaking conditions. **Table V** lists the results.

Table V. Effect of polyaluminum compound on rosin sizing.

Additive	Rosin (%)	pH	$Cobb_{60}$ (g/m^2)
$[Al(H_3PO_4)_{0.2}(OH)_{0.8}(SO_4)_{1.1}]_n$	0.06	7.2	50
$[Al(H_3PO_4)_{0.2}(OH)_{0.8}(SO_4)_{1.1}]_n$	0.12	7.2	35
(P/Al)=2.6	0.06	7.2	82
(P/Al)=2.6	0.12	7.2	61

Table V shows polyaluminum phosphate, particularly a polyaluminum phosphate sulphate compound can get good sizing results using rosin size at neutral-alkaline conditions.

Polyamine

Polyamines are known to improve rosin size efficiency in neutral-alkaline papermaking systems because of their larger cationic charge densities in the neutral pH region and high molecular weights. Research in this area has mainly focused on polyamines by themselves, polyamine/metal ions, and modified polyamines.

Effects of polyamine

Biermann [10] studied several polyamines as mordants for rosin size used from pH 3 to pH 10 (see **Table VI**).

Table VI. Effect of polyamine (7 lb rose size/Ton of pulp).

Polyamine	Dosage (lb/Ton)	Alum (lb/Ton)	pH	HST (sec)
-	-	12.2	4.75	13
-	-	33	4.75	105
PEI (Polyethyleneimine)	6.7	3.3	8.0	260
PAA (Polyallylamine)	4.1	0	7.0	400
PAA (Polyallylamine)	4.1	3.3	7.0	980

Tanaka, et al. [11-14] reported the effect of several polyamines on rosin sizing at neutral-alkaline papermaking conditions. The results are shown in **Figs. 2-4**, and listed in **Table VII**.

Table VII. Sizing features of paper with rosin size-polyamines at pH 7.5 and emulsion rosin sizing (1%).

Additive	Dosage (% on pulp)	Size content (mg/g paper)	Sizing degree (sec)
PDADMAC	1	0.53	0
PEI	1	0.92	0
PTAA/AAm	1	3.10	3
APNVF	1	4.30	10
Alum: APNVF	5:1	4.25	25

PDADMAC-poly(diallyldimethylammonium chloride)
PEI— polyethyleneimine
PTAA/AAm-copoly(trimethylaminoethyl acrylate acrylamide)
APNVF—aminated poly-N-vinylformamides

Based on the above experimental results, the effect of polyamines on rosin sizing at neutral-alkaline papermaking systems can be summarized as follows:

- Several polyamines (polyallyl amine, polyvinyl amine, aminated poly-N-vinylformamides et al.) can increase the rosin sizing efficiency at neutral-alkaline papermaking conditions, even if they can't improve the paper strength properties such as tensile strength. However, comparing emulsion rosin size with rosin soap size, it seems the effect of polyamines on emulsion rosin size is more efficient and different polyamines have greatly different efficiency. Generally, the polyamines with linear structures were more effective. The smaller the side chains of the linear polyamine, the greater the sizing with the rosin emulsion size with the polyamine; the polyamine with some amide groups and relatively lower density is more efficient.

- Polyamine-alum as a dual retention aid system, even if both dosages are small, still could achieve a much higher degree of rosin sizing at neutral-alkaline conditions.

Effect of polyamine/metal ions

Biermann, et al., [15] researched polyethyleneimine (PEI)/metal ions as mordants for rosin soap size for two types of pulp: unbleached kraft and thermomechanical pulp (TMP). The main results are listed in **Table VIII** and shown in **Fig. 5**.

Table VIII. Effect of metal ions/polyethyleneimine mordants on rosin sizing.

Pulp	Mordant	Amount added (%)	pH	Cobb (g/m^2/2 min)
Unbleached Kraft Pulp	Alum	1.0	4.5	23.5
	Fe^{3+}/PEI	1.0/0.5	7.0	29.6
	Fe^{2+}/PEI	1.5/0.5	7.0	24.1
	Fe^{2+}/PEI	0.5/0.5	7.5	30.1
	Fe^{2+}/PEI	0.5/0.5	6.5	26.3
	Fe^{2+}/PEI	0.5/0.5	6.5	24.6
	Cu^{2+}/PEI	1.5/0.5	7.0	24.8
	Cu^{2+}/PEI	1.7/0.5	8.0	25.5
	Cu^{2+}/PEI	2.5/0.5	9.0	27.2
Thermomechanical Pulp	Alum	1.0	4.5	32.1
	Fe^{2+}/PEI	1.5/0.5	7.0	22.1
	Cu^{2+}/PEI	1.5/0.5	7.0	22.8
	Cu^{2+}/PEI	2.5/0.5	8.0	16.9
	Cu^{2+}/PEI	2.5/0.5	9.0	18.3

Table VIII and Fig. 5 suggest the following:

- Fe^{2+}/PEI and Cu^{2+}/PEI can induce very high levels of rosin sizing using various pulps in neutral-alkaline papermaking systems.
- In a pH range of 6-9, rosin sizing for Cu^{2+}/PEI mordant is not sensitive, particularly for Cobb values.

Effects of modified polyamines

Deng, et al., [16] reported the sizing effect obtained using modified polyamine-polyethyleneimine-epichlorohydrin (PEI-epi) mordant/rosin system at neutral-alkaline conditions was comparable with that of an alum-rosin system at acidic conditions. They described two possible ways for PEI-epi to anchor rosin: through electrostatic force and/or covalent bond. **Figures 6-12** show the main experimental results based on the 3^3 designed experiments.

The effects of PEI-epi on rosin sizing at neutral-alkaline papermaking systems can be summarized as follows:

- Rosin/PEI-epi at neutral-alkaline conditions can achieve the same sizing effect as alum-rosin at acidic conditions.
- The dosage of rosin and ratio of rosin to PEI-epi are both very important. Rosin should be ~1% and the ratio should be 1.2:1. The effect of PEI-epi on unbleached pulp is much more efficient than on bleached pulp.
- There are several critical parameters for the this system, such as stock temperature (~35ºC), pH (6.5) and reaction time (0.5 min.)
- The effect of PEI-epi on ER is more efficient that that of RS.

Ehrhardt et al [17] studied the effect of modified polyamine (polyamine-epichlorohydrin) on rosin sizing at different pH values. The results showed that good rosin sizing at neutral conditions can be achieved by using polyamine-epichlorohydrin, though results are better with alum. The results are listed in **Table IX**, and shown in **Figs. 13 and 14**.

Table IX. Effect of modified polyamine on rosin sizing (pH = 7.5 and 0.4% rosin).

Modified polyamine	**Dosage (%)**	**Alum (%)**	**HST (sec)**
No	no	0	0
No	no	0.25	16
Bis-hexamethylenetriamine-epichlorohydrin	0.4	0	172
Bis-hexamethylenetriamine-epichlorohydrin	0.4	0.25	536
Polyamidoamine-epichlorohydrin HYMENE® 557H	0.4	0	0
Polyamidoamine-epichlorohydrin HYMENE® 557H	0.4	0.25	125
Polyamine-epichlorohydrin RETEN® 201	0.4	0	0
Polyamine-epichlorohydrin RETEN® 201	0.4	0.25	29

From that data, Ehrhardt's results can be summarized as follows:

- At neutral conditions, a good rosin sizing can be achieved by using two modified polyamines-(bis-hexamethylenetriamine-epichlorohydrin and diethylenetriamine-dicyandiamide-epichlorohydrin with a small amount of alum (0.25%).

- Rosin sizing will be increased as the dosage of bis-hexamethylenetriamine-epichlorohydrin increases.

The effects of modified polyamine on rosin sizing at neutral-alkaline papermaking systems can be summarized as follows:

- Modified polyamine (polyamine-epichlorohydrin) can greatly improve the sizing efficiency of rosin sizing at neutral-alkaline conditions, even achieving better sizing levels than that of alum-rosin at acidic conditions.
- Polyamine-epichlorohydrin-rosin is a very complex system. Factors that must be taken into account include the rosin type and dosage, the ratio of polyamine-

epichlorohydrin to rosin, polyamine, dosage of alum, pH, stock temperature, and reaction time.

CONCLUSIONS

It is very interesting and valuable to study rosin sizing at neutral-alkaline papermaking conditions for solving problems associated with traditional, acid-based sizing agents. In this review, although physical technology-premixing sizing procedure and polyaluminum chloride (PAC) have been used by the paper industry, there is little information concerning their activation mechanism. Modified polyamine-epichlorohydrin resin is the best prospective chemical agent to greatly improve the efficiency of rosin sizing in neutral-alkaline conditions, if one hopes to achieve better sizing levels than that of alum-rosin at acidic conditions.

Much work is still needed to develop highly efficient technologies for rosin size under neutral-alkaline papermaking conditions. We need to completely understand the physical and chemical mechanisms that can greatly increase the sizing level of rosin size under these conditions. We also need to find the most efficient and economic polyamine-epichlorohydrin chemical for rosin sizing at neutral-alkaline conditions. Research should also focus on developing new rosin-based sizes that are very efficient at neutral-alkaline conditions and new sizes (not AKD or ASA) to blend with rosin size so that they are highly efficient at neutral-alkaline conditions. Finally, we must determine the optimal technological conditions for commercializing this potentially highly efficient technology.

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INSIGHTS FROM THE AUTHORS

We are developing anionic resin and rosin with other sizes, such as AKD, to be used in neutral-alkaline papermaking conditions. This study allowed us to critically examine the technologies for rosin sizes used in neutral to alkaline papermaking systems.

Our challenge is to completely understand the mechanisms of highly efficient sizing technologies. We plan to do this by evaluating particle size, microphotographs, and product properties (physical and chemical).

We were particularly interested to find that some chemical agents can greatly improve the rosin or anionic resin size efficiency in neutral-alkaline papermaking conditions. Mills can directly use the premixing process sizing or use some chemical modification rosin to reduce costs.

In future studies, we will focus sizing mechanisms and how to blend other sizes with rosin sizes used at neutral-alkaline papermaking systems.

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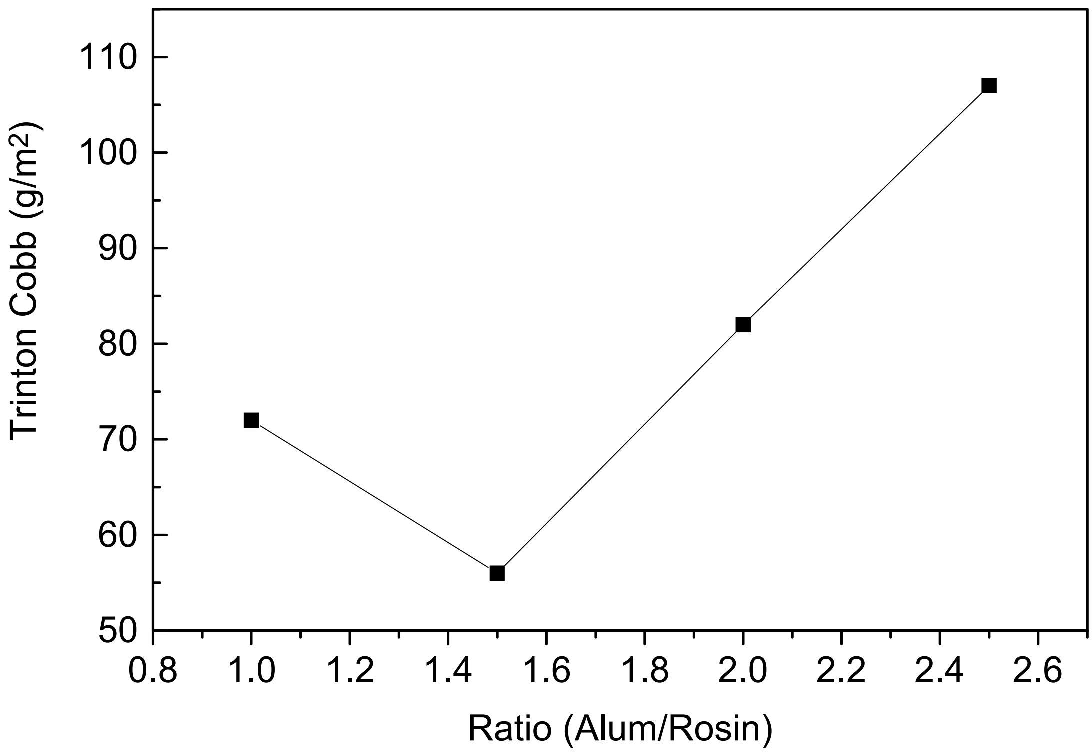

Figure 1. Effect of the ratio of alum to Rosin based on premixing Alum/Rosin.

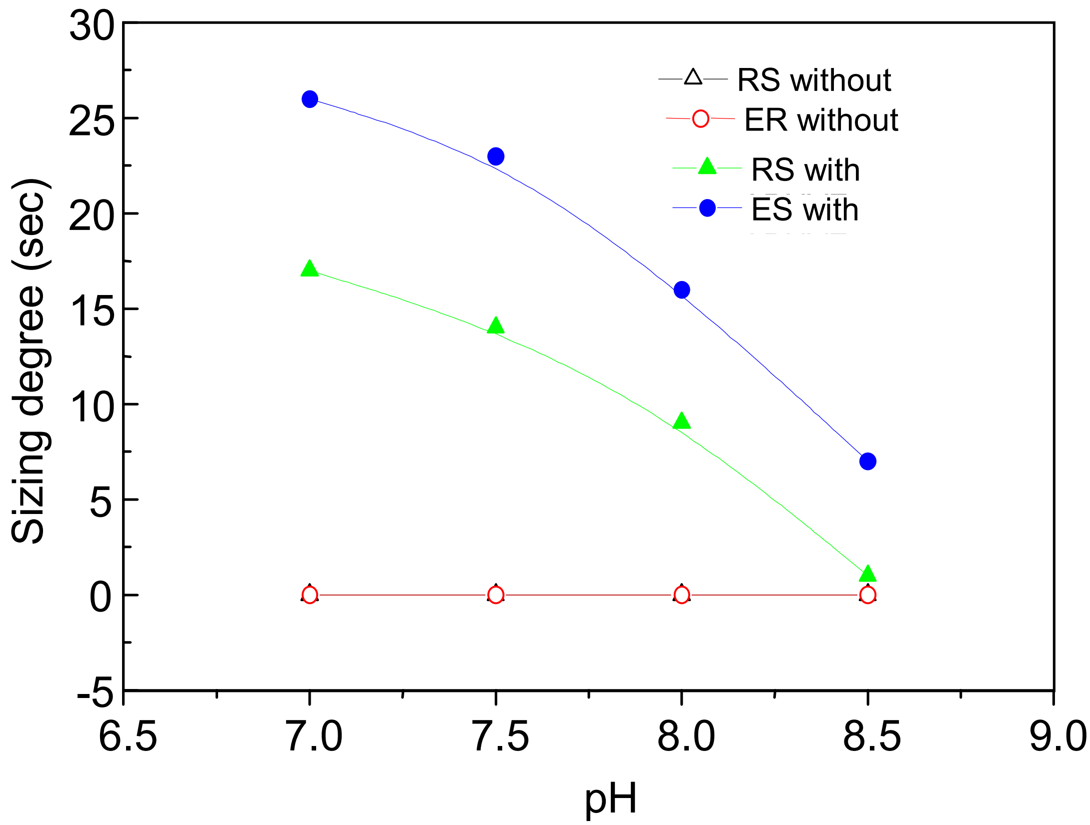

Figure 2 Effect of APNVF (aminated poly-N-vinylformamides) on Rosin sizing at neutral-alkaline conditions at 0.5% emulsion rosin size (ER) or 0.5% rosin soap size (RS) and 1% alum.

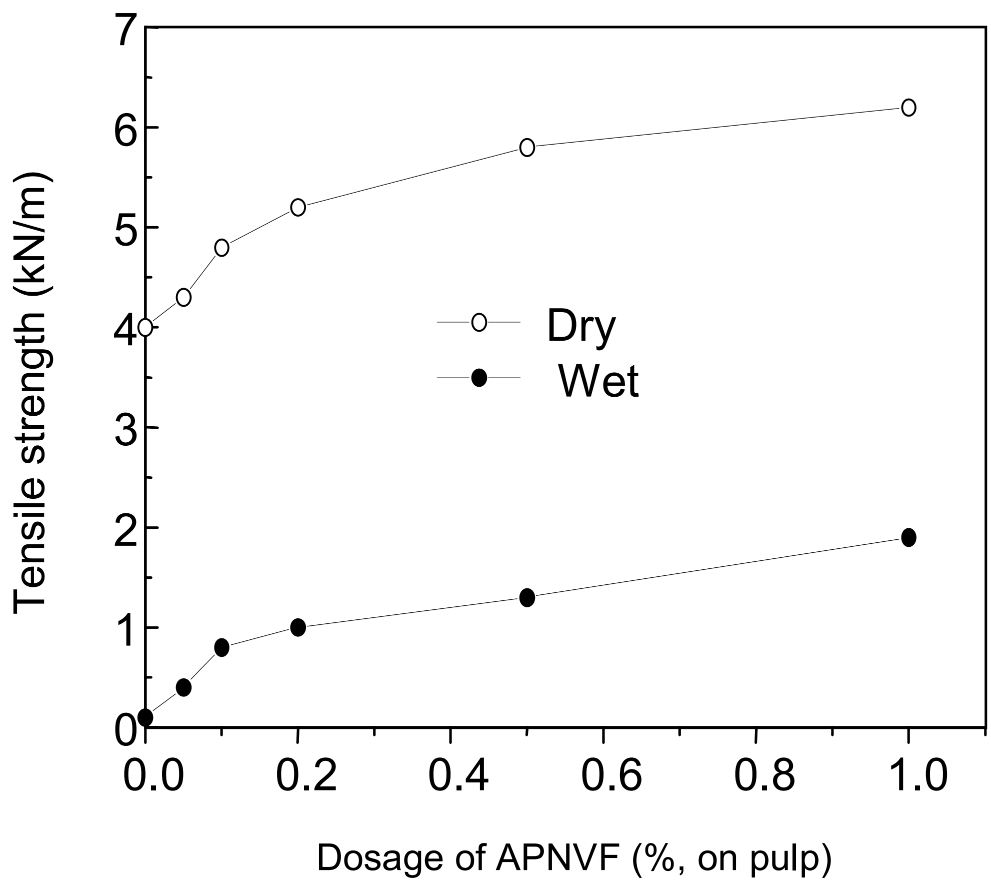

Figure 3 Effect of dosage of APNVF on the tensile strength of dry paper and wet paper at 1% emulsion rosin size and 1% alum, pH = 7.5.

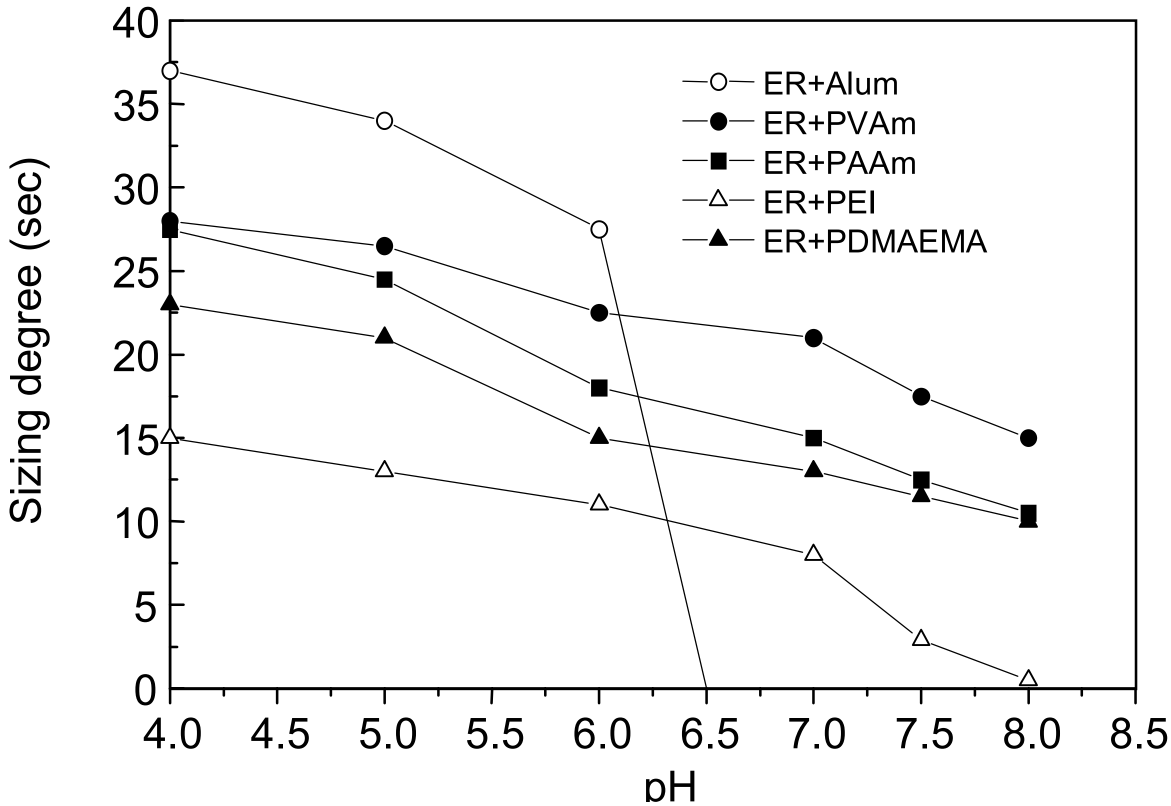

Figure 4 Effect of pH on emulsion rosin sizing (ER) with alum, polyvinyl amine (PVAm), polyallyl amine (PAAm), Poly (dimethylaminoethylmethacrylate) (PDMAEMA) and polyethyleneimine (PEI) at ER (0.5%), polyamines (1%) and alum (2%).

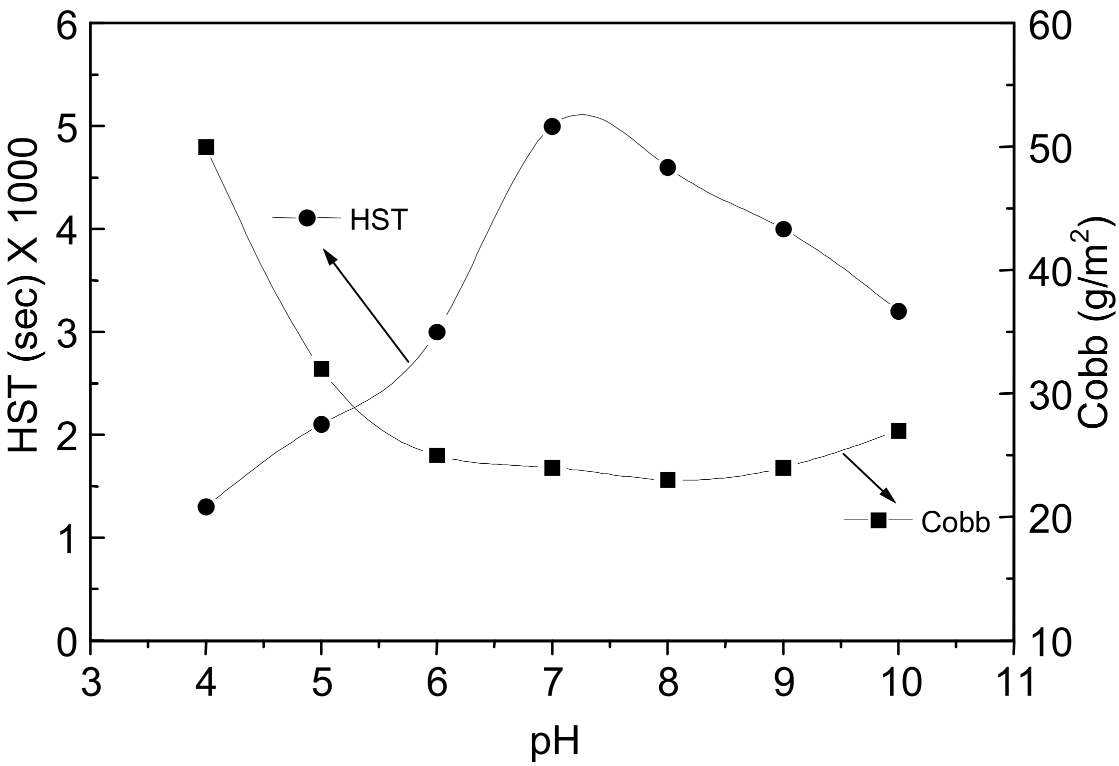

Figure 5 Effect of pH on Rosin sizing as rosin soap (0.5%),Cu^{2+} (2.5%), PEI (0.5%) for Bleached hardwood KP.

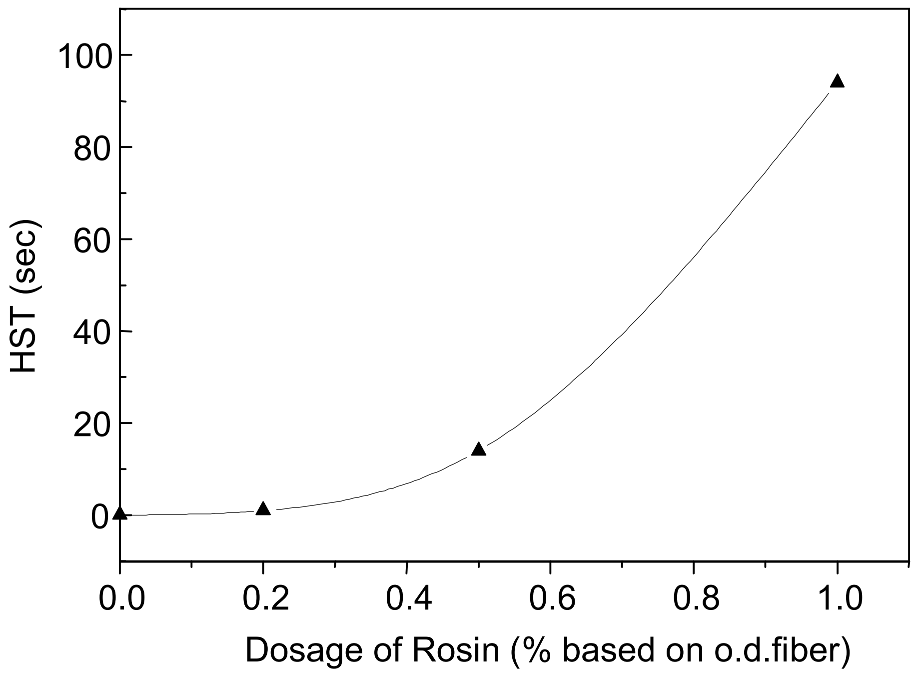

Figure 6 Effect of Rosin amount on sizing at pH = 8.1.

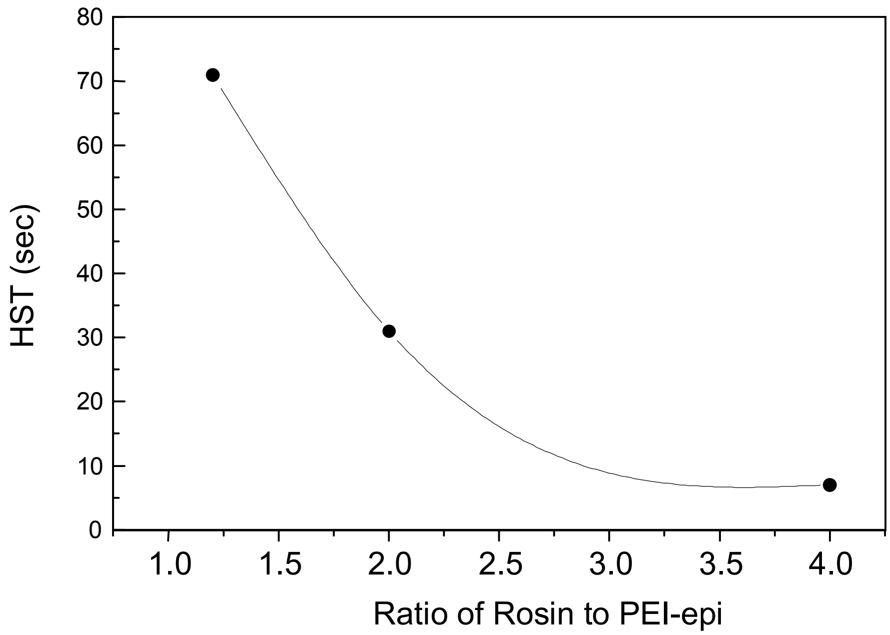

Figure 7 Effect of ratio of rosin to PEI-epi on sizing at pH = 8.1.

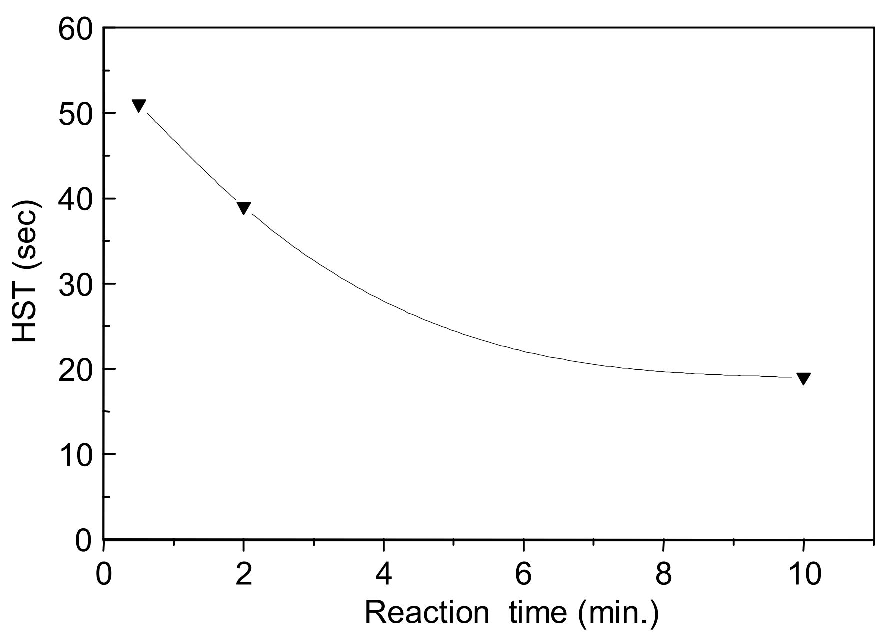

Figure 8 Effect of reaction time on sizing at pH = 8.1.

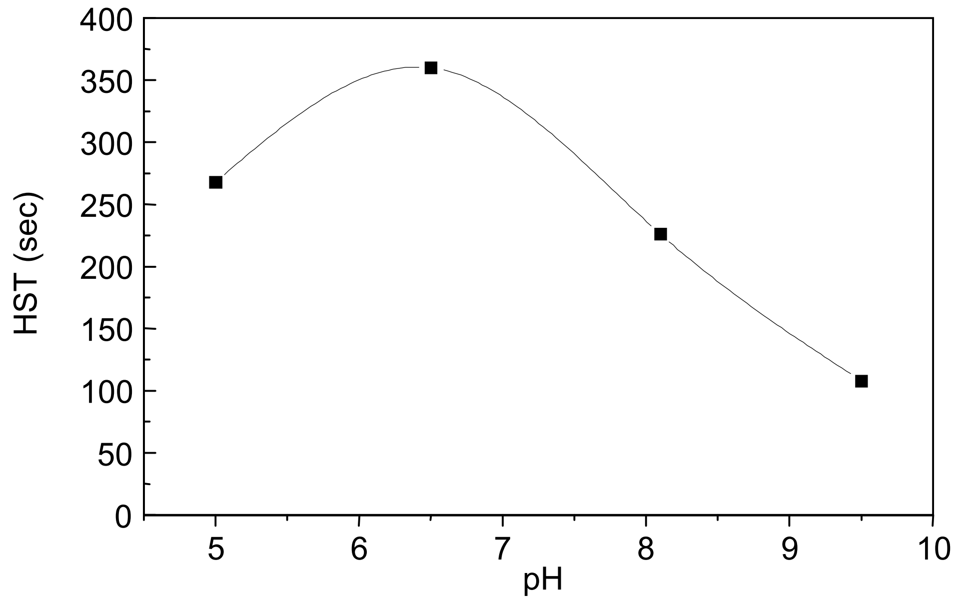

Figure 9 Effect of pH on sizing at rosin (1.0%), rosin:PEI-epi (1.2), reaction time (0.5 min).

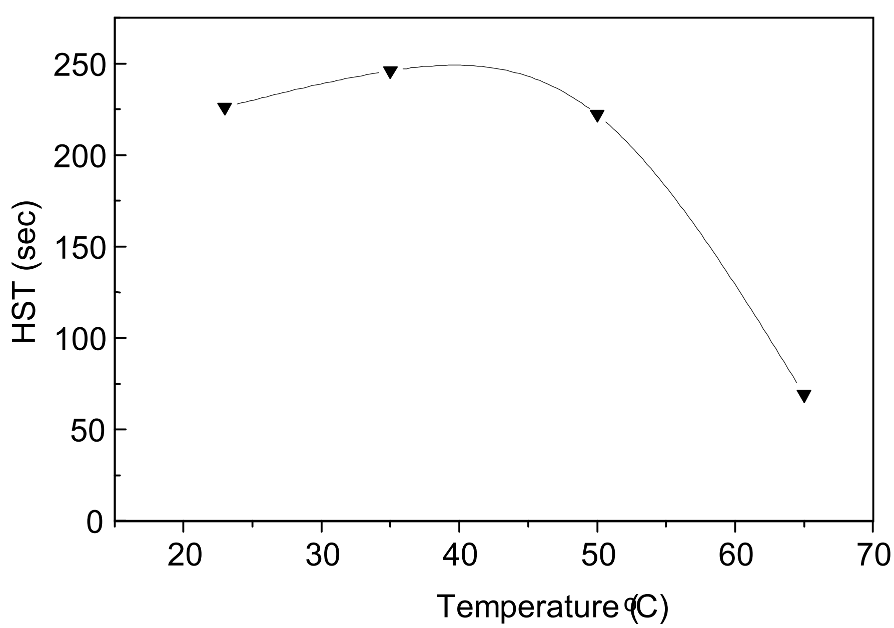

Figure 10 Effect of stock temperature on sizing at rosin (1.0%), Rosin:PEI-epi (1.2), reaction time (0.5 min). and pH = 8.1.

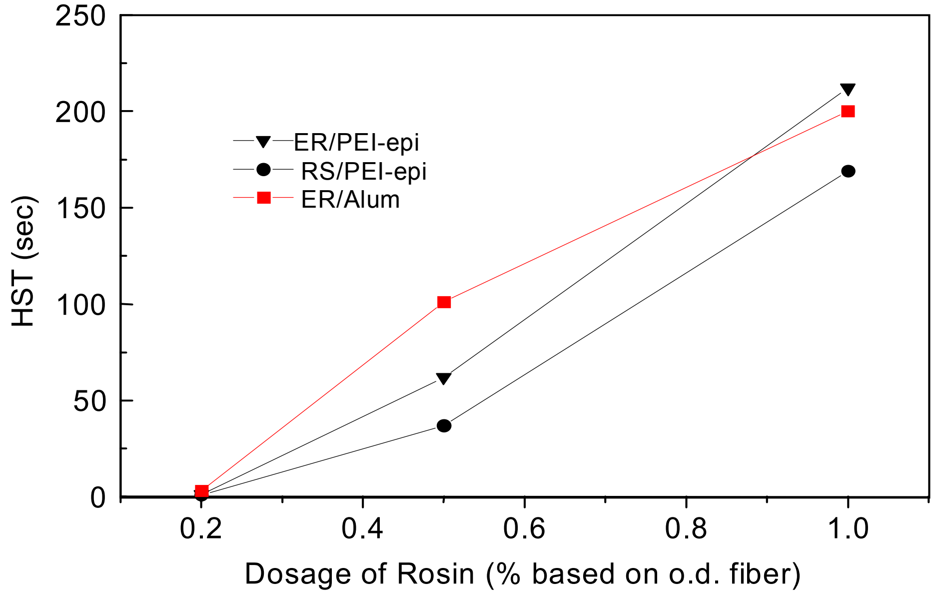

Figure 11 rosin/PEI-epi vs. rosin/alum sizing at (rosin/PEI-epi: 1% rosin, rosin/PEI-epi = 1.2, pH 8.1, 0.5 min.; rosin/alum: 1% rosin, rosin/alum = 1, pH 4.8, 0.5 min.).

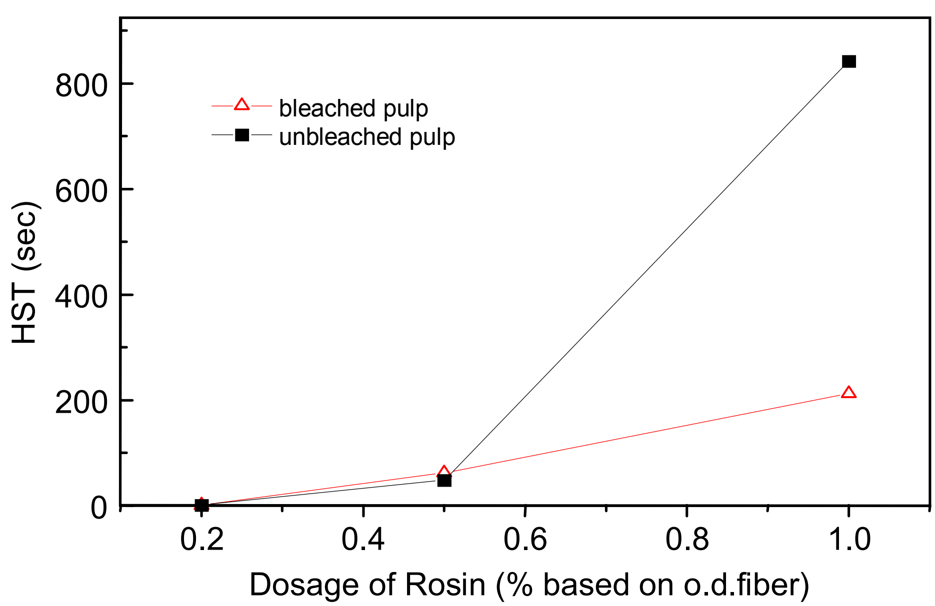

Figure 12 Effect of pulp (bleached and unbleached) on Rosin/PEI-epi sizing at rosin/PEI-epi=1.2, reaction time=.5 min. and pH = 8.1.

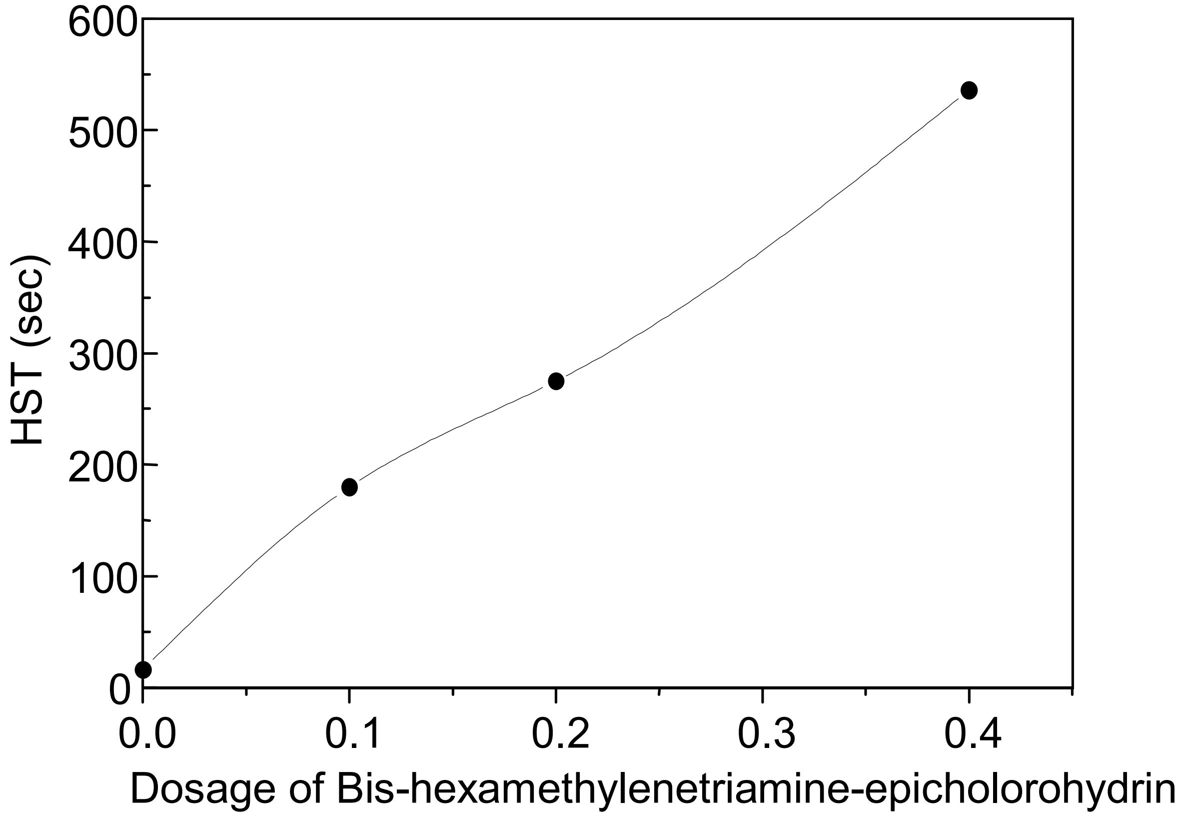

Figure 13 Effect of dosage of bis-hexamethylenetriamine-epichlorohydrin on rosin sizing at rosin (0.4%), alum (0.25%) and pH 7.5.

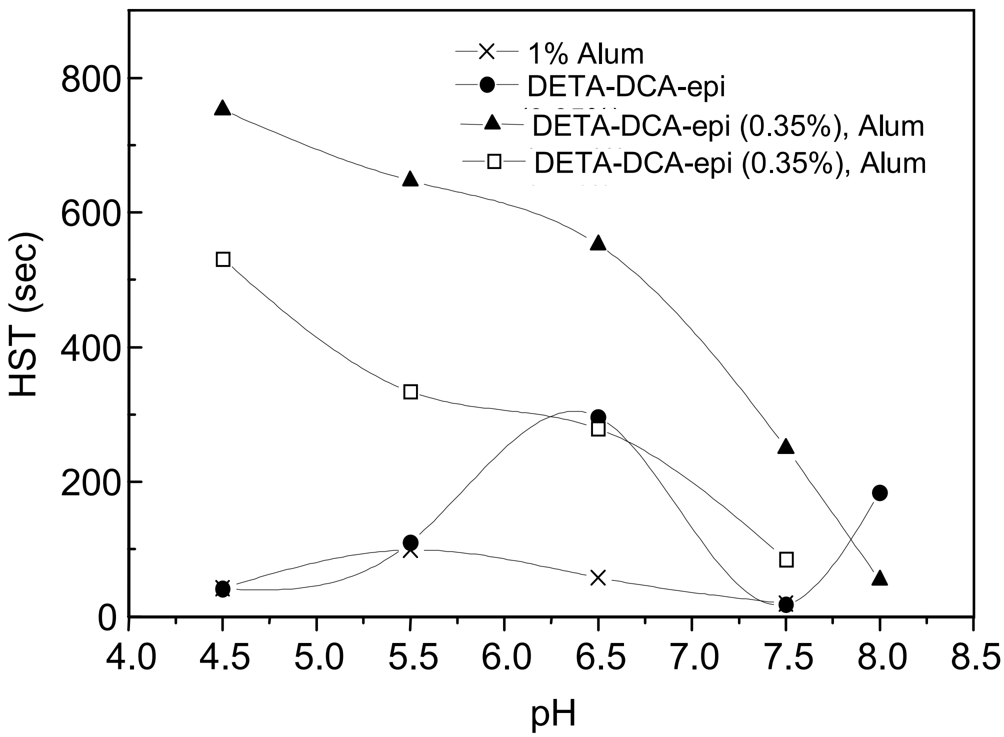

Figure 14 Effect of pH and dosage of alum on diethylenetriamine-dicyandiamide-epichlorohydrin (DETA-DCA-epi)-rosin sizing at rosin (0.35%).