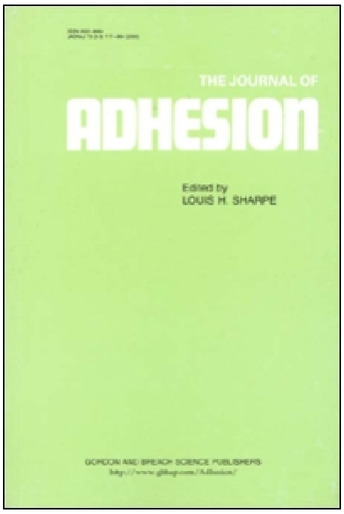

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The Effect of Adding Lignin to Poly(Dimethyl Siloxane)–Poly(Vinyl Chloride) Blends

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A new adhesive sealant with improved mechanical properties has been prepared by blending a sealant based on poly(dimethyl siloxane)-(PDS) with poly(vinyl chloride)-(PVC) and Kraft lignin (L). During this study, California redwood was used as substrate. Two commercial primers were also used to examine their effects on the adhesion of joints. By adding a small amount of L, the modulus of the sealant based on PDS + 10% PVC is improved. The application of primers to the wood substrate has significantly improved the adhesion of PDS, PDS + 10% PVC and PDS + 10% PVC + L polyblends. Improvement in adhesion increased the stress-strain values of the joints. Statistical inference of the experimental results are also discussed.

KEY WORDS Poly(dimethyl siloxane); poly(vinyl chloride); lignin; primers; blending; confidence intervals.

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1 INTRODUCTION

When building envelopes are exposed to wind and other environmental factors, joints between the prefabricated elements often undergo extensive deformations. As the deformations become non-uniform, conventional caulkings (mortar filling, cement filling) are not capable of keeping the buildings weather-tight. Since conventional materials could not meet the modern requirements, new materials such as sealants are developed. Excellent performance of sealants has attracted the attention of architects, building engineers and road builders. However, additional research work seems to be vitally important in improving their durability.

Blending polymers offers a means of engineering into one material combination of desirable characteristics exhibited by the individual polymers. In many situations the goals are to obtain improved mechanical behaviour, better durability and an optimum cost-to-benefit ratio. This project was a continuation

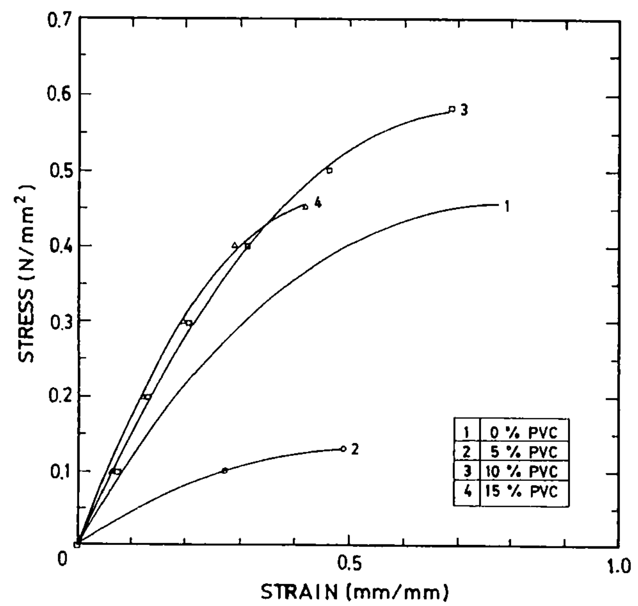

FIGURE 1 Stress-strain curves obtained with PDS–PVC polyblends on a wood substrate.[1]

of previous research work on polymer mixtures, involving the study of blends of PDS with vinyl polymers[1] and some elastomeric copolymers.[2]

As shown in Figure 1, one conclusion of the former study[1] was that the polyblends of PDS with 10% PVC have better mechanical properties and durability than PDS itself in conjunction with a wood substrate. It was also observed that during tensile strength testing of this binary system the failures were almost exclusively cohesive in the adhesive. In this study, the blending technique was used to develop a tertiary system based on poly(dimethyl-siloxane)-(PDS), poly(vinyl chloride)-(PVC), and lignin (L). The aim of adding a third polymer into PDS + 10% PVC was mainly to prevent the cohesive failures.

Lignin, a natural polar polymer, was chosen because of its low cost, very limited utilization and the interesting results that we have already obtained in other studies.[3–5] Also, hydrophilic (polar) adhesives make good joints with wood by virtue of the chemical affinity between the adhesive and wood, which leads to good wetting properties.[6] Lignin is an abundant macromolecular compound with a phenolic structure which makes it an interesting raw material for a wide variety of industrial applications. Recently lignin was used in the composition of wood adhesives[7] and in blends with different synthetic polymers.[8]

This paper will present and discuss the influence of a third polymer (L) on the binary system. Effects of two commercial primers on the adhesion and on the durability of the joints of the newly-formed tertiary system with wood were also investigated. Thirdly, a statistical analysis has been carried out to evaluate the reliability of the various experimental data for the best decision-making. The plan of the paper is as follows. Section 2 will describe briefly the experimental methodology which includes the properties of different materials used. In section 3 the various experimental results are presented and a detailed discussion of the findings are made. The last section is dedicated to the statistical inference of the experimental observations.

2 EXPERIMENTAL METHODOLOGY

a Materials

All materials used in the preparation of the tertiary polyblends are commercial products. The basic material was a silicone sealant based on PDS. Dow Corning 699 was selected because of its excellent blending properties and commercial availability.[1]

Poly(vinyl chloride) was a suspension type (Geon resin) produced by B. F. Goodrich. Even though it has a relatively high specific gravity for a plastic (1.4), its price in terms of volume is still more than competitive against other thermoplastics in the market. Another reason for PVC selection is its unique quality that enables it to be easily blended with a variety of polymers in order to obtain new compounds with new characteristics.[2]

Kraft lignin (Tomlinite-Domtar) is a commercial product extracted from a mixture of hardwoods (maple, beech, elm), precipitated from the black liquor with sulphuric acid and pH adjusted to a level between 6–7 with carbon dioxide.

Primer 1: (Dow Corning 1200 primer coat) is used to promote adhesion of certain silicone sealants and coatings to a variety of construction materials.

Primer 2: (Dow Corning 1205 primer coat) has a different composition than primer 1 and it is applied as any other primer before the adhesive to improve adhesive-substrate bond performance.

The wood (California redwood) substrates were cut lengthwise along the grains, thus subjecting the sealant only to the lengthwise grains.

b Procedure:

The experimental program was comprised of two parts:

- testing of specimens without primer coatings and
- testing the specimens with primer coatings.

Each part of the program had three steps: specimen preparation, curing and testing for load deformations.

The test specimens (12.5 by 12.5 by 50 mm) consisted of a bead of material cast between two prismoidal pieces of wood. These specimens were prepared in accordance with ASTM method C719–79, as well as with CAN2–19.0–M77, method 12.1, 1978. Seven different sets of samples were prepared having different ingredients as shown in Table I. The components were mixed manually and the

TABLE I
The composition of the tested specimens

Set #	Notation	Details of components
Set 1	●	100% PDS
Set 2	△	90% PDS + 10% PVC
Set 3	□	89% PDS + 10% PVC + 1% Lignin
Set 4	■	88% PDS + 10% PVC + 2% Lignin
Set 5	○	87% PDS + 10% PVC + 3% Lignin
Set 6	×	86% PDS + 10% PVC + 4% Lignin
Set 7	▲	85% PDS + 10% PVC + 5% Lignin

mixing time was kept constant. Curing was done in laboratory conditions (24°C and 35% RH) over a period of 14 days.

Tensile (stress-strain) measurements were performed at 24°C with an Instron Model 1125 Universal Testing Machine, using a 500 Kg load cell with a cross-head speed of 2 mm/min, and a chart speed of 20 mm/min. For each set a minimum of ten samples were prepared and examined. For some cases, up to twenty samples were prepared in order to keep the experimental errors as low as possible. The butt joint was formed along the 12.5 × 50 mm opposite side of the sealant bead. Tensile forces were applied on the specimens and testing was conducted until there was a visible adhesive or cohesive failure or until the results recorded on the chart indicated a sharp decrease in load. Various preventive measures during sample preparation and testing are reported elsewhere.[9]

3 RESULTS AND DISCUSSIONS

Experimental observations are presented and discussed in this section, whereas the reliability of the data is statistically analyzed in the next section. In each graph seven sets of results are given and they represent, respectively, the seven different ingredients as explained in Table I, which indicates their percentages by weight. The amount of PVC was always kept constant and thus any increase in L will lead a direct decrease in PDS. Even though both set 1 and set 2 are free from L, set 2 is always viewed as the control specimen because of its greater strength than set 1 as reported previously.[9]

Arithmetical mean values of the failure loads were determined from their individual failure loads. From these mean loads, conventional tensile stresses were computed and they are shown in Figure 2. Figure 2 also includes the maximum stresses as well as the minimum stresses that were recorded during the testing of all specimens. Mean stresses reveal that the PDS tensile strength has been improved by the addition of 10% PVC. Addition of L to PDS + PVC polyblends produces little changes in the stress values. Figure 3 has the same format as Figure 2 but the strains are shown. It is clear that the strain of the butt joint is about 0.8 mm/mm which is reduced to 0.4 mm/mm as the amount of L increases. The observations of PDS and PDS + PVC polyblends are same as reported earlier by Beznaczuk.[9]

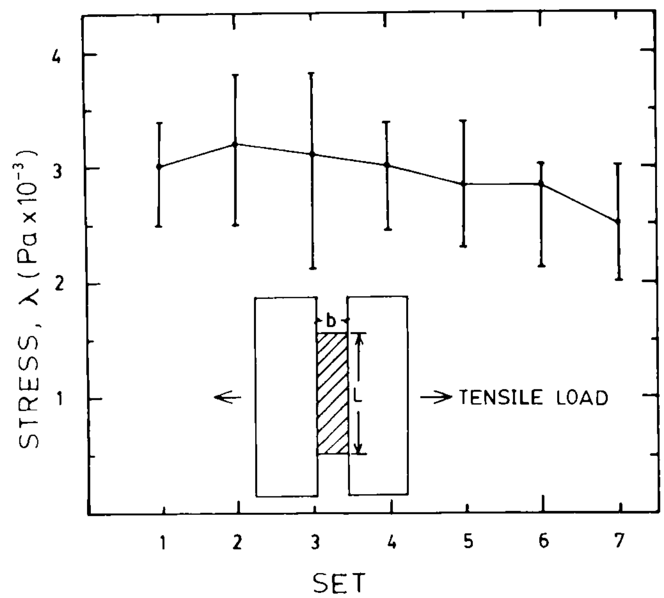

FIGURE 2 Range of measured tensile stresses (λ) of various amounts of L added to PDS–PVC polyblends with wood substrate.

Stress-strain diagrams based on the individual data are drawn in Figure 4, to evaluate the spreading nature of the loads for various specimen strains. The graph also gives an idea of the scatter of the values. In the graph, for some cases, a lesser number of data points appear than the number of specimens tested. This is because the same experimental observation occurred for more than one specimen. Detailed statistical analysis of the observations and confidence intervals are

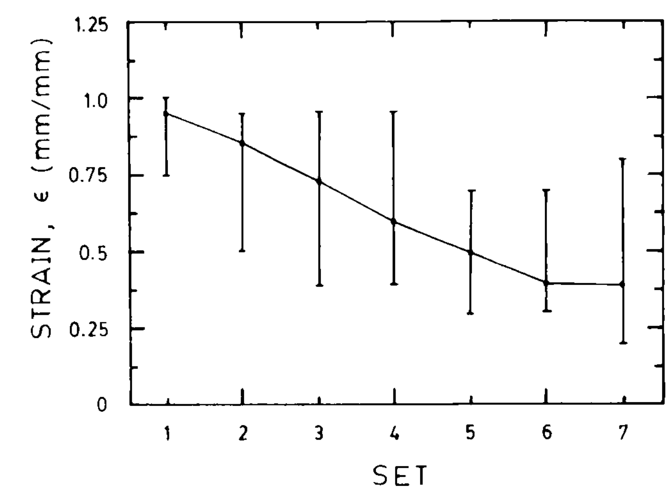

FIGURE 3 Range of measured tensile strain (ε) of various amounts of L added to PDS–PVC polyblends with wood substrate.

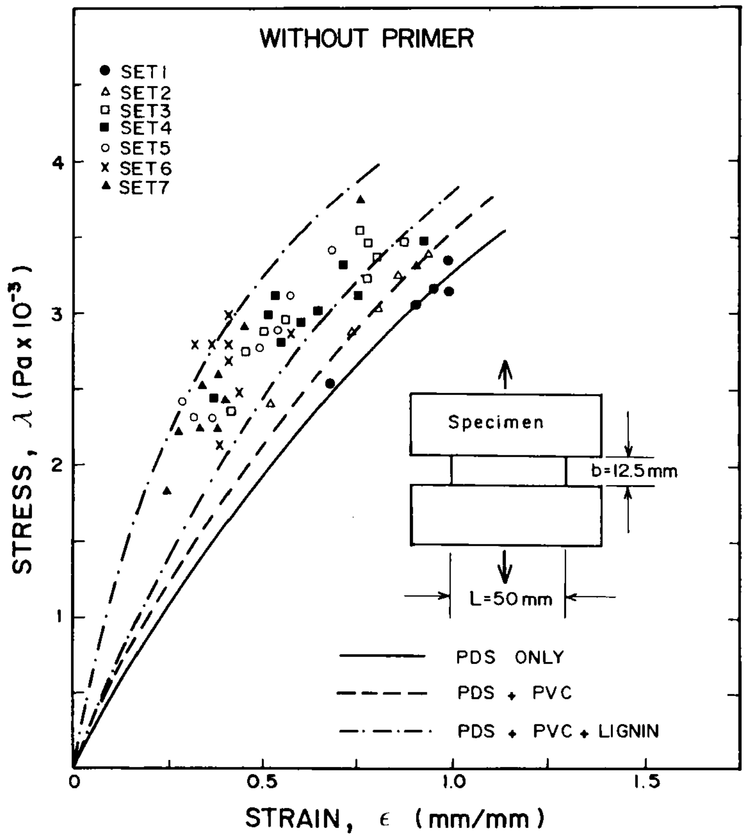

FIGURE 4 Tensile stress-strain behaviour of PDS and its polyblends (wood substrate, without primer).

presented in the next section. From the graph, it is obvious that the addition of lignin decreases the ultimate tensile strain of the joint. Since the various amounts of L added to PDS + 10% PVC polyblends play a lesser role in the ultimate stress-strain, their dispersions are represented by two curves, respectively, for the lower and upper limits. The other two curves in the graph represent the case of PDS and PDS + 10% PVC. All sets with lignin contents in excess of 1% show a clear decline both in stress and strain. Unlike the cohesive failures observed in the case of the binary system PDS + 10% PVC, the failures with L are always due to lack of adhesion of PDS to the substrate. Since the failure of the substrate never occurred and the strain levels decline more than the stress levels, a rise in modulus is revealed.

It is likely that the improvement in the modulus of the tertiary poly-blend is due to the interactions between L and PVC. As the result of increased rigidity, the tertiary system PDS + 10% PVC + L can only sustain less strain than that of the PDS + 10% PVC blend. Thus, the failure of the new system is found to be a lack of adhesion. To prevent adhesive failures and to improve joint durability, primers were applied on the specimen edges.

The use of primers on joint substrates enhances the integral adhesion of sealants, expecially where sealants are exposed to severe environmental conditions. Primers are particularly recommended for porous substrates such as wood, masonry, etc. A variety of primers based on solutions of chlorinated rubbers, urethanes, silanes or asphalt emulsions are commercially available. For wood surfaces the polyurethane primers are often used. Selection of the primers and their use can be best determined by the sealant composition and the substrate characteristics.[10]

Recorded load/deformations with primer coatings are transformed into stress-strain values and they are displayed in Figure 5 for the case of the first primer. As we may identify from the graph, both and failure stresses and failure strains are significantly increased. This was also found in the case of polyblends with L added. Nevertheless, the increase in the amount of L did not result in a linear

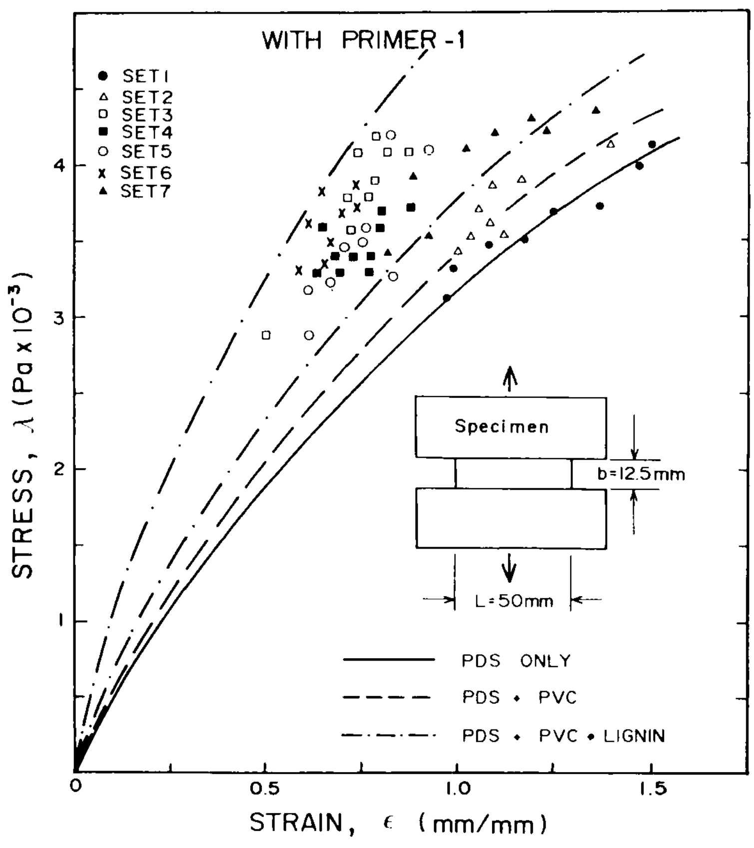

FIGURE 5 Tensile stress-strain behaviour of PDS and its polyblends (wood substrate, primer-1).

increase in ultimate stress. Same trend is also observed for primer 2. Thus, priming of the specimens will enhance the durability of the joints.

To understand the priming effect on the ternary system, a more straightforward comparison is made in Figures 6–9. Both stresses and strains are compared for the systems with the two different primers. The X-axis value indicates the stress or strain data obtained with the particular primer, whereas the vertical axis denotes either stress or strain for the same experimental set without primer. The seven different set values are included in the figures to show the global effect of the primer application. However, the plotted values are same as Figure 5 only for the case of primer-1 but in a different representation. A common line (45°) is also drawn in all the figures. Points above the 45° line indicate a negative effect of the primer while points below the line indicate a positive effect. The points on the line represent no influence of primer. This is the common evaluation of a graph of this format.

It is very clear from Figures 6–9 that the values obtained by utilizing primers are often better. This is found to be true for both stress and strain. This implies that the specimens will take more load under large extension, once the primer is applied. However, the improvements in the stresses are less than those of the

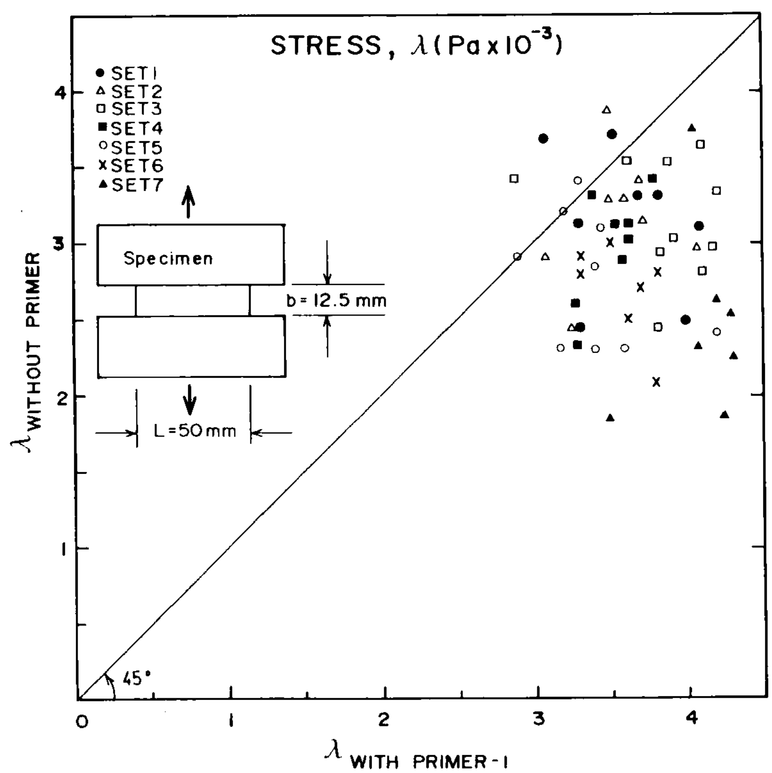

FIGURE 6 Comparison of the tensile stresses (λ) of various specimens; wood substrate treated with primer-1.

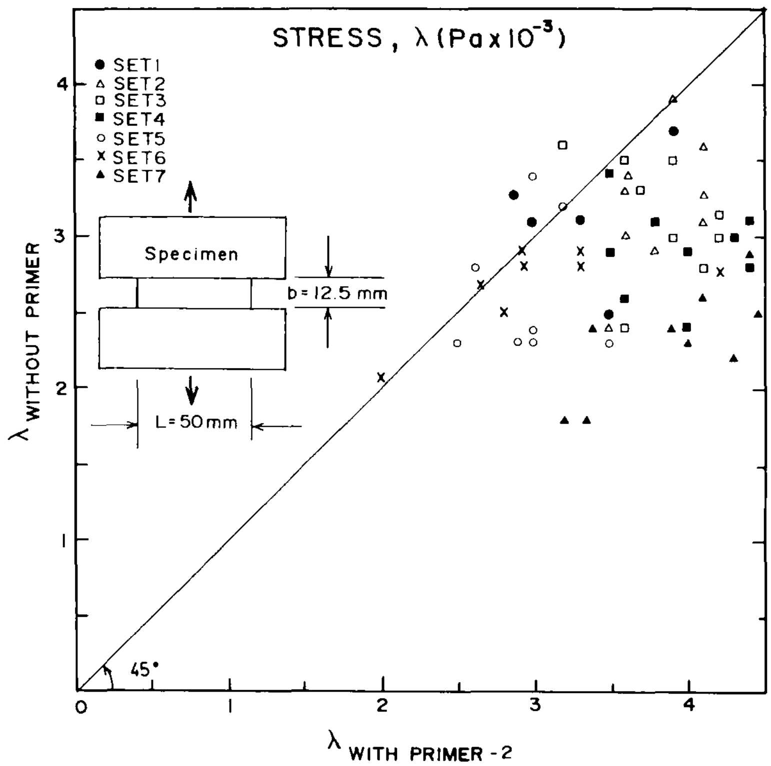

FIGURE 7 Comparison of the tensile stresses (λ) of various specimens; wood substrate treated with primer-2.

strains. Only a very few points fall above the reference line (45°) and that may be due to the random errors produced during the preparation and/or testing.

The effect of lignin in improving the strength of the joint was less significant than that of the primer. On the other hand, irrespective of the amount of lignin added, the performance of the lignin-filled polyblends with primed substrates is always preferable to those specimens without lignin. When comparing the efficiency of the primers, primer-2 will yield more extension than that of primer-1. However, the spreading of the values indicate that the trend in primer-2 is not constant. This may be due to its sensitivity to sample preparation. In any event, both primers seem to increase the mechanical performance of the studied polyblends. Thus, the use of primer strengthens the polyblend/wood interface.

4 STATISTICAL INFERENCE OF THE EXPERIMENTAL RESULTS

In the previous section, the experimental observations were presented and discussed. All explanations were made exclusively based on a single number from a set of observed data to represent the parameter of the underlying population.

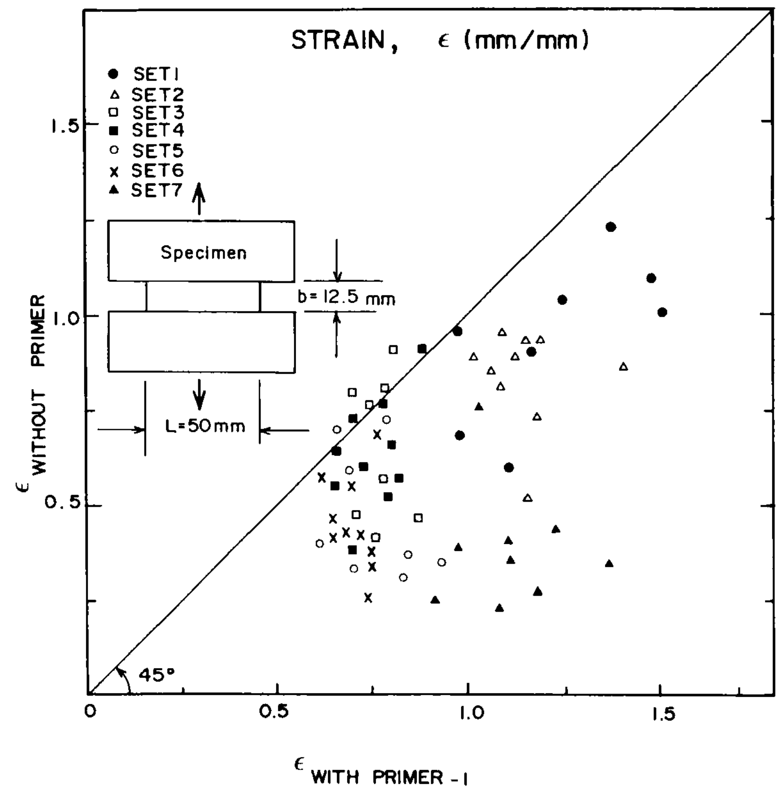

FIGURE 8 Comparison of the relative deformations (ε) of various specimens; wood substrate treated with primer-1.

The single number is called the unbiased population mean which can represent the maximum likelihood of the observations. However, those numbers do not convey information on the degree of accuracy. For this reason, the intervals over which a parameter may lie is often used to supplement the point estimation of the same parameter. Such intervals are called the confidence intervals and their method of estimation is known as intervals estimation. Detailed procedures for the calculations of these intervals can be found elsewhere.[11]

Calculations for the confidence intervals of the measured data have been made and the results are presented in Table II. The table includes the upper, mean and lower limits of the calculated stress values for the three different cases. All the displayed values have a confidence level of 90%. Thus, we can be 90% confident that the population mean will lie between the upper and lower limit values.

The behaviour of the various conclusions made in the previous sections can be identified by careful examination of Table II. Rows 1, 4 and 7 represent the lower limit of the stresses whereas 3, 6 and 9 reveal the upper limits, respectively, for without primer, with primer-1 and with primer-2 cases. The conventional mean stress values of the specimens with and without primer coatings are also inserted

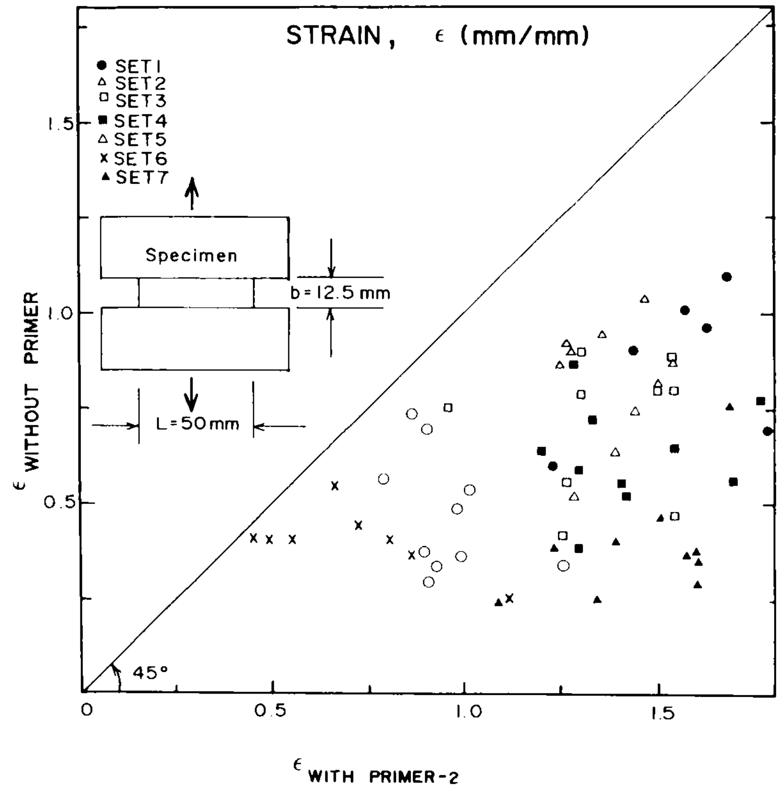

FIGURE 9 Comparison of the relative deformations (ε) of various specimens; wood substrate treated with primer-2.

TABLE II
90% Confidence interval stress values
(Row 1, 4 and 7 lower limits: Row 2, 5 and 8 mean values: Row 3, 6 and 9 upper limits)

	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7	Row #
Stress (10^{-3} Pa) without primer	2.6	2.6	2.7	2.7	2.4	2.4	2.2	1
	3.0	3.2	3.1	3.0	2.7	2.7	2.5	2
	3.3	3.7	3.5	3.2	3.0	3.0	2.8	3
Stress (10^{-3} Pa) with primer-1	3.4	3.5	3.5	3.2	3.2	3.4	3.8	4
	3.6	3.7	3.8	3.5	3.5	3.6	4.0	5
	3.9	4.0	4.2	3.8	3.8	3.6	4.3	6
Stress (10^{-3} Pa) with primer-2	2.9	3.7	3.2	3.5	2.6	2.5	3.3	7
	3.2	3.7	3.8	3.9	2.9	2.9	3.9	8
	3.6	4.1	4.4	4.3	3.2	3.3	4.3	9

TABLE III
Percentages of probable error estimates in the measured tensile stressess

	Set 1	Set 2	Set 3	Set 4	Set 5	Set 6	Set 7
Stress (%) without primer	8	17	14	7	11	12	5
Stress (%) with primer-1	6	5	7	7	6	4	5
Stress (%) with primer-2	10	4	24	9	9	13	8

in the table to identify their deviations from the confidence limits. It is worth mentioning that the mean stress values of unprimed specimens are the same as shown in Figure 2, whereas the upper and lower limits are calculated with 90% confidence of the mean values.

By comparing them it is evident that the primer plays a significant role in improving the adhesive nature of the joints. Moving along the row values shows the smaller/negative influence of the newly-added polymer, L. Nevertheless, for 1% (set 3) and 5% (set 7) L-added polyblends show considerable gain in their stress values after priming. To establish the presence of specific molecular interactions in the polyblends with PVC and L, IR spectrophotometry and FTIR photoacoustic spectrophotometry experiments were carried out. Because of the small amount of L used such interactions could not be identified.

Computations were also made to estimate the probable errors of the measurements by using statistical estimation theory.[12] Table III displays the percentages of probable error estimated in stress values for each set of data. The reliability of the observations that have been discussed so far can be assured from these errors. The table shows that for all the experimental cases the probable error is always within 15%, except for the values of set 2 without primer coating and set 3 with primer-2 coating which have a probable error of 17% and 24%, respectively. Thus, the statistical inference provides direct indication of the reliability of the experimental data discussed in this paper.

CONCLUSIONS

The following conclusions can be reached based on the above discussions:

1) A rise in modulus of the polyblend was observed when a small amount of lignin was added to the PDS + 10% PVC sealant.

2) Lignin-added polyblends failed due to lack of adhesion during the tensile testing.

3) Application of commercial primers to the surface of a California redwood increases the adhesive property of PDS, PDS + 10% PVC and PDS + 10% PVC + L polyblends to this substrate.

4) The confidence intervals and the probable errors for the observed data are computed by using statistical estimation theory which supports the above findings.

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