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SEALANT POLYBLENDS WITH LIGNIN

Michael A. Lacasse

A Thesis
in the
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ABSTRACT

Sealant Polyblends with Lignin

Michael A. Lacasse

An investigation was conducted to establish the viability of blending lignin, a naturally occurring, readily available polymer resource, with various sealants, namely: silicone, polyurethane, polysulfide, acrylic, and butyl.

Preliminary testing of standard specimens revealed that the tensile properties of polyurethane, acrylic, and butyl based sealants were enhanced when mixed with 10 parts by weight of lignin.

These sealants were tested in a more detailed program, where specimens of lignin-sealant blends, having blend ratios varying between 0 and 20%, were prepared on substrates of aluminum, mortar, and wood, and subjected to laboratory control, accelerated aging and natural aging conditions. Results of tension testing showed that generally, lignin acts as a reinforcing agent which adds rigidity to the polymeric matrix, as indicated by the increase in toughness and modulus of blended sealants with the addition of lignin.

Light microscopy and scanning electron microscopy, used to determine the morphology of polyurethane blends, in conjunction with thermographic analysis by differential scanning calorimetry, disclosed the two-phase behavior of lignin-polymer blends.

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LIST OF SYMBOLS

Symbol	Description
A	Acrylic sealant
AA	Accelerated aging
Al	Aluminum substrate
ASTM	American Society for Testing and Materials
B	Butyl sealant
C	Control specimens
CSA	Canadian Standards Association
CGSB	Canadian Government Standards Board
DSC	Differential scanning calorimeter
L	Lignin
LM	Light microscope
M	Mortar substrate
NA	Natural aging
PBW	Parts by weight
Ps	Polysulfide sealant
PU	Polyurethane sealant
PVAc	Polyvinyl acetate
S	Silicone sealant
SBR	Styrene-butadiene rubber
SEM	Scanning electron microscope
Tg	Glass transition temperature
UV	Ultra-violet radiation

1. INTRODUCTION

One of the prime functions of the building envelope is to prevent air, dust and water from penetrating inside the enclosure. The effectiveness of any given shell to perform this function however, is dependent on the degree to which its joints, inherent to any structure, are sealed. Materials used to seal joints are subject to repeated cycles of strain in the most extreme weather conditions, and their resilience and durability are of importance in maintaining an effective seal. Presently, polymer based sealants are the most widely used materials capable of meeting the requirements imposed by the environment in which they function.

The size of the combined sealant retail and construction markets is 72% of the overall consumption of sealants in the United States, representing a value of 440 million dollars (U.S.) in 1985, and a projected combined market value of 483 million dollars (U.S.) in 1990 (1). Consequently, the promotion and research of improved sealants is of continuing importance.

The objective of this research program is to characterize the properties of sealant polyblends with lignin. The intent is to help develop more resilient, durable, and economical sealants and to aid in cultivating a market for lignin, a highly underutilized renewable polymeric material, readily available from industry.

The experimental program was set in two parts. A preliminary program evaluated the viability of blending lignin with five different sealants, representative of the most widely used sealants presently available on the market, namely silicone, polyurethane, polysulfide, butyl, and acrylic. The evaluation was based on the adhesive and cohesive tensile strength of specimens prepared on three standard size testing substrates: aluminum, mortar, and wood. The sealant blends whose tensile properties were enhanced with the addition of lignin were tested in a second more detailed program. The detailed program further characterized the properties of particular sealants in terms of their morphological structure, curing mode, thermal behavior, tensile response, and durability to accelerated and natural weathering conditions.

2. USE OF SEALANTS IN THE BUILDING INDUSTRY

2.1 Function of a Sealant

The envelope of a building may be made of a variety of building materials, including metal, glass, concrete or stone panels, masonry cladding, or even wood or plastic panels. Whatever the combination used, this series of plates or elements, when properly positioned and correctly attached to the building frame, assures a suitable climatic barrier between the exterior and interior of the building enclosure, provided precautions have been taken to effectively seal the panel extremities. The function of a sealant is to provide this effective seal as economically as possible. An effective seal implies the weatherproofing of the building; hence the prevention of water entry which may cause damage to interior finishes and even lead to structural damage; the prevention of air passage, which may include dust and undesirable odours when infiltrating a building; or the loss of heat energy and conditioned air when exfiltrating from the building.

An effective seal is achieved not only from proper sealant selection, but also from adequate joint design. Since the choice of sealant is based on the joint geometry and anticipated joint movement, an appreciation of joint types and joint seals is beneficial in being able to classify jointing materials and to assess their effectiveness in various jointing configurations.

2.2 Classification of Joints

A distinction must be made between joint types and joint seal or joint design. A joint type identifies the fashion in which the sealant, which links the joint faces, functions and the mode in which it functions, be it in tension, compression, shear, or in combined stress situations. Joint seal relates to the weatherproofing design.

2.2.1 Joint type

There are essentially two basic types of joints: working and non-working (2). Working joints change size and shape with the relative movement of adjoining parts. Examples of working joints are given in Table 1. In working joints, the sealant material must withstand repeated cycles of stress and strain without failure. Most working joints may be classified as being either butt joints or lap joints. Butt joints subject the sealant to alternating tensile and compressive stresses as shown in Figure 1. It can also be seen that lap joints subject the sealant to lateral deformations causing shear stresses to develop upon joint movement.

Joint type	Example
butt	-exterior panel joints
	-expansion joints
	-control joints on masonry walls
lap	-exterior panel-to-mullion joints
	-exterior panel-to-sill joints
	-joints in sheet roofing or siding

Table 1 - Examples of Working Joints (2)

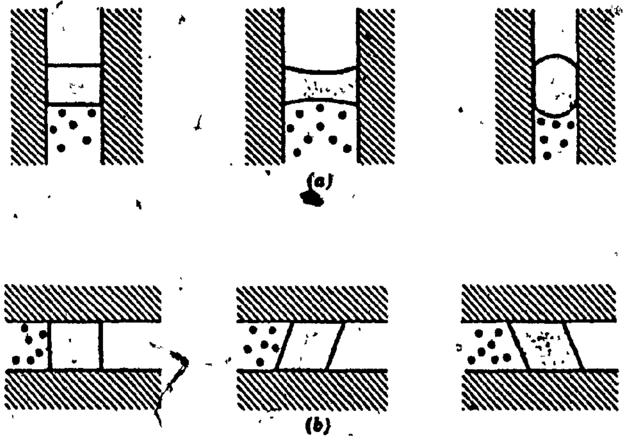


Figure 1 - Deformation of Sealant Beads (2)

Non-working joints are characterized by the minimal relative movements of adjacent parts, consequently the sealant functions primarily as a filler and is subject to little or no stress (2).

2.2.2 Joint seal

Joint seal or joint design relates to the manner in which weatherproofing is achieved. A one-stage seal, for example, attempts to restrict the movement of air, water, and water vapour through the joint at the exterior wall face, in a single step. On the other hand, two-stage seals separate the water barrier and air barrier functions, combined in the one-stage seal. The water barrier in a two-stage seal is placed on the outside face of the exterior wall sections. Behind this initial seal is a drained and ventilated cavity, the back of which forms the front on the second seal, which acts as an air barrier. Although the air barrier or seal is ventilated to the outdoors, it is protected from direct contact with the elements of nature. Consequently it is not as susceptible to degradation by ultraviolet radiation from sunlight, nor to excessive wetting or continuous exposure to rain which may penetrate the outer weather barrier. In the latter situation, the geometry of the joint is such that water is drained from the joint cavity by the forces of gravity. A comparison between one- and two-stage seals for concrete panels is illustrated in Figure 2.

SEALANT FUNCTIONS:

A) Combined water and air barrier at the same point.
B) Rainscreen, with ventilated & drained air space behind.
C) Air barrier.
D) Vapor barrier.

Joint Configuration Terms: a - nib; b - threshold; c - lid; d - groove; e - pressure equalization chamber; f - rebate.

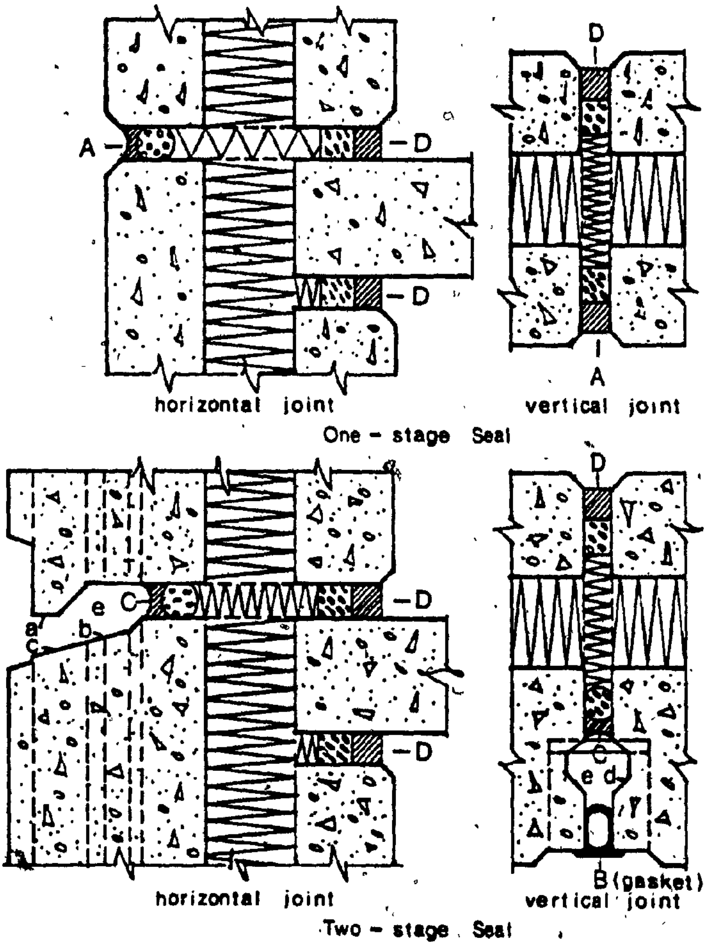


Figure 2 - One- and Two-stage Seals (3)

2.3 Joint Movement

The overall stress and strain to which a sealant is subjected is dependent on the degree of movement at the joint, and the width and depth of the sealant bead. Thus for proper sealant selection, an estimate of the magnitude of movement must be obtained whereby the anticipated elongation or compression of the joint may be matched to a sealant of adequate movement capacity.

Joints on the exterior cladding of buildings tend to exhibit the most extreme cyclical movement (4). They are also the most critical from the point of view of providing a seal since they are subjected to the most severe service conditions.

Joint movement may be estimated by first distinguishing between irreversible and reversible movements in buildings (5). Building settlements, deflection under dead load, creep and shrinkage effects are irreversible movement. Reversible movements are those induced by thermal changes, moisture content changes, and wind loads. The magnitude of the irreversible movements must be assessed in order to determine their overall effect on the joint.

In terms of reversible movement, wind effects become important in high rise buildings which deflect under wind load. Moisture changes affect the rate of thermal expansion in certain building materials, and thus may be of importance to verify potential interaction between thermal and moisture effects at building locations which are often subject to water accumulation.

The correlation between joint movement and air temperature was established for building expansion joints (6), joints between precast concrete panel cladding (7), and brick panel cladding (8). Generally, it can be stated that cladding materials which are subjected to daily and seasonal change in temperature, tend to change in dimension accordingly. Thus movement at a joint may be estimated by evaluation of the temperature range at the joint, determining the distance between panel points, and applying the appropriate coefficient(s) of thermal expansion to the calculation. The effect of temperature change on joint width is illustrated in Figure 3, which shows the monthly variation in joint movement at the top level of a southwest-facing wall of a highrise apartment building. The corresponding monthly temperature fluctuations for this joint are also depicted, and it can be seen that there is a definite correlation between temperature change and joint movement. As is expected, joints open in cold temperatures and close in warmer temperatures; are widest in winter and closest in summer.

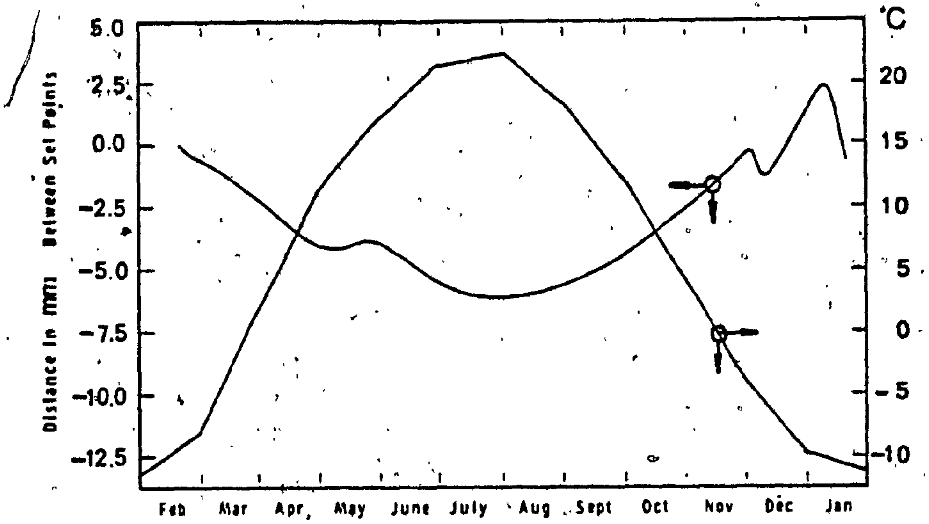


Figure 3 - Joint Movement and Average Temperatures (6)

2.4 Stresses and Strains in Sealants

Of primary importance in determining the performance of a sealant is its shape and dimension. The actual width chosen would be determined from an estimation of the potential movements the sealant might be subjected to. However, the shape or configuration is of prime importance in limiting the stress and strain on the sealant to appropriate values. There is a definite relationship between the depth (D) of the seal and the width (W) of a joint that determines the amount of strain in a sealant (2). Essentially, the strain of the sealant surface is a function of the extension, and of the D/W ratio, and necessarily will be higher than the amount of the joint strain. Thus for a joint extension of 30%, a joint strain in the sealant surface of approximately 90% will be induced in a joint depth to width ratio of four (D/W = 4), and a joint strain in the sealant surface of 35% in a joint of depth to width equal to one (D/W = 1). The lower the depth to width ratio, the less strain is induced on the surface of the sealant for a given joint extension. The effects of strain and corresponding substrate stresses are shown in Figures 4 and 5, which compare two seals having D/W = 4 and D/W = 1 at 100% extension.

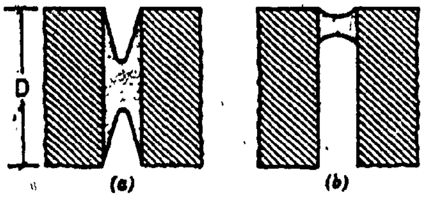


Figure 4 - Comparison of Maximum Strains (a) For 50mm deep seals. Extension of joint: 100%; sealant strain: 550%. (b) For 12.5mm deep seals. Extension of joint: 100%; sealant strain: 160% (2)

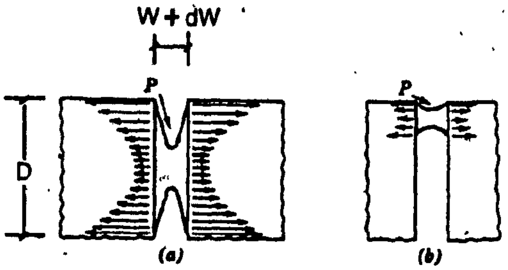


Figure 5 - Comparison of Substrate Stresses for (a) 50mm deep seals; and (b) 12.5mm deep seals (2)

It can be observed from Figure 6 that the stress distribution at 40% extension for a 12.5mm deep joint (D/W = 1) has a similar stress distribution pattern as a 50mm deep joint at D/W = 2, at 20% elongation (2). This stresses the importance of the depth to width ratio. From a practical standpoint, a depth to width ratio of one is used, since lower ratios would result in more shallow depth seals, which may be prone to irregular application and hence eventual joint failure.

2.5 Types of Joint Failure

Depending on the type of sealant, failure may occur due to lack of adhesion, cohesion, or spalling of the substrate to which the sealant is bonded. Failure may also arise from the intrusion of foreign material in the joint.

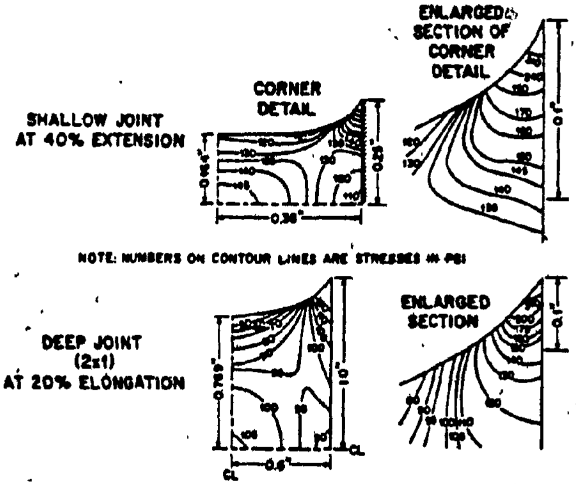


Figure 6 - Comparison of Deformation and Stress Distribution Patterns in Edges of 12.5mm deep versus 50mm deep Ps Sealant on Extension (9)

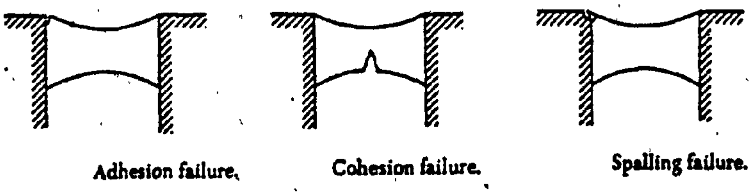

Adhesion failure. Cohesion failure. Spalling failure.

Figure 7 - Types of Failure (2)

Adhesive failure is characterized by the loss of bond between the sealant material and its substrate as illustrated in Figure 7. Cohesive failure occurs within the body of the sealant, and is dependent on the type of sealant and the rate of applied stress. The substrate may fail by spalling off those edges which are under the highest degree of stress (e.g. Fig. 6). If the cohesive strength of the sealant is greater than that of the substrate, the substrate will fail. The deposition of foreign particles on the surface of an extended sealant eventually abrades the surface upon repeated cycles of extension and contraction. The sealant is progressively reduced and eroded to the point that it may fail.

2.6 Sealant Classification and Properties

2.6.1 Classification

There are various ways in which sealants may be classified. Gjelsvik proposed a wide-ranging comprehensive classification of jointing materials, in which sealants are divided into eight sub-groups, according to their end use, as shown in Table 2, and further subdivided by type, in consideration of the mode and method of application (3).

Damusis (10) classifies sealants according to their formulation, viscosity, and mode of application. Essentially, it is elastic type sealants which are classified as being either one or two component formulations. One component sealants do not require premixing, but have a limited shelf-life because the

SEALANT TYPE	SEALANT CHARACTERISTIC
Rapid hardening	-Wood sash putties
	-Metal sash putties
Plastic glazing compounds	-Plastic glazing compounds, knife grade, one-part
	-Plastic glazing compounds, knife grade, two-part
	-Plastic glazing compounds, gun grade, one-part
	-Plastic glazing compounds, gun grade, two-part
Skin-forming plastic sealants	-Standard quality gun grade skin-forming plastic sealants
	-Standard quality knife grade skin-forming plastic sealants
	-Glazing quality gun grade skin-forming plastic sealants
	-Glazing quality knife grade skin-forming plastic sealants
Non-skinning plastic sealants	-Non-skinning plastic sealants, gun grade
	-Non-skinning plastic sealants, knife grade
Tough plastic sealants	-Standard quality gun grade tough plastic sealants
	-Glazing quality gun grade tough plastic sealants
	-Narrow joint gun grade tough plastic sealants
Thermoplastic sealants	-Hot-poured thermoplastic sealants for horizontal joints in horizontal construction
	-Thermoplastic sealants, hand applied at slightly elevated temperatures
Strip sealants	-Standard quality non-drying plastic strip sealants
	-Standard quality partly cured plastic/elastic strip sealants
	-Glazing quality partly cured plastic/elastic strip sealants
	-Standard quality thermoplastic sealants
Elastic sealants	-Standard quality two-part gun grade elastic sealants
	-Glazing quality two-part gun grade elastic sealants
	-Standard quality one-part gun grade elastic sealants
	-Glazing quality one-part gun grade elastic sealants
	-Traffic bearing two-part gun grade elastic sealant
	-Traffic bearing one-part gun grade elastic sealants
	-Traffic bearing two-part cold poured elastic sealants

Table 2 - Classification of Sealants for Building Construction (3)

moisture sensitive curing agent, which is pre-blended with the base material, is often susceptible to premature curing. Two-component sealants require mixing of the base material and the curing agent, thus premature curing is not a problem and the sealant components may have an extended shelf-life. Blending permits adjusting the curing time, pot life (in mixing bowl), and physical properties.

One- and two-component sealants may be subdivided into self-leveling and non-sagging types, the former are used in horizontal joints, whereas the latter are used for vertical joints. Self-leveling sealants are inherently less viscous than non-sagging types, and tend to more effectively wet, and hence adhere to, the surface of the substrate. Non-sagging sealants used in vertical joints are required because less viscous sealants tend to flow out of the joint.

Sealants my be further classified according to their mode of application. They may be: gun grade, suitable for use with a gun-type applicator; knife grade, capable of being applied with a putty knife or spatula. Gun grade sealants are less viscous than knife grade sealants.

Sealants may also be classified according to their main chemical binder. The principal binders used in sealant formulation are listed in Table 3, in order of their capability to recover from elastic deformation.

Degree of Recovery	Sealant Binder
- High-recovery group	silicones urethanes
- Moderate-recovery group	polysulphides polymercaptans
- Low-recovery group	chlorosulphonated polyethylene acrylics polychloroprenes
- Very low-recovery group	butyl mastic and tapes polyisobutylenes

Table 3 - Classification of Sealant Binders (10)

2.6.2 Sealant Properties

The properties of sealants are dependent on the chemical and physical nature of the polymer building blocks (10). The main factors determining the properties of cured sealants are:

1) shape and symmetry of polymer chemical groups
2) ratio between: rotating flexible segments
and
cohesive rigid groups

3) ratio between: amorphous blocks
and
crystalline blocks,
4) ratio between: linearity
and
crosslinking

The melting point and degree of softness of a sealant binder depends on the cohesive energy (i.e. intermolecular forces) of the chemical groups and their freedom of rotation around the bond axis. Generally, polymeric structure linked with aromatic groups tend to have higher melting points, since aromatics contribute cohesive energy to the system.

In consideration of the symmetry of the molecule, it may be said that lack of symmetry enhances the distortion amplitude of vibrating polymeric segments upon heating, resulting in lower melting or softening points for molecules of low symmetry and correspondingly higher values for those molecules with a high degree of symmetry. It follows then that the chemical groups with a high degree of rotational freedom tend to have lower melting points than those with more restrained linkages.

The cross-linking of polymer chains is the chemical characteristic which imparts elasticity to a substance; high molecular weight linear polymers cause viscous flow. Sealants are viscoelastic materials which demonstrate both elastic and viscous behaviour. A purely elastic material will, upon removal of an applied stress, return to the original shape, whereas a viscoelastic material will exhibit a certain amount of viscous flow during stressing, which permanently deforms the substance.

Properties of sealants are characterized by chemical and physical tests, which permit not only the quantification of certain properties of a particular material, but also direct comparison between the various sealants offered on the market. Properties of various sealants are given in Table 4.

In terms of performance, sealants are often graded according to their capacity for movement, cost, ease of application and joint preparation, and other criteria, as presented by Fisher (11) in Table 5.

2.7 Polyblending and Sealant Polyblends

Polyblending is the physical blending of two or more polymers. The usefulness of polymers can be considerably increased by polyblending carefully selected polymers in appropriate proportions, such that the end product has more desirable properties than those of its components. The combining of two or more structurally dissimilar polymers is of commercial interest due to the potential of developing materials to meet the specific functional needs in industry. Curing time, durability, mechanical performance, or other properties may be altered to suit industrial requirements;

cost reductions are possible through suitable selection of materials without sacrificing the inherent properties of the functional polymer (12-13).

Most polymers are incompatible with each other, so that blending two polymers usually leads to a class of materials whose properties are due to the presence of two phases. This does not imply undesirable properties, but, in fact, the occurrence of synergistic effects which may yield superior properties within the polyblend compared to those of either component.

The properties of polymers are changed by polyblending because the macromolecular environment of the polymeric matrix is modified; bond energies and chain flexibility between molecular groups and blocks are altered due to adhesion and interaction between distinct polymeric phases. Hence phase morphology and adhesion are important considerations in polymer blend technology since they critically influence many properties and subsequent uses of the end products.

Polymers may also be blended with particulate fillers or extenders, which may alter the properties of the base polymer as would polyblending. The mechanical properties of these blends are dependent on the moduli and the quantity of the individual components in the blend. Hence in two-phase, polymer-particulate systems, where a rigid high modulus phase is incorporated into a lower modulus, such as a polymer, the modulus of the composite is increased in some

PROPERTIES	BUTYL SEALANT	ACRYLIC SEALANT	POLY-SULFIDE	SILICONE	POLY-URETHANE
Tack free time @75F 250° / R.H.	2-4 hr	2-8 hr	12-48 hr	2-4 hr	12-48 hr
Cure time 6mm x 6mm (days)	120	30	60	5	30
Tensile strength (kPa)	70-140	275-415	690-1380	415-1040	1730-3450
Elongation	25%	25-60%	150-200%	100-200%	300-450%
Modulus @100% elongation	(NR)	(NR)	75-100	40-80	30-80
Shore A initial	10-18	20-40	30-45	25-35	30-50
Recovery after 100% elongation	15	20	45	83	90
Continuous service range (deg. C)	-30 100	-23 100	-40 120	-70 200	-50 135
Water immersion properties	Fair	Fair	Good	Good to Fair	Fair to Good
Dilute acid resistance	Very good	Fair	Very good	Good	Good
Dilute alkali resistance	Fair	Fair	Good	Fair	Very good
Solvent resistance	Poor (NR)	Good	Excell.	Excell.	Excell.
Aging properties	Good	Very good	Very good	Excell.	Excell.

Table 4 - Sealant Properties (2)

SEALANTS	ADVANTAGES	DISADVANTAGES
Butyl (±7.5% Movement Capacity)	Good adhesion Good water resistance Good color stability Little surface prep Caps neoprene gaskets	Slow curing High shrinkage Low recovery Relatively soft
Solvent-based Acrylics (±7.5% to ±12% Movement Capacity)	No primer required Excellent adhesion Excellent UV resistance Good chemical resistance Non-staining Tough curing	18mm maximum width Poor recovery Strong curing odor Poor water resistance Slow curing
Polysulfides (±25% Movement Capacity)	Good UV/water resistance Won't stain masonry Fast through cure Good adhesion/durability Broad color range	Slight curing odor Less UV resistance/recovery than the following Primers for porous surfaces
Urethanes (±25% Movement Capacity)	Excellent UV/ozone/tear/chemical resistance Excellent recovery Little shrinkage Joints up to 150mm wide 20-30 year life	Light colors can discolor Poor water immersion resistance Surface priming required
Silicones (±25% to ±50% Movement Capacity)	Excellent UV/ozone/heat resistance No shrinkage 20-30 year life Excellent recovery Non-staining	Critical surface preparation Slight curing odor Dirt pickup Concrete/aluminum adhesion difficult

Table 5 - Sealant Comparison (11)

proportion to the volume fraction of the filler added.

The behavior of these composites depends not only on the individual properties of the two components and on their relative proportions, but also on the size, shape, and state of agglomeration of the minor component, and on the degree of adhesion between the filler and the matrix (15).

Particulate phases are usually referred to as fillers, or if the interphase adhesion is high, reinforcing fillers. Interphase adhesion or reinforcing is brought about by chemical or physical bonds which develop between the filler and polymer. It has also been shown that there exists a correlation between reinforcement and specific surface area of the fillers (15). Reinforcement begins when particles have greater than 50 m^2/g of surface area, which corresponds to a spherical particle having a diameter of 500A. This is the same order of magnitude as the distances between crosslinks, and consequently may affect the manner in which the polymer chains behave under mechanical stress.

Sealants are polymer based substances to which have been added compounding agents such as : fillers, extenders, pigments or plasticizers, and may or may not be a polyblend depending on the nature of the agents added. Sealants behave as particulate-polymer systems, where the polymer phase may also be a polyblend.

3. LIGNIN AND LIGNIN-ELASTOMER SYSTEMS

3.1 Characterization and Isolation of Lignin

Lignin is a relatively abundant renewable polymer material possessing physical and chemical characteristics which potentially render it a suitable blending agent for various polymeric substances. Of appreciable importance is the occurance and function of lignin in nature, its physical and chemical structure and properties, and the methods by which lignin is isolated on an industrial scale.

3.1.1 Sources, function and structure of lignin

Lignin is one of the three major chemical systems in wood. The relationship between the chemical components is illustrated in Figure 8, which indicates that extraneous substances may account for five per cent (5%) of the weight of dry wood, lignin twenty-five per cent (25%), and polysaccharides (holocellulose) seventy per cent (70%). Holocellulose is made of both cellulose (50% by weight of wood) and hemicellulose (20% by weight of wood), high molecular weight carbohydrates, the latter of which is a mixture of shorter chain polysaccharides (16).

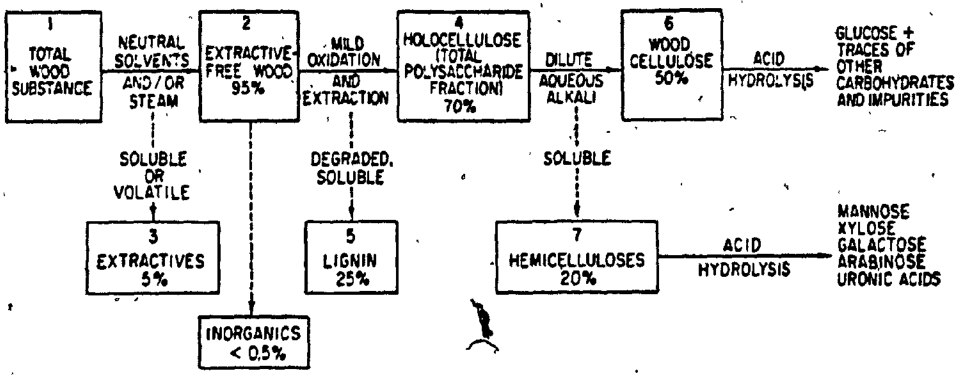


Figure 8 - The chemical components of wood (16)

These substances combine to form the components of wood which is made up of elongated cells (1-7mm in length). The lignin network is concentrated between and in the outer layers of the wood cell. It is this network which gives wood its structural rigidity, by stiffening and holding the cells together. Although the function of lignin is clearly understood, its chemical makeup is more difficult to define. Essentially it is the chemical characteristics of lignin which permit it to function as a binder for the cellulosic fibrillar structure of wood.

Lignin is a highly branched, randomly structured, three-dimensional polymer consisting of phenylpropane units held together by ether and carbon-carbon bonds. Consequently, lignin is totally amorphous in structure (no melting point and softens at 70-110°C), has a strong absorption capacity (surface area: 180 m^2/g). The molecular weight of isolated lignin (opposite of protolignin or in situ lignin) ranges from 1000 to 12000 depending on the extent of chemical degradation during isolation. Although the chemical structure of lignin is extremely complex and difficult to characterize, several speculative structures have been postulated, one of which is shown in Figure 9.

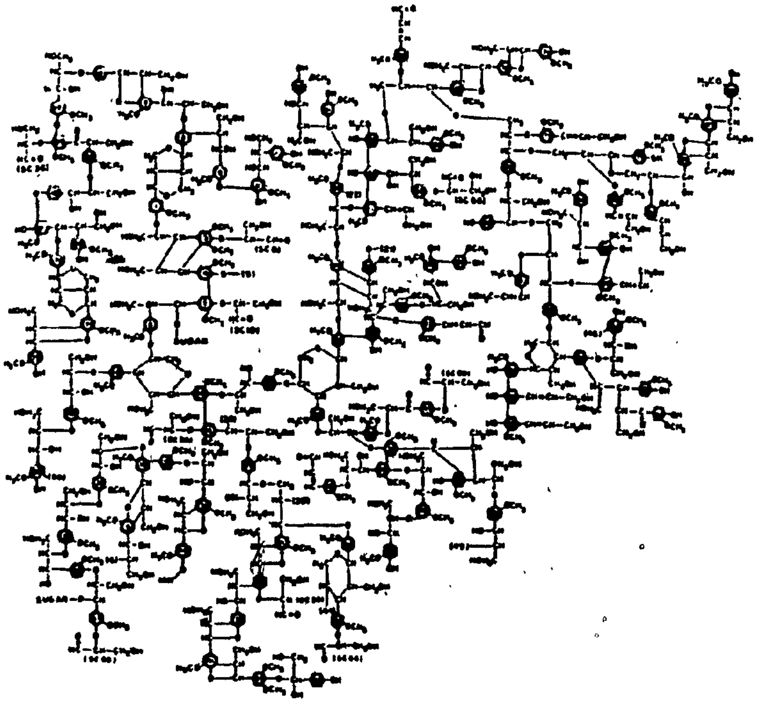


Figure 9 - Softwood lignin model designed by computerized evaluation (17)

3.1.2 Isolation of lignin for technical purposes

There are a number of methods by which lignin may be isolated both in the laboratory and in industry. It is the pulping process industry, however, which provides the greatest source of lignin (20×10^6 tons in the U.S. in 1980 (18)), and consequently lignin derived from this industry is readily available at low cost, as seen in Table 6.

Source	Material	Price/Pound (1980, $U.S.)
Pulping Industry	Kraft lignin	0.10 - 0.15
	Lignosulphonates	0.03 - 0.07
Petroleum	Crude oil	0.15 ($35/bbl)
	Petroleum sulphonate	0.50 - 0.70
	Polyacrylamide	0.80 - 1.50
	Polyacrylate	0.60 - 1.40
	Polyalkylphosphate	1.50 - 2.50

Table 6 - Prices of lignin in comparison to chemical raw materials (18)

The major methods used to pulp or delignify wood are the alkali process and the sulphite process (19).

The sulphate or kraft process and the soda process are the two principal alkaline pulping methods. Sodium hydroxide is the principal cooking chemical in both processes, while in sulphate pulping, sodium sulphide is an additional active pulping component. Wood, introduced into a digester in the form of wood chips, is delignified by the action of the cooking chemicals which dissolve the lignin into black liquor, leaving a residue of pulp. Normally, the lignin in kraft black liquor is used as a source of heat for the manufacture of steam, which is subsequently utilized in the industrial production of paper. However, the dissolved alkali lignin can be precipitated by acidification of the solution, yielding a brown amorphous powder which may be referred to as Kraft lignin.

In the sulphite process, lignin in wood is converted into soluble lignosulphonates by the action of bisulphites and free sulphurous acid at 130 to 140°C. The cooking process is completed in a digester, as above, and the wood chips are impregnated with the acid sulphite solution. After sufficient time, delignification occurs, breaking down the bonds between the units of the lignin macromolecule. The sectioned molecules are in the form of soluble lignosulphonates.

3.2 Utilization of Lignin for Polymeric Products

3.2.1 Introduction

The present and future utilization of lignin is an extensive and increasingly important field (20). Reasons for this development can be seen in the increasing appreciation of renewable raw material for organic chemical by-products. Total market volume for non-fuel uses was estimated at more than 7.5×10^5 t/yr. for 1980, and projections for the year 2000 could total 6.25×10^6 t/yr. (non-fuel uses) representing an eight-fold increase in demand (20).

Technical lignins and modified products have found a wide range of applications as shown in Table 7. It is considered that the most important future application will be based on the adhesive properties of lignin products for thermosetting resins and phenols (17). Wood composites, such as plywood, particle board and fibre boards, have been made using lignin and phenol formaldehyde as the adhesive binders (21). The strength and durability characteristics of these new wood composites were comparable to conventionally glued products, with lignin replacing 70% of the phenolic binder. This represents a saving in cost of expensive phenolic polymer.

Dispersants for:	Carbon black Insecticides Herbicides Pesticides Clays Dyestuffs Pigments Ceramics
Emulsifiers, stabilizers, extenders for:	Soils Road surfaces Asphalt Waxes Oil in water Rubbers Soap Latex Fire foam
Metal sequestrants for:	Industrial water Agricultural micronutrients
Additives for:	Drilling muds Concrete Cement grinding Industrial cleaners Tanning agents Rubbers Vinylplastics
Binder and adhesives for:	Animal-feed pellets Printing inks Minerals Laminates Foundry cores Ores
Coreactant for:	Urea-formaldehydes Phenolics Furans Epoxides Urethanes
Others:	Protein coagulants Protective colloids in steam boilers Ion-exchange resins Oxygen scavenger Components in negative plate expanders for storage batteries

Table 7 - Utilization of alkali lignins, lignin sulphonates and modified lignins. (17)

3.2.2 Lignin-elastomer systems

There also exists a great potential for the use of lignin as a constituent within polymer-elastomer systems. Some synthetic elastomers, such as silicone rubber, have quite a high cost to volume ratio. The use of lignin, an abundant and relatively low-price substance, in a system with high-priced elastomers, would serve not only to improve properties, but to reduce final product costs as well.

The use of lignins in conjunction with elastomers is hampered by their performance deficiencies, which are related to both physical and chemical properties (18). Factors which contribute to these deficiencies include:

1) The structural complexity of lignin
2) The tenacious resistance of lignin to any kind of degradation
3) The inherent variability of lignin , which is aggravated in isolation (22)

These significant factors have not served as a deterrant to continuing research however, which indicates the optimism of researchers with respect to overcoming these difficulties.

Reinforcing fillers such as carbon black are widely used for reinforcing the mechanical strength of polymer-elastomer systems. While many reinforcing agents can be dry milled into elastomers, this method cannot be utilized with lignins. Attempts to dry mill lignin into styrene-butadiene rubber (SBR) showed almost no reinforcing effect. This can be attributed to the fact that lignin particles, under the influence of heat generation, coalesce by hydrogen bonding and thus cannot be finely dispersed into the rubber (18).

Lignin must be incorporated into rubber by latex masterbatching in order that its reinforcing properties can be realized. To prepare a lignin-rubber masterbatch, it is usual to dissolve the lignin in an aqueous alkali, then add the alkali-lignin solution to the rubber latex. This mixture is heated and co-coagulated by running the mixture into an acid solution with adequate agitation. The reinforcing characteristics of a lignin in a masterbatch can be affected by several variables:

1) Concentration of the alkaline-lignin solution and the rubber latex
2) Concentration of the coagulating solution
3) Temperature of the ingredients
4) Order of addition of the ingredients
5) Rate of agitation during co-coagulation (23)

Lignin precipitation temperature and particle size also affects its reinforcing characteristics (Fig. 10). The tensile strength of SBR reinforced with purified Kraft lignin is very sensitive to the precipitation temperature at which the lignin was isolated. When the particle size of lignin is reduced below a critical limit (which gives a surface area of 45 m^2/g or more), the lignin undergoes excessive coalescence and thus loses its reinforcing ability within elastomers. The type of lignin used can affect results, as hardwood technical lignins are inferior to their softwood counterparts as dispersants, emulsion stabilizers and elastomer reinforcing agents (18).

Keilen et al. (24-26) have demonstrated that lignin (sulfate process) coprecipitated with natural, styrene-butadiene (Fig. 11), nitrile, or Neoprene (Fig. 12) rubbers can yield tensile strengths comparable (at the same volume loadings) to carbon blacks. This could potentially consume large quantities of polymeric lignin for commercial markets.

To improve the reinforcing characteristics of lignin, various modifications have been proposed. Raff and Tomlinson (27) observed that the reinforcing ability of alkaline lignin, for GR-S rubber, was greatly enhanced with increasing oxidation of the lignin prior to coprecipitation with the latex. Lignin rubber masterbatches that are at least partially treated with a diisocyanate can exhibit improved hot tensile strength, abrasion, and reduced torsional hysterisis (28). Heating of lignin synthetic rubber masterbatches for 5-40 minutes at 150-175°C tends to improve abrasion resistance and lower torsional hysterisis (29).

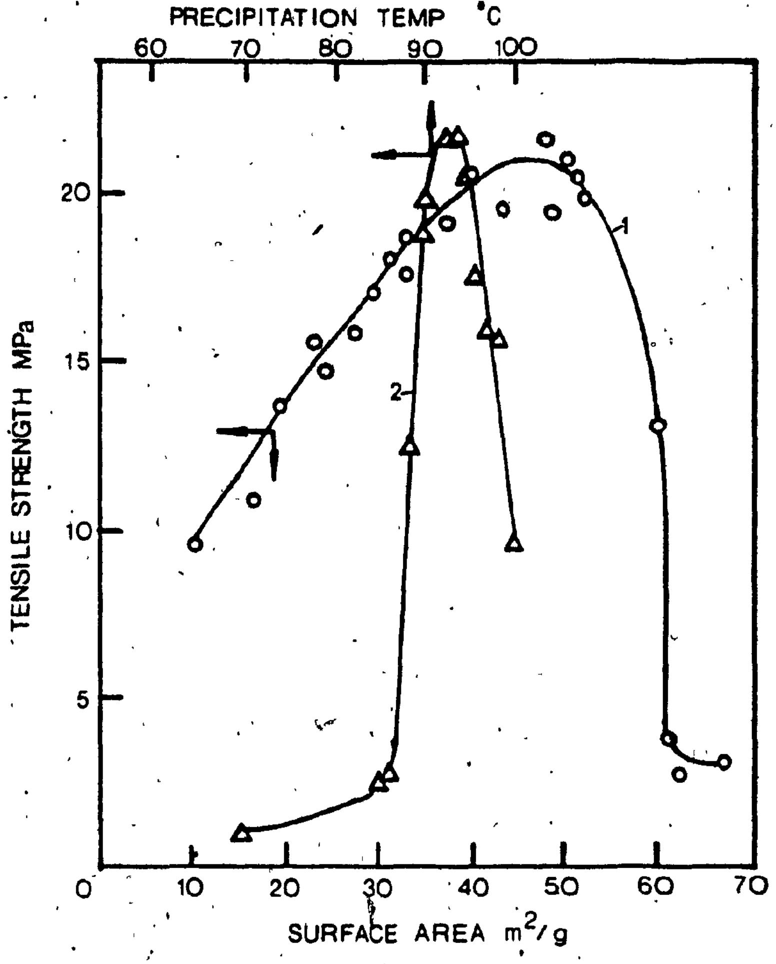


Figure 10 - Relationship between tensile strength of reinforced SBR and surface area (1); between tensile strength and precipitation temperature (2) of KRAFT lignin (18).

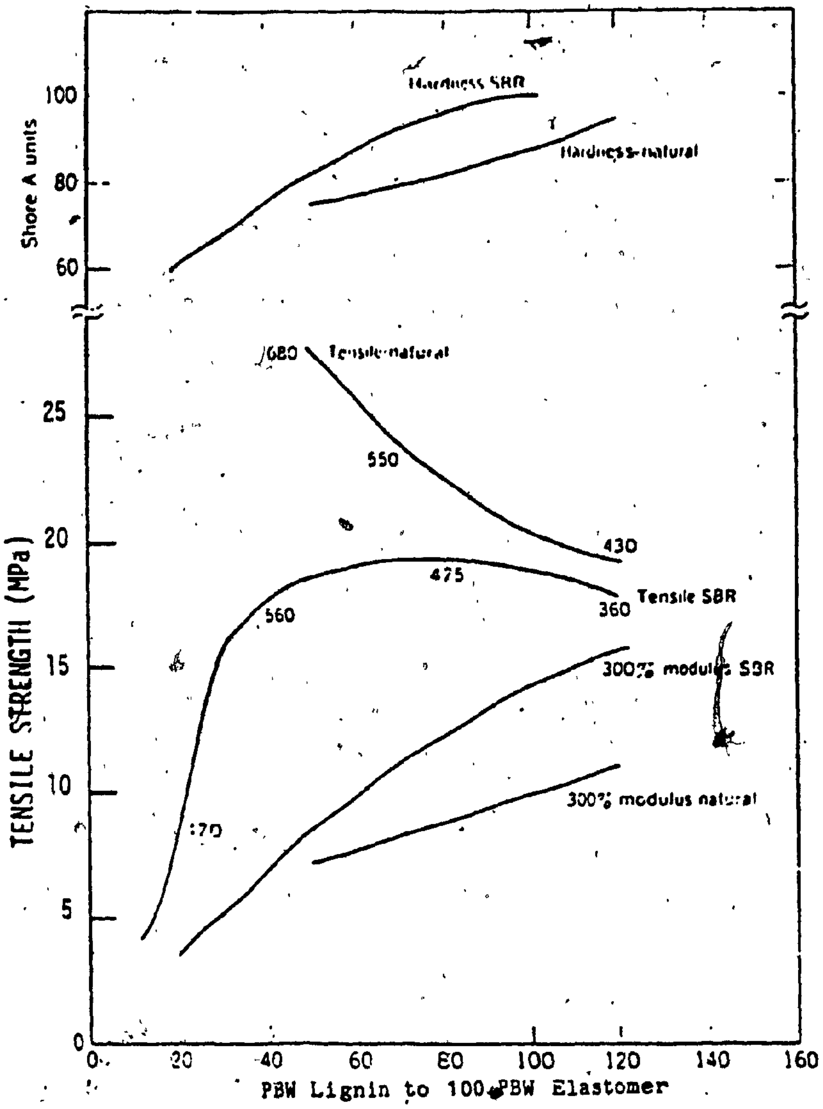


Figure 11 - Vulcanizate properties vs. lignin loading for SBR and natural rubbers. Numbers on tensile curve represent ultimate elongation (29)

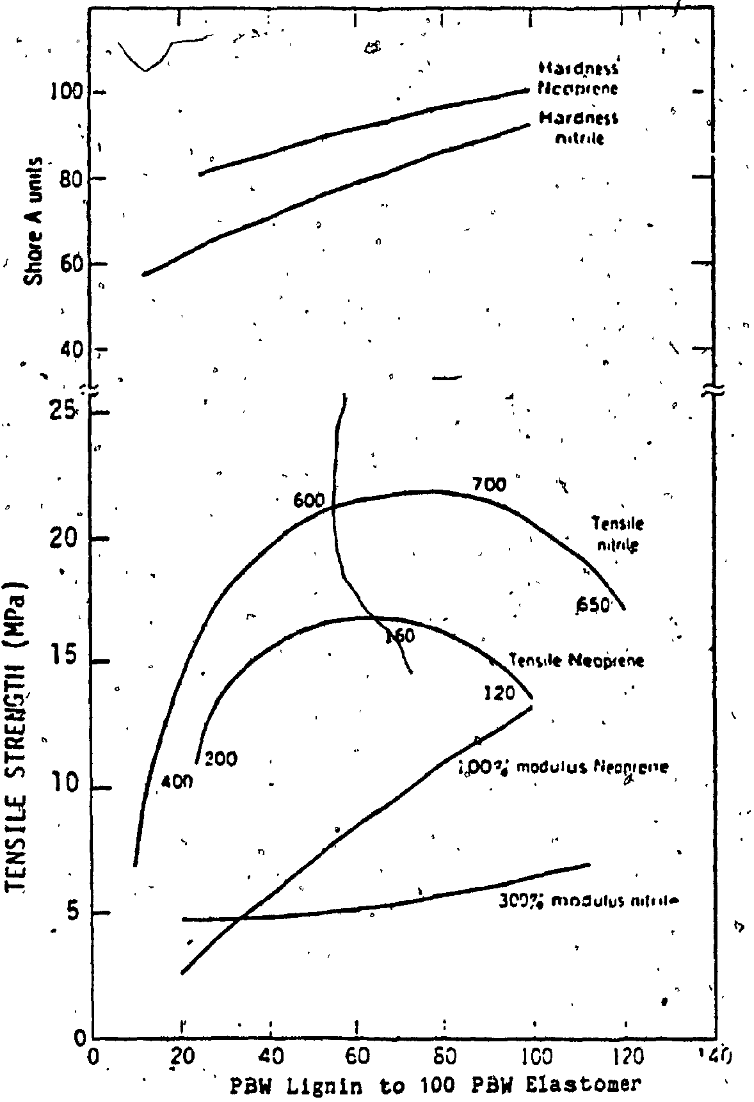


Figure 12 - Vulcanizate properties vs. lignin Loading for nitrile and Neoprene rubbers. Numbers on tensile curve represent ultimate elongation (29)

The polyblending of silicone rubber sealants with lignin does not require the involved process of latex masterbatching. Recent investigations by Beznaczuk (30) utilized the uncured silicone sealant (building construction grade), based on polydimethylsiloxane (PDS), and Kraft lignin, polyblended by mechanical mixing only. 12.5mm butt joint specimens (5, 10, and 15% lignin by weight) were cast between substrates of wood, aluminum and mortar. After a 14-day cure, specimens were exposed to laboratory control conditions (24°C, 35% R.H.), accelerated weathering (4 cycles daily between -30°C and +30°C for a total of 400 cycles), and natural weathering conditions in a relatively polluted location of downtown Montreal. In comparison with neat PDS sealants, there were two cases where tensile testing revealed that higher strengths and/or toughness were obtained with polyblending (Table 8).

The first case was that of the 5% lignin polyblend on a mortar substrate in control conditions, where the toughness (area under the characteristic stress-strain curve) of this polyblend was twice that of its PDS counterpart. After accelerated and natural weathering, however, toughness of the polyblend decreased significantly to a level far below that of PDS.

The second case was that of the 5% lignin polyblend on an aluminum substrate. Both the control and the accelerated weathering specimens were very slightly tougher than their corresponding PDS specimens. As in the first case, after

SPECIMEN	SUBSTRATE	TOUGHNESS (MPa)		
		Exposure conditions		
		Control	Accelerated	Natural
PDS	Wood	0.23	0.14	0.17
PDS	Aluminum	0.04	0.01	0.08
PDS	Mortar	0.12	0.05	0.05
PDS-lignin (5%)	Wood	0.04	0.01	0.01
PDS-lignin (5%)	Aluminum	0.04	0.01	0.01
PDS-lignin (5%)	Mortar	0.22	0.04	0.02
PDS-lignin (10%)	Wood	0.02	0.01	0.03
PDS-lignin (10%)	Aluminum	0.01	0.01	0.01
PDS-lignin (10%)	Mortar	0.09	0.04	0.02
PDS-lignin (15%)	Wood	0.02	0.02	0.01
PDS-lignin (15%)	Aluminum	0.01	0.01	0.02
PDS-lignin (15%)	Mortar	0.07	0.03	0.00

Table 8 - Toughness of PDS-Lignin polyblends (30)

natural weathering the toughness value for this decreased (down to 20% of the PDS toughness).

In both cases, all tensile testing failures were adhesive, indicating that lignin may in fact be a suitable reinforcement of silicone sealants if the adhesive bond to the substrate can become more reliable. One possible solution is the use of a primer on substrates prior to sealant application. Since control specimens indicated a higher toughness than weathered specimens, the loss of adhesive strength can be partially attributed to various weathering factors (U.V. light, wet/dry cycles, pollution, etc.).

Lignin has the potential for providing various other properties to elastomers besides mechanical strength reinforcement. Murray and Watson (31) have observed that lignin acts as a stabilizing agent, against oxidation, for SBR. De Paoli, Furlan and Rodrigues (32) investigated the use of lignin from sugar cane bagasse as a photostabilizer for butadiene rubber. The photostabilizing effect of lignin was further enhanced by the addition of dioctyl-p-phenylenediamine, and can be compared to commercially used stabilizers.

Thus the potential for widespread commercial use of lignins in conjunction with elastomers exists if researchers can demonstrate that all performance requirements can be satisfied. Lignin, for example, can compete actively with carbon black as a reinforcement for rubber if hardness can be reduced and modulus improved. This and other industrial uses of lignin-elastomer systems would prove to be beneficial worldwide, giving a useful function to a by-product of the wood pulping process.

4. EXPERIMENTAL PROGRAM

4.1 Introduction

4.1.1 Purposes and objectives

The experimental research program has a dual purpose. It first intends to aid the development of more resilient and economical sealants for the building industry. Secondly, it is hoped that further research in the area of lignin-polymer systems will cultivate new markets for lignin, a low-cost renewable material which is readily available from industry.

To be purposeful, then, the main objectives of the research program are to characterize the properties of lignin polyblended sealants in terms of their morphology, curing characteristics, thermal behavior, as well as their durability and resilience as measured by their cohesive and adhesive strength in tension.

To achieve these objectives, the research program was set in two parts, the initial portion being a preliminary program to select those sealants which display the greatest potential for improving their characteristic properties from lignin polyblending. The scope of this program is detailed in section 4.1.3. The second part of the program entails completing more detailed work to characterize the properties of selected polyblends, including the use of differential scanning calorimetry, light and scanning electron microscopy, curing tests, and tensile tests. The detailed program is described in section 4.1.4.

4.1.2 Materials

The sealants used as the matrix for polyblending were representative of the five most important generic sealants presently available on the market. They are:

1) Silicone (S) - one part self-curing sealant (MULCO - Silicone 25 years)
2) Polyurethane (PU) - one part self-curing, non-sag sealant (MULCO - Maxiflex)
3) Polysulfide (Ps) - one part self-curing, non-sag sealant (MULCO - GC-9).
4) Butyl (B) - self curing rubber-based caulking (MULCO - Butam 15 years)
5) Acrylic (A) - one part self-curing sealant (MULCO - Mulco 20 years)

All sealants were obtained from Mulco of St. Hubert, Que., in self-contained cartridges of 300 ml.

Kraft lignin (L), obtained from Domtar of Cornwall, Ont., was the base polymer with which each of the sealants were blended. The lignin was formed by the sulfuric acid precipitation of black liquor, itself derived from the pulping of various hardwoods (maple, beech, elm). The pH of the precipitate was adjusted with carbon dioxide to a level between 6 and 7.

4.1.3 Preliminary program

The preliminary program served to evaluate the viability of blending lignin with silicone (S), polyurethane (PU), polysulfide (Ps), butyl (B), and acrylic (A) sealants, thus narrowing the field of research to those sealants whose functional properties were enhanced with lignin polyblending.

The evaluation was based on the adhesive and cohesive characteristics of each specimen, determined by direct tension testing of standard size sealant specimens to failure. Samples were evaluated by comparing tension test results obtained from blended and unblended specimens. The discrete phase of the blend comprised 10 parts by weight of lignin and the matrix phase comprised 100 parts by weight of sealant. Hence the lignin-sealant (eg. L:S) blend ratio was 10:100 (hereafter referred to as a blend ratio of 10%).

Three specimens were cast between three standard size substrates of aluminum (Al), mortar (M), and wood (W) for each set of blended and unblended (control) samples, representing a total of 90 samples cast in all. The experimental procedure used to prepare the specimens is outlined in section 4.2.1. The tension testing procedure is outlined in section 4.2.2.4. Results of the preliminary testing program are detailed in section 5.1. Those sealants whose properties were enhanced with the addition of lignin were tested in a more detailed program, oulined in the next section.

4.1.4 Detailed program

The detailed testing program consisted primarily of tension testing of lignin-polymeric blends. Accordingly, three series of six specimens were cast between aluminum, mortar and wood substrates over six different blend ratios for each generic sealant tested. Hence 324 specimens were cast for each sealant tested, 108 per series, and 36 specimens for each substrate in a series. The three series, a control (C), natural aging (NA), and accelerated aging (AA) series, were cast to accommodate the requirements of the durability testing program described in section 4.2.2.5. The specimens were formulated with lignin-sealant blend ratios of 0, 5, 10, 12.5, 15, and 20%.

The blends were prepared as described in section 4.2.1, and then subjected to tension testing as outlined in section 4.2.2.4.

The remainder of the detailed program was used to investigate the morphology, curing, and thermal characteristics of lignin-polyurethane polyblends, and is described in sections 4.2.3.1 to 4.2.3.3 respectively. The utility of each test method in evaluating and characterizing polymers and polymer blends is described, and the apparatus and testing procedures used in performing each test are reviewed.

4.2 Experimental Procedure

4.2.1 Tensile testing specimen preparation

Each specimen was prepared by first assuring the size, configuration and cleanliness of the substrates. The substrates were placed in specially prepared casting plates such that specimens could be cast in lots of six to twelve, depending on the length of the plate. The mixture was formulated, mixed thoroughly by hand, and placed in the mold formed by each pair of appropriately spaced substrates. The details of each step in the preparation of the specimens is given below.

4.2.1.1 Preparation of substrates

There were three different substrates used to prepare specimens: aluminum, mortar, and wood. It is considered that these substrates are representative of the majority of building materials which generally come into contact with sealants. The size and configuration of both the substrate and the specimen were chosen according to CGSB CAN2-19.0M77, and are depicted in Figure 13.

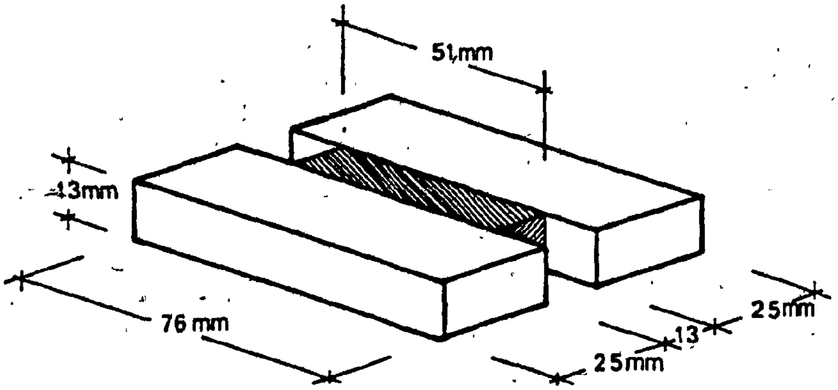


Figure 13 - Size and configuration of specimens

4.2.1.1 a) aluminum -- The aluminum bars were obtained from local metal distributors in lengths of ten feet, cut to size, and burrs along their edges were removed by filing. Visible dirt and grime or adhered material were removed using an abrasive pad (steel wool), soap and water. To further ensure as clean a surface as possible, the bars were placed in a solution of sulphuric acid and sodium bichromate at 70°C for three minutes. Once removed from the solution, the bars were thoroughly rinsed in water and wiped dry with paper towels, after which they were stored for subsequent usage in specimen preparation.

4.2.1.1 b) wood -- The wood substrates were made from California redwood strips (of 13x26mm nominal dimension), obtained from local wood distributors and cut to the specified length. Prior to use, the wood substrates were brushed free of surface dust in order to prevent surface contamination between the substrate and the polyblend.

4.2.1.1 c) mortar -- The mortar substrates were prepared from mixing 1 part high early strength Portland cement (CSA A5) and 2 parts by mass of clean, well graded fine aggregate (ASTM C33) in sufficient water to produce the desired consistency, as specified in the mortar consistency test (ASTM C109). The mortar was placed in steel molds of specified dimensions and allowed to cure at room temperature (23±2°C) for one day in moist air (95-100% R.H.), and six days (minimum) in water at 23±2°C. The mortar substrates were then removed from the water and were oven dried to constant mass at 104-110°C. Those mortar bars whose testing surfaces were found to have pits or cavities greater than 2mm were rejected. All remaining bars were stored for subsequent usage in specimen preparation.

4.2.1.2 Preparation of molds

Casting plates, fabricated in plywood, were made to accommodate six to twelve specimens as shown in Figure 14. The sealant bead was cast in the area between the two substrates, the width of which was gauged with wooden spacers. Prior to mounting the substrate bars and spacers onto the casting plate, the bottom of the plate was lined with wax paper, to prevent the sealant from adhering to the wooden plate, and hence to facilitate removal of the cured specimens. The end spacers were similarly prepared using adhesive cellophane tape. Having positioned the bars and spacers onto the plate, care was taken to ensure: proper alignment between substrate bars (parallel edges); correct mold dimensions as defined by the distance between pairs of spacers in a given specimen mold; and effective contact with the plate base, such that no visible paths could be detected through which a low viscosity sealant might flow. The specimens thus formed were prevented from moving by being jammed between wood blocks set at the end of each casting plate.

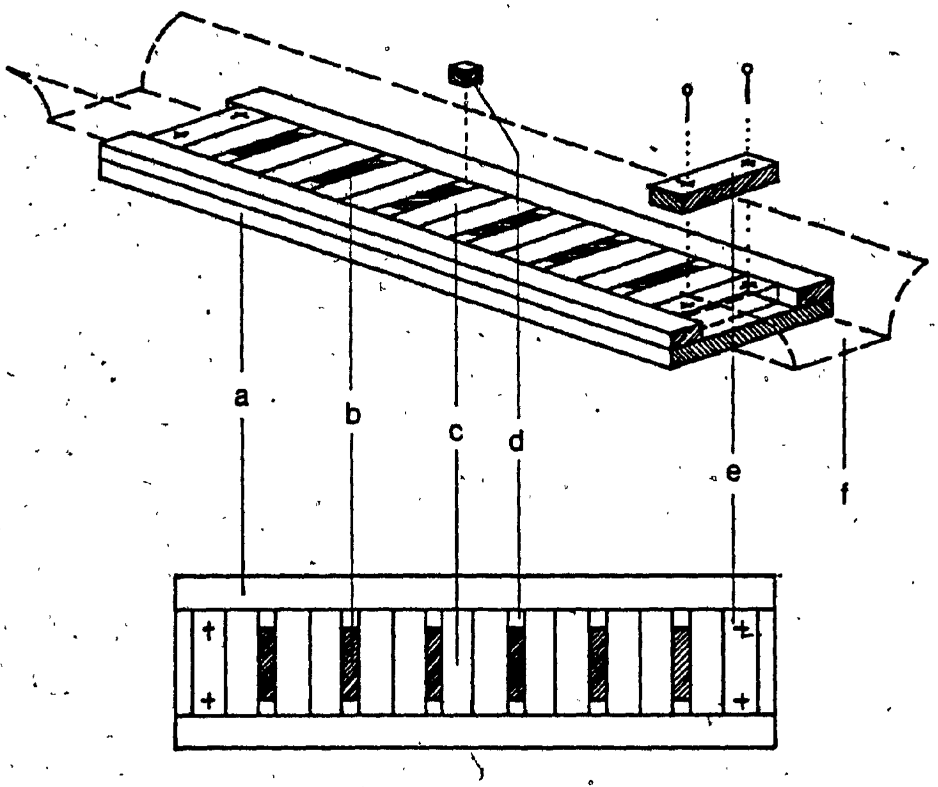


Figure 14 - Specimen molds (a) casting plate
(b) sealant bead
(c) substrate bar
(d) spacers
(e) end block
(f) lining paper

4.2.1.3 Preparation of polyblends

Depending on the number of specimens to be cast, a sufficient amount of sealant was placed in a pre-weighed mixing bowl and its mass measured and recorded. Having obtained the weight of the sample, a predetermined proportion of lignin powder, by mass of sealant, was weighed and mixed thoroughly by hand with a steel spatula. Rapid or uncontrolled mixing movement during blending was avoided as it was found to cause the formation of voids within the polymer matrix, a condition that is undesirable from the viewpoint of producing homogeneous specimens. Those specimens which, after the blends had set, were found to have visible voids or cavities, were rejected and replaced by newly batched specimens.

4.2.1.4 Casting of specimens

The specimens were cast at room temperature ($23 \pm 2^{o}C$) and relative humidity of 35%, and permitted to cure on the casting plates for a period not exceeding one week. The technique used to cast the specimens depended on the viscosity of the mixture. Less viscous polyblends were poured directly from the mixing bowl into the mold. A glass rod was used to ensure the blend touched and hence wetted all surfaces in the mold. More viscous polyblends were placed in the mold with a steel spatula, being careful to distribute the mixture evenly throughout the mold. Air pockets, voids or bubbles which may have formed were worked out with the aid of a spatula or glass rod. Excess mixture on either side of the substrate was removed by scraping it off with the steel utensil.

4.2.1.5 Curing of specimens

After the initial one-week curing period, the specimens were removed from the casting plate and classified in groups for either immediate testing or further curing. The minimum curing time was not less than that specified by the manufacturer. Those specimens requiring further curing were monitored regularly to check on the relative condition of their cure. When practical, the end spacers were detached from the ends of the beads, but retained in such a positioned as to ensure the specimens maintained the appropriate configuration during further curing. This permitted the more complete and rapid cure of the specimen. Curing times for the different specimen blends are given in Appendix 1.

4.2.2 Specimen testing

4.2.2.1 Microscopic testing

Obtaining the maximum information about the morphology of polymers requires the use of a variety of techniques, including the use of light microscopy as well as scanning electron microscopy.

4.2.2.1 a) light microscopy (LM) -- Reflected light microscopy is valuable for examining the texture of solid opaque materials. Furthermore, the presence and connectivities of polymer phases, hence the degree of miscibility, may be determined by direct visual confirmation, through the use of a reflected light microscope (33,34). Light microscopy requires a minimum of difference in refractive index between phases for contrast, and can be best obtained with differences in opacity or color (35).

Accordingly, a series of color as well as monochrome photomicrographs were made using a Leitz orthoplan light microscope with dark field incident light illumination. Magnifications of 20, 40, 60, 100, 120 and 300X were used to view the features of the polyblends. Surface and sectional area features of control and aged polyblends, having a L-PU blend ratio of 15%, were observed. Sectional specimens were prepared by slicing the sealant across its section with a razor blade. Results of these tests are presented in section 5.2.

4.2.2.1 b) scanning electron microscopy (SEM) -- SEM is increasingly being used in phase studies, because contrasts between phases can often be detected by changes in surface texture and topography, and SEM permits a considerable depth of field in comparison to those obtained using LM or transmission electron microscopy techniques (33,35).

In SEM analysis (Fig. 15), a fine beam of electrons is scanned across the surface of an opaque specimen to which a uniform covering of conductive material, such as gold, has been applied. Secondary electrons, back scattered electrons, or x-ray photons emitted when the beam hits the specimen, are collected to provide a signal used to modulate the intensity of the electron beam in a television tube, scanning in synchronism with the microscopic beam. Because the beam is small in comparison to the distances relative to the specimen, the images obtained from the SEM have a great depth of field, resulting in photomicrographs which have a natural, three-dimensional appearance (33,36).

An ISI SS-60 SEM was used to analyse lignin particles as well as various L-PU specimens. Photomicrographs were made of the control specimens having L-PU blend ratios of 0, 10, 15, and 20%.

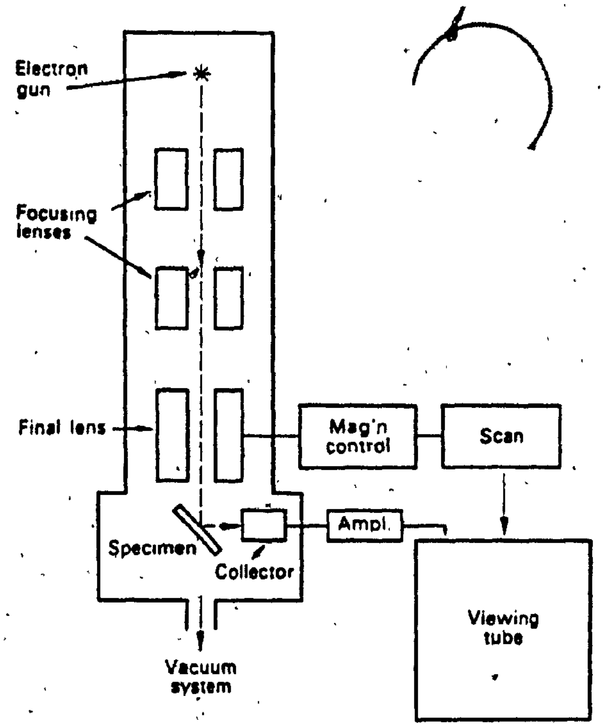


Figure 15 - Block diagram of scanning electron microscope (SEM) (35).

The effect of AA on L-PU blends having a 15% blend ratio was also investigated. All specimens were sputter coated with gold to suppress charging and increase electron emmission. Magnifications of 50, 500, 1500, 3000, 10000, and 15000X at a 10kV beam intensity were used to expose the surface conditions of L-PU blends. Lignin particles were scanned at magnifications of 3000, 9000 and 10000X. Results of SEM analysis are summarized with a series of photomicrographs in section 5.2.

4.2.2.2 Hardness testing

Cure within the body of an elastomeric sealant is the process which endows the sealant with its elastoplastic properties. The curing of elastomeric sealants usually involves the formation of cross linkages between polymer molecules, and advances inwards from the exposed surface. Hence body cure may first be detected as a hardened outer layer which overlays an uncured zone of sealant (37). With time the cure process proceeds through the sealant, and thus may be monitored by sequence hardness testing.

A testing program was devised to monitor the curing mode of L-PU blends. The hardness of the various blends was determined according to ASTM C661-70, using a Shore type A-2 durometer. The durometer is a device which measures the hardness of an elastomer by the indentation of a conical tipped hardened steel rod into the specimen being tested. The indentation hardness, measured on a scale of 0 to 100, is inversely related to the penetration of the indentor, and is dependent on the elastic and viscoelastic properties of the polymer blend.

Test specimens were made for six L-PU blend ratios varying from 0 to 20%. Each specimen was blended as described in article 4.2.1.3 and cast on aluminum plates (80x150mm) in brass frame molds having inside dimensions of 6x40x130mm.

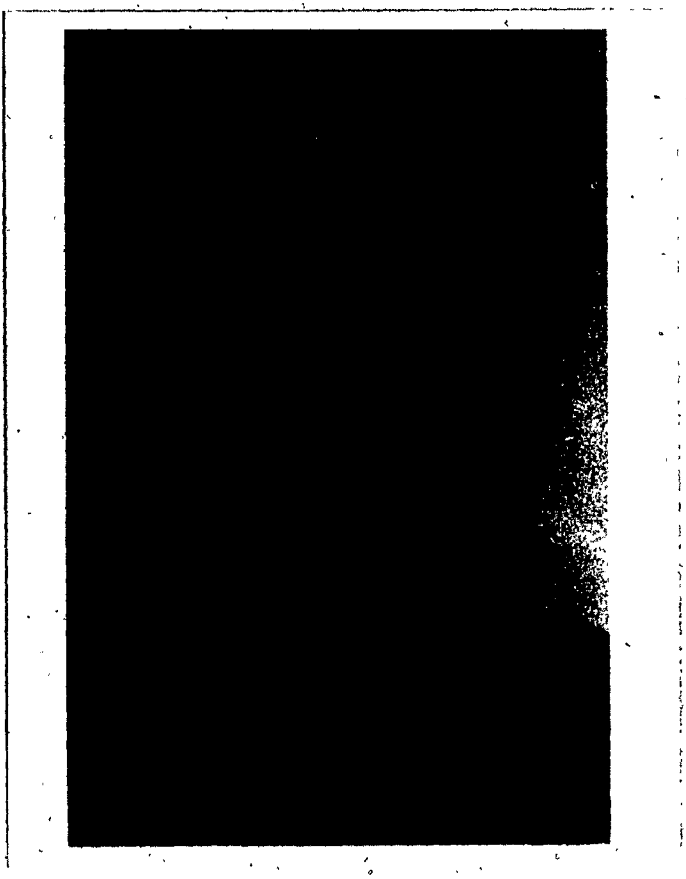


Figure 16 - Constant load operating stand with durometer used for sequence hardness testing.

An individual test consisted of placing the specimen in a lever-actionned constant load operating stand, to which was affixed the durometer, as shown in Figure 16. The action of the lever caused the specimen to come into contact with the indentor, such that values could be obtained from the durometer gauge. For each test sequence, hardness values were recorded at application of the weighed indentor, at 10 seconds, and at 60 seconds. The hardness at 10s provides an indication of the degree of cure at or near the exposed sealant surface, whereas the 60s reading indicates the degree of cure deeper within the body of the sealant.

The testing sequence was arranged such that the indentation hardness values were obtained at predetermined time intervals, enabling a more comprehensive plot of the values on a log time scale. At each specified time interval, three indentation hardness tests were performed on each of two specimens, totaling six tests for each blend ratio tested. The average value of the 10 second reading was plotted against a log time scale to illustrate the change in hardness with time. Results from the curing tests are evaluated in section 5.3, and the testing sequence and hardness data are given in Appendix 2.

4.2.2.3 Thermal testing

The most commonly used method for establishing compatibility in a polymer blend is through determination of the glass transition temperature in the blends versus that of the unblended constituents (35). The glass transition temperature (Tg) is the temperature at which the polymer changes from a relatively hard brittle material, to a softer more plastic material upon heating. On a molecular level, this represents a change from a more ordered to a less ordered arrangement of the molecular chains. Above Tg, the polymer has acquired sufficient thermal energy for isomeric rotational motion, or for torsional oscillations to occur about most of the bonds in the main chain which are capable of such motion (38). Constraints to motion can arise from the barrier to rotation, which in turn is raised by the magnitude of cohesive forces between the molecular chains.

The blend of two or more polymers alters the cohesive forces of the respective polymers in such a fashion as to cause a shift in the value of Tg. In the case of compatible polymer blends, a single Tg between the Tg's of the component polymers will occur, with a sharpness in transition similar to that of the components. In cases of borderline miscibility, two separate transitions between those of the constituents may occur (35).

The glass transition temperature may be determined by using a differential scanning calorimeter (DSC) in which the differences in heat capacity of a reference and sample material is analysed over a predetermined time-temperature program (33,35). Reference and sample specimens are placed in individual cells or pans which sit on a thermoelectric disc (as shown in Fig. 17). Heat is transferred through the disc and into both the reference and sample via the specimen pans, at a constant rate of heating. The differential temperature of the specimens is monitored by area thermocouples located on the underside of the disc beneath each specimen pan. Since the thermal resistance to the specimens is held constant, differential temperatures are directly proportional to differential heat flows. At Tg, the sample temperature remains constant until the heat of transition has been supplied, whereas the reference specimen continues to increase in temperature, causing the differential temperatures and hence a negative heat flow is observed in this region.

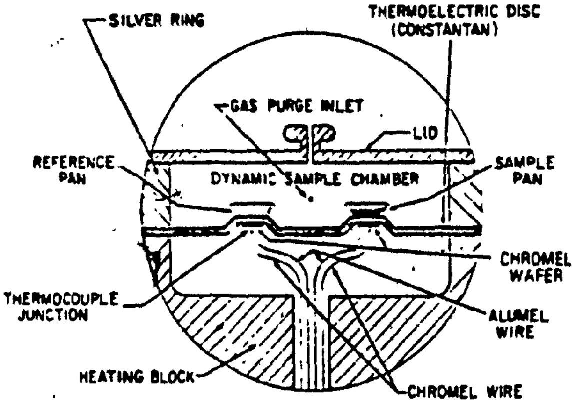


Figure 17 - DSC cell cross-section

A Dupont 910 differential scanning calorimeter (DSC) was used to analyse various L-PU blends according to ASTM 3418-8L. Control as well as NA and AA specimens of L-PU sealants having blend ratios of 0, 10, 15, and 20% were tested. Samples, whose weights varied from 17-25 mg, were placed in DSC cells at room temperature. The thermographs were determined between -100 and 200oC, at a heating rate of 20oC/min, and maintained in a nitrogen atmosphere provided by a gas flow of 50 l/hr.

The DSC analysis of lignin was also included in this test program, and results for all tests are summarized in section 5.4.

4.2.2.4 Tension testing

The Instron Universal Testing Instrument, model 1125, was used for tension testing. The machine is made up of three major systems: the load cell system, which measures and transmits the loading data to the recording system; the cross head drive system, which moves the load cell in a direction to cause loading and ultimately deformation of the specimen; the recording system, which receives the loading and extension data and plots the information on an automatic plotting device.

The load cell is mounted on the cross head frame as illustrated in Figure 18. The load cell exhibits very little deflection under an applied load, therefore the motion of the cross head alone may be used to determine the specimen extension. The moving cross head is operated by two vertical lead screws that are driven by a d.c. motor via a gearbox. The speed at which the cross head operates may be selected from ten different settings between 0.05 and 500 mm/min.

A specimen is attached to the load cell by a pair of tensile grips whose tips rest on the horizontal surface of each substrate, as illustrated in Figure 19. As the cross head drive system is activated, the cross head frame moves in the upward direction, causing tensile forces to develop along the sealant bead - substrate interface. The load cell measures the load and transmits the data to the control unit, which plots the data on a 250mm wide strip chart recorder, integral to the control unit. The rate of crosshead speed is related to the chart speed such that the load-strain data may be read directly from the chart. A 500 kg load cell was used to test the specimens. A cross head speed of 2 mm/min was used in conjunction with a 20 mm/min chart speed to produce a reasonably comprehensible plot of the stress-strain data. The cross head speed of 2 mm/min was chosen because it was a compromise between previously estimated rates of joint movement in buildings (considering movement due to thermal, vibrational, or wind effects), and practical considerations concerning the time required for the experiment.

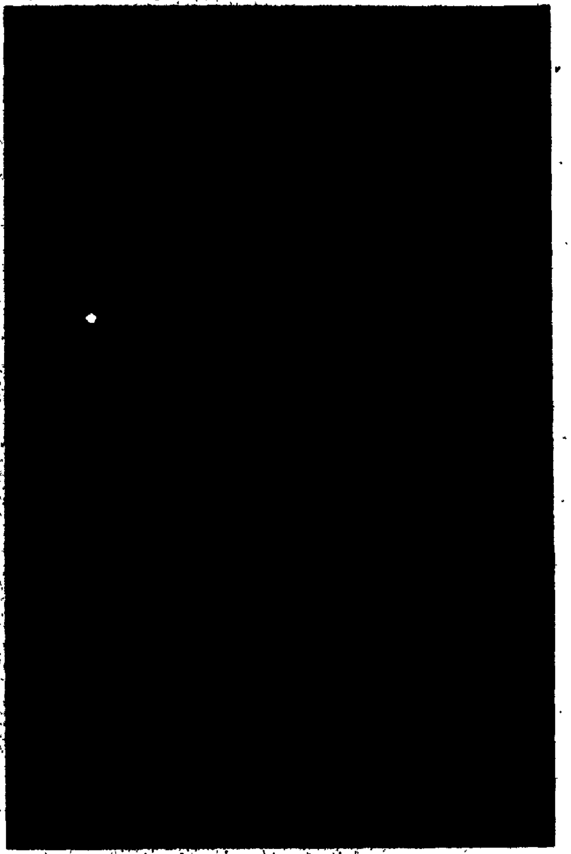


Figure 18 - Instron testing instrument

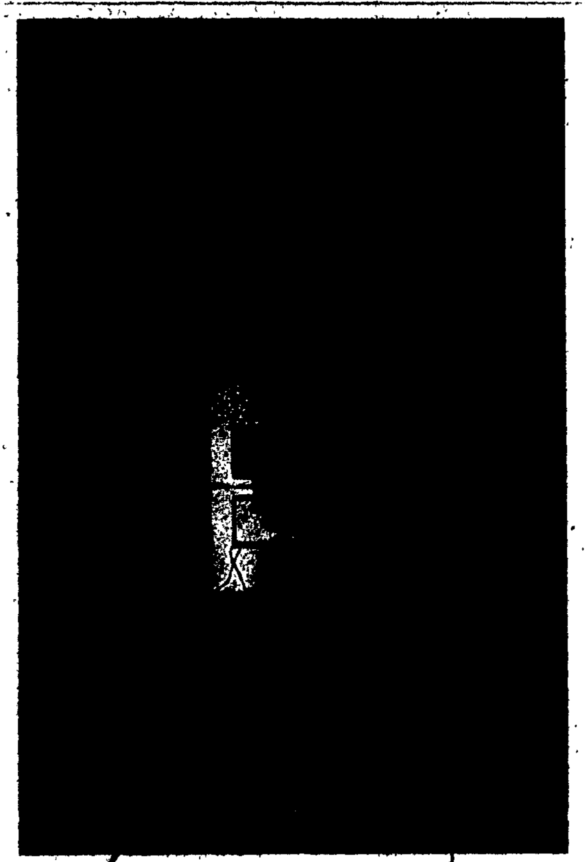


Figure 19 - Extension of specimen

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. The stress on the specimen was calculated by dividing the tensile load, obtained from the load cell and recorded on the chart, by the nominal area under tensile stress, which is equal to 645 mm^2 (12.7x50.8mm). The strain is equal to the ratio of the recorded extension to the width of the sealant bead (12.7mm). The data obtained from the plotter was used to plot the stress-strain curves characteristic of each sealant type and polyblend. The toughness of the sealants was evaluated by calculating the area beneath the stress-strain curve at yield. The modulus was defined as the slope of the line tangent to the stress-strain curve at 5% strain.

4.2.2.5 Durability testing

A weathering chamber was used to artificially age (AA) a series of lignin-polymer specimens. The chamber was set to cycle between -30°C and 40°C, four times every 24 hours. Ultra-violet lamps within the chamber exposed the specimens to radiation 12 hours a day, simulating exposure to the sun. Samples were tested continuously for 720 cycles over a period of 180 days. Specimens were also subject to a natural aging (NA) program whereby a series of lignin-polymer specimens was exposed to exterior weather conditions for 37 weeks, between July 15, 1985 and March 31, 1986. Specimens were placed in wooden racks which kept the specimens upright and sufficiently separated to allow equal exposure to all specimens. The temperature variation during the exposure time is given in Figure 20, including the mean weekly maximum and minimum temperatures, and also the mean monthly temperatures. Maximum and minimum temperatures recorded during this period were 32.6°C and -26.7°C respectively. The mean monthly hours of bright sunshine over the exposure period are shown in Figure 21, indicating maximum intensity at the begining of the exposure period, and a minimum at week 23 (December). The durability of each blend was evaluated by comparing tension test results between laboratory control specimens and aged specimens. Results of these tests are discussed, in relation to the type of polyblend and the substrate to which it is adhered, in sections 5.5 to 5.7. As well, the effects of accelerated aging on the surface morphology of PU blends is presented in section 5.2.

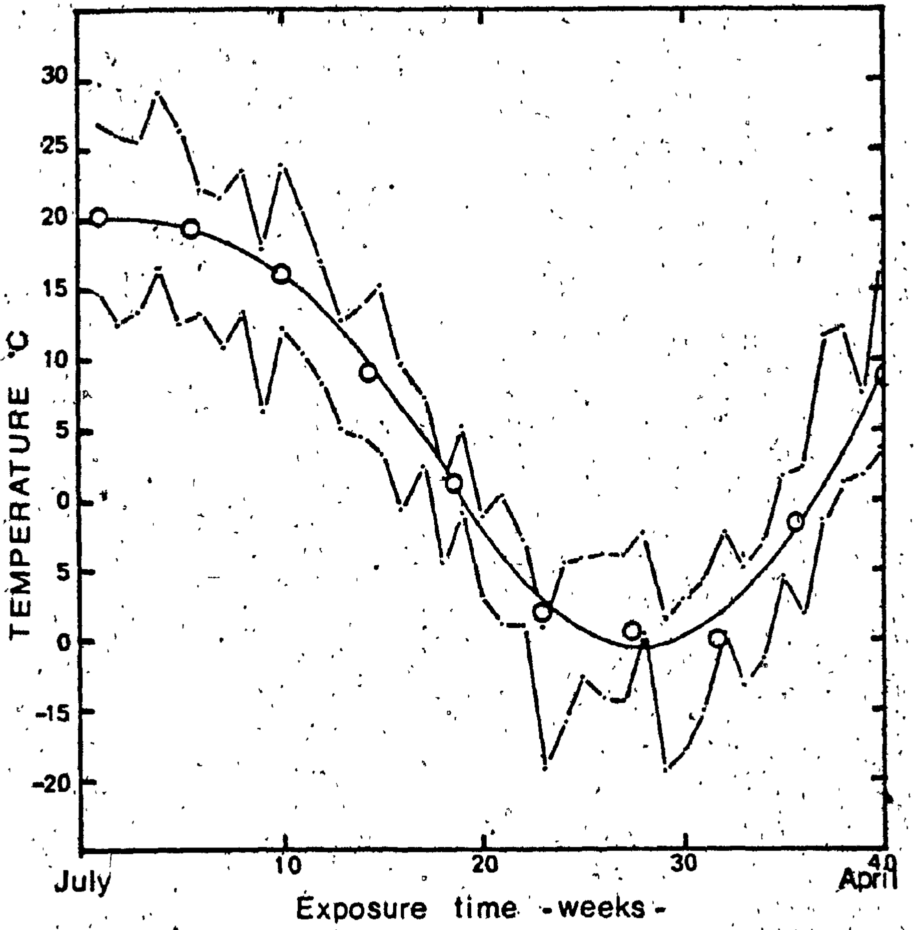


Figure 20 - NA exposure conditions: average weekly maximum and minimum temperatures, and average monthly temperatures

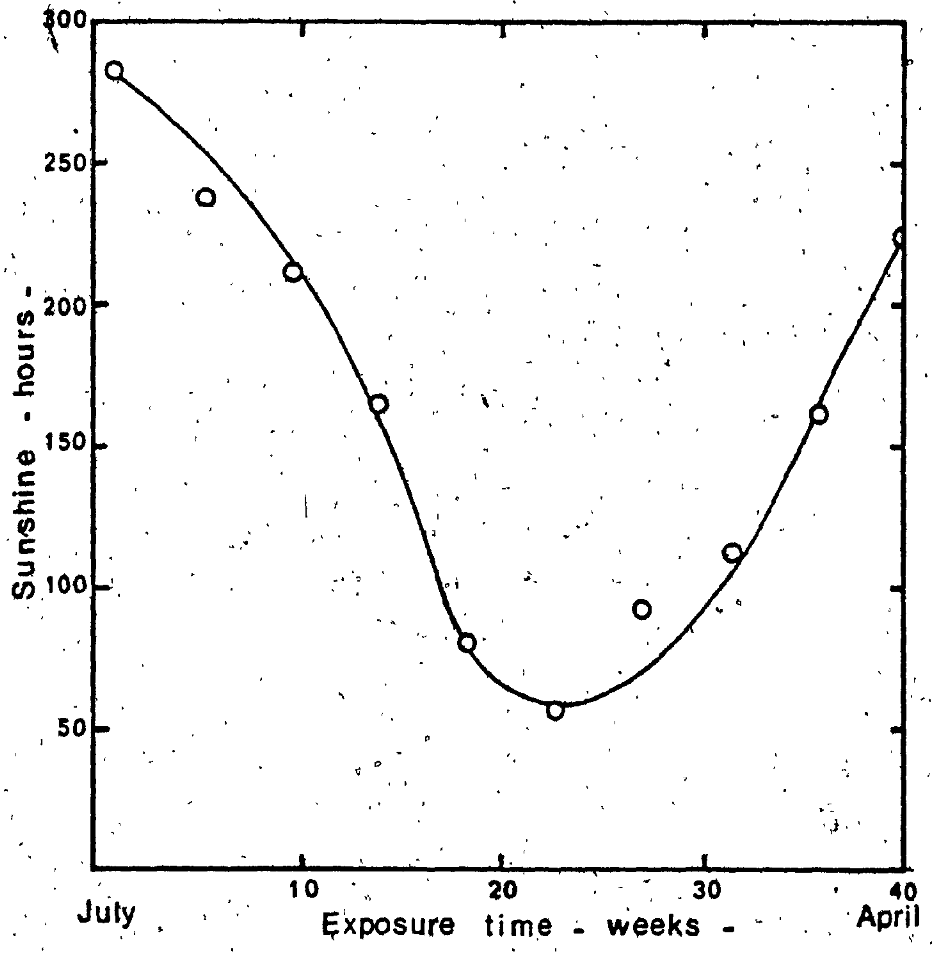


Figure 21. - NA exposure conditions: average monthly hours of bright sunshine

5. EXPERIMENTAL RESULTS

5.1 Preliminary Program

The results obtained during the preliminary program indicate that the addition of lignin to Ps and S sealants has not been beneficial. However, the results of this initial program do indicate enhanced performance of Pu, A, and B sealants blended with lignin. The results of the detailed testing program are presented in subsequent sections of chapter 5. The present section outlines the results obtained from preliminary tests.

The effect of adding lignin to Ps, S, and Pu sealants cast on aluminum substrates is illustrated in Figure 22, where it is observed that the yield stress and strain of Ps and S specimens modified with lignin at a blend ratio of 10%, is reduced and hence blended specimens possess a lower value of toughness than do the non-blended specimens. However, as it is clearly shown, better results have been obtained in the case of PU specimens. The maximum tensile stress and the toughness at failure have both increased approximately 40%. Similarly, for specimens cast between wood substrates, as shown in Figure 24, there is a general tendency for decreased stress and toughness values in the case of Ps and S blends. For Ps specimens, the maximum tensile stress at failure increased 10% with the addition of lignin, yet the corresponding decrease in strain resulted in a decrease in toughness of 20%. For L-PU blends, both the maximum tensile stress at yield and the toughness increased by 45%. The effects of lignin on blends cast between mortar substrates is shown in Figure 23, where, again, Ps and S blends show diminished performance with the addition of lignin. PU sealants polyblended with lignin indicate an increase in tensile stress at failure of 65%, and a corresponding increase in toughness of 100%. Results obtained from tensile tests of L-B and L-A blends are shown in Figure 25, indicating a two fold increase in tensile stress at yield for B samples, and 150% increase in yield stress for acrylic samples on aluminum substrates. Testing of these polyblends adhered to mortar and wood substrates indicate a 200% and - approximately 100% increase in tensile stress at yield for L-B and L-A specimens respectively (Figs. 26 and 27).

Based on the results from this initial test series, PU, A, and B sealants were selected for further testing in the detailed program.

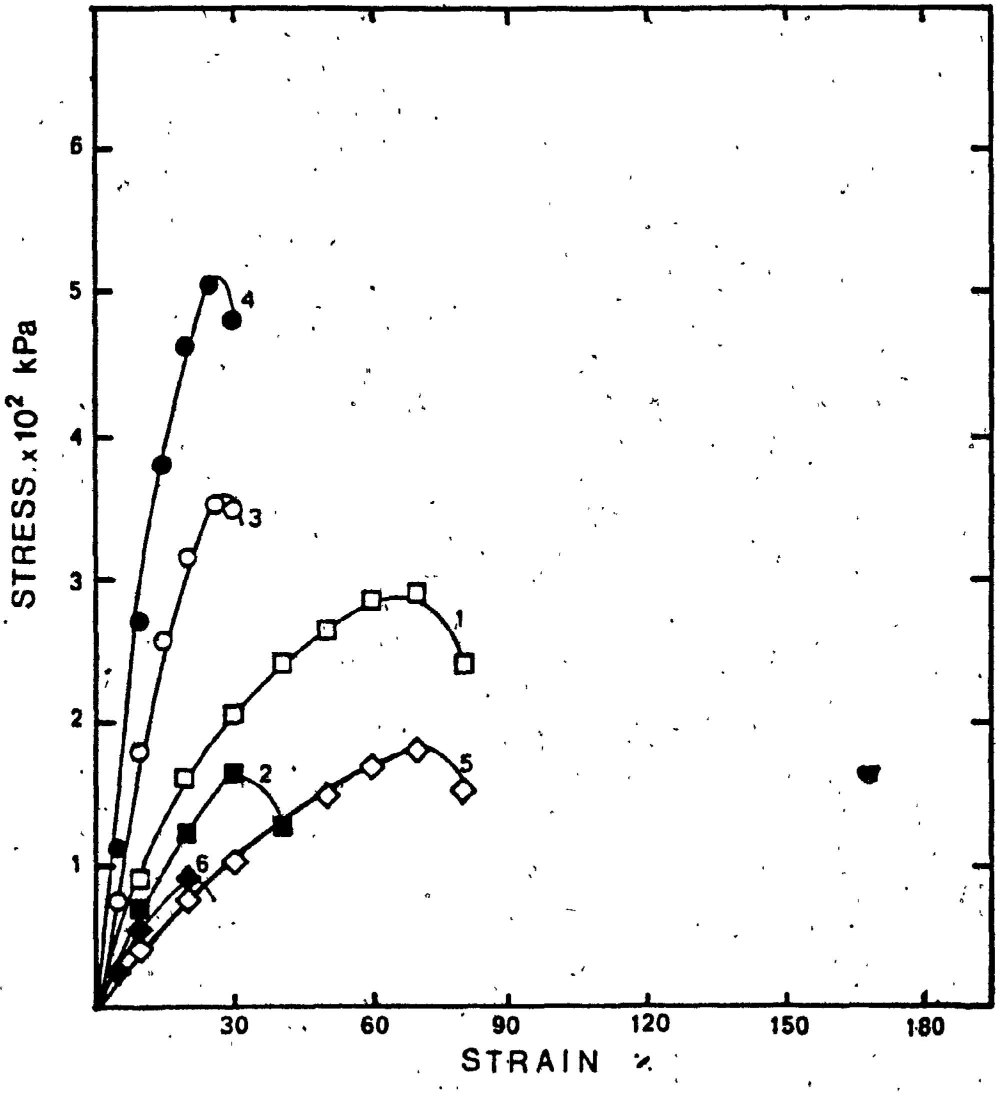


Figure 22 - Tensile stress-strain curves obtained from L-S, L-PU, and L-Ps polyblends on aluminum substrates. Curve 1: L-S, 0:100; 2: L-S, 10:100; 3: L-PU, 0:100; 4: L-PU, 10:100; 5: L-Ps, 0:100; 6: L-Ps, 10:100

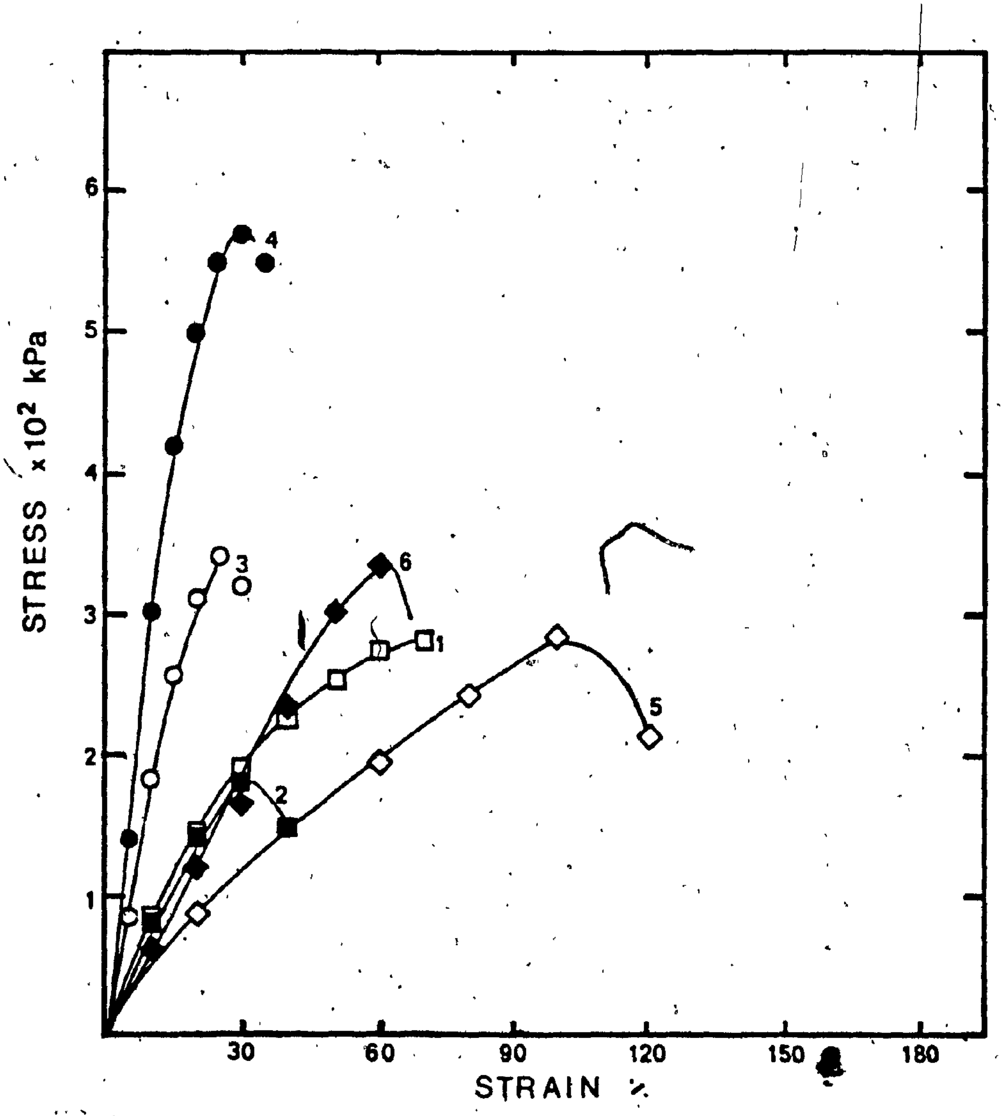


Figure 23. - Tensile stress-strain curves obtained from L-S, L-PU, and L-Ps polyblends on mortar substrates. Curve 1: L-S, 0:100; 2: L-S, 10:100; 3: L-PU, 0:100; 4: L-PU, 10:100; 5: L-Ps, 0:100; 6: L-Ps, 10:100

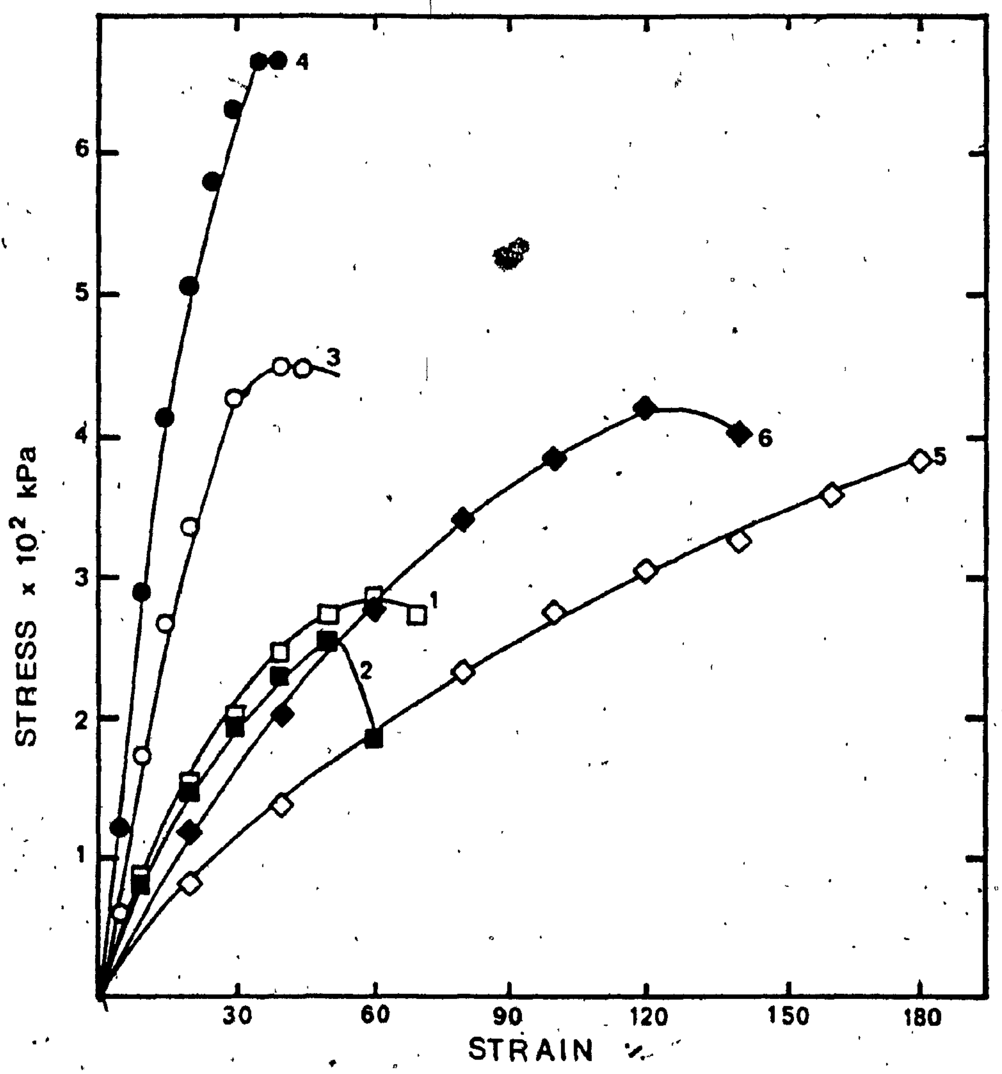


Figure 24 - Tensile stress-strain curves obtained from L-S, L-PU, and L-Ps polyblends on wood substrates. Curve 1: L-S, 0:100; 2: L-S, 10:100; 3: L-PU, 0:100; 4: L-PU, 10:100; 5: L-Ps, 0:100; 6: L-Ps, 10:100

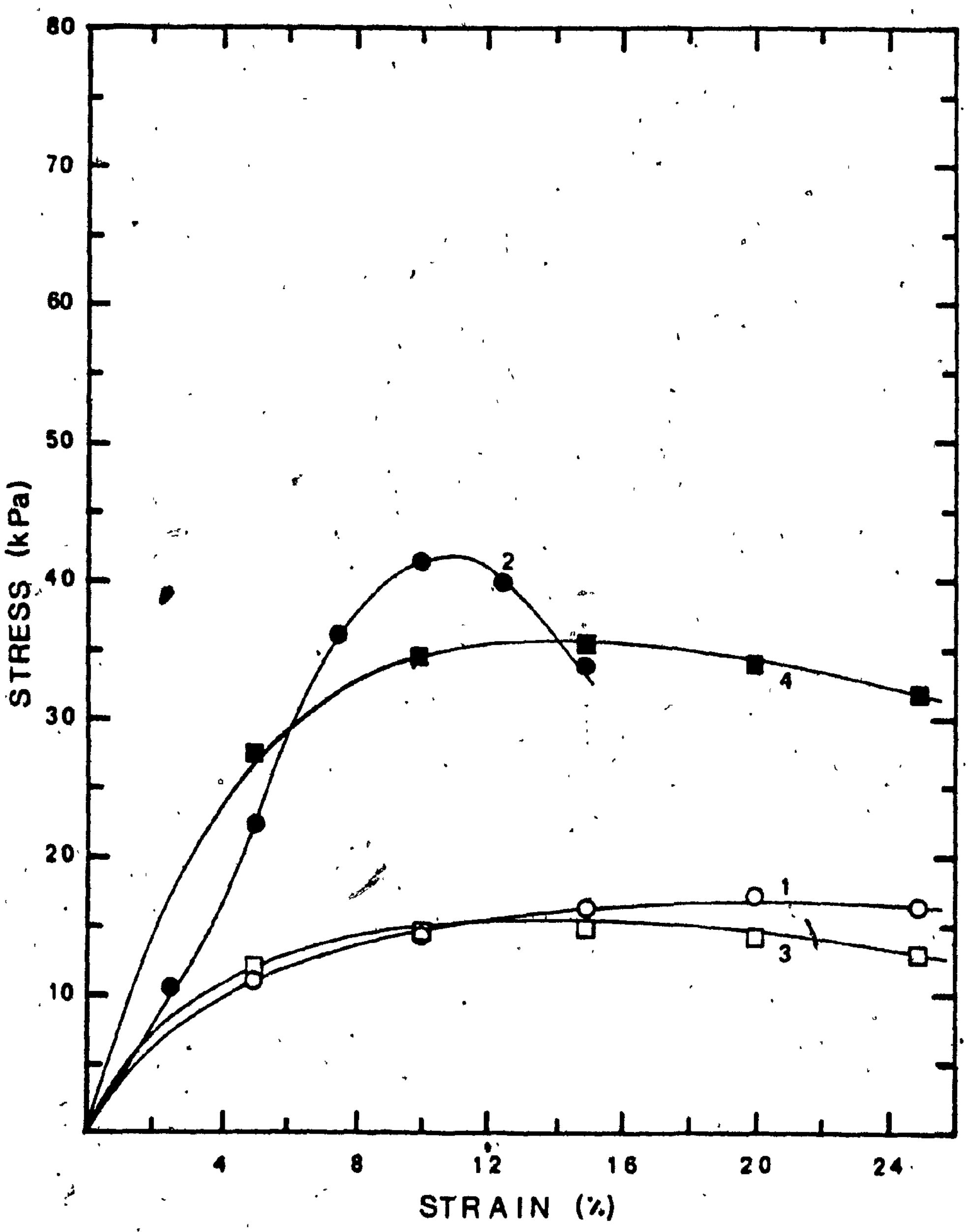


Figure 25 - Tensile stress-strain curves obtained from L-B and L-A polyblends on aluminum substrates. Curve 1: L-B, 0:100; 2: L-B, 10:100; 3: L-A, 0:100; 4: L-A, 10:100

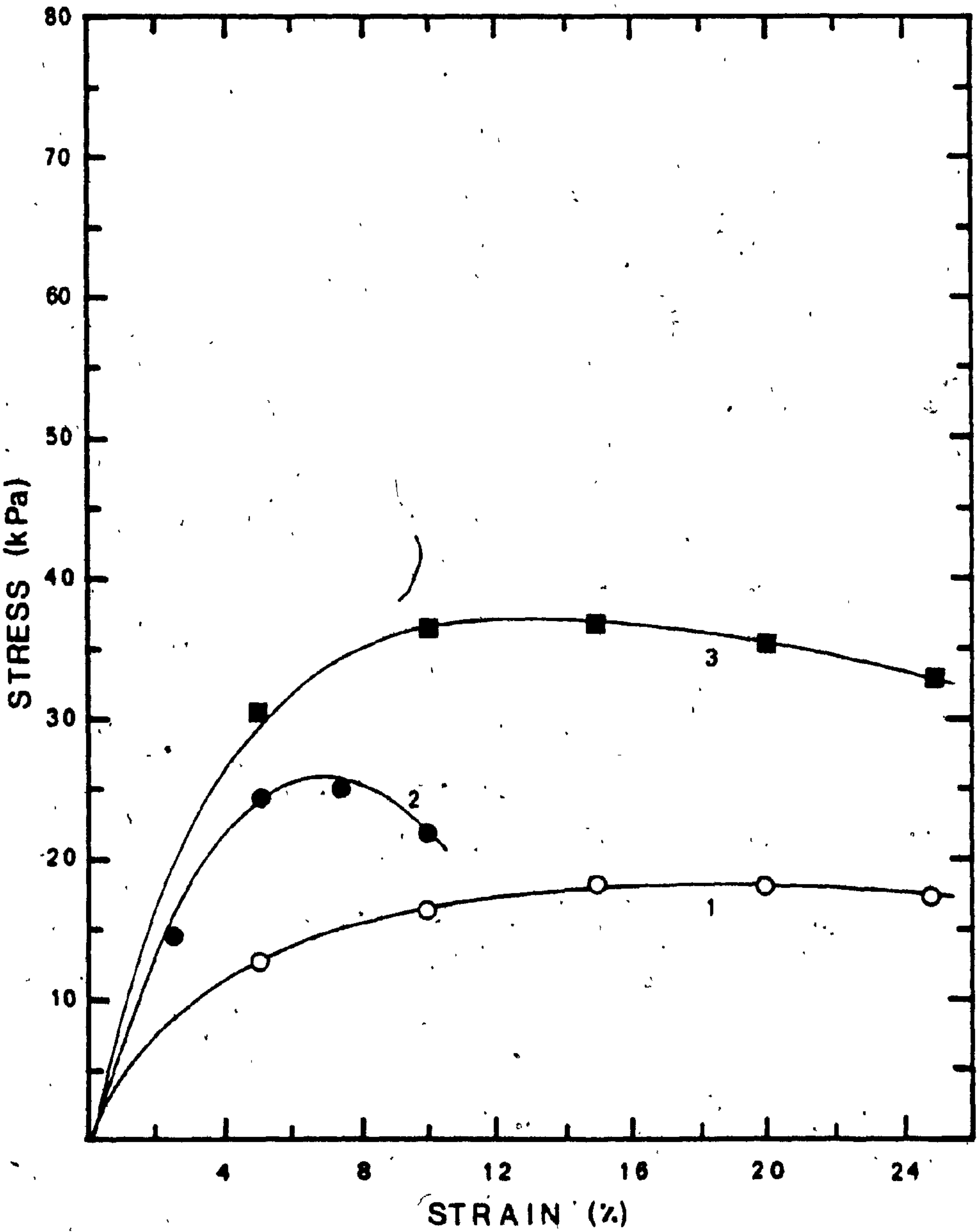


Figure 26 - Tensile stress-strain curves obtained from L-B and L-A polyblends on mortar substrates. Curve 1: L-B, 0:100; 2: L-B, 10:100; 3: L-A, 10:100.

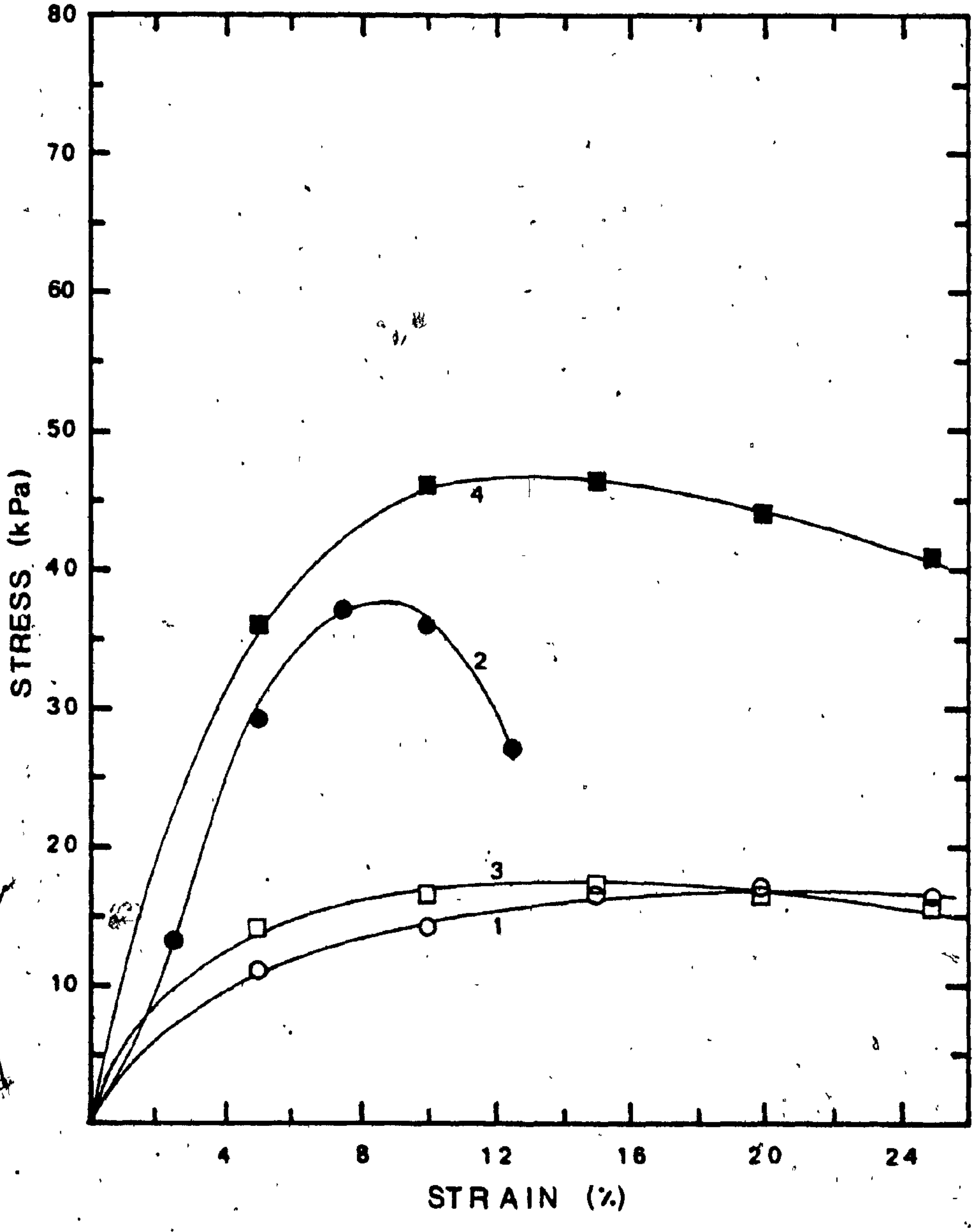


Figure 27 - Tensile stress-strain curves obtained from L-B and L-A polyblends on wood substrates. Curve 1: L-B, 0:100; 2: L-B, 10:100; 3: L-A, 0:100; 4: L-A, 10:100

5.2 Morphology

The results of morphological analysis using optical light microscopy (LM) are presented in color photomicroprints shown in Figures 28 to 32. In order to facilitate comparison between prints, all photomicroprints presented depict surface or sectional features at 40X magnification except Figure 32, which is magnified 120X for purposes of illustrating sectional details of the polymer blend. Furthermore, this series of photomicroprints serves to illustrate the effect of accelerated aging (AA) on polyblends having a blend ratio L:PU of 15%. Control and AA specimens are contrasted in surface and sectional views of the first pair and second pair of photomicroprints, respectively.

The initial figure (Fig. 28) shows the surface features of a control specimen of blended PU sealant. The color clearly identifies the brown lignin particles entrapped in the PU matrix. The craters which can be identified on the surface are indicative of the mode of curing of the sealant, which releases carbon dioxide by its reaction with the moisture in the air. The release of the gas causes bubbles to form on the surface of the sealant, which later collapse and form the texture seen in the photomicroprints.

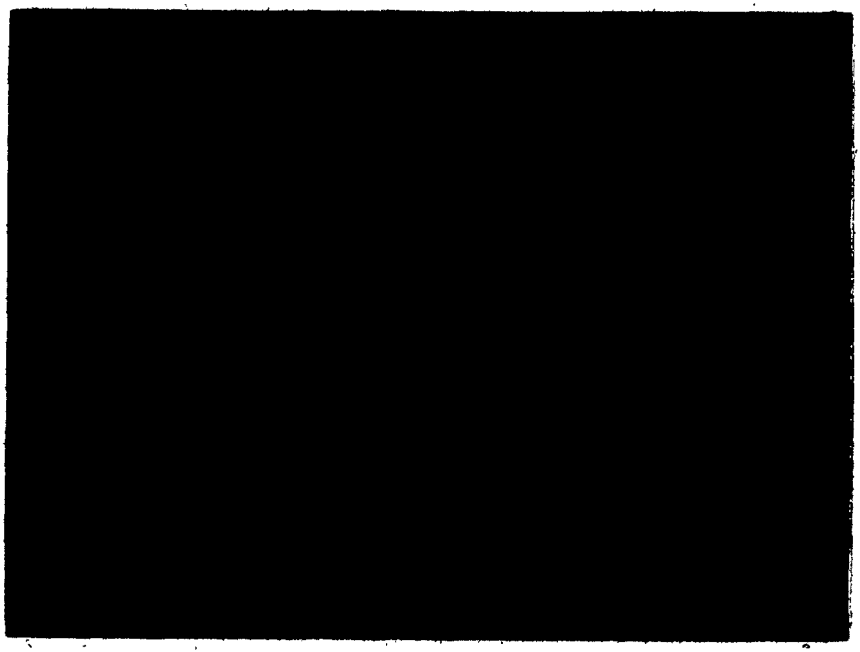


Figure 28 - Surface features of L-PU polyblend (15:100) control specimens using LM (40X)

Figure 29 - Surface features of L-PU polyblend (15:100) AA specimens using LM (40X)

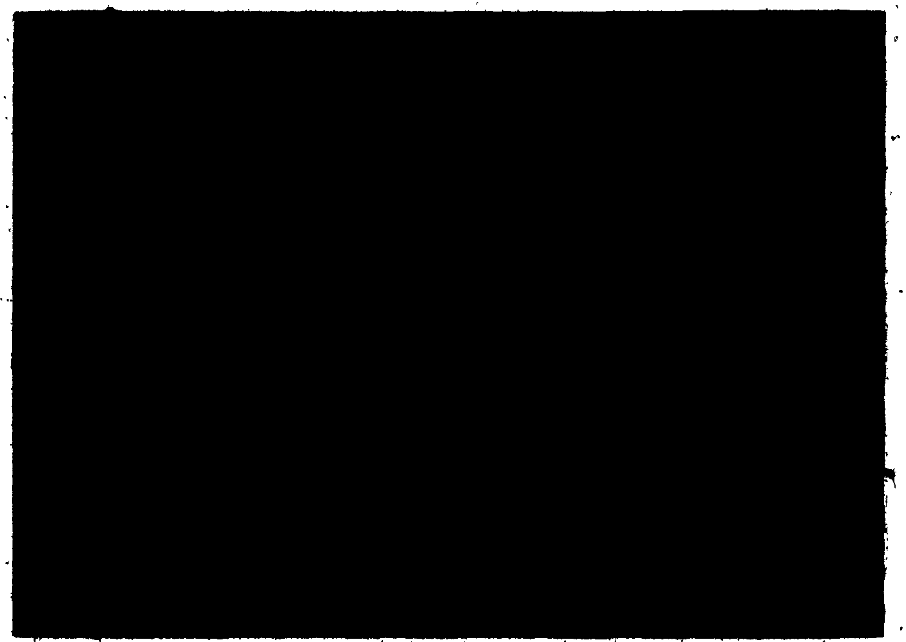


Figure 30 - Sectional features of L-PU polyblend (15:100) control specimens using LM (40X)

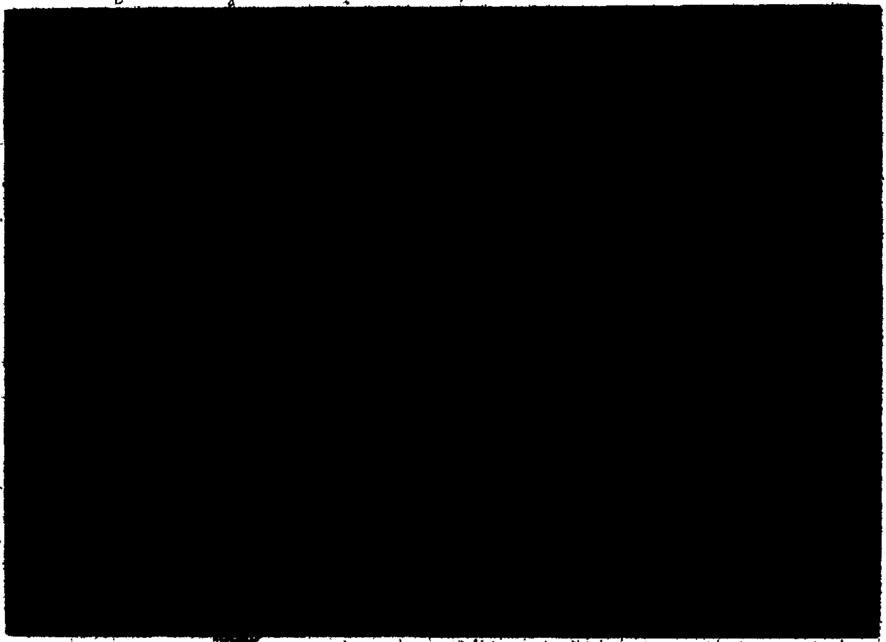


Figure 31 - Sectional features of L-PU polyblend (15:100) AA specimens using LM (40X)

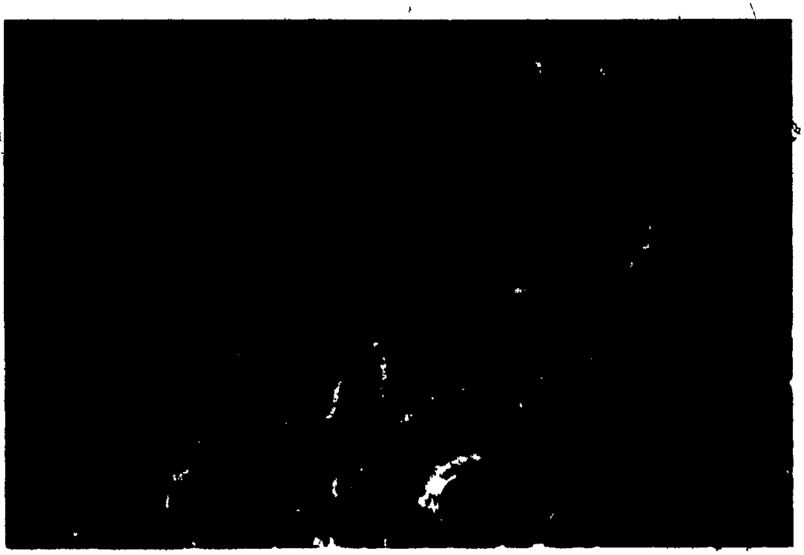


Figure 32 - Sectional features of L-PU polyblend (15:100) AA specimens using LM (120X)

These craters are areas where the effects of aging are pronounced. Figure 29 shows the size and extent of cratering is increased over the surface of the sealant, indicating that the specimen is susceptible to degradation under AA conditions.

A sectional view of a control specimen is shown in Figure 30, where it is seen that the lignin is coalesced around voids in the sealant conglomeration. Similar features can be seen in the sectional view of the AA specimen (Fig. 31) although no outward differences can be detected between the control and the AA samples from these views. A detailed view of an AA specimen more clearly shows the effects of AA

(Fig. 32).

Photomicrographs of lignin and L-PU polyblends obtained from SEM are shown in Fig. 33 to Fig. 38. The initial photomicrograph (Fig. 33) depicts lignin particles magnified 3000X. The lignin particles have a noticeably angular configuration, although some particles have edges which are rounded or smooth. The size of the particles varies from a fraction of a um up to approximately 6 or 7 micrometers.

The size distribution of the particles appears generally uniform, roughly ranging between 1 to 4 um in width. It is also observed that the porosity of the lignin particles is homogeneous, there being little or no evidence of pores or pore structure detectable on their surface.

These lignin agglomerations may be easily recognized in L-PU blends, as their distinctive morphology is in contrast to that of a neat (unblended) PU sealant, whose surface texture is more smooth, undulating, and to a certain extent cratered, as seen in Figure 34. The craters or voids are most probably produced by the release of carbon dioxide during the airing process.

The contrasting morphologies of lignin and PU are exemplified in SEM photomicrographs showing surface features of L-PU blends with blend ratios of 10% and 20%, Figures 35 and 36 respectively. The inclusion of lignin particles within the polymeric matrix is clearly depicted in both figures, and they are generally evenly distributed throughout the polymeric matrix. There are areas where the particles form larger agglomerations, as shown in Figure 36. The reason for lignin particles lining the edge of certain craters is not immediately apparent, however it may be that carbon dioxide gas is more easily expelled in areas where lignin particles coalesce.

The final two photomicrographs clearly illustrate the effect of AA on the surface texture of L-PU polyblends having a 15% blend ratio. In Fig 37, the surface features of a control specimen are contrasted to that of an AA specimen in Figure 38. The smooth surface texture of the control specimen has been aged by thermal shock and ultraviolet radiation, to leave lignin particles entrapped in the polymeric matrix. The surface of the PU matrix has eroded to expose a fibrillar structure of more resistant urethane linkages.

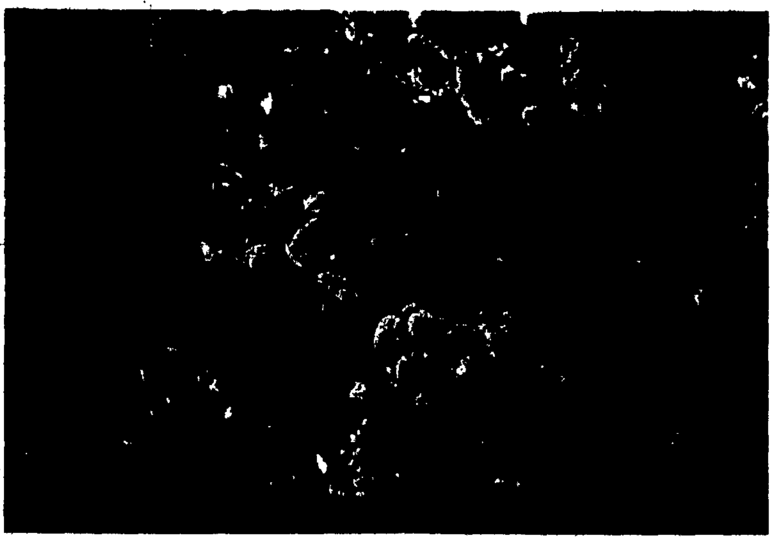


Figure 33 - SEM of lignin particles (3000X)

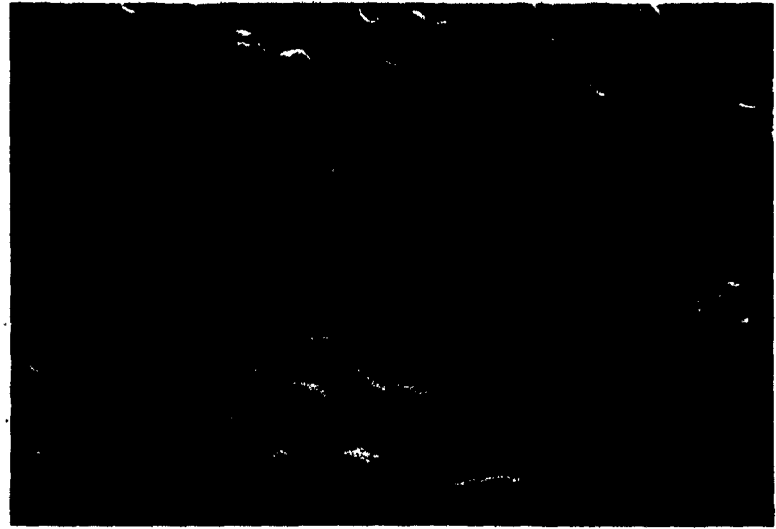


Figure 34 - SEM of neat PU surface (500X)

Figure 35 - SEM of L-PU polyblend surface (10:100) (500X)

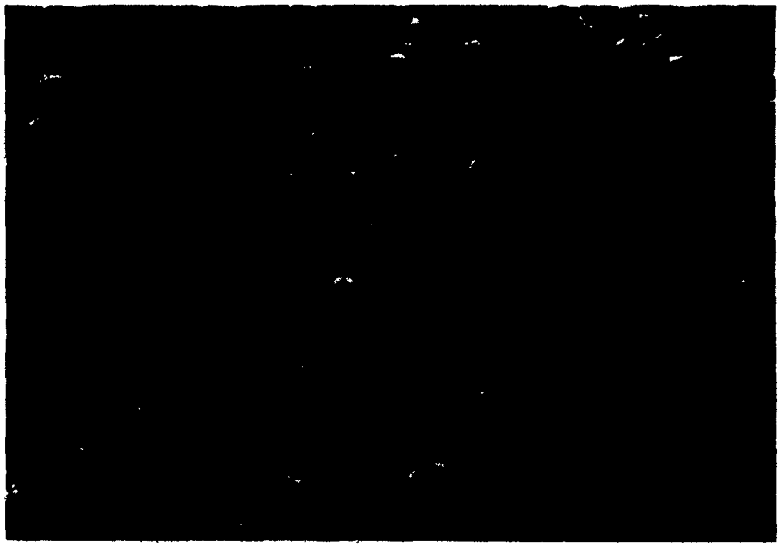


Figure 36 - SEM of L-PU polyblend surface (20:100) (500X)

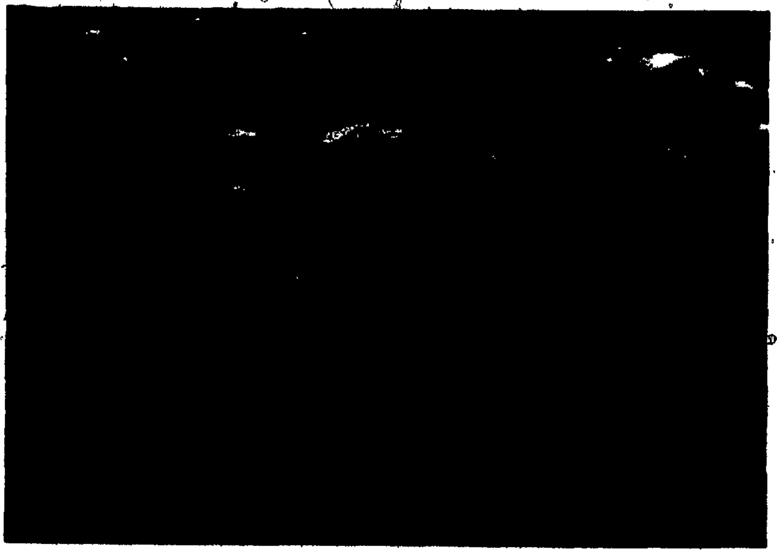


Figure 37 - SEM of L-PU polyblend surface (15:100) control specimen (500X)

Figure 38 - SEM of L-PU polyblend surface (15:100) AA specimen (500X)

5.3 Curing Characteristics

Results of indentation hardness testing for the unblended PU sealant are shown in Figure 39. For the neat PU blends, the initial hardening test may be recorded after approximately 25 hours have elapsed since the initial casting time. In the next 23 hours, the sealant reaches 40% of the hardness obtained in one week, and 70% of the total weekly hardness in the following 24 hours. The weekly hardness is 95% of the average hardness over 1519 hours, indicating that most of the cure occurs in the first week after initial set. It may also be observed that a number of months may elapse before a second hardening stage occurs. It is not yet apparent what causes the subsequent hardening of the sealant after two months of curing.

For L-PU blends of 20 PBW of lignin (Fig. 40), the initial hardness reading may be taken at 20 hours, representing a 20% decrease in initial set time for this blended sealant in comparison to the neat sealant. The polyblend reaches 35% of its one week hardness after 24 hours, 72% of its hardness in 48 hours, and 85% of its hardness after 72 hours from initial set. Generally, this is indicative of a more rapid cure for blended sealants in comparison to neat PU.

This is all the more evident when considering the results shown in Figure 41 which depicts curing tests for L-PU blend ratios of 0, 10, and 20%. The curing time,as measured by sequence hardness testing, is affected by the amount of lignin blended with the base sealant. Furthermore, it may be shown, by refering to Appendix 2, that at any given time, the ratio of 10s to 60s hardness decreases with increasing amounts of lignin, indicating a more rapid hardening process for blended vs. unblended sealants. Although the rate of curing appears to be similar for blended and unblended sealants, as indicated by the straight line portion of the curves, overall, blended sealants harden more quickly than unblended sealants in direct proportion to the amount of lignin present in the blend.

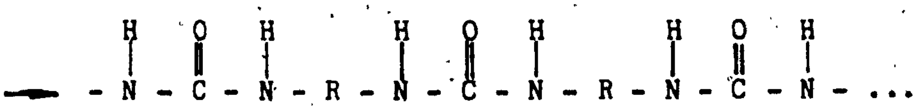
To explain this phenomena, it is desireable to understand the basic chemistry involved with the formation of PU, more specifically one component polyurethane sealants. Polyurethane one component sealants are produced by the reaction of moisture (water) and an isocyanate terminated prepolymer such as alkyl trimethyl triisocyanate, which is referred to as:

$$R - (NCO)_3$$

Combining three moles of water with the isocyanate yields an amine (1), which further reacts with the isocyanate to form urethane linkages (2), i.e.:

1. $$3H_2O + R - (NCO)_3 \longrightarrow \underset{\text{amine}}{R - (NH_2)_3} + 3CO_2\uparrow$$

2. $R - (NH_2)_3 + R - (NCO)_3$



$$-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\ldots$$

urethane

The rate of cure is affected by the activity of the functional end groups (i.e. OH and NCO), and the presence of catalysts. The hardness of the cured products depends on the crosslinking density between molecular chains and the rigidity of the chains, which increases with a corresponding increase in the number of aromatic groups along the chain. Furthermore, the crosslink density is a function of the type of prepolymer used in the sealant formulation. It is surmized that the incorporation of lignin into the PU matrix may be seen as adding to the crosslink density by increasing the concentration of aromatic groups within the polymeric network.

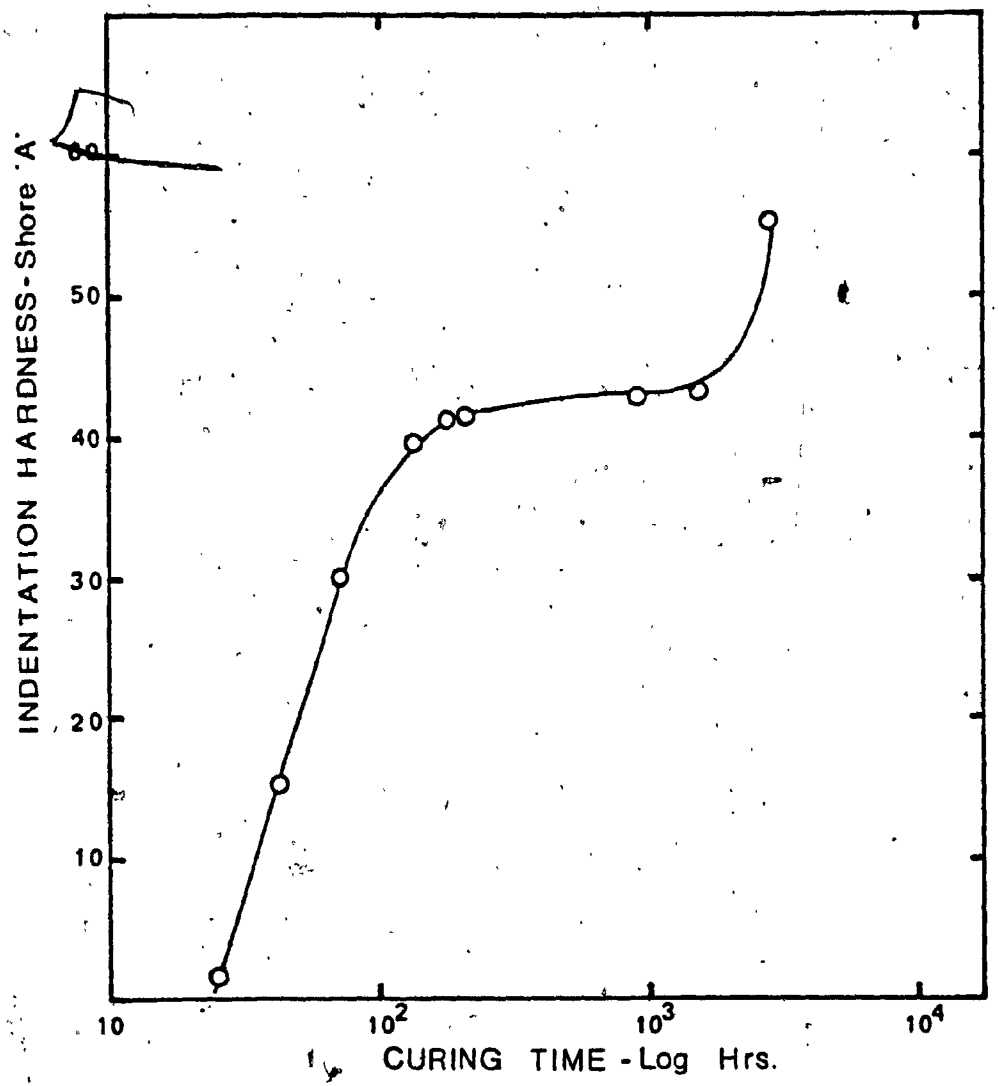


Figure 39 - Indentation hardness of neat PU sealant in relation to curing time

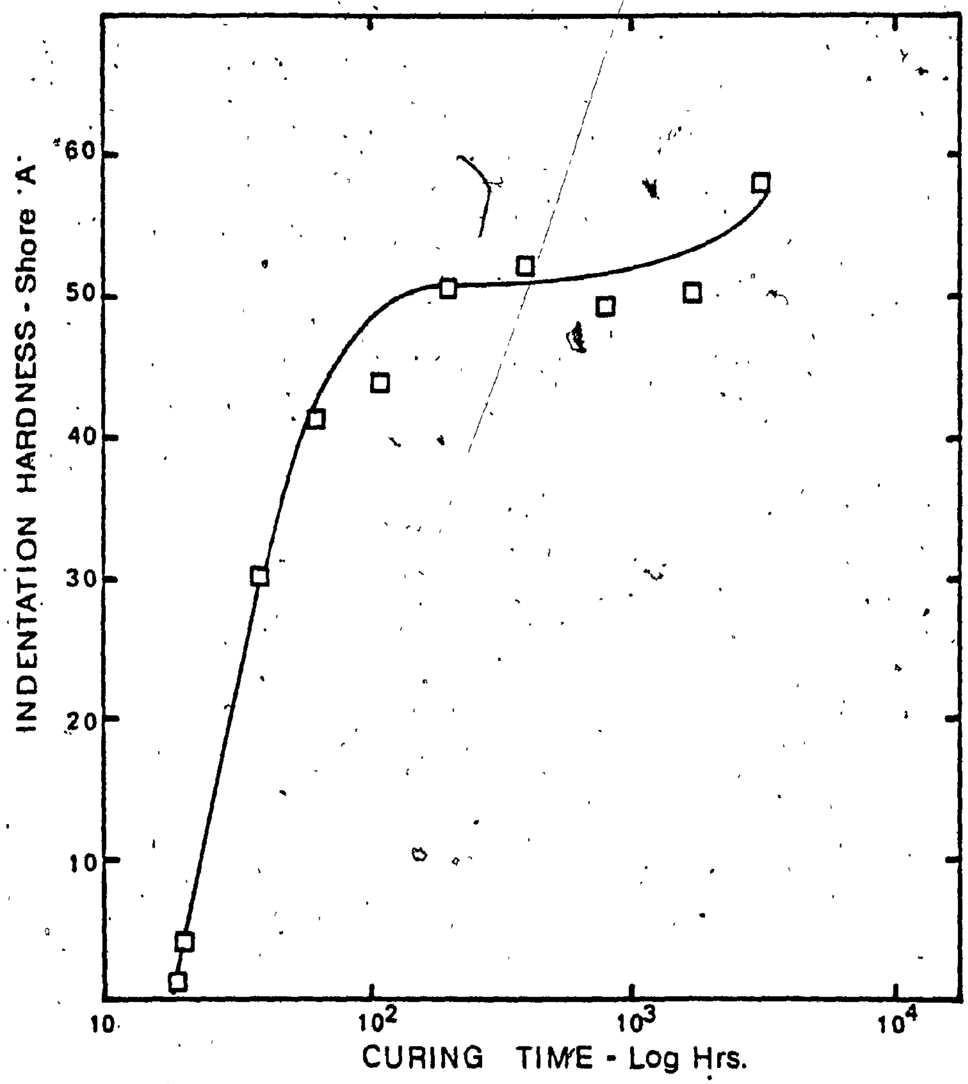


Figure 40 - Indentation hardness of L-PU polyblend with 20% blend ratio in relation to curing time

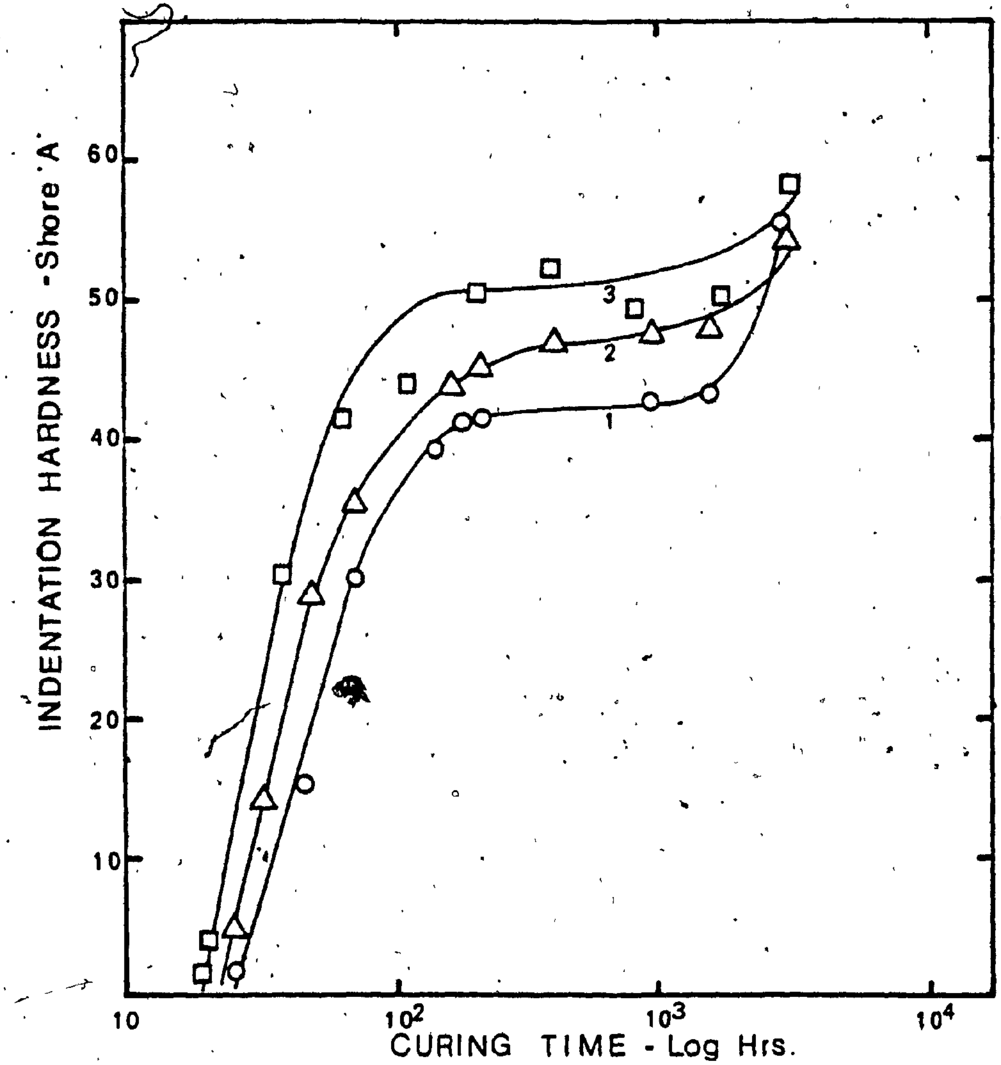


Figure 41 - Indentation hardness of L-PU polyblends in relation to curing time. Curve 1: L-PU; 0:100

2: L-PU; 10:100

3: L-PU; 20:100

5.4 Thermal Testing

Results of DSC thermographs are given in Figure 42. The thermographs plotted are those for lignin, blended control specimens (designated C-L0-, L10-, L20-PU, depending on the blend ratio), and unblended specimens which were subjected to NA and AA conditions. The location of the curve on the thermograph is dependent on the specimen size, greater size causing a depression in the graph. This is due to the increase in differential heat flow between the reference and sample specimens.

As is evident from Figure 42, there is not a significant modification of thermographs with the addition of lignin. Values obtained for the glass transition temperature of neat PU sealant are in the range of -55°C and are not observed to shift with an increase in the amount of lignin in the blends. This indicates that L-PU blends are not miscible, and hence exist in two distinct phases. The physical properties of these blends are determined by the interfacial adhesion between the phases. Similar dispersive and polar forces between these phases would suggest a good interfacial adhesion, which, for example, would be marked by an increase in tensile modulus with corresponding increase in polymer loading.

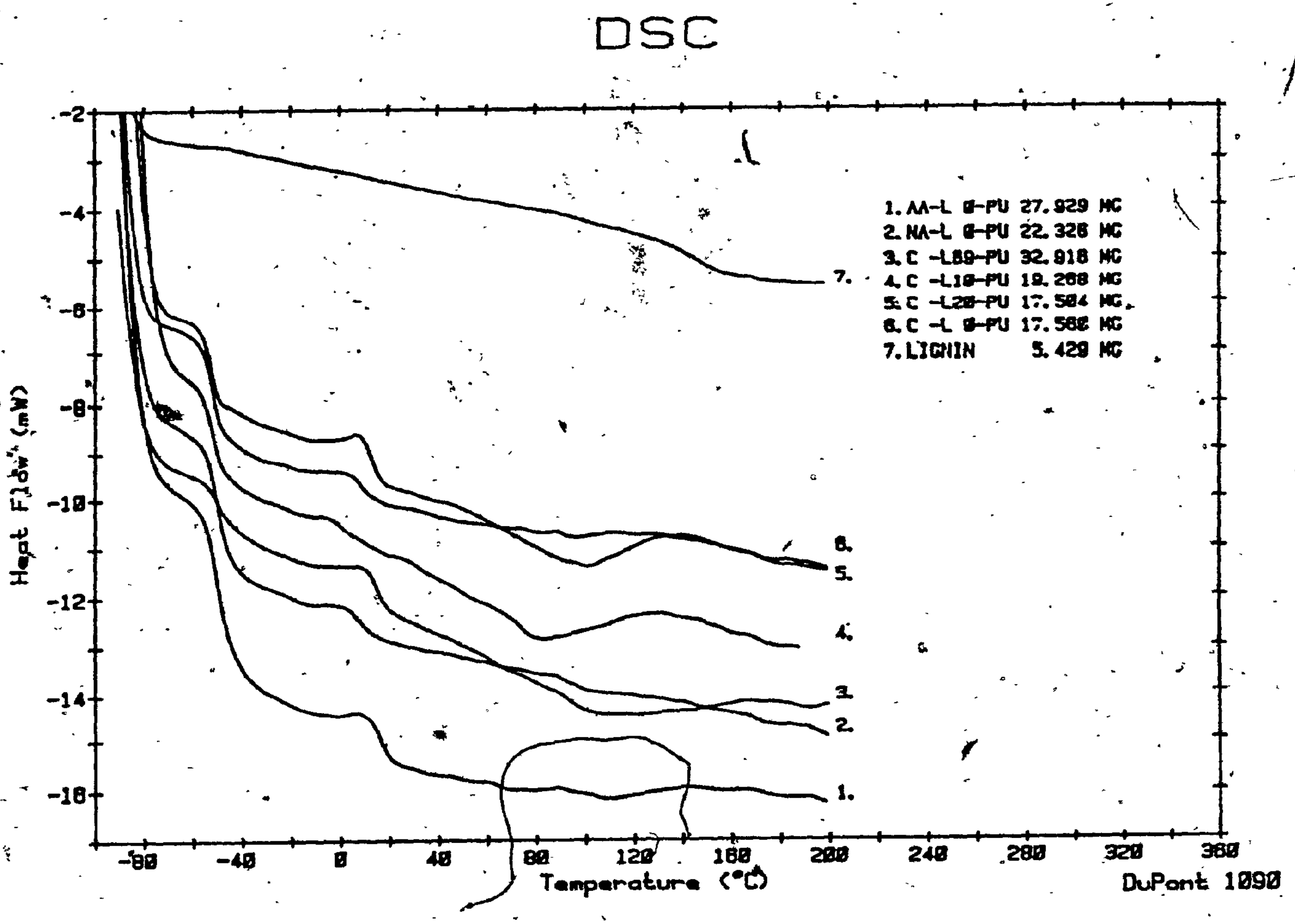


Figure 42 DSC thermograph of lignin and L-PU polyblends

5.5 Tension Testing of Lignin-Butyl (L-B) Polyblends

5.5.1 L-B polyblends on aluminum substrates

Control (C) and naturally aged (NA) specimens were found to exhibit a decrease in toughness with the addition of lignin to the polyblend (Table 9). This, in large part, is due to the decrease in strain at yield despite an increase in the yield stress (Table 10). The toughness of these blends decreased 64% for the control specimens, and 24% for the NA specimens with the addition of 5 parts by weight (PBW) of lignin, and further decreases in toughness are shown for increased lignin loads. However, this condition is not prevalent for specimens subjected to accelerated aging (AA), where in contrast there is shown to be a 40% increase in toughness with the addition of up to 10 PBW of lignin.

The tangent modulus of L-B polyblends on aluminum substrates increases from 6 to 40% with the addition of 5 PBW of lignin, and for AA and NA specimens there is a progressive increase in modulus with additional lignin loading. In the case of control specimens, the incorporation of lignin into the matrix beyond 5 PBW of lignin is shown to diminish the tangent modulus. The increase in modulus is met with a corresponding increase in yield stress for both AA and NA specimens (Figs. 44, 45). Only the C specimens showed a decrease in yield stress with the addition of lignin (Fig. 43).

Strain at yield decreased with increased lignin loading for all specimens tested (Table 10). Lignin loadings above 5 PBW of sealant for control specimens and above 12.5 PBW of sealant for AA and NA specimens reduced the modulus sufficiently for the specimens to fail exclusively in adhesion. The effect of AA and NA on L-B polyblends is characterized by a stiffening of the polymeric matrix, which is observed by a small or negligible loss of yield stress, and a much larger loss of strain at yield with a correspondingly higher modulus. The stiffening of the matrix is shown to increase the incidence of adhesive failure along the sealant-substrate interface. Although lignin is able to increase the toughness, yield stress and modulus of some blends, it stiffens the polymeric matrix sufficiently to cause adhesive failure, characterized by much lower yield strains, and consequently its use in butyl blends can not be considered beneficial to the performance characteristics of the sealant.

The incompatibility of the polymers may account for the diminished performance of the L-B polyblends. Generally, non-polar substances are not compatible with polar substances, as is the case with the butyl sealant, a non-polar polymeric blend, and lignin, a naturally occurring polar substance. The reduced mechanical performance of L-B polyblends is not entirely unexpected in consideration of their incompatibility.

TOUGHNESS (KPa)

Polyblend L:B	Exposure Conditions C	 AA	 NA
0:100	5.7	4.4	4.8
5:100	2.1	5.4	3.6
10:100	-	6.2	3.3
12.5:100	-	4.1	3.9

TANGENT MODULUS (KPa)
at 5% strain

Polyblend L:B	Exposure Conditions C	 AA	 NA
0:100	18.4	16.7	21.3
5:100	19.5	22.2	29.9
10:100	2.6	42.8	47.9
12.5:100	9.7	70.9	62.9

Table 9 - Toughness and tangent modulus of lignin-butyl polyblends on aluminum substrates

YIELD STRESS (KPa)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	30.9	26.1	30.7
5:100	22.5	38.0	35.3
10:100	-	67.8	43.9
12.5:100	-	71.8	67.5

YIELD STRAIN (%)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	18.5	16.7	15.6
5:100	9.2	14.2	10.4
10:100	-	9.2	7.4
12.5:100	-	5.5	5.8

Table 10 - Yield stress and yield strain of lignin-butyl polyblends on aluminum substrates

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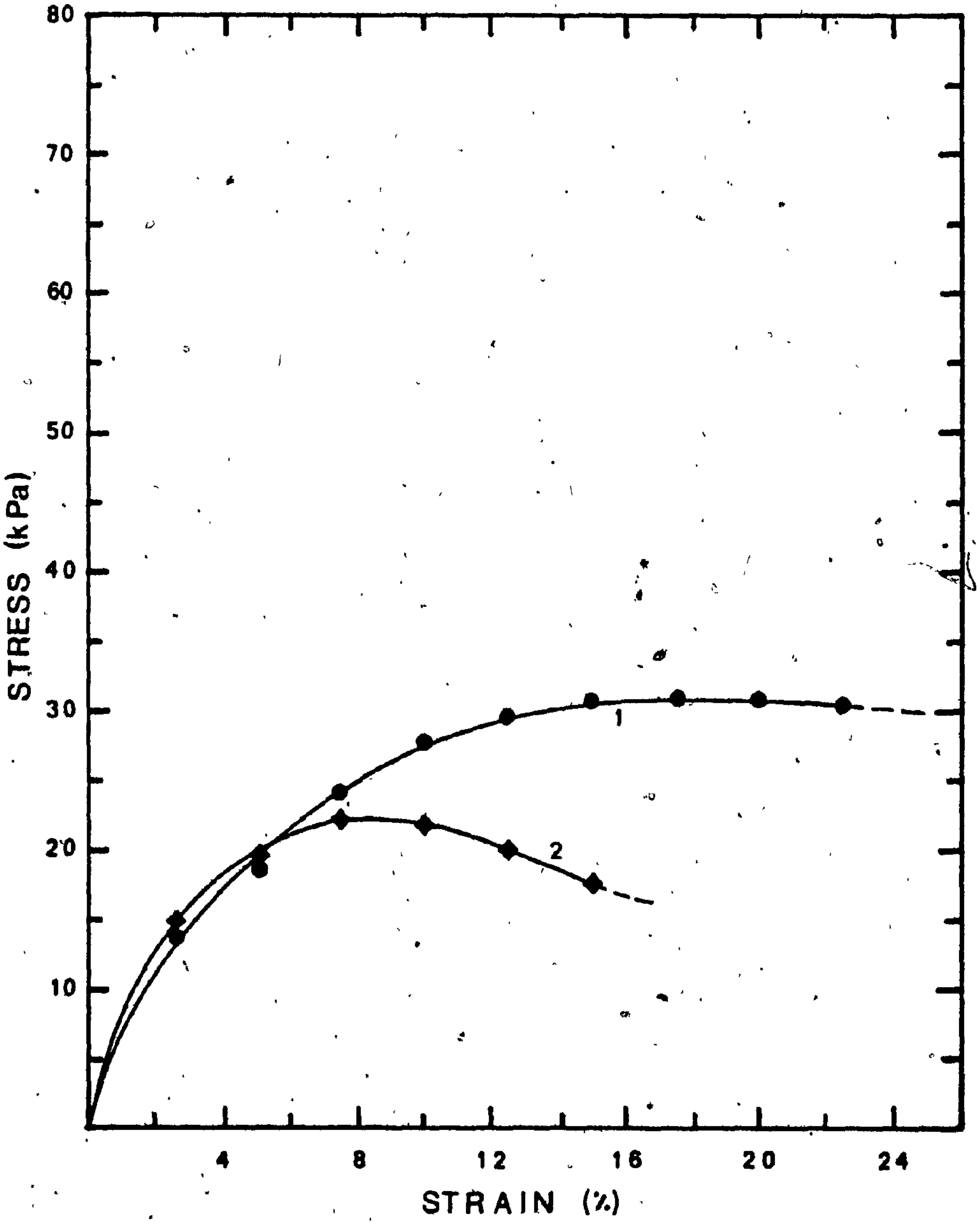

Figure 43 - Tensile stress-strain curves obtained from control, L-B polyblends on aluminum substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: L-B; 4: L-B; 5: L-B;

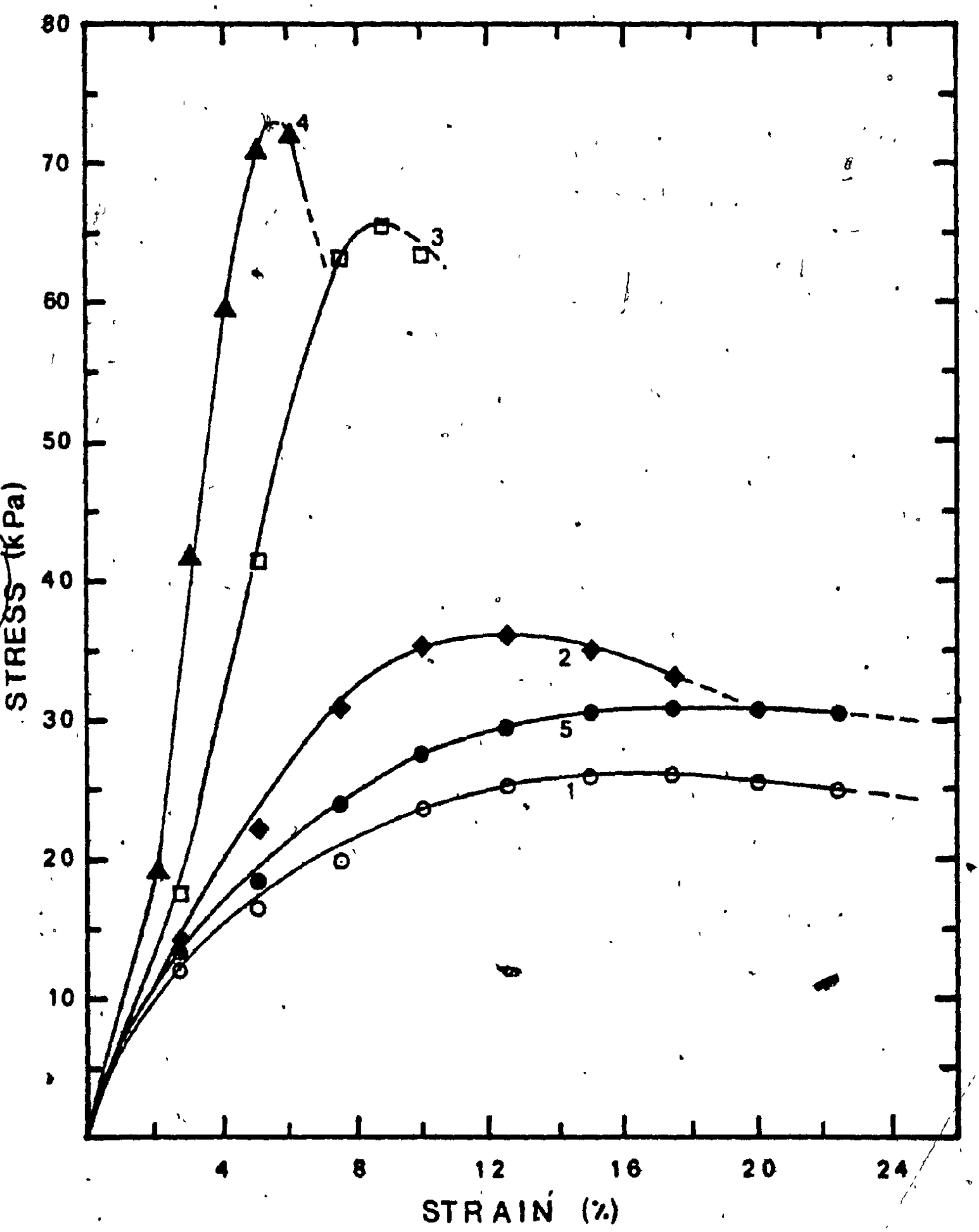

Figure 44 - Tensile stress-strain curves obtained from AA, L-B polyblends on aluminum substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: L-B, 10:100; 4: L-B, 12.5:100; 5: Control curve, L-B, 0:100

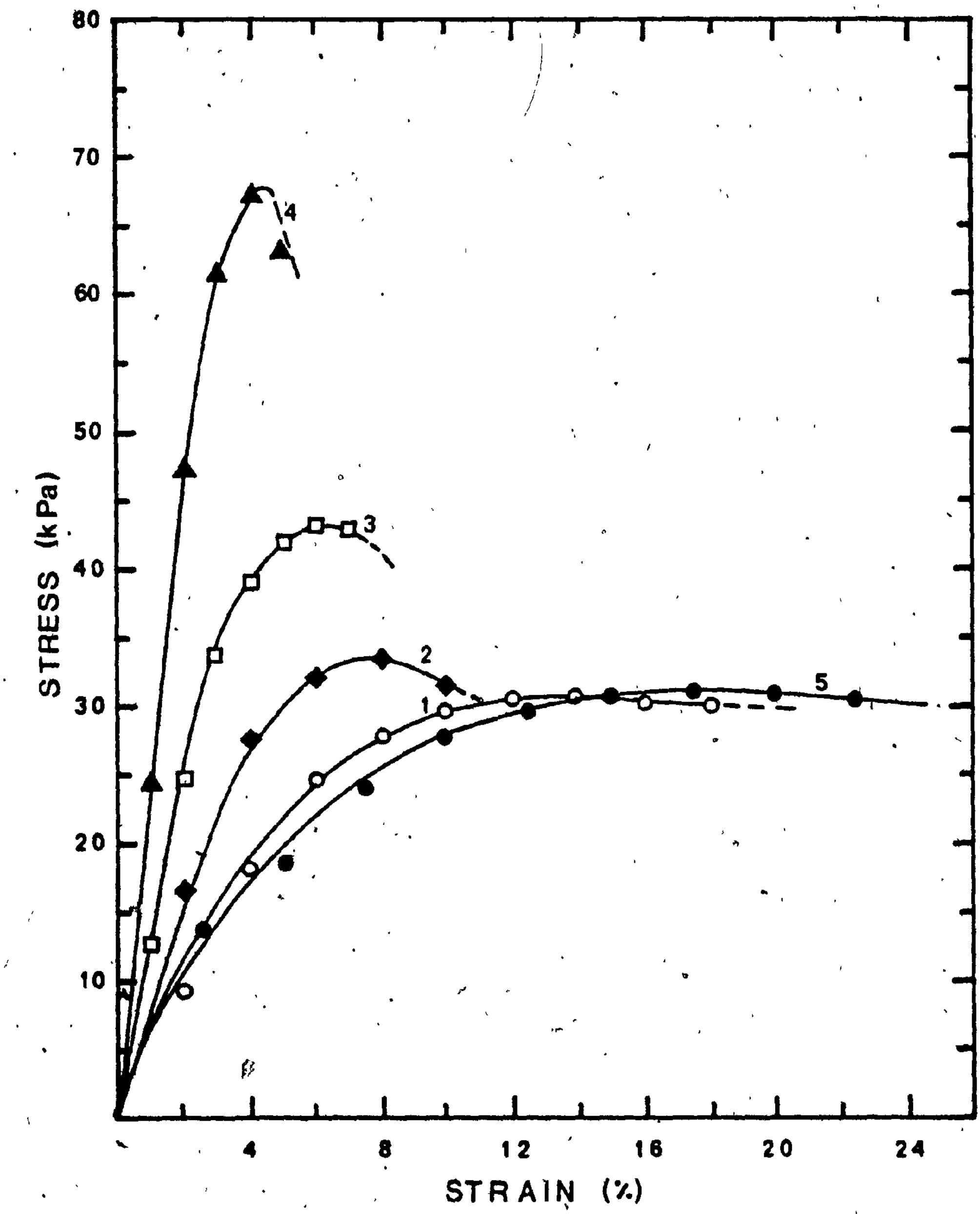

Figure 45 - Tensile stress-strain curves obtained from NA, L-B polyblends on aluminum substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: L-B, 10:100; 4: L-B, 12.5:100; 5: Control curve, L-B, 0:100

5.5.2 L-B polyblends on mortar substrates

The toughness of L-B polyblends adhered to mortar substrates is reduced with the addition of lignin, where a 20 to 60% loss in toughness is observed with the addition of 5 PBW of lignin to the polyblend (Table 11). The loss in toughness is met with a corresponding loss of yield strain recorded in all blends tested, despite, for some specimens tested, increases in yield stress of up to 23% (Table 12).

The addition of lignin is seen as a stiffening agent, characterized by an increase in modulus of 40% for AA and NA specimens. In contrast, there is a decrease in modulus for C specimens with the addition of 5 PBW of lignin. This is due to the adhesive failure of the specimens as indicated by the low values of stress and strain at yield, as shown in Figure 46. The stiffening of the butyl matrix with the addition of small quantities of lignin is shown to display even more undesirable characteristics in the case of sealants adhered to mortar substrates.

The improved performance of AA and NA specimens in comparison to C specimens is difficult to assess (Figs. 47, 48). Results from tests on aluminum substrates indicate that the toughness of AA and NA specimens is inferior to that of the control specimens, but is in the same order of magnitude as test results obtained from mortar substrates, ranging between 4 and 5 KPa. This indicates that the control specimens on mortar substrates have abnormally low values of toughness, which may be accounted for by their loss of adhesion while curing. This phenomena is not prevalent with L-B blends on wood substrates. The during mode of the L-B control specimens is seemingly affected by a series of complex interactions between the sealant and the substrate causing premature adhesive failure. Further investigations would necessarily be required in order to identify these interactions, and to clarify the manner in which they combine to affect the sealant-substrate interfacial bond. Presently, these test results show that the addition of lignin to B sealant has not enhanced the functional properties of the sealant.

TOUGHNESS (KPa)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	1.3	4.9	4.2
5:100	0.5	3.9	2.5

TANGENT MODULUS (KPa)
at 5% strain

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	14.5	17.7	25.7
5:100	10.1	24.9	36.8

Table 11 - Toughness and tangent modulus of lignin-butyl polyblends on mortar substrates

YIELD STRESS (KPa)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	1.12	2.0	2.1
5:100	0.69	2.5	2.0

YIELD STRAIN (%)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	7.5	16.0	13.4
5:100	4.9	10.3	8.1

Table 12 - Yield stress and yield strain of lignin-butyl polyblends on mortar substrates

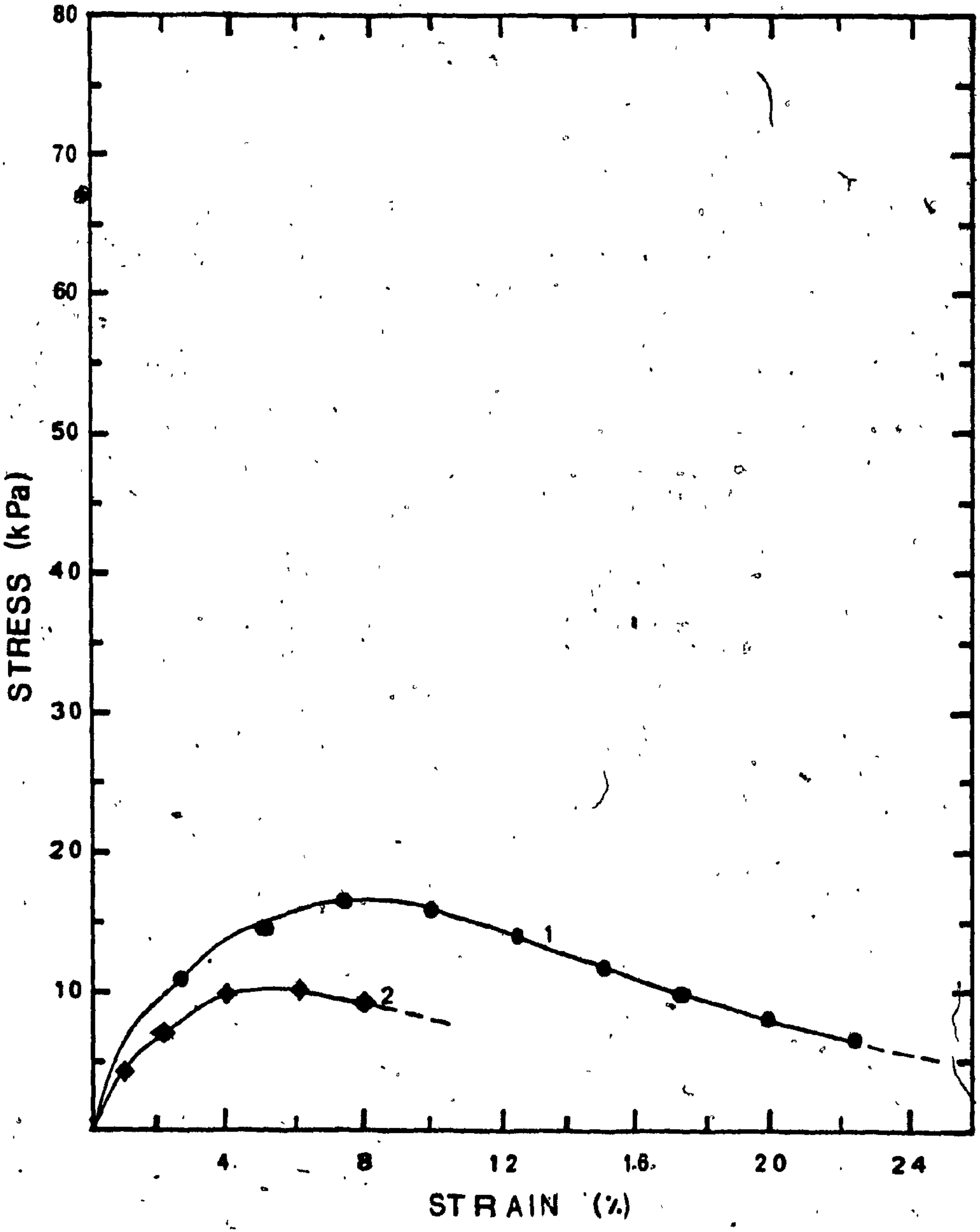

Figure 46 - Tensile stress-strain curves obtained from control, L-B polyblends on mortar substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100

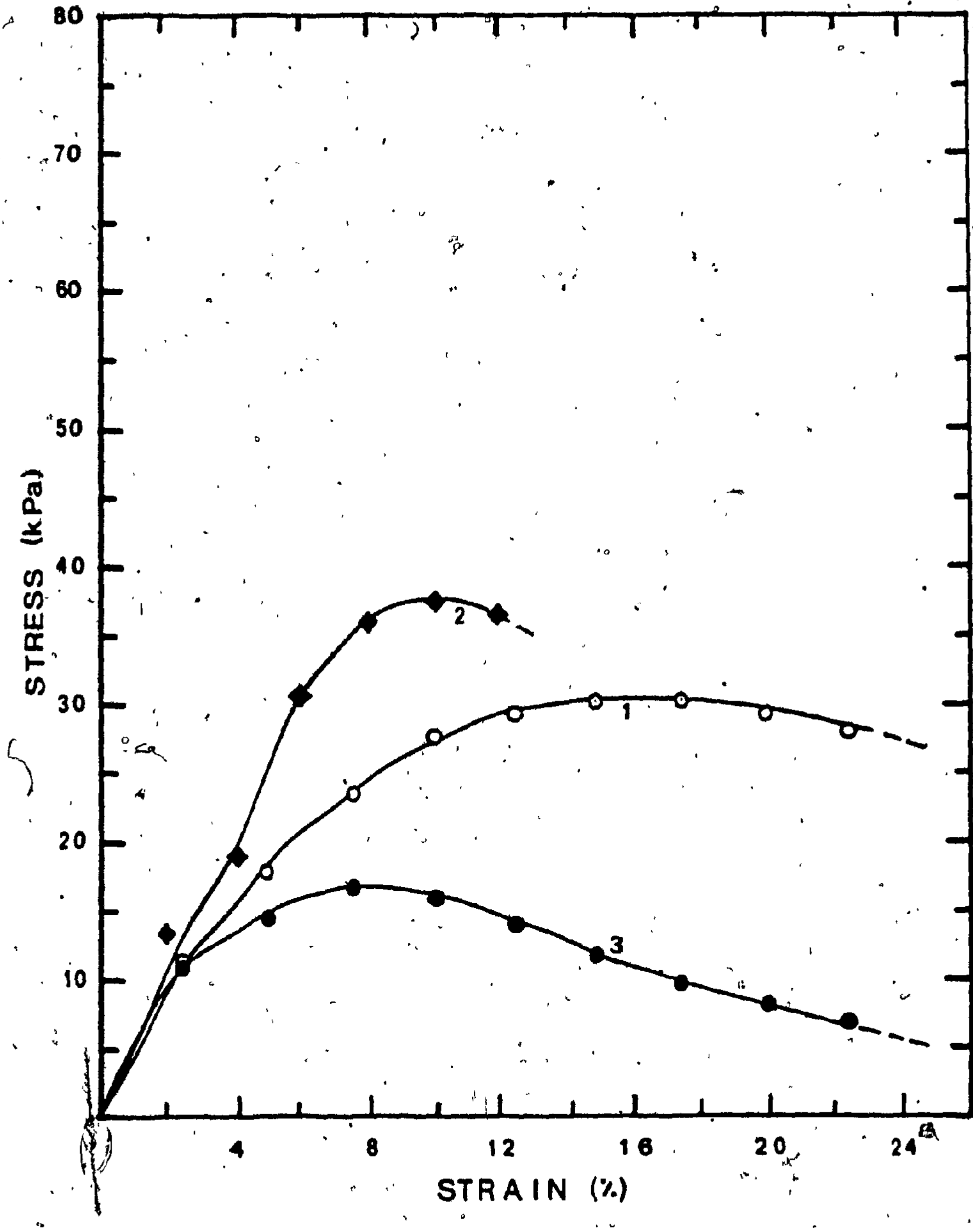

Figure 47 - Tensile stress-strain curves obtained from AA, L-B polyblends on mortar substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: Control curve, L-B, 0:100

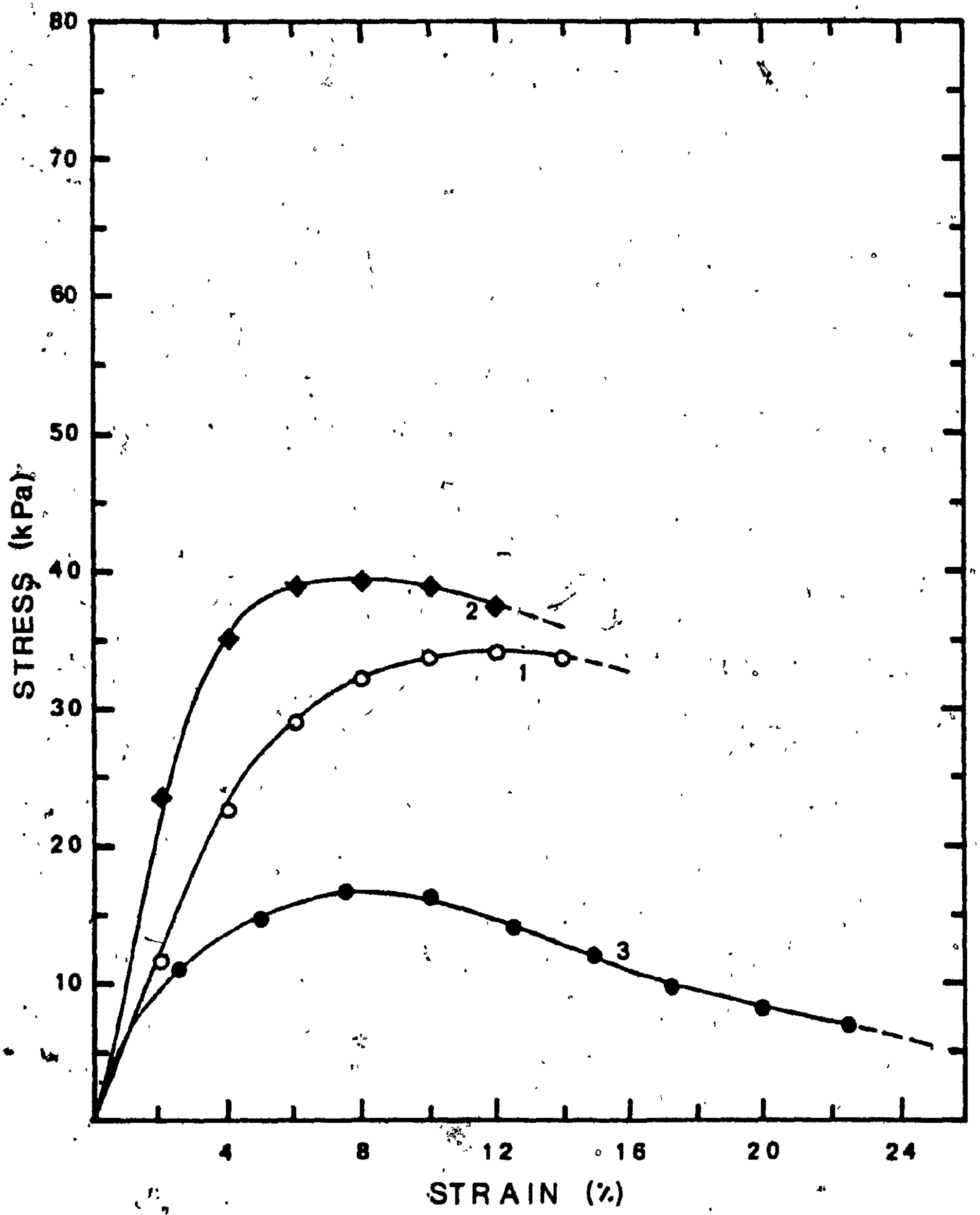

Figure 48 - Tensile stress-strain curves obtained from NA, L-B polyblends on mortar substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: Control curve, L-B, 0:100

5.5.3 L-B polyblends on wood substrates

Generally, the addition of lignin to B sealants on wood substrates reduces their toughness. This is due to a stiffening of the matrix characterized by an increase in modulus with a corresponding increase in lignin loading (Table 13). The stiffened matrix causes premature adhesive failure at the sealant-substrate interface, which may be observed in a reduced strain at yield (Table 14). The addition of 5 PBW of lignin reduced the yield strain 24 and 28% in the case of NA and AA specimens respectively, and up to 54% for the C specimens as shown in Figures 49, 50 and 51. Specimens which had higher lignin loadings were prone to adhesive failure upon casual handling and could not be tested.

Since butyl sealants cure by solvent release, then it is expected that the effect of elevated temperature induced by thermal shock and/or natural or simulated solar radiation would cause a more rapid cure of the sealant. Hence specimens subjected to NA or AA may cure more rapidly in comparison to C specimens as characterized by their increase in tangent modulus. It is also observed that the modulus of NA specimens is greater than that of AA or C specimens, which suggests that the effects of NA on B and L-B blends is more pronounced that that of AA conditions. This may be due to the effect of moisture (in the form of rain and snow), to which NA specimens were exposed in contrast to AA specimens.

The addition of lignin may also accelerate the cure by causing a more rapid release of the solvent, or by adsorption of the solvent onto the surface of the lignin particles, due to its porosity.

These combined conditions account for the increase in modulus of NA specimens in comparison to AA and C specimens. Furthermore, both the aging process and the addition of L affect the overall performance characteristics of L-B blends, however the manner by which they combine to modify the mechanical properties is not apparent, and further study and experimentation are required for useful conclusions to be drawn.

TOUGHNESS (KPa)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	5.5	5.2	4.8
5:100	3.3	5.3	3.6
10:100	-	2.5	-

TANGENT MODULUS (KPa)
at 5% strain

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	16.4	16.0	22.9
5:100	18.7	21.3	30.1
10:100	8.8	32.8	-

Table 13 - Toughness and tangent modulus of lignin-butyl polyblends on wood substrates

YIELD STRESS (KPa)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	1.9	1.8	2.1
5:100	1.5	2.5	2.1
10:100	-	2.5	-

YIELD STRAIN (%)

Polyblend	Exposure Conditions		
L:B	C	AA	NA
0:100	19.0	19.0	15.2
5:100	8.8	13.8	11.6
10:100	-	6.8	-

Table 14 - Yield stress and yield strain of lignin-butyl polyblends on wood substrates

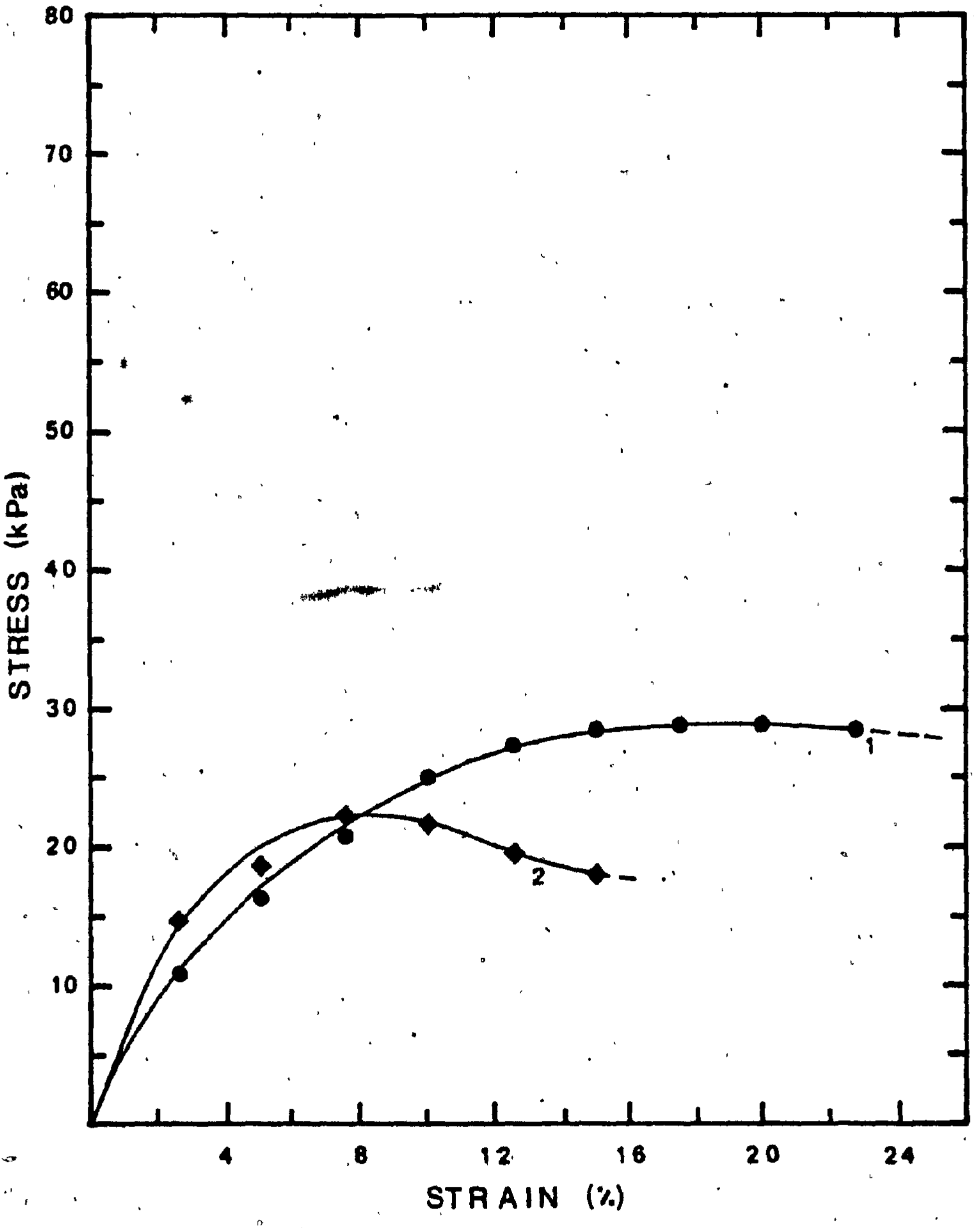

Figure 49 - Tensile stress-strain curve obtained from control, L-B polyblends on wood substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100

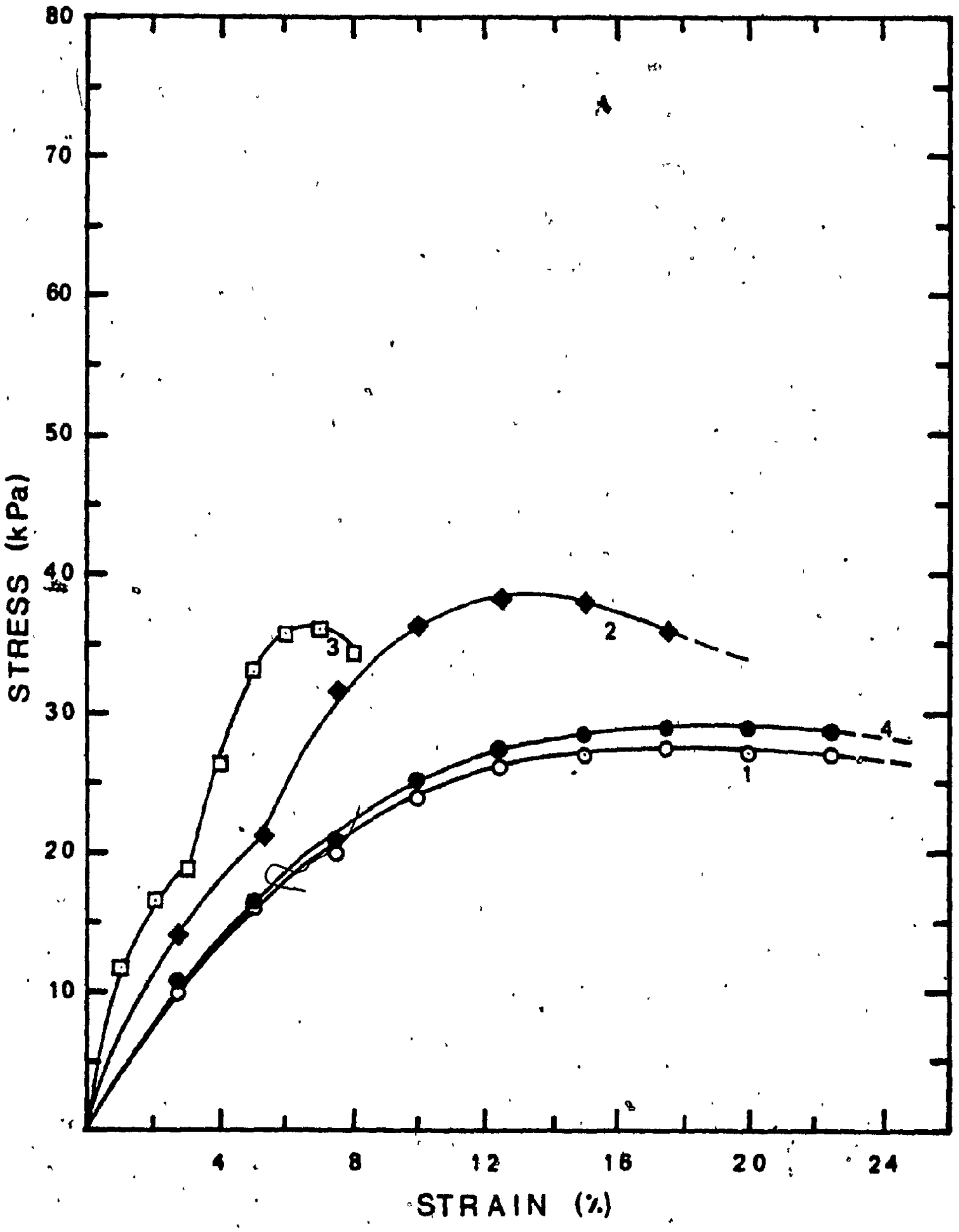

Figure 50 - Tensile stress-strain curves obtained from AA, L-B polyblends on wood substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: L-B, 10:100; 4: Control curve, L-B, 0:100

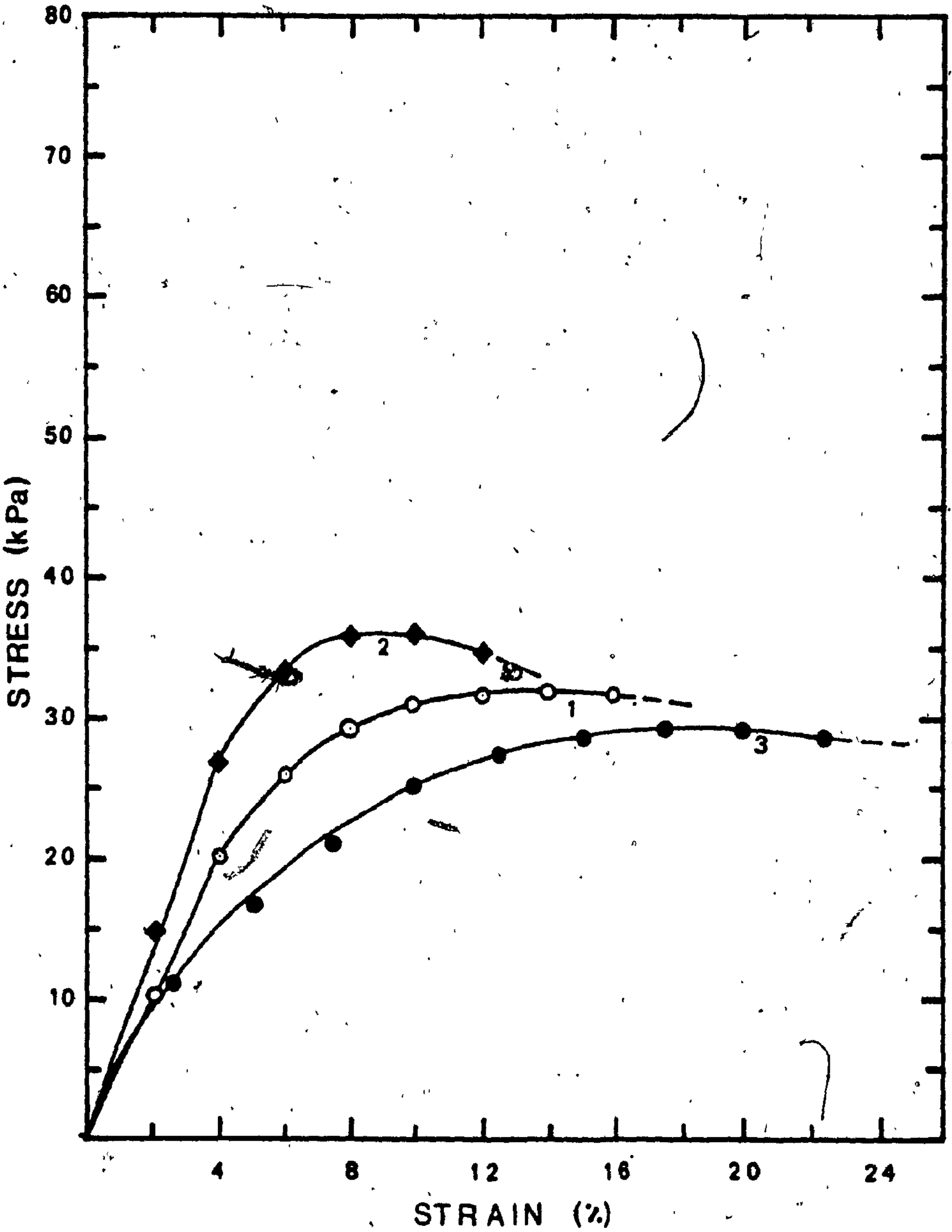

Figure 51 - Tensile stress-strain curves obtained from NA, L-Pu polyblends on wood substrates. Curve 1: L-B, 0:100; 2: L-B, 5:100; 3: Control curve, L-B, 0:100

5.5.4 Discussion and Conclusions

The addition of lignin to the polymeric matrix of butyl sealants stiffens the polyblend such that adhesive failure is more easily initiated in zones of high stress concentrations, located along the edge of the sealant-substrate interface. The stiffened matrix is characterized by an increased modulus with increased polymer loading and lower values of strain at yield, with corresponding reductions in toughness of the blend. Lower yield strains are indicative of a loss in adhesive strength.

The increase in toughness is brought about by the addition of L to the sealant blend, as well as the AA and NA processes. The addition of L may cause a more rapid release of solvent from the polymer, which in turn accelerates the curing process. However, it is felt that the effects of elevated temperatures are more important in initiating and propagating the release of solvent from the B matrix to complete a cure. Neither the extent nor the mode of interaction between the addition of L and the aging process is known. Lignin most likely behaves as a particulate filler, where the incorporation of L in the B matrix generally increases the modulus, and the mechanical properties are dependent on the interfacial adhesion between the lignin phase and the B phase. Morphological studies and thermal analysis would aid in confirming the existence of two phase behavior in L-B blends. Furthermore, hardness testing in relation to time would help clarify the role of lignin in the curing mode of L-B polyblends. Although the addition of lignin does not appear to be beneficial in enhancing the properties of B sealants, it might be used to replace filler substances with which B sealants are generally compounded, although the incompatibility of L and B must also be considered. In this respect, lignin may find a role in replacing extender pigments such as whitings or thixotropic agents (i.e. fibrous talc), both of which are used in considerable quantities in the formulation of B sealants (e.g. 42.5% and 12.7% by weight of sealant for whiting and fibrous talc respectively, in a typical one-part, non-sagging butyl-based sealant formulation). The size of calcium carbonate whiting ranges from 0.05 to 40 microns, and for fibrous talc from 3 to 8 microns, which is in the same order of magnitude of lignin particle sizes previously observed from SEM photomicrographs in section 5.2. The market for butyl sealants is expected to reach approximately 23000 tonnes by 1990, and the incorporation of lignin as an extender or reinforcing agent potentially may considerably increase the current demand for lignin, which is in the range of 40000 tonnes/yr.

5.6 Tension testing of lignin-acrylic (L-A) polyblends

5.6.1 L-A blends on aluminum substrates

The toughness of L-A blends on aluminum substrates increases with a corresponding increase in lignin loading for all specimens tested, as shown in Table 15. Increases of 25% in toughness were observed for control specimens having a 12.5 PBW lignin loading. For AA specimens, a maximum increase of 300% in toughness was achieved with the same lignin loading, whereas a 540% increase in toughness over non-modified L-A blends was obtained in the case of NA specimens loaded with 20 PBW of lignin. In general, these increases in toughness may be attributed to the addition of lignin, which causes an increases in both stress and strain at yield, as shown in Figures 52, 53, and 54.

Yield stress for control specimens increased 94, 188 and 321% for lignin loadings of 5, 10, and 15 PBW respectively, but decreased to 80% with addition of 20 PBW to the blend, representing a loss in yield stress, over the specimens blended with 15 PBW of lignin, of 57%.

This loss of stress at yield may be attributed to a stiffening of the L-A matrix, causing an increased incidence of adhesive failure, as observed during tensile testing. The failure mode of L-A polyblends on aluminum substrates was predominantly cohesive in nature for lignin loadings of 0 and 5 PBW, cohesive-adhesive in nature for lignin loadings of 10 and 12.5 PBW, and adhesive in nature for the remaining specimens. In the case of AA specimens, the yield stress increased 94, 144, and 300% with the addition of 5, 10, and 15 PBW of lignin, respectively, but only 258% when 20 PBW of lignin were added to the blend. Again, the loss in yield stress is due to a stiffened L-A matrix which enhances adhesive failure initiated at the point of highest stress concentrations along the sealant-substrate interface. NA specimens were found to behave in a similar fashion, where gains in yield stress of 38, 138, 246, and 407%, over unblended sealant, were obtained with the addition of 5, 10, 15, and 20 PBW of lignin, respectively.

In terms of durability, there is a loss in toughness with a corresponding loss in stress and strain for aged (ie. AA and NA) specimens in comparison to C specimens. It can also be seen from Table 15 that the loss in toughness is greater with NA specimens than with AA specimens. This may be due to the different aging conditions NA specimens are subjected to, as they are exposed to moisture in the form of water, ice, and snow. Furthermore, the often highly polluted and acidic nature of the rain may also play a part in reducing the resilience of NA specimens, although it is not possible to presently estimate to what extent this factor contributes to the weathering process.

A loss of modulus for aged specimens in comparison to control specimens was also observed. The effects of thermal shock, natural or simulated solar radiation and, in the case of NA specimens, moisture on the aged specimens may cause scission of the polymer chains and/or reductions of the crosslinking density, which in turn lowers their modulus.

As was reported earlier, the addition of lignin enhances the mechanical properties of L-A polyblends. However, when comparing the percentage increase in mechanical properties of AA and NA with C specimens, results do not conclusively support the premise that lignin improves the durability of A sealants. For unblended sealants (ie. L:A; 0:100), there is a 25% loss of modulus and a 15% loss of toughness due to the aging process. The addition of lignin does not reduce the % loss of toughness or modulus with aging, although blended sealants do have a greater modulus and toughness relative to the control specimens of neat sealant.

In general, the improvements in mechanical properties of L-A blends on aluminum substrates are due to the inclusion of lignin in the sealant blend. Lignin acts as a reinforcing filler, which stiffens the matrix sufficiently to progressively increase its mechanical properties up to a point at which adhesive failure is predominant. This point occurs at much higher lignin loadings for L-A blends in comparison to L-B blends, attesting to the superior adhesive tenacity of A sealants.

Lignin-A polyblends behave as a two-phase material, with the mechanical properties determined by the interfacial adhesion betweeen phases. The polar nature of A and L polymers enables the formation of intermolecular forces or secondary bonds to develop at the phase interface, which may account for the enhanced mechanical performance of these blends. Furthermore, both polymers have functional reactive groups, which may also react, forming covalent bonds.

TOUGHNESS (KPa)

Polyblend L:A	C	Exposure Conditions AA	NA
0:100	2.23	2.2	1.6
5:100	4.5	3.2	1.9
10:100	7.2	4.7	4.5
12.5:100	8.0	6.6	5.5
15:100	7.5	8.9	7.2
20:100	3.2	4.9	10.2

TANGENT MODULUS (KPa)
at 5% strain

Polyblend L:A	C	Exposure Conditions AA	NA
0:100	14.7	10.1	12.0
5:100	27.6	19.4	16.7
10:100	41.9	27.7	29.0
12.5:100	57.2	33.1	34.3
15:100	67.7	40.5	37.2
20:100	27.2	5.0	51.2

Table 15 - Toughness and tangent modulus of lignin-acrylic polyblends on aluminum substrates.

YIELD STRESS (KPa)

Polyblend L:A	Exposure Conditions C	 AA	 NA
0:100	17.8	14.8	13.6
5:100	34.5	25.8	18.7
10:100	51.3	36.1	32.3
12.5:100	65.9	44.6	40.1
15:100	74.9	59.1	47.0
20:100	32.1	5.3	69.0

YIELD STRAIN (%)

Polyblend L:A	Exposure Conditions C	 AA	 NA
0:100	12.5	15.0	11.7
5:100	13.1	12.5	10.0
10:100	14.0	13.0	13.8
12.5:100	12.1	14.8	13.7
15:100	10.1	15.0	15.3
20:100	10.1	9.3	14.8

Table 16 - Yield stress and yield strain of lignin-acrylic polyblends on aluminum substrates.

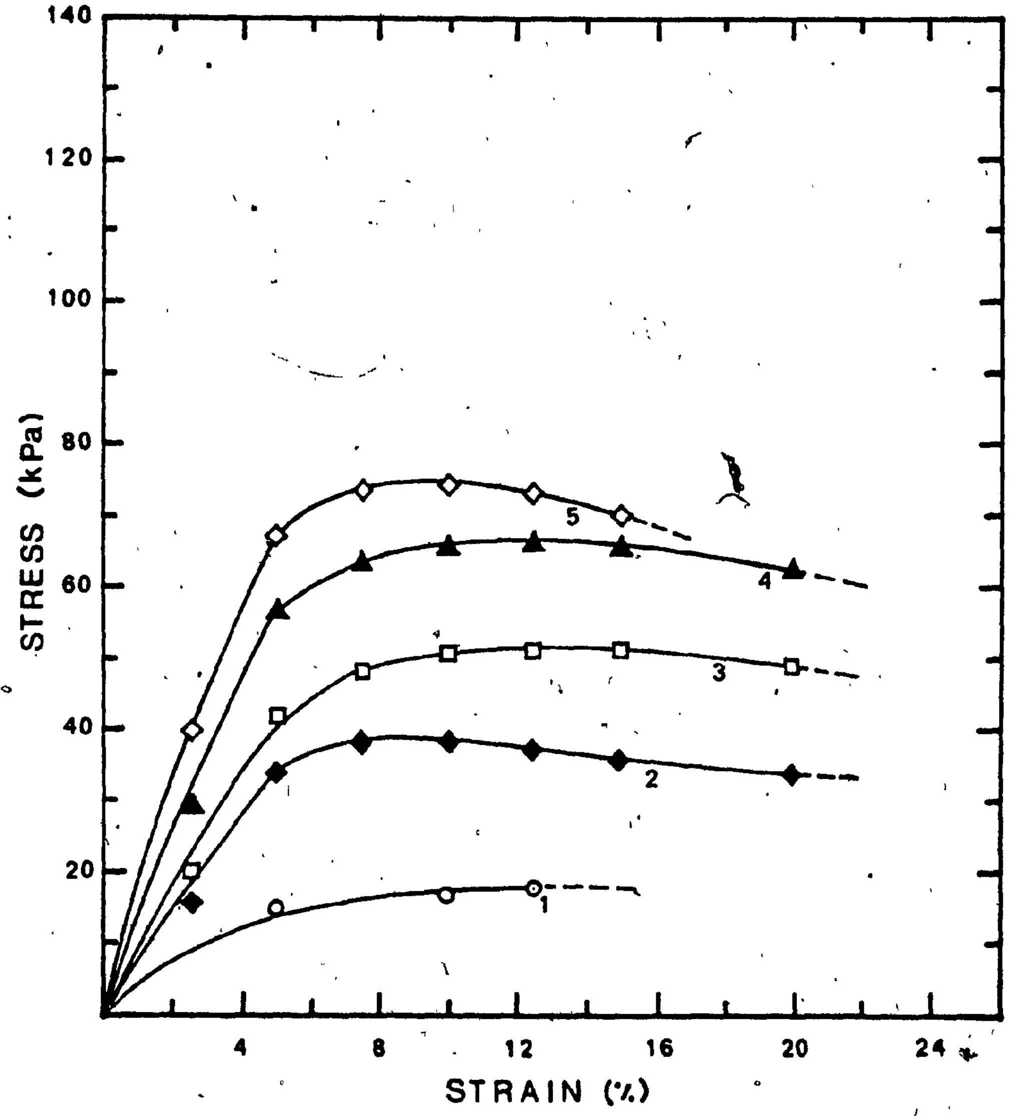

Figure 52 - Tensile stress-strain curves obtained from control, L-A polyblends on aluminum substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: L-A, 20:100; 7: Control curve, L-A, 0:100

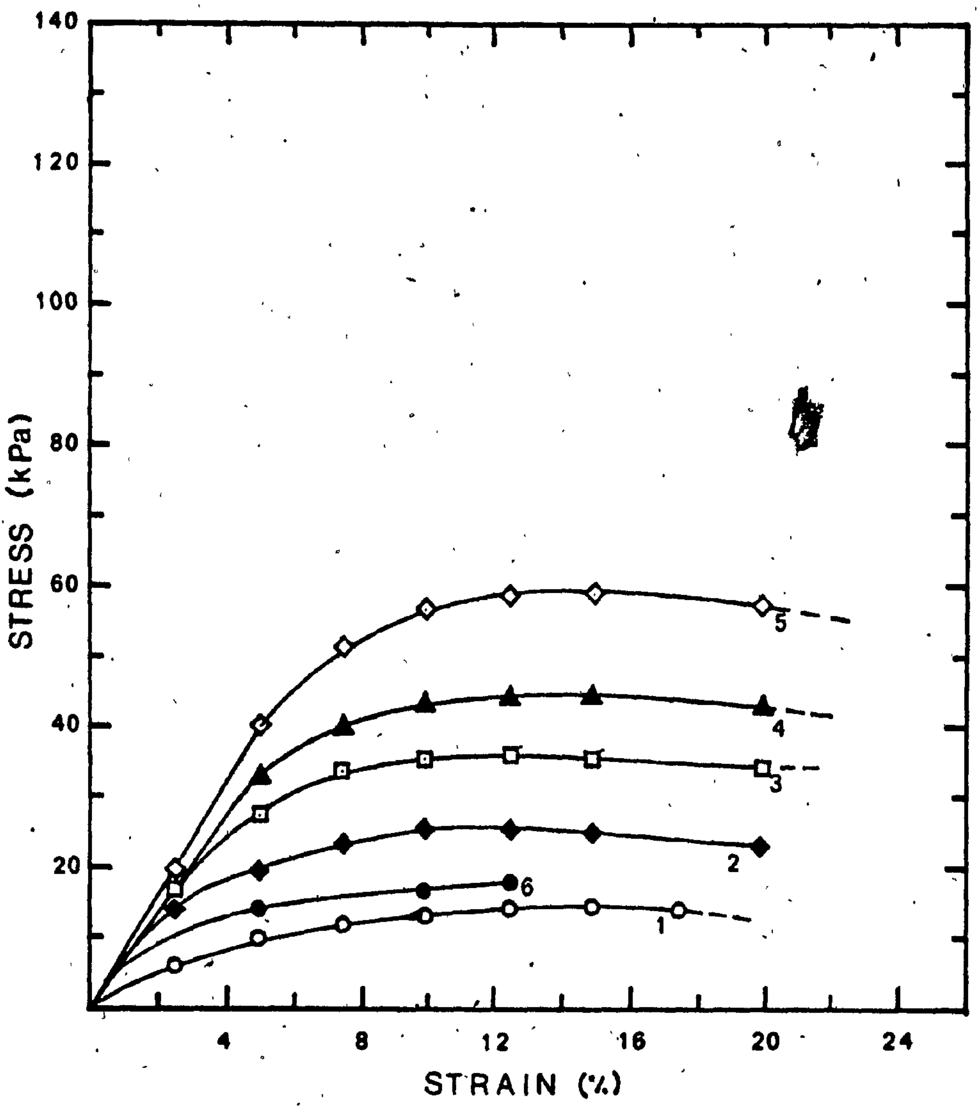

Figure 53 - Tensile stress-strain curves obtained from AA, L-A polyblends on aluminum substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: Control curve, L-A, 0:100

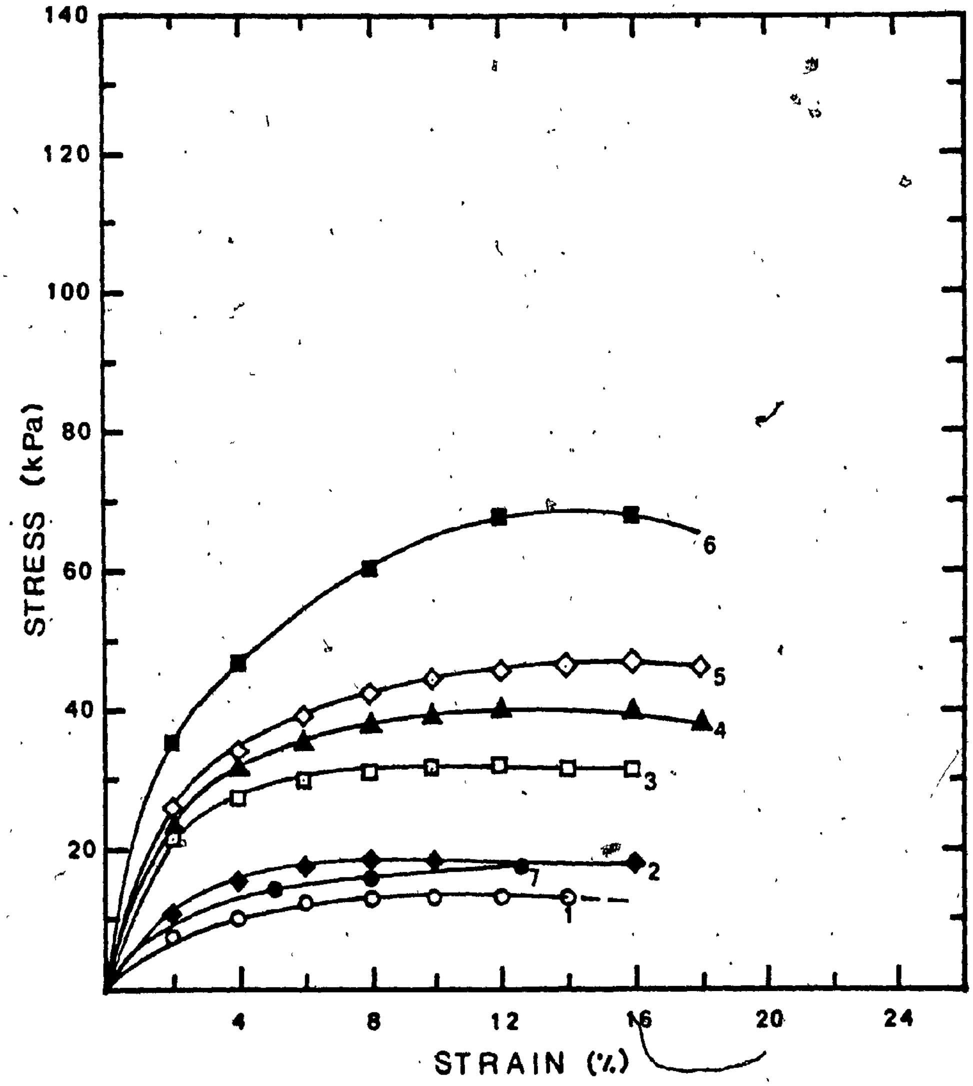

Figure 54 - Tensile stress-strain curves obtained from NA, L-A polyblends on aluminum substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: L-A, 20:100; 7: Control curve, L-A, 0:100

5.6.2 L-A blends on mortar substrates

The toughness of L-A polyblends on mortar substrates generally increases with the addition of lignin in the blend (Table 17). The maximum toughness of control specimens is 280% greater than the unblended sealant achieved at a L-A loading of 12.5 PBW. For NA and AA specimens the maximum respective toughness is 371% and 447% at 12.5 and 15 PBW of lignin respectively.

The modulus of L-A polyblends generally increases with increased lignin loading (Table 18), with control and AA specimens increasing 30 and 240% with addition of 5 PBW of lignin, and increasing 154 and 295% with a further addition of 5 PBW of lignin. Thereafter, any additional lignin is shown to reduce the modulus of the polyblend. The NA specimens display a more progressive increase in modulus with an 88, 223, 291 and 492% increase in modulus with the incorporation of 5, 10, 12.5, and 15 PBW of lignin respectively within the polymeric matrix. Hence the addition of lignin progressively stiffens the sealant, with corresponding increases in stress and strain at yield. Control, AA, and NA specimens exhibit an increase in yield stress with the addition of lignin, as shown in Figures 55, 56, and 57. For control specimens, 10 PBW of lignin added to the sealant matrix increased the stress at yield by 150%, however any further additions were not beneficial in terms of yield stress. AA and NA specimens displayed a similar trend in stress increase with lignin addition. The yield stress of AA specimens were shown to increase 210 and 391% for lignin loadings of 10 and 15 PBW respectively, in comparison to NA specimens which increased 220 and 441% for comparable lignin loadings. The increase in stress at yield is indicative of a more cohesive, higher modulus material, whose adhesive strength is still capable of withstanding the higher stresses imposed at the edges of the sealant-substrate interface.

The yield strain for L-A polyblends on mortar substrates is seen to limit the stress at yield obtainable in the sample. Values of stress and strain at yield below 9% are indicative of a sealant matrix which is too stiff, and failure tends to occur in adhesion in the zone of highest stress concentration along the sealant-substrate interface. This was evident for those AA specimens blended with 5 PBW of lignin, where the strain at yield was 8.9% and a high value yield stress was obtained in comparison to C or NA specimens. This was due to the reinforcing effect of backing paper which remained adhered to the sealant surface of the specimen.

The durability of L-A sealants on mortar substrates is not as sensitive to the addition of lignin as was found for L-A specimens on aluminum substrates. In general, the toughness and modulus of the specimens decreases with aging, more so for NA than AA specimens. As suggested earlier, the general trend is due to the effect of thermal cycling and solar radiation, and the more severe effects observed from results on NA specimens, due to these combined effects as well as the effect of moisture. However, in contrast to results obtained from blends on aluminum substrates, those from mortar substrates indicate that the percentage loss of mechanical properties of AA and NA neat sealant is greater than that of blended specimens. Hence in this case the addition of lignin would appear to be beneficial in improving the durability of L-A polyblends.

Lignin-A polyblends on mortar substrates generally behave in the same fashion as those adhered to aluminum substrates. The role of lignin is to reinforce the polymeric matrix and, in consequence, the mechanical properties are dependent on the interfacial adhesion between the lignin particles and the acrylic polymer matrix. This is a trait found in two phase particulate composites.

TOUGHNESS (KPa)

Polyblend	Exposure Conditions		
L:A	C	AA	NA
0:100	2.6	2.6	1.6
5:100	3.6	4.3	2.6
10:100	7.3	6.6	5.2
12.5:100	4.6	7.6	7.6
15:100	3.3	14.0	7.3
20:100	-	10.8	-

TANGENT MODULUS (KPa)
at 5% strain

Polyblend	Exposure Conditions		
L:A	C	AA	NA
0:100	21.4	11.0	11.2
5:100	27.9	37.0	21.1
10:100	54.4	43.5	36.2
12.5:100	53.0	43.1	43.8
15:100	43.9	59.4	66.3
20:100	-	105.5	-

Table 17 - Toughness and tangent modulus of lignin-acrylic [illegible]yblends on mortar substrates.

YIELD STRESS (KPa)

Polyblend	Exposure Conditions		
L:A	C	AA	NA
0:100	27.8	18.4	13.4
5:100	34.1	49.2	23.7
10:100	70.3	57.0	42.9
12.5:100	59.0	61.1	55.7
15:100	46.9	90.4	72.5
20:100	-	120.8	-

YIELD STRAIN (%)

Polyblend	Exposure Conditions		
L:A	C	AA	NA
0:100	9.4	14.0	12.0
5:100	10.4	8.9	10.8
10:100	10.4	11.5	12.2
12.5:100	7.8	12.5	13.6
15:100	7.1	15.5	10.0
20:100	-	9.0	-

Table 18 - Yield stress and yield strain of lignin-acrylic polyblends on mortar substrates.

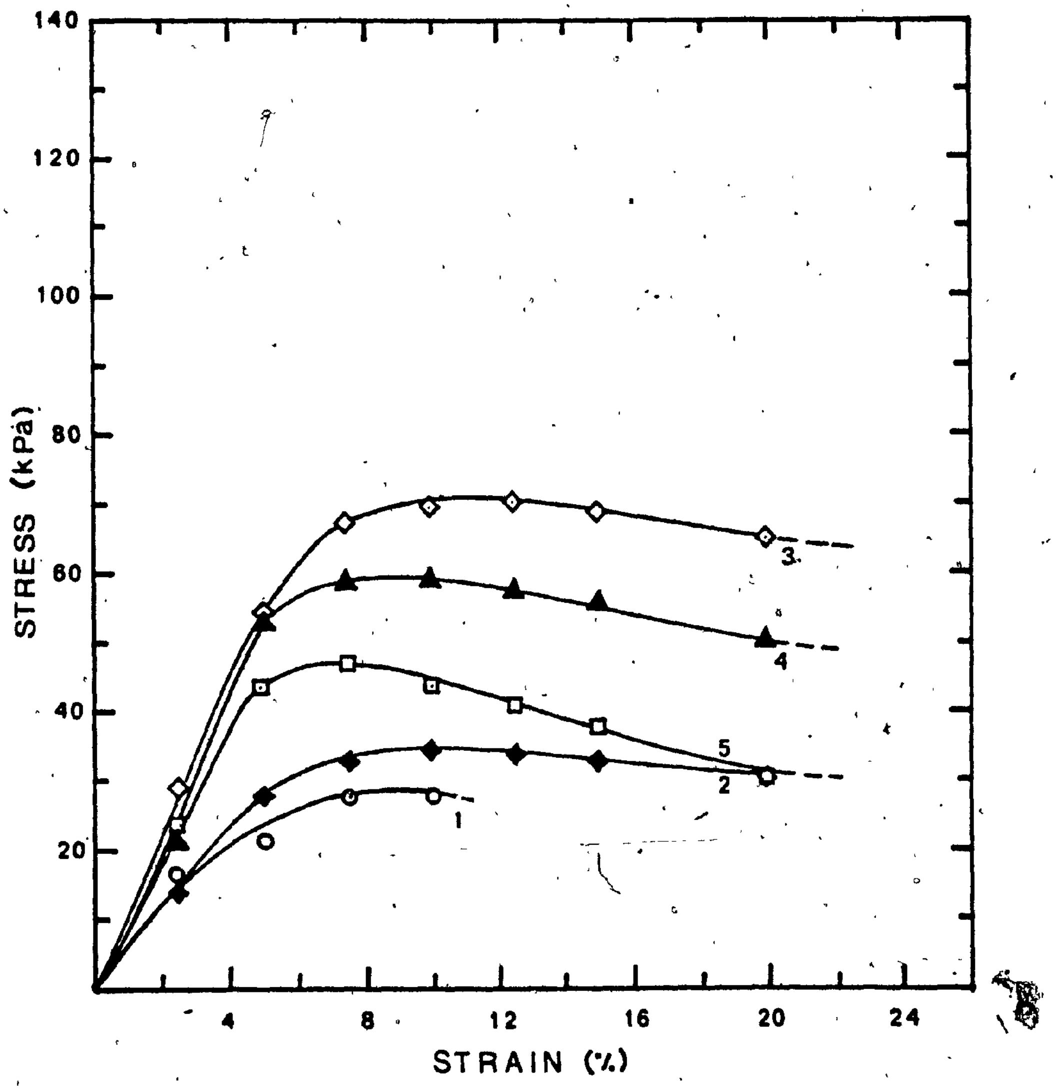

Figure 55 - Tensile stress-strain curves obtained from control, L-A polyblends on mortar substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: Control curve, L-A, 0:100

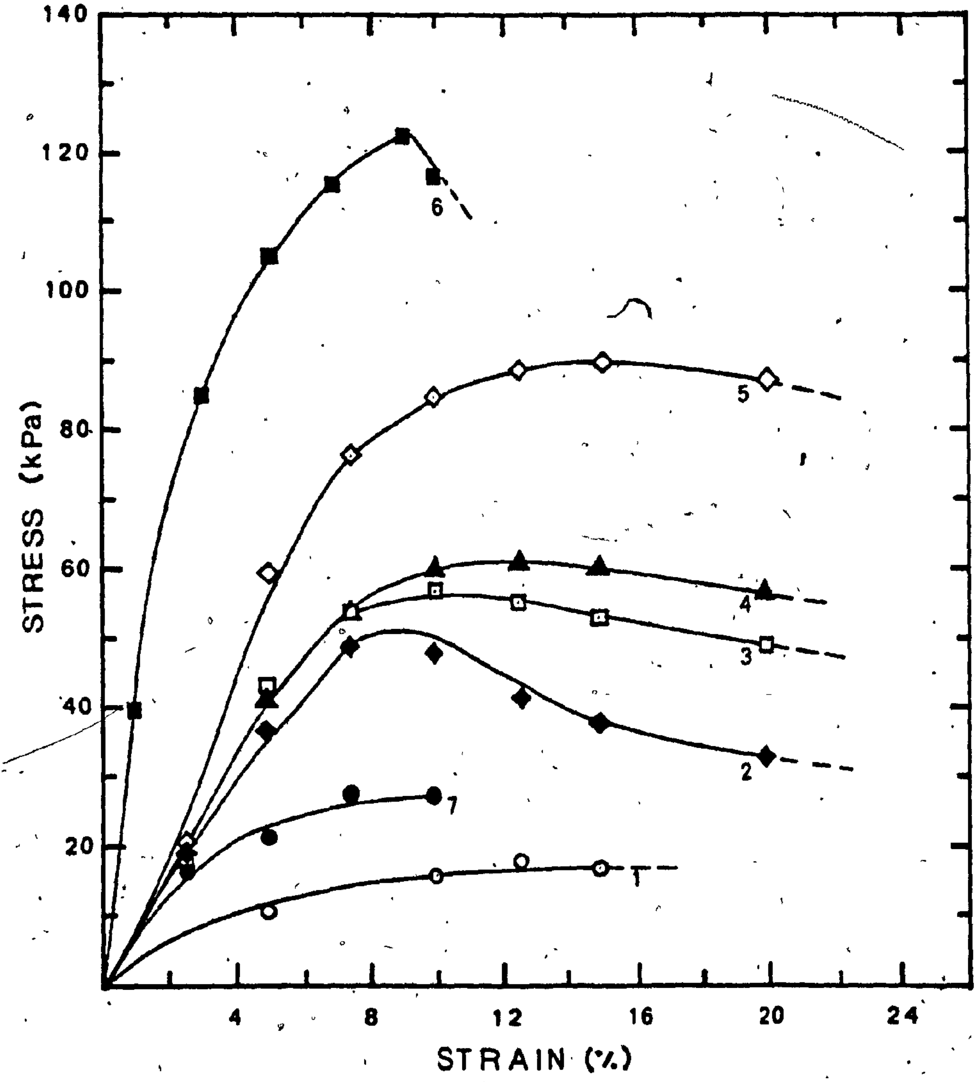

Figure 56 - Tensile stress-strain curves obtained from AA, L-A polyblends on mortar substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: L-A, 20:100; 7: Control curve, L-A, 0:100

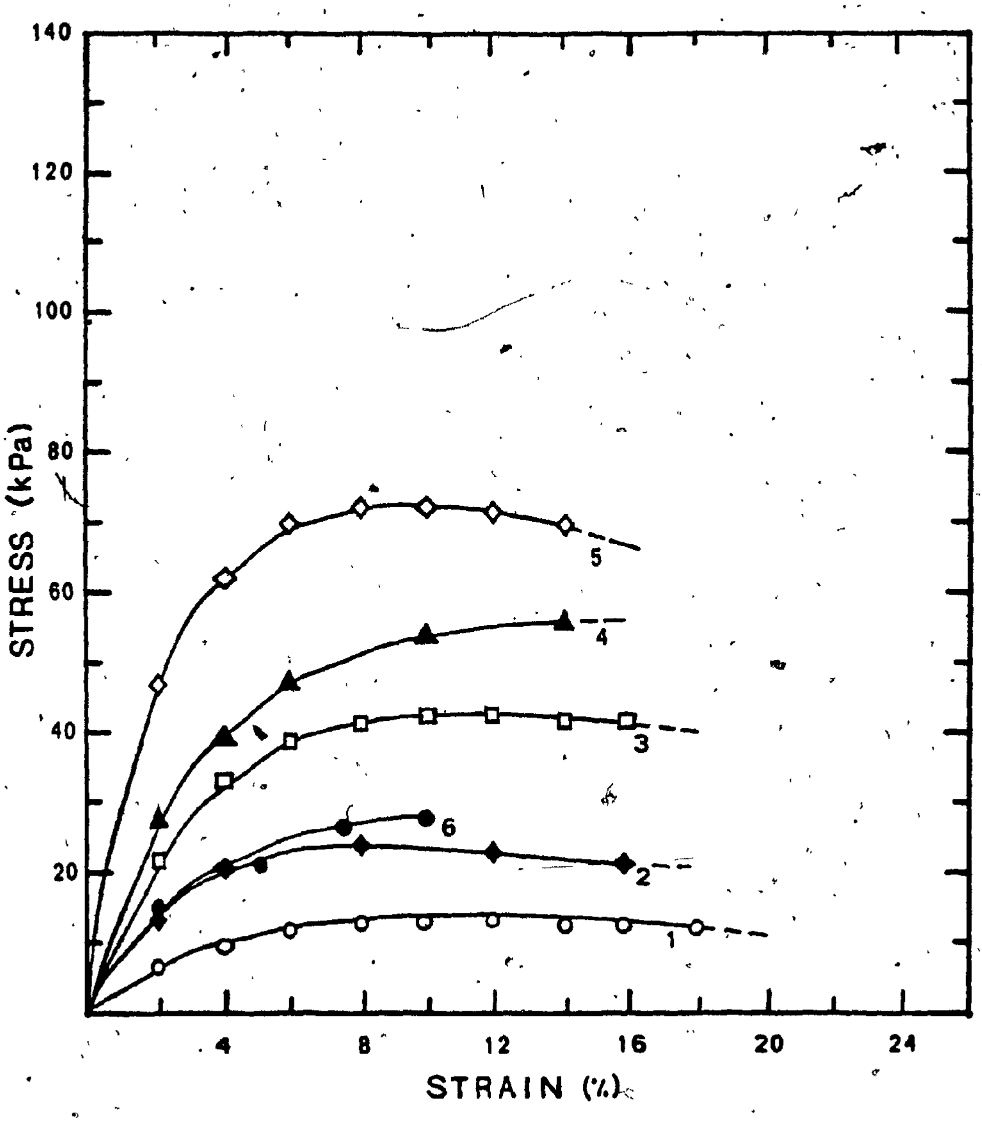

Figure 57 - Tensile stress-strain curves obtained from NA, L-A polyblends on mortar substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: Control curve, L-A, 0:100

5.6.3 L-A blends on wood substrates

The toughness of L-A polyblends on wood substrates is shown to increase with the addition of lignin, with the greatest gains recorded at 15 PBW lignin loading, giving 330% and 217% increase in toughness for NA and AA specimens respectively (Table 19). Beyond this loading factor, the toughness diminished 30% for both types of specimens. Control specimens exhibited a maximum increase of 200% over unblended sealant at 15 PBW loading. These increases were due to the addition of lignin which stiffened the matrix, as indicated by higher values of stress and strain at yield (Fig. 58, 59, and 60). The stress at yield increased progressively for all specimens tested, with maximum stresses attained at 20 PBW lignin loading (Table 20).

Reductions in toughness beyond 15 PBW lignin loading were due to adhesive failure, which is characteristic of an even stiffer polymeric matrix, and is illustrated by the lowering of yield strain at high lignin loadings. The stiffening of the matrix is also shown by the increase in modulus with the addition of lignin (Table 19). Control specimens exhibited a modulus increase of 153 and 388%; AA specimens a modulus increase of 152 and 490%; NA specimens a modulus increase of 123 and 480%, for loadings of 10 and 20 PBW respectively.

The durability of L-A blends on wood substrates is in general agreement with the results obtained for blends on mortar substrates. There is a loss of toughness and modulus with aging, and a more important loss in toughness for NA specimens than for AA specimens. However, the loss in modulus of NA specimens is not as significant as that of AA specimens and is, for blended sealants on average, less than that found for neat sealants. This may indicate an increased durability with the addition of lignin for NA specimens, in contrast to results obtained for AA specimens, which show a greater percentage loss of modulus with blended sealants than with neat sealant. Clearly the results obtained are inconclusive with respect to the role of lignin in enhancing the durability of A blends.

In comparison to L-A polyblends on aluminum and mortar substrates, L-A polyblends on wood substrates behave in much the same manner, with lignin acting as an active reinforcing agent which stiffens the overall polymeric matrix and enhances the mechanical properties of the blend.

TOUGHNESS (KPa)

Polyblend L:A	Exposure Conditions C	 AA	 NA
0:100	2.4	2.7	2.1
5:100	3.2	3.0	2.7
10:100	6.4	5.1	4.0
12.5:100	6.4	7.1	4.5
15:100	7.3	8.5	8.9
20:100	4.2	6.0	6.1

TANGENT MODULUS (KPa)
at 5% strain

Polyblend L:A	Exposure Conditions C	 AA	 NA
0:100	16.2	13.7	13.2
5:100	34.7	15.8	23.6
10:100	41.0	34.5	29.5
12.5:100	45.4	39.0	40.7
15:100	62.4	45.1	53.5
20:100	79.1	80.8	76.6

Table 19 - Toughness and tangent modulus of lignin-acrylic polyblends on wood substrates.

YIELD STRESS (KPa)

Polyblend L:A	Exposure Conditions C	 AA	 NA
0:100	20.0	17.9	16.2
5:100	38.4	24.7	26.4
10:100	52.8	42.9	34.2
12.5:100	56.9	53.2	46.1
15:100	72.5	62.0	64.4
20:100	79.2	83.3	79.8

YIELD STRAIN (%)

Polyblend L:A	Exposure Conditions C	 AA	 NA
0:100	12.0	15.0	12.8
5:100	8.3	12.3	10.0
10:100	12.1	11.9	11.7
12.5:100	11.3	13.3	9.8
15:100	10.0	13.8	13.8
20:100	5.3	7.2	7.6

Table 20 - Yield stress and yield strain of lignin-acrylic polyblends on wood substrates.

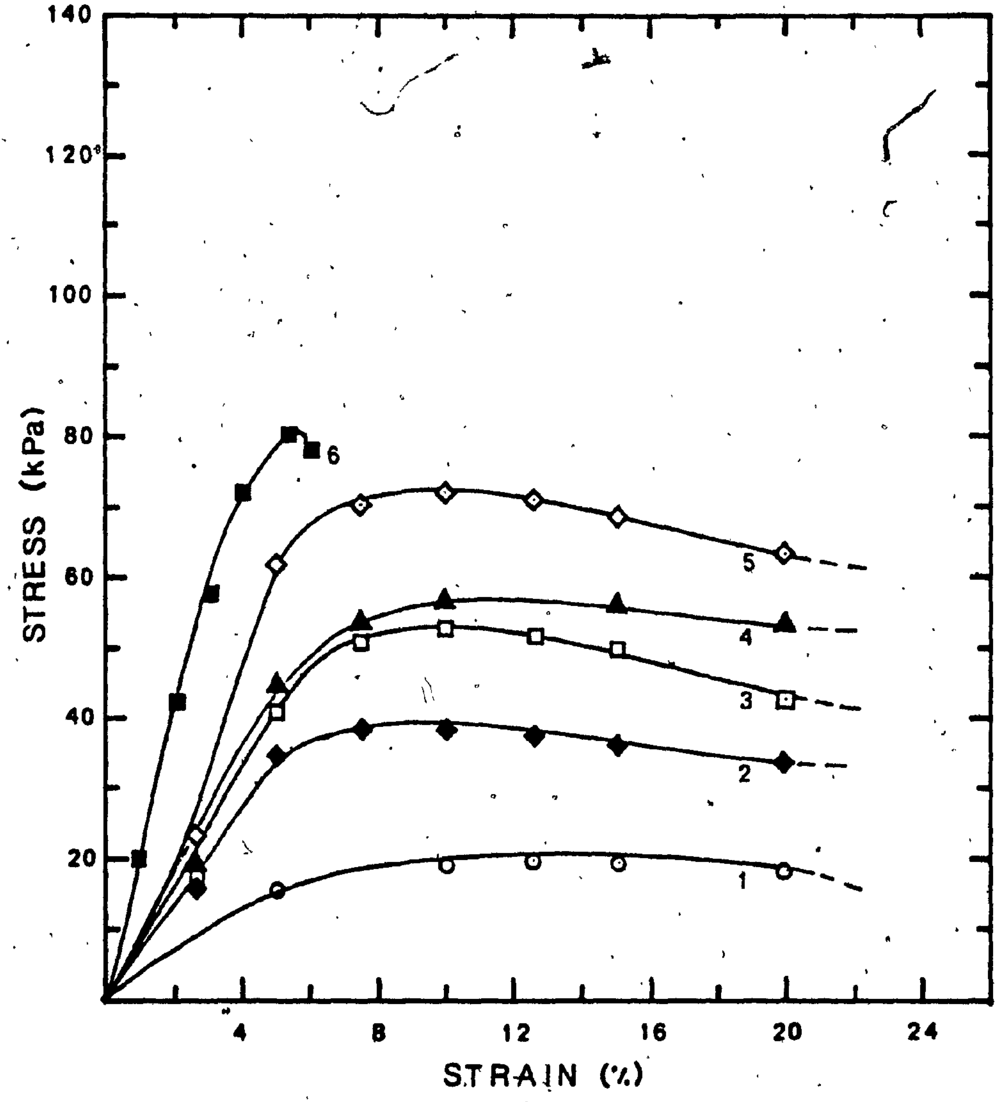

Figure 58 - Tensile stress-strain curves obtained from control, L-A polyblends on wood substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: L-A, 20:100

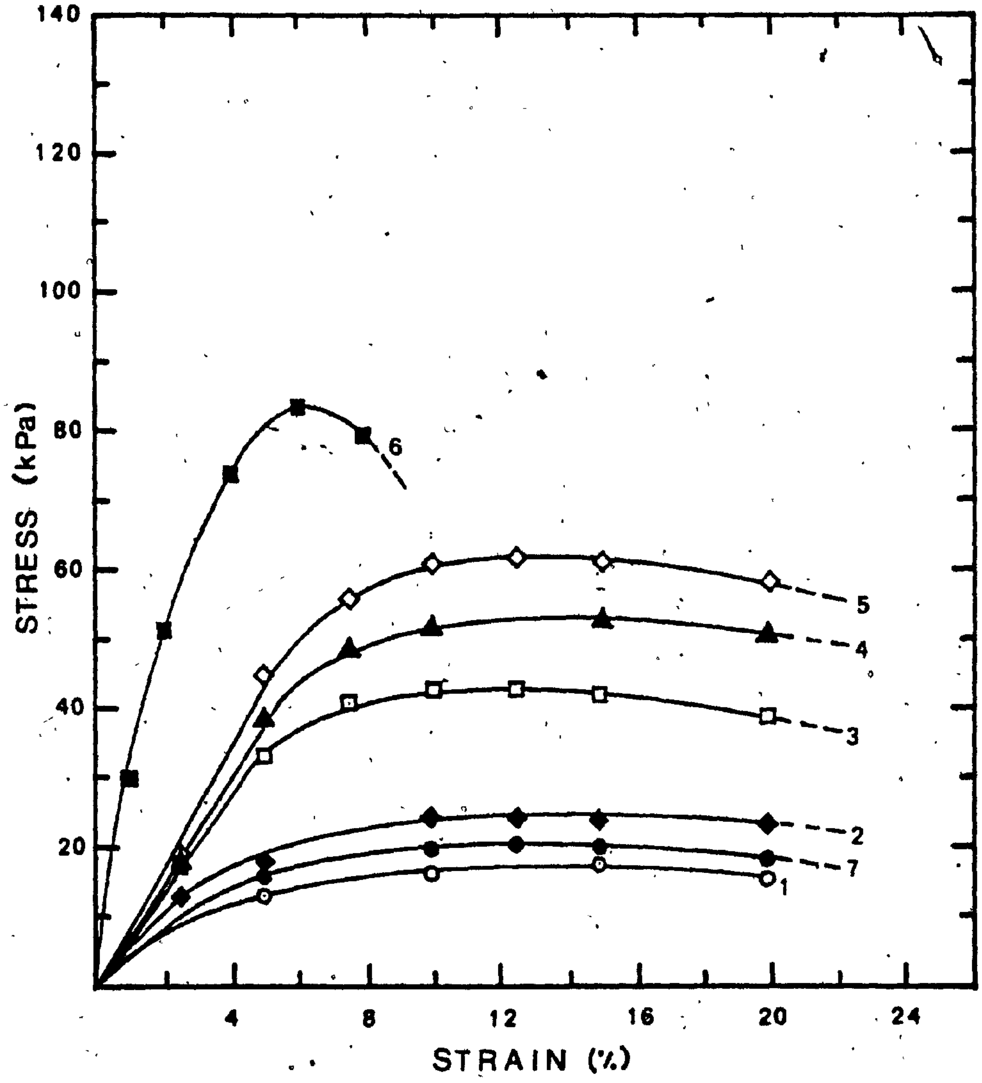

Figure 59 - Tensile stress-strain curves obtained from AA, L-A polyblends on wood substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: L-A, 20:100; 7: Control curve, L-A, 0:100

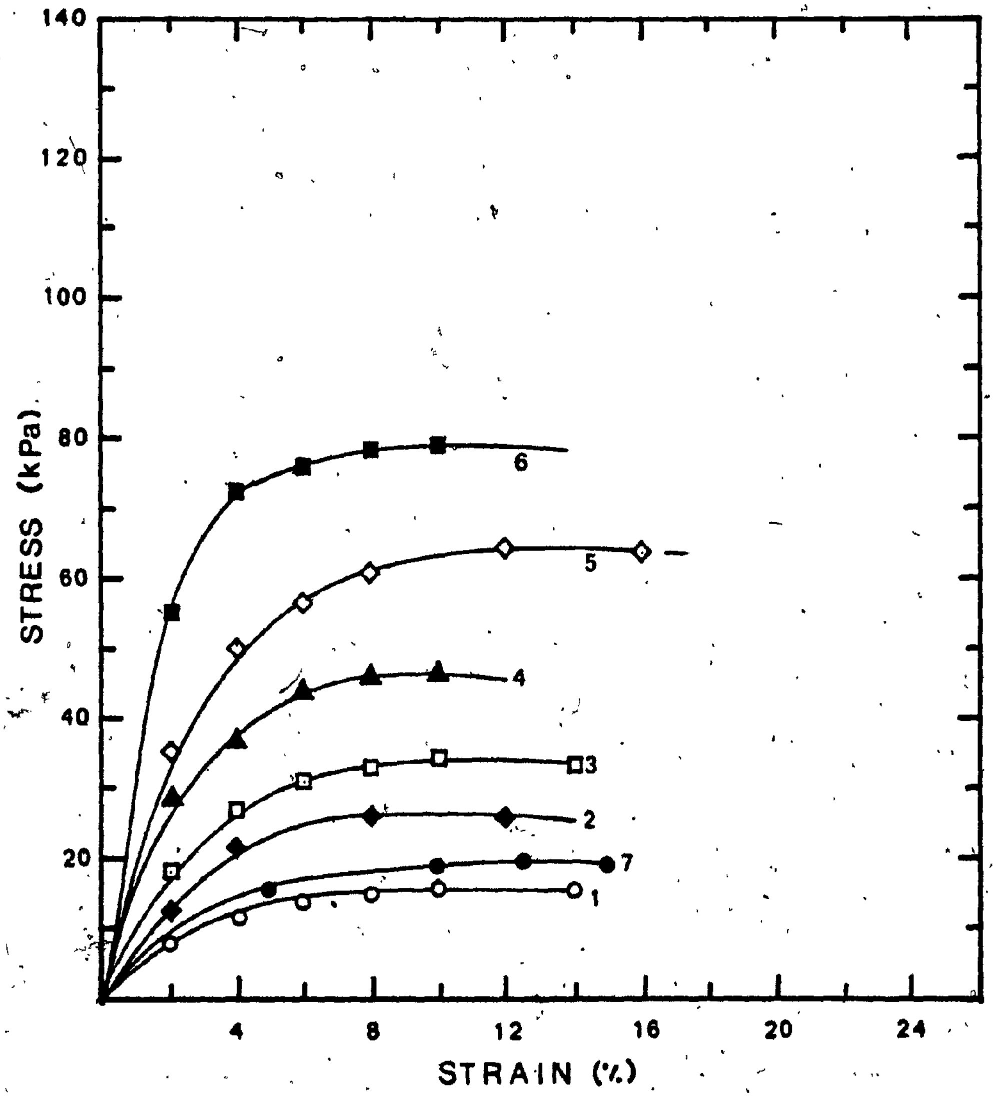

Figure 60 - Tensile stress-strain curves obtained from NA, L-A polyblends on wood substrates. Curve 1: L-A, 0:100; 2: L-A, 5:100; 3: L-A, 10:100; 4: L-A, 12.5:100; 5: L-A, 15:100; 6: L-A, 20:100; 7: Control curve, L-A, 0:100

5.6.4 Discussion and Conclusions

The incorporation of 12.5 to 15 PBW of lignin in L-A polyblends increases the toughness, modulus, and stress and strain at yield. The increase in toughness of blends adhered to aluminum substrates averaged approximately 360%, ranging between 257% for C specimens and 542% for NA specimens. Polyblends adhered to mortar substrates averaged 330% increase in toughness, whereas those blends on wood substrates averaged an increase in toughness of 250%. These significant increases in toughness are due to the reinforcing capabilities of lignin. The polymer acts in a two phase system, as a strengthening agent, where the mechanical properties of the combined phases are dependent on the interaction between each phase. This is common of two component composite blends of a weak low modulus matrix, in which is dispersed a higher modulus particulate. Their properties are a function of the interfacial adhesion between each phase. Evidence of phase separation could be obtained by studying the morphology of the blends using SEM in conjunction with LM. In this way, different material textures would identify each phase. The use of a DSC thermograph would aid in discerning the existence of one or two phases, by illustrating the changes (if any) in glass transition temperatures.

More investigations are also required to clarify if L acts as a simple filler in the L-A polyblend system or, as is surmised, as an active reinforcement with possible chemical interactions. Infra-red spectroscopy would provide a useful means to analyse the differences between blended and unblended specimens.

In general, there is a progressive increase in modulus with a corresponding increase in lignin loading for all blend ratios tested (Figures 61 & 62). However, with respect to C specimens, this trend is reversed for those adhered to mortar and aluminum substrates beyond blend ratios of 10:100 (L:A) and 15:100 (L:A) repectively. That is to say, there exists a decrease in modulus with the addition of lignin in these specimens, although the absolute value of the modulus is in excess of the neat A sealant. In a similar fashion, the modulus of AA specimens adhered to aluminum substrates decreases beyond a blend ratio of 15:100 (L:A). Loss of modulus in specimens with high L loading (20:100::L:A) is more apparent for those adhered to aluminum or mortar substrates (Figure 62) than those adhered to wood. Specimens having a high lignin loading failed primarily in adhesion, and in the case of those adhered to aluminum or mortar substrates, failure occured before significant values of strength or modulus could be recorded.

It may also be observed that a lower modulus is obtained with specimens adhered to aluminum than to wood substrates. This is more evident for specimens tested in the AA and NA series than the C series. There may be some chemical interactions between the mortar and the L-A sealant in the zone closest to the sealant substrate interface which produces a stiffening of the polymeric matrix.

The effects of AA on specimens may be observed from Figure 62. For specimens adhered to wood and aluminum substrates, the value of the modulus for AA and NA specimens is less than that of C specimens. However, it is also observed that the percentage increase in modulus between corresponding increases in L loading are similar for all aging conditions. For specimens adhered to mortar substrates, the effects of aging are not as apparent, in consideration of the inconsistent results obtained for C specimens in comparison to results of the other test series.

In general, in may be stated that there is a loss of modulus observed in specimens subjected to AA and NA in comparison to C conditons, brought about by the combined effects of thermal shock and UV radiation, and in the case of NA specimens, the added efeects of moisture.

Furthermore the durability of L-A polyblends is neither improved nor hindered with the addition of lignin, and further testing in this area is required to establish more conclusively, the role of lignin in their aging process.

An analysis of the yield strain of L-A specimens (Figures 63 & 64) indicates that there is a loss of strain at yield for specimens having a high blend ratio in comparison to the neat sealant. Beyond this initial observation, the manner in which the yield strain is affected by the addition of lignin is not immediately apparent. As can be seen from the figures, the correlation between yield strain and lignin loading is difficult to establish. The L-A blend is seemingly capable of absorbing certain quantities of L filler up to a blend ratio of 15:100 (L:A) without unduely affecting the strain at yield. The adhesive tenacity of these blends prevents premature adhesive failure along the sealant substrate interface up to this limiting value of lignin loading.

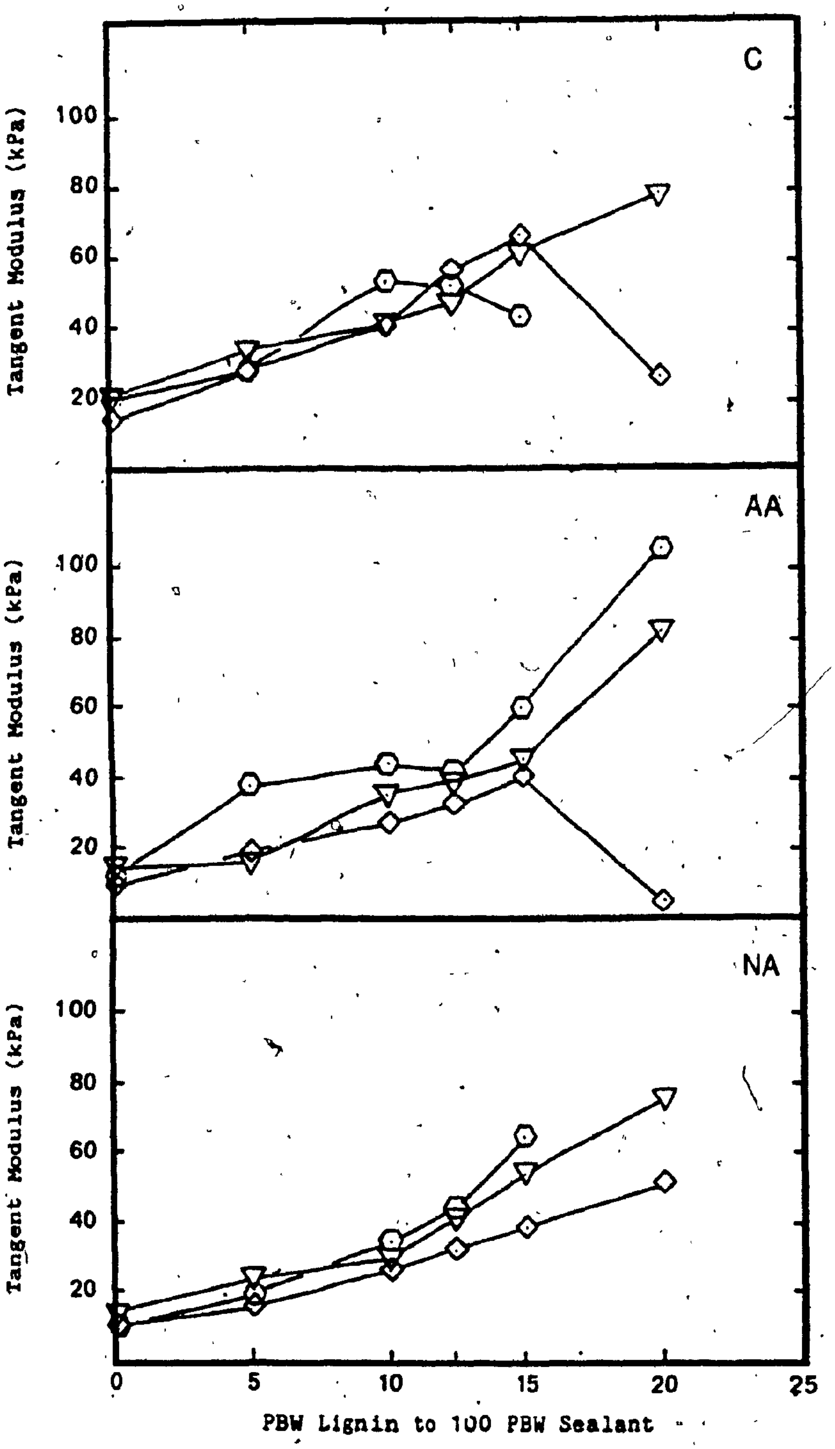

Figure 61 - Tangent modulus of L-A polyblends as a function of L loading in C, AA, NA conditions.

Substrates: ▼ - wood; ⬡ - mortar; ◇ - aluminum

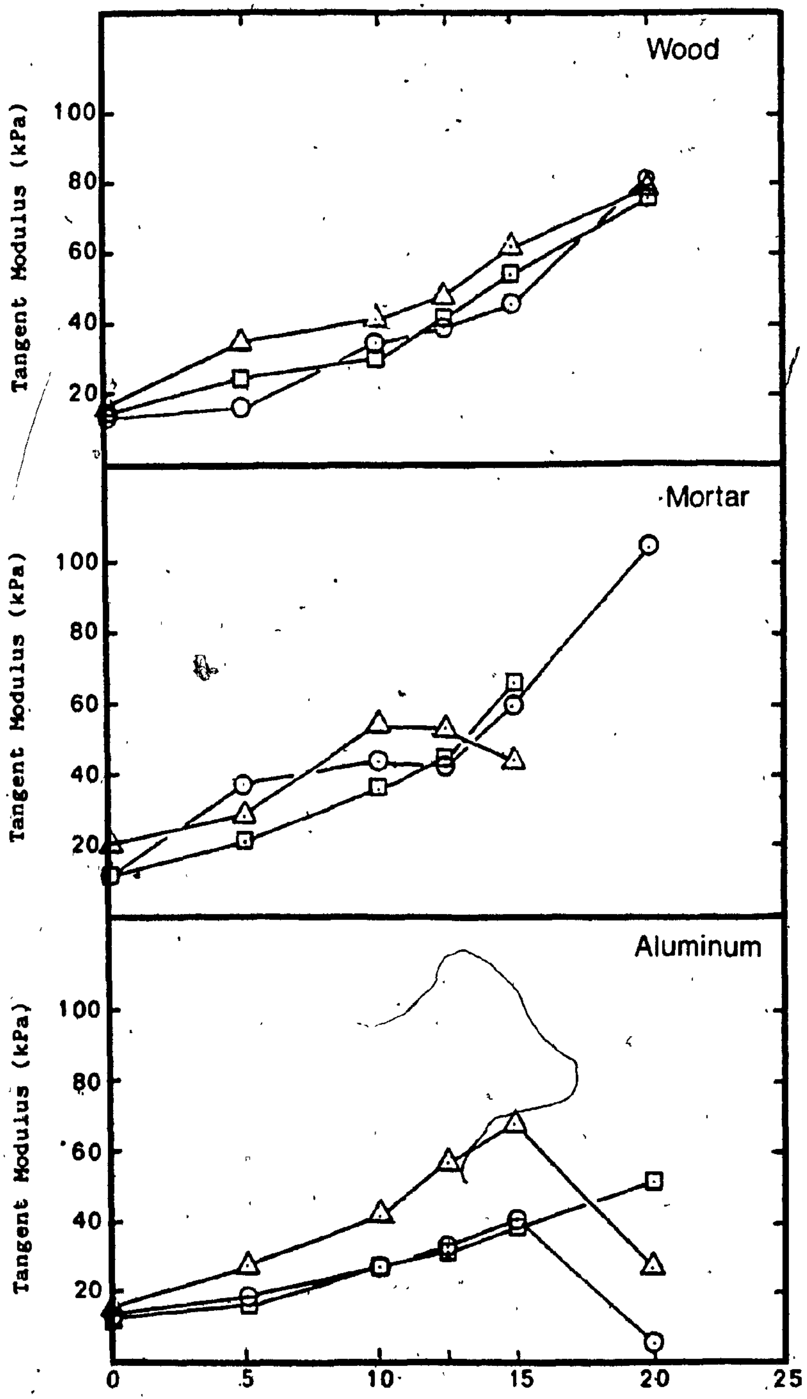

Figure 62 - Tangent modulus of L-A polyblends as a function of L loading on wood, mortar, and aluminum. Aging conditions: △ - C; ○ - AA; □ - NA

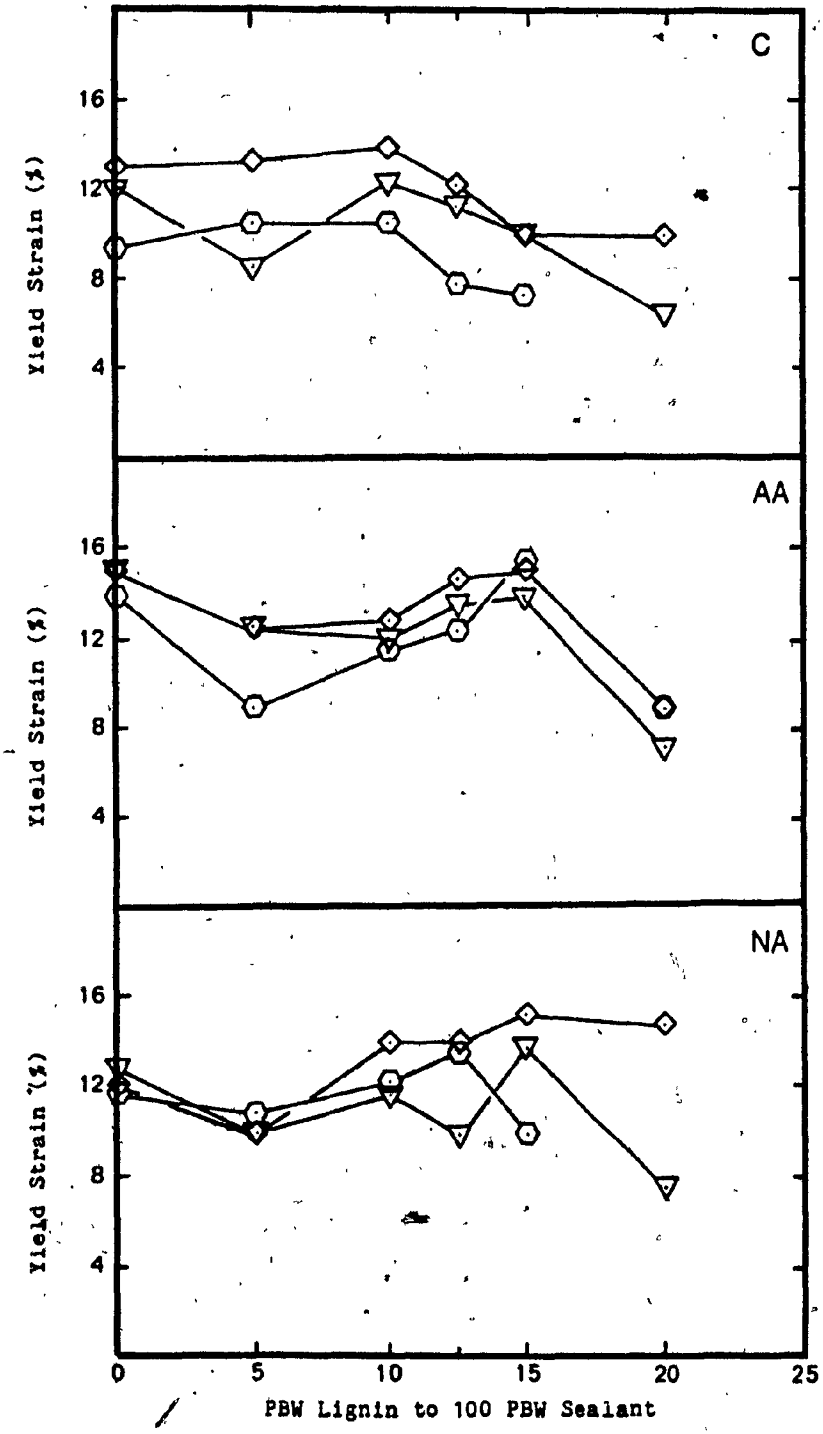

Figure 63 - Yield strain of L-A polyblends as a function of L loading in C, AA, NA conditions. Substrates: ▽ - wood; ⬡ - mortar; ◇ - aluminum

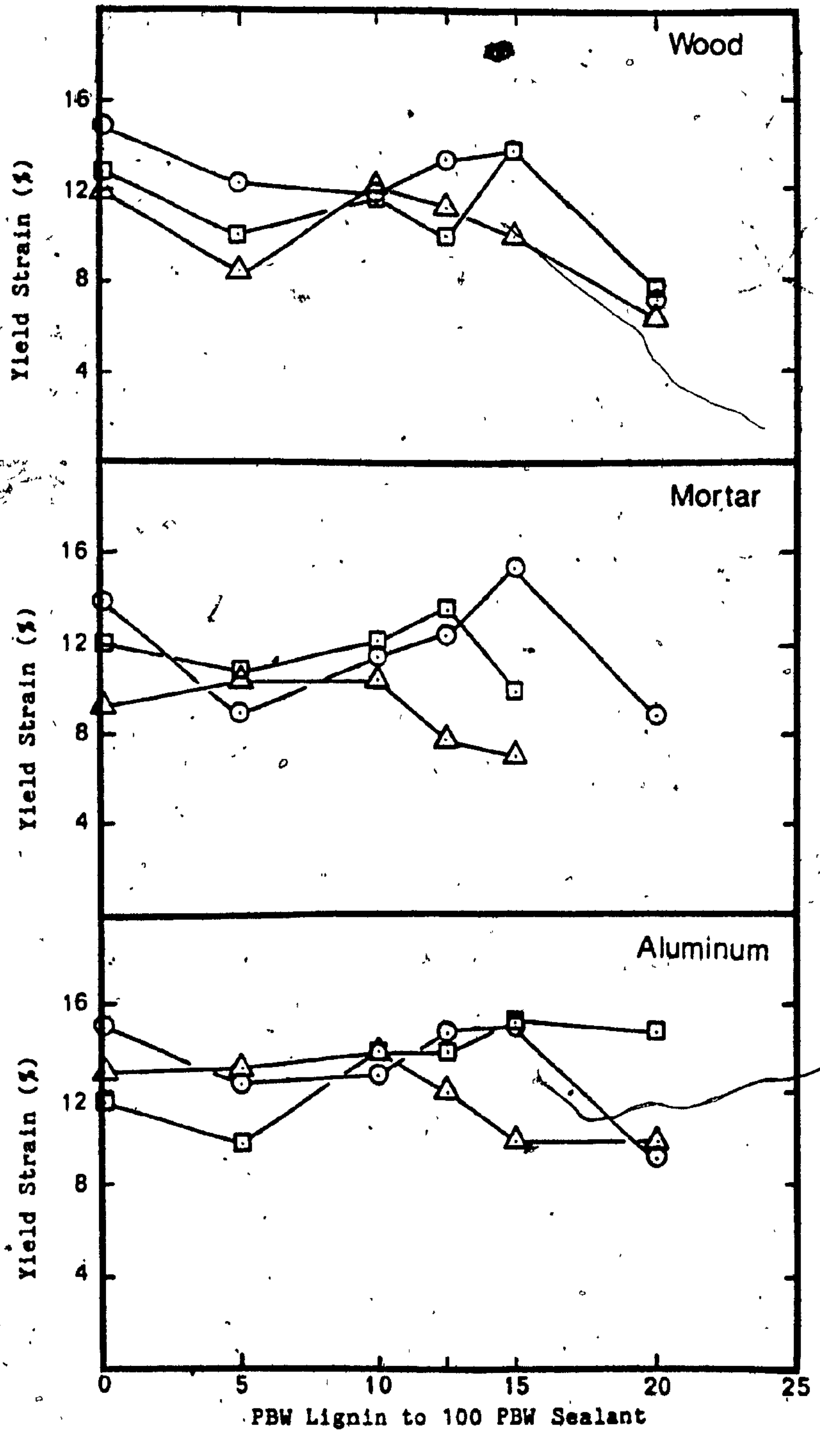

Figure 64 - Yield strain of L-A polyblends as a function of L loading on wood, mortar, and aluminum. Aging conditions: △ - C; ○ - AA; □ - NA.

5.7 Tension Testing of Lignin-Polyurethane (L-PU) Polyblends

5.7.1 L-PU blends on aluminum susbtrates

An increase in toughness, tangent modulus, and stress and strain at yield is observed for blends having 5 PBW of lignin in the matrix (Tables 21, 22). Any additional lignin added to the mixture increases both the stress and strain at yield, as well as the toughness of the blend, but not as significantly as was shown for specimens blended with 5 PBW of lignin. The modulus is seen to progressively increase with the addition of lignin; control specimens exhibited an increase in modulus of 5, 24, 51 and 92% with the addition of 5, 10, 15 and 20 PBW, respectively, of lignin to the PU. This data suggests a linear correlation between the amount of lignin present in the polyblend and the tangent modulus, however, it is felt that the present data is insufficient to establish such a relationship, and further testing would be required to validate this hypothesis. Furthermore, this relationship is altered by the action of accelerated as well as natural aging conditions, since it is seen that there is not as patterned a response in tangent modulus with the addition of lignin in the blend occurring in these specimens. For AA specimens, there is a 10% decrease in modulus with the addition of 5 PBW of lignin, whereas an increase of 18% in modulus is observed for NA specimens with the same lignin loading. Despite the initial inconsistencies, a more coherent pattern may be established for the effect of lignin addition on the tangent modulus of AA and NA polyblends. Overall , the addition of lignin stiffens the PU matrix such that with 20 PBW of lignin incorporated in the blend, an average increase of 100% in modulus is achieved for all specimens adhered to aluminum substrates.

The toughness of L-PU polyblends increased by 18, 21, and 24% for NA, C, and AA specimens respectively. Thereafter, the addition of lignin caused a slight drop of 17 to 35% in toughness with 10 PBW of lignin in the blend. The initial increases in toughness are seen as a result of increases in both stress and strain yield, which improved 8 to 14% and 4 to 16% respectively (Fig. 61, 62, 63). The loss in toughness is largely attributed to a loss in yield strain, which ranged, for specimens blended with 10 PBW of lignin, between 16 and 24%, in comparison to loss of yield stress, determined to be almost insignificant, in the order of 0 to 8%.

TOUGHNESS (KPa)

Polyblend L:PU	C	AA	NA
		Exposure Conditions	
0:100	427	446	400
5:100	518	555	473
10:100	362	362	395
12.5:100	371	273	369
15:100	358	266	243
20:100	224	251	267

TANGENT MODULUS (KPa)
at 5% strain

Polyblend L:PU	C	AA	NA
		Exposure Conditions	
0:100	310	269	202
5:100	324	246	239
10:100	385	337	309
12.5:100	436	365	327
15:100	469	433	363
20:100	595	509	465

Table 21 - Toughness and tangent modulus of lignin-polyurethane polyblends on aluminum substrate

YIELD STRESS (KPa)

Polyblend L:PU	C	AA	NA
0:100	1191	1191	1038
5:100	1315	1281	1183
10:100	1225	1174	1186
12.5:100	1255	1059	1214
15:100	1283	1140	1078
20:100	1146	1183	1167

YIELD STRAIN (%)

Polyblend L:PU	C	AA	NA
0:100	35.8	37.5	38.5
5:100	39.4	43.0	40.0
10:100	29.6	30.8	33.3
12.5:100	29.6	25.8	30.4
15:100	27.9	23.3	22.5
20:100	19.6	21.3	22.9

Table 22 - Yield stress and yield strain of lignin-polyurethane polyblends on aluminum substrates

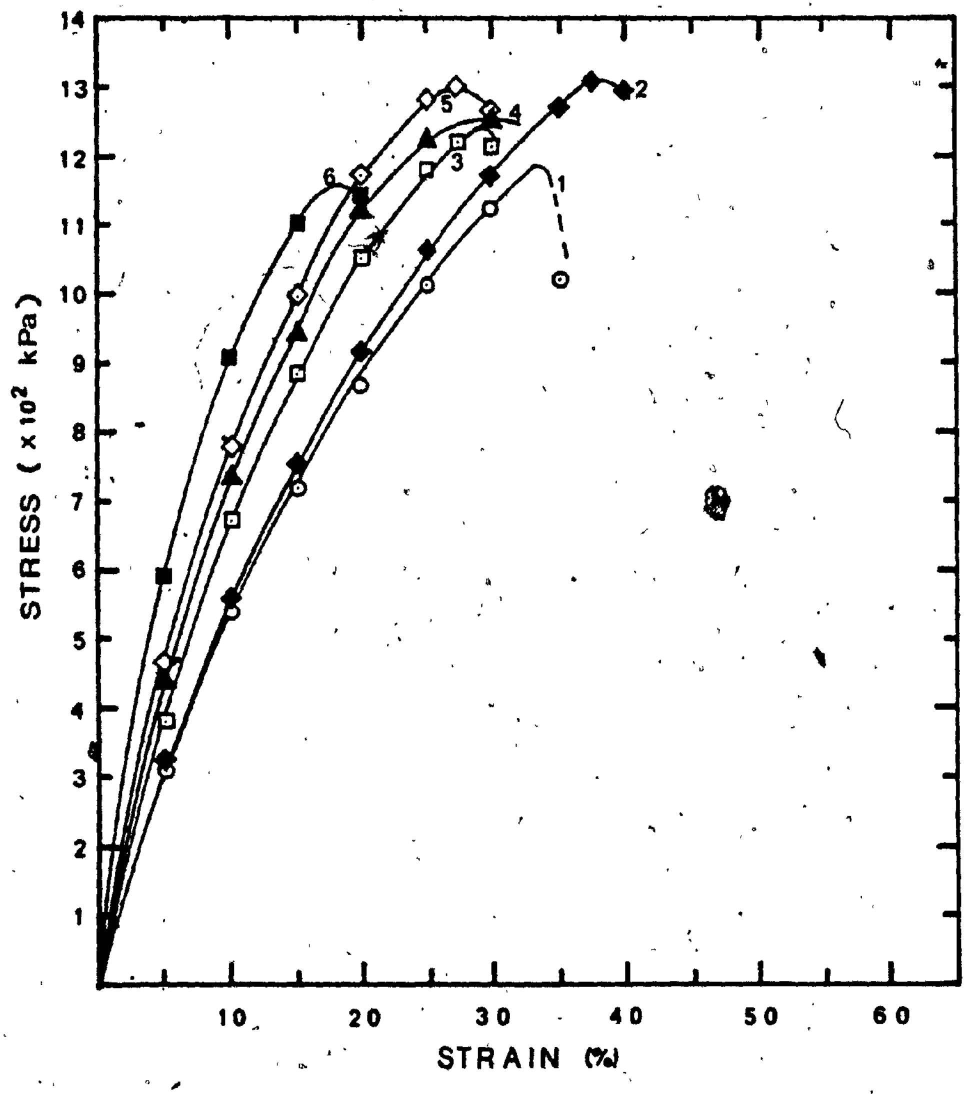

Figure 65 - Tensile stress-strain curve obtained from control, L-PU polyblends on aluminum substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100

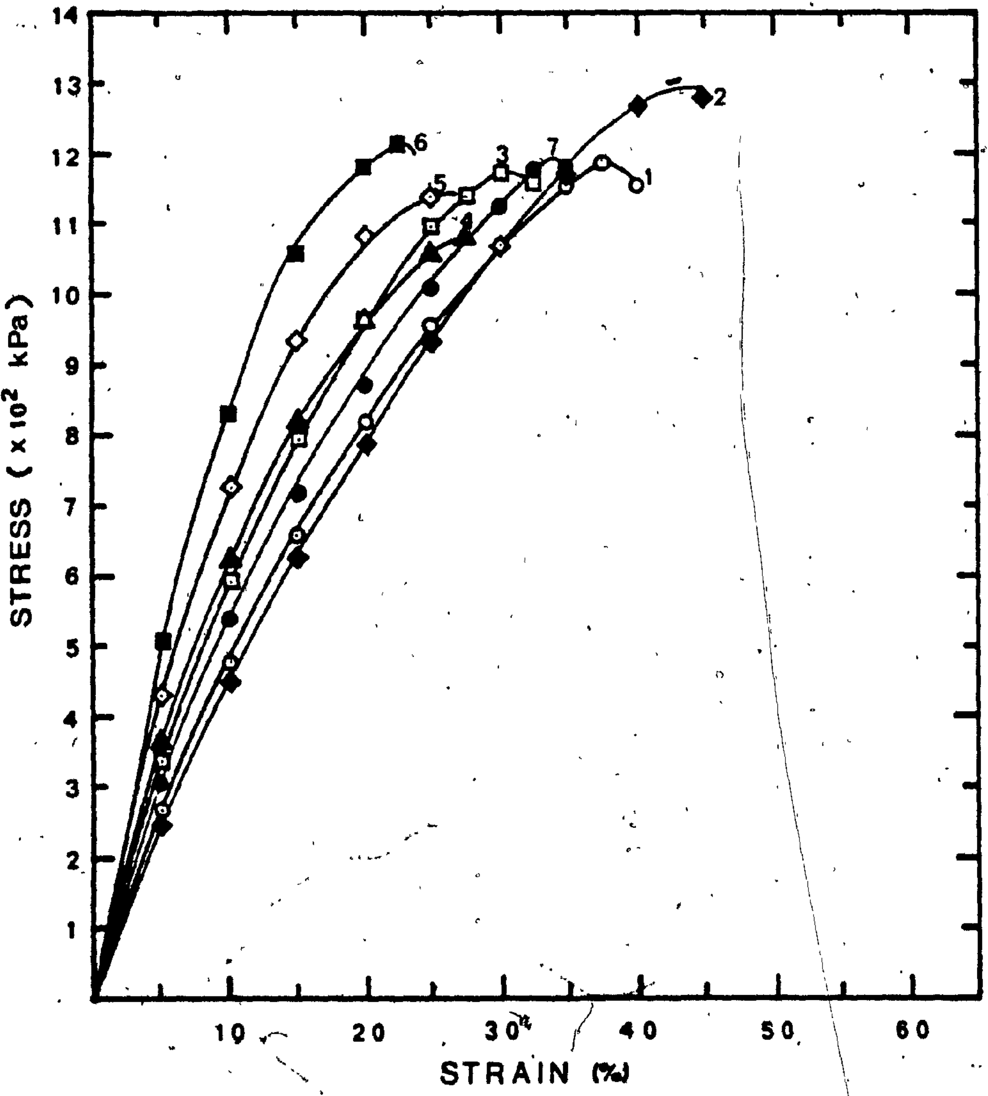

Figure 66 - Tensile stress-strain curves obtained from AA, L-PU polyblends on aluminum substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100; 7: Control curve, L-PU, 0:100

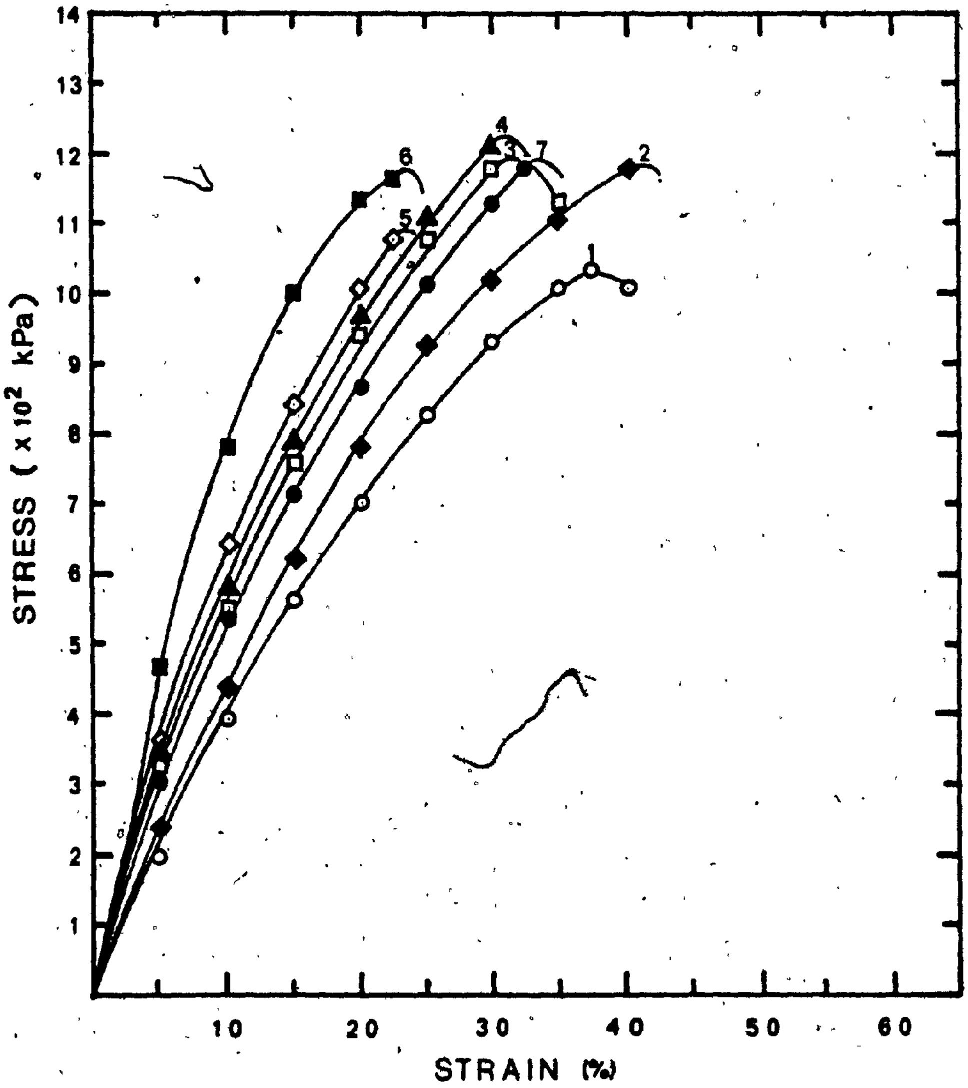

Figure 67 - Tensile stress-strain curves obtained from NA, L-PU polyblends on aluminum substrates Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100; 7: Control curve, L-PU, 0:100

5.7.2 L-PU polyblends on mortar substrates

The toughness of L-PU polyblends decreased for both the control and AA specimens with addition of 5 PBW of lignin, in contrast to a 94% increase in toughness for NA specimens, for the same lignin loading (Table 23). This decrease was also accompanied by a loss of strain at yield, which was a consequence of both the stiffening of the matrix as well as the condition of the substrate surface, and the substrate as a whole. For control specimens, the failure mode was dominantly adhesive in nature, placing a limit on the amount of stress induced in the sealant. Thus, for control specimens, it is observed that the yield stress (Table 24, Fig. 64, 65, 66),at 5 and 12.5 PBW lignin loading, are higher thanthose for 10 and 15 PBW lignin loading, underlining the inconsistency of the results, which places emphasis on the condition of the substrate surface and the adhesive tenacity of L-PU polyblends to mortar substrates. For mortar specimens subject to AA conditions, it was observed that a considerable number of specimens had extensive microcracking visible on their surfaces, and the failure mode of these specimens was dominantly initiated in the substrate, being localized in zones of high stress concentration. The failure mode was then adhesive in nature. The deterioration of the mortar substrate was due to the combined action of moisture on the substrate surface, brought about by condensation in the cooling chamber, and the freeze-thaw action of the AA process. This reduced the ability of the substrate to withstand tensile testing, and moreover precluded the possibility of accurately assessing the results. This is more easily visualized by considering Figure 65, which shows the stress-strain curves for AA specimens, in conjunction with the toughness of the specimens (Table 23). It is shown that a marked inconsistency in results is obtained for AA specimens, in comparison to control or NA specimens.

TOUGHNESS (KPa)

Polyblend L:PU	Exposure Conditions C	 AA	 NA
0:100	421	98	173
5:100	402	59	336
10:100	357	138	233
12.5:100	393	63	285
15:100	222	43	237
20:100	246	22	132

TANGENT MODULUS (KPa)
at 5% strain

Polyblend L:PU	Exposure Conditions C	 AA	 NA
0:100	263	208	203
5:100	307	238	199
10:100	366	366	269
12.5:100	362	284	277
15:100	372	398	365
20:100	497	414	354

Table 23 - Toughness and tangent modulus of lignin-polyurethane polyblends on mortar substrates

YIELD STRESS (KPa)

Polyblend L:PU	Exposure Conditions C	AA	NA
0:100	1203	451	693
5:100	1237	428	915
10:100	1223	672	875
12.5:100	1329	491	1012
15:100	1067	474	1037
20:100	1282	414	836

YIELD STRAIN (%)

Polyblend L:PU	Exposure Conditions C	AA	NA
0:100	35.0	21.8	25.0
5:100	32.5	13.8	36.0
10:100	29.2	20.6	26.0
12.5:100	29.6	12.9	28.1
15:100	20.8	9.2	22.9
20:100	19.2	5.4	15.8

Table 24 - Yield stress and yield strain of lignin-polyurethane polyblends on mortar substrates

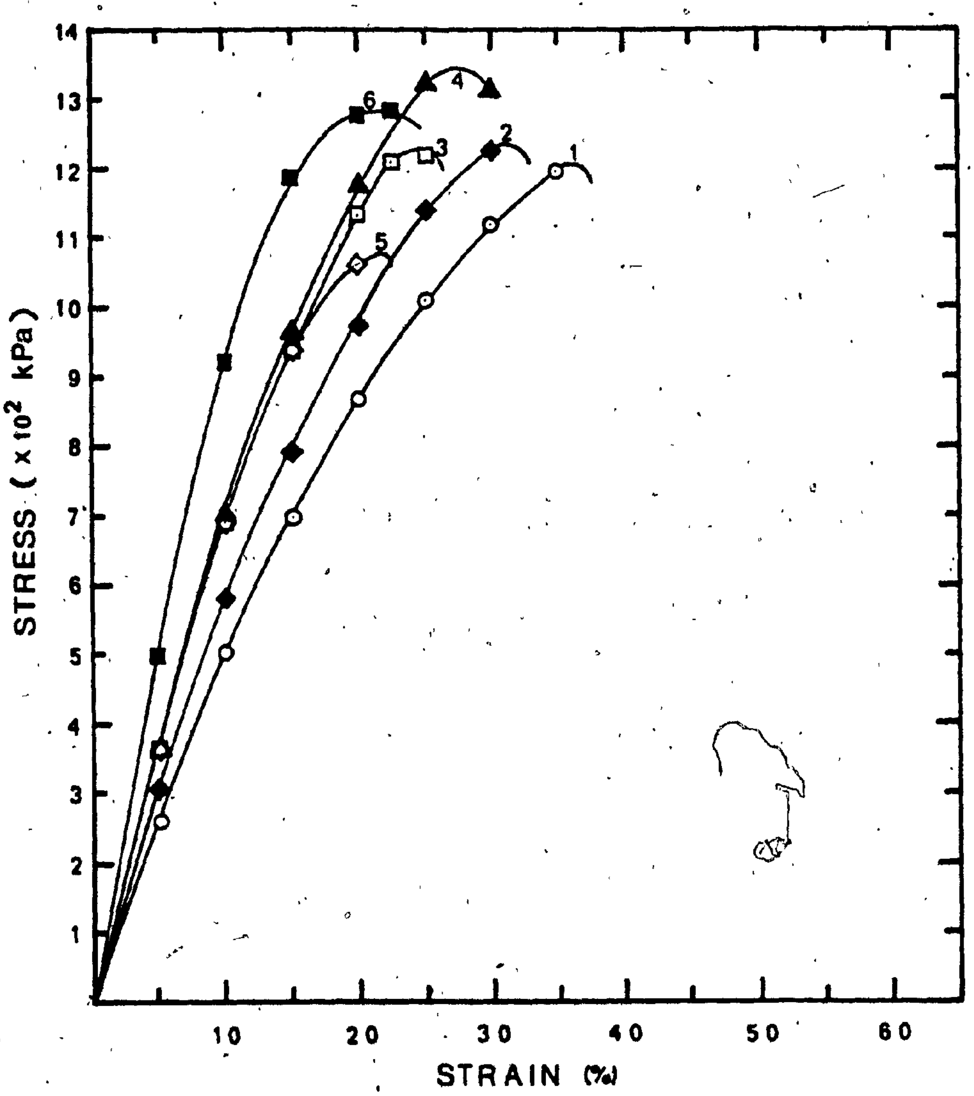

Figure 68 - Tensile stress-strain curve obtained from control, L-PU polyblends on mortar substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100

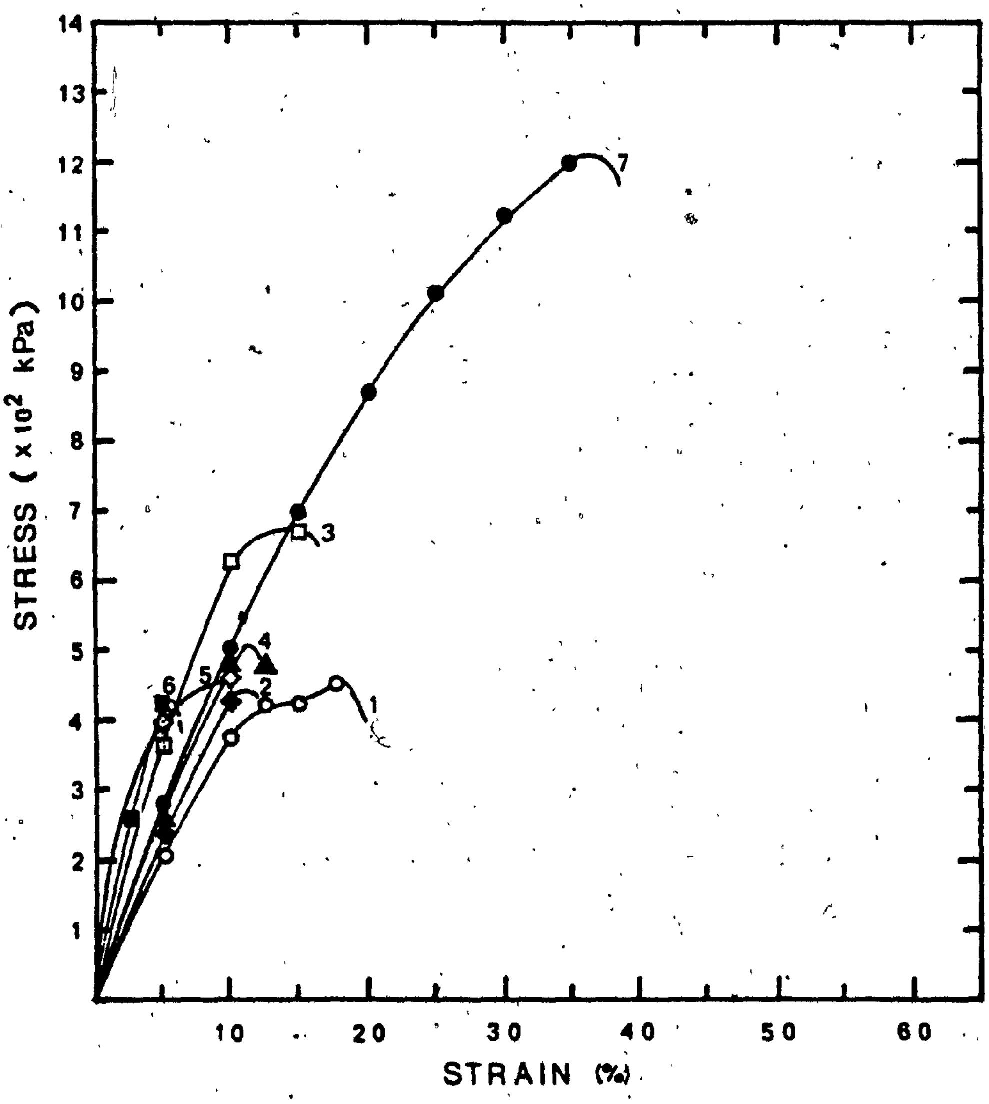

Figure 69 - Tensile stress-strain curves obtained from AA, L-PU polyblends on mortar substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100; 7: Control curve, L-PU, 0:100

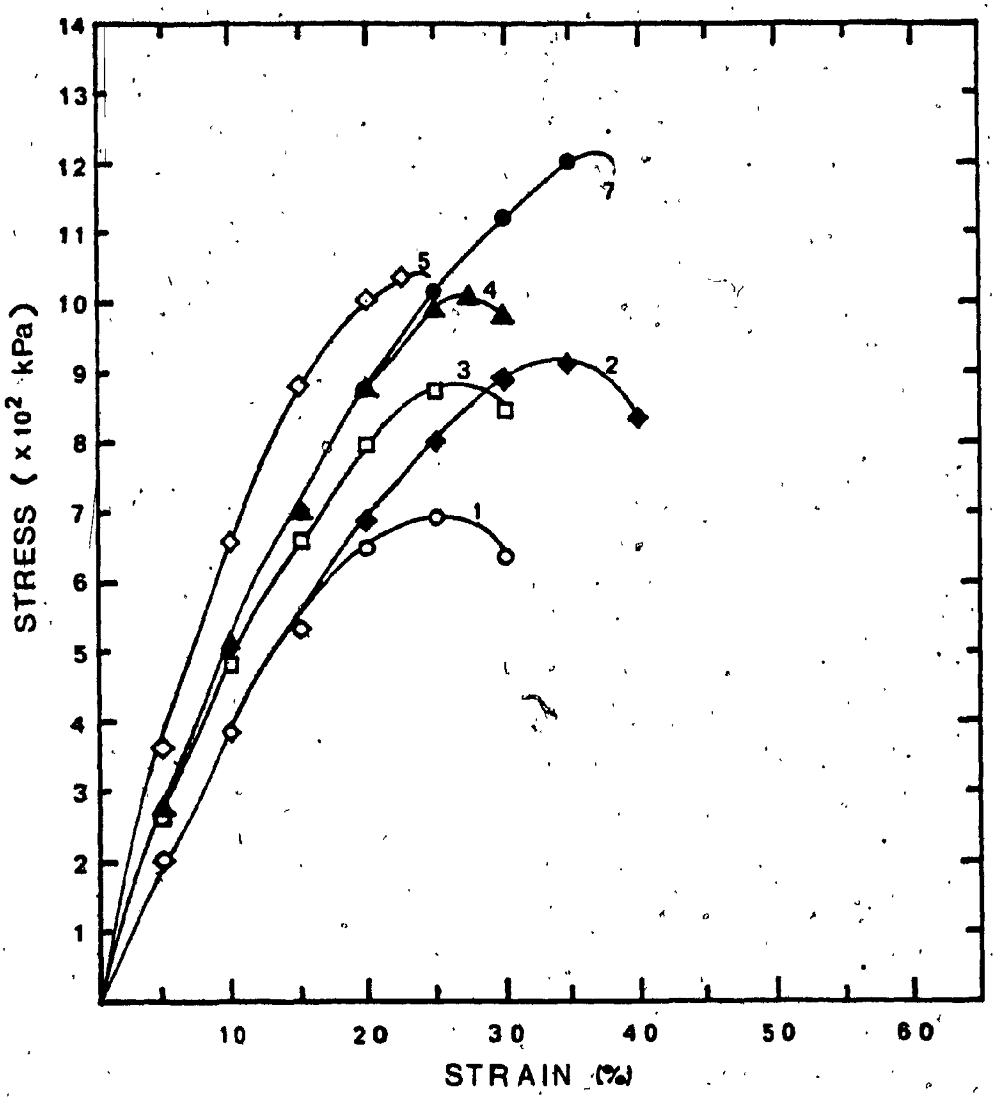

Figure 70 – Tensile stress-strain curves obtained from NA, L-PU polyblends on mortar substrates Curve 1: L-PU, 0:100; 2: L-U, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100; 7: Control curve, L-PU, 0:100

5.7.3 L-PU blends on wood substrates

Lignin-polyurethane blends on wood substrates exhibit lower values for toughness, modulus, and stress and strain at yield, in comparison to values obtained from specimens adhered to aluminum and mortar substrates. This is due to the initiation of failure in the substrates, which limits the strain to which the sealant may be subjected to, and consequently reduces the ultimate stress and toughness of these specimens.

However, in the case of control and AA specimens, increases in toughness were observed with addition of 5 PBW of lignin (Table 25), thereafter, the addition of lignin caused a reduction in toughness. With NA specimens, there was a 16% loss of toughness with the addition of 5 PBW of lignin. The higher values for toughness of specimens having 15 and 20 PBW lignin can only be attributed to higher sustained load at the initial substrate or wood failure.

The tangent modulus of control specimens is observed to increase 12, 37, 62, and 70% for lignin loadings of 5, 10, 15, and 20 PBW, respectively (Table 25). There is a similar progressive increase in modulus with the addition of lignin, shown for both AA and NA specimens; for lignin loadings of 5, 10, 15, and 20 PBW there are increases in modulus of 11, 49, 94, and 123% respectively for AA specimens, and increases in modulus of 6, 35, 73, and 98% respectively for NA specimens. The increased modulus is due to the stiffening of the L-PU matrix, which causes higher yield stress to develop (Table 26), as observed by the increase of up to 62% in stress at yield for AA specimens of 5 PBW loading (Fig. 68). A further increase of 5 PBW of lignin loading increases the yield stress from 1 to 12% for AA and NA specimens respectively, whereas there is a decrease in stress at yield for all subsequent lignin addition in the case of control specimens (Fig. 67, 69).

There is a loss of strain at failure with the addition of more than 5 PBW of lignin, although this condition is not prevalent for NA specimens which show a general downward trend, but with no discernable pattern in relation to the amount of lignin present in the blend. Since the yield strain is to a considerable degree a function of the initial substrate failure, which itself is dependent on the nature as well as the orientation of the grain of the wood. It is understood that the data obtained for strain at yield often does not show consistent trends,and may vary considerably depending on the specimen being tested.

TOUGHNESS (KPa)

Polyblend L:PU	Exposure Conditions C	 AA	 NA
0:100	190	110	177
5:100	198	246	148
10:100	140	181	171
12.5:100	89	115	136
15:100	100	124	216
20:100	43	50	204

TANGENT MODULUS (KPa)
at 5% strain

Polyblend L:PU	Exposure Conditions C	 AA	 NA
0:100	253	192	173
5:100	282	214	184
10:100	347	286	234
12.5:100	374	322	231
15:100	410	372	300
20:100	431	428	342

Table 25 - Toughness and tangent modulus of lignin-polyurethane polyblends on wood substrates

YIELD STRESS (KPa)

Polyblend L:PU	Exposure Conditions C	AA	NA
0:100	801	550	674
5:100	833	893	682
10:100	800	906	761
12.5:100	715	766	724
15:100	802	826	917
20:100	575	674	943

YIELD STRAIN (%)

Polyblend L:PU	Exposure Conditions C	AA	NA
0:100	23.8	20.0	26.5
5:100	23.8	27.5	21.7
10:100	17.5	20.0	22.5
12.5:100	12.5	15.0	18.8
15:100	12.5	15.0	23.5
20:100	7.5	7.5	21.7

Table 26 - Yield stress and yield strain of lignin-polyurethane polyblends on wood substrates

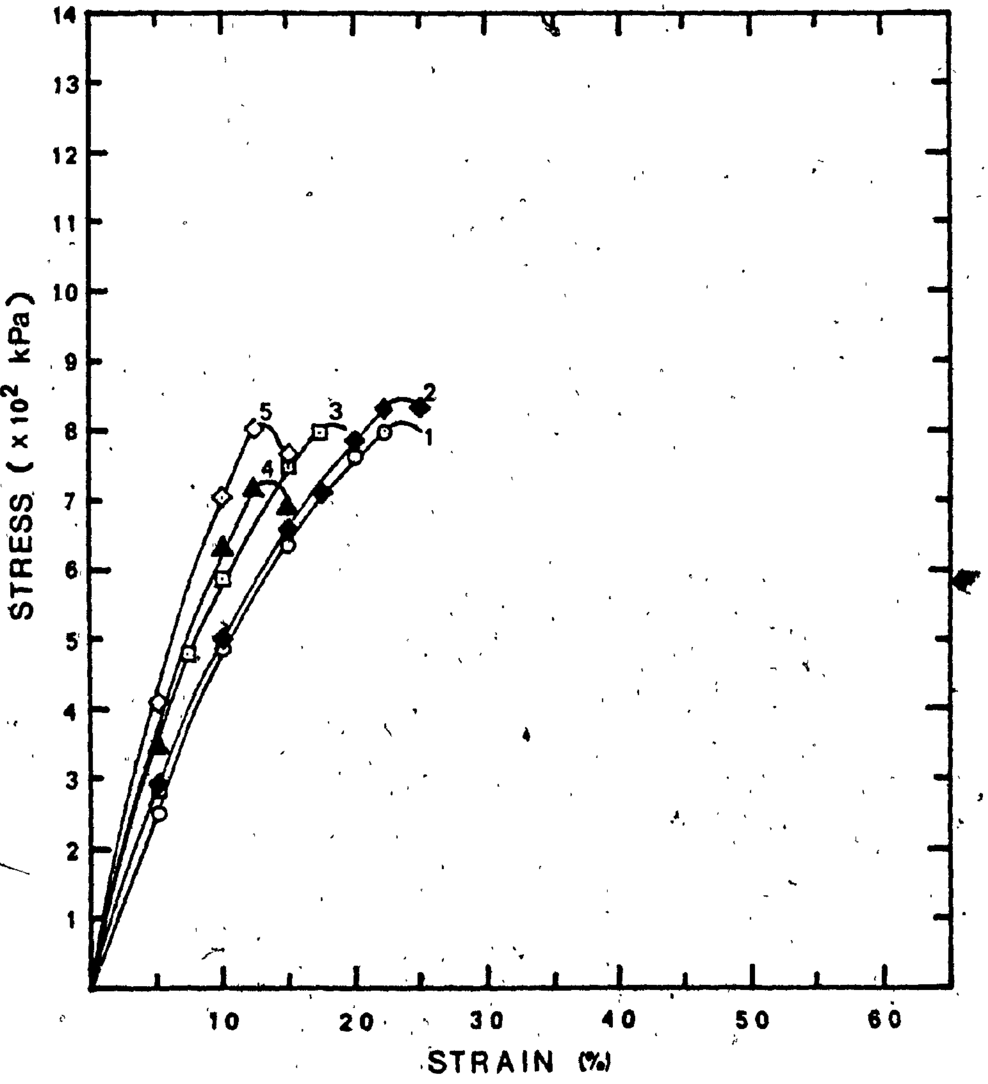

Figure 71 - Tensile stress-strain curve obtained from control, L-PU polyblends on wood substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100

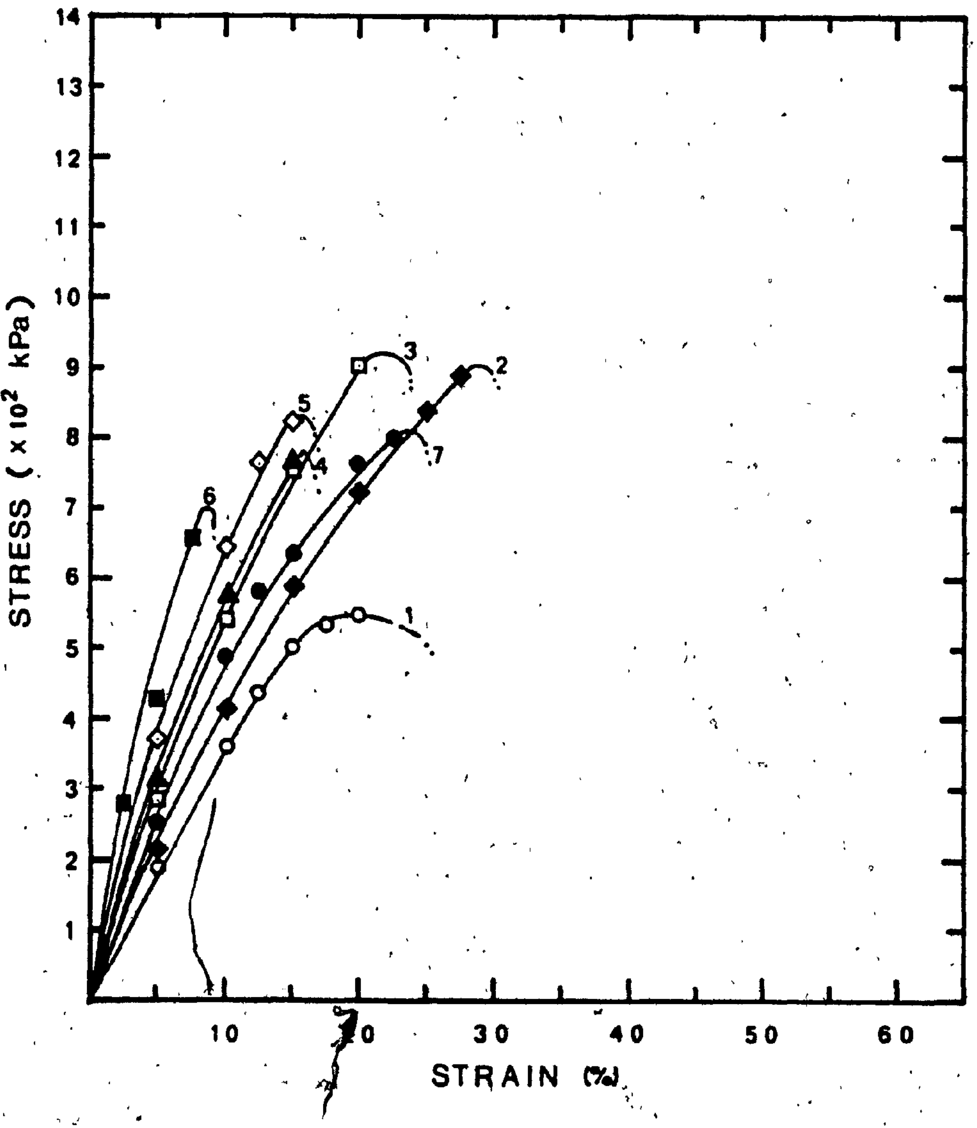

Figure 72 - Tensile stress-strain curves obtained from AA, L-PU polyblends on wood substrates. Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100; 7: Control curve, L-PU, 0:100

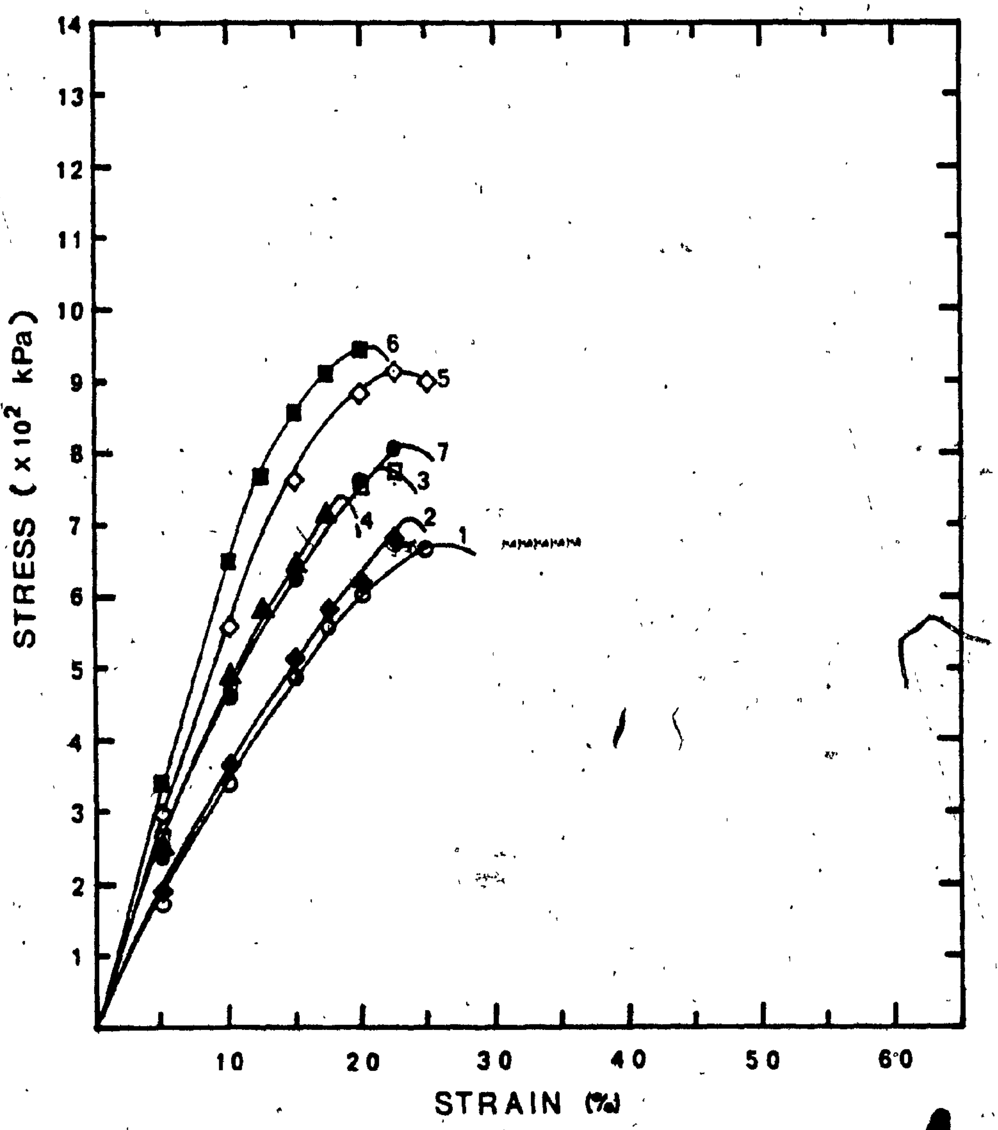

Figure 73 - Tensile stress-strain curves obtained from NA, L-PU polyblends on wood substrates Curve 1: L-PU, 0:100; 2: L-PU, 5:100; 3: L-PU, 10:100; 4: L-PU, 12.5:100; 5: L-PU, 15:100; 6: L-PU, 20:100; 7: Control curve, L-PU, 0:100

5.7.4 Discussion and conclusions

Small amounts of lignin blended with a polyurethane sealant increase the toughness, modulus, and stress and strain at yield of the polyblend. Additional quantities of lignin incorporated in the PU matrix are not seen as beneficial for the toughness of the sealant since too stiff a blend causes higher stresses in the zones located along the edges and extremities of the sealant-substrate interface. A stiffer blend is characterized by an increase in modulus with increased polymer loading. Incidence of higher stresses in failure zones are borne by the decrease in strain at yield with lignin loadings above 5 PBW.

The tangent modulus of L-PU blends increases progressively with a corresponding increase in lignin loading for all specimens tested (Figures 74 & 75). Furthermore, at any given L loading, the modulus of specimens adhered to aluminum substrates is generally greater than that of either mortar or wood substarates, and in this respect, the modulus of specimens adhered to mortar is greater than those adhered to wood.

The increase in modulus is to be expected since the lignin acts as a reinforcing filler, which , as mentioned previously, stiffens the blend. Lower values of modulus obtained for specimens adhered to mortar and wood substrates is indicative of the mode of failure of these specimens, which primarily failed in the substrate. Hence the type and the condition of the substrate affected the test results, as can be clearly demonstrated in the case of AA mortar spwcimens. The considerable deterioration of these substrates due to the aging process rendered them unsuitable for proper testing and evaluation of the blends.

Figure 75 clearly shows a loss of modulus with aging: there is a 20% loss of modulus in AA specimens, and a 30% loss of modulus for NA specimens in comparison to C specimens. This indicates that the effects of NA are more severe than that of AA conditions. The AA process does not subject the specimens to the efeects of moisture, hence this factor may in part account for the differing results between aging methods.

It has also been observed that the addition of lignin reduces the loss of modulus in L-PU blends. Hence it may be concluded that in general, the addition of small quantities of lignin to the L-PU matrix is beneficial in terms of both strength and durability.

An analysis of Figures 76 and 77 reveals that, in general terms, the yield strain decreases with the addition of lignin. This relationship is not continuous since, in the case of specimens adhered to aluminum substrates, there is seen to be an increase of strain at yield at a blend ratio of 5:100 (L:PU), and this condition is also observed for other data as well (i.e. M-NA; W-C; W-AA). It is difficult to establish if this a phenomena particular of specimens adhered to aluminum substrates or a general trend that is prevalent for all tested substrates, since the data obtained from tests on mortar and wood is inconsistent in this respect. Nonetheless, in the case of aluminum substrates, the addition of lignin has clearly been beneficial.

The effect of substrate type on the values of yield strain is evident from Figure 76. The highest percentage strains in all aging conditions are those obtained from specimens adhered to aluminum substrates, and the lowest values from specimens adhered to wood substrates. This is an entirely expected result in light of the failure criteria of these specimens, which is dominated by the strength of the substrate. Of course the exception to this trend is found in AA mortar specimens which have significantly lower values of yield strain than either aluminum or wood.

There does not seem to be any apparent relationship between the aging conditions and the yield strain as shown from Figure 77. What is evident is the loss of strain at yield with increase lignin loading, except , as previously noted, in the case of specimens adhered to aluminum

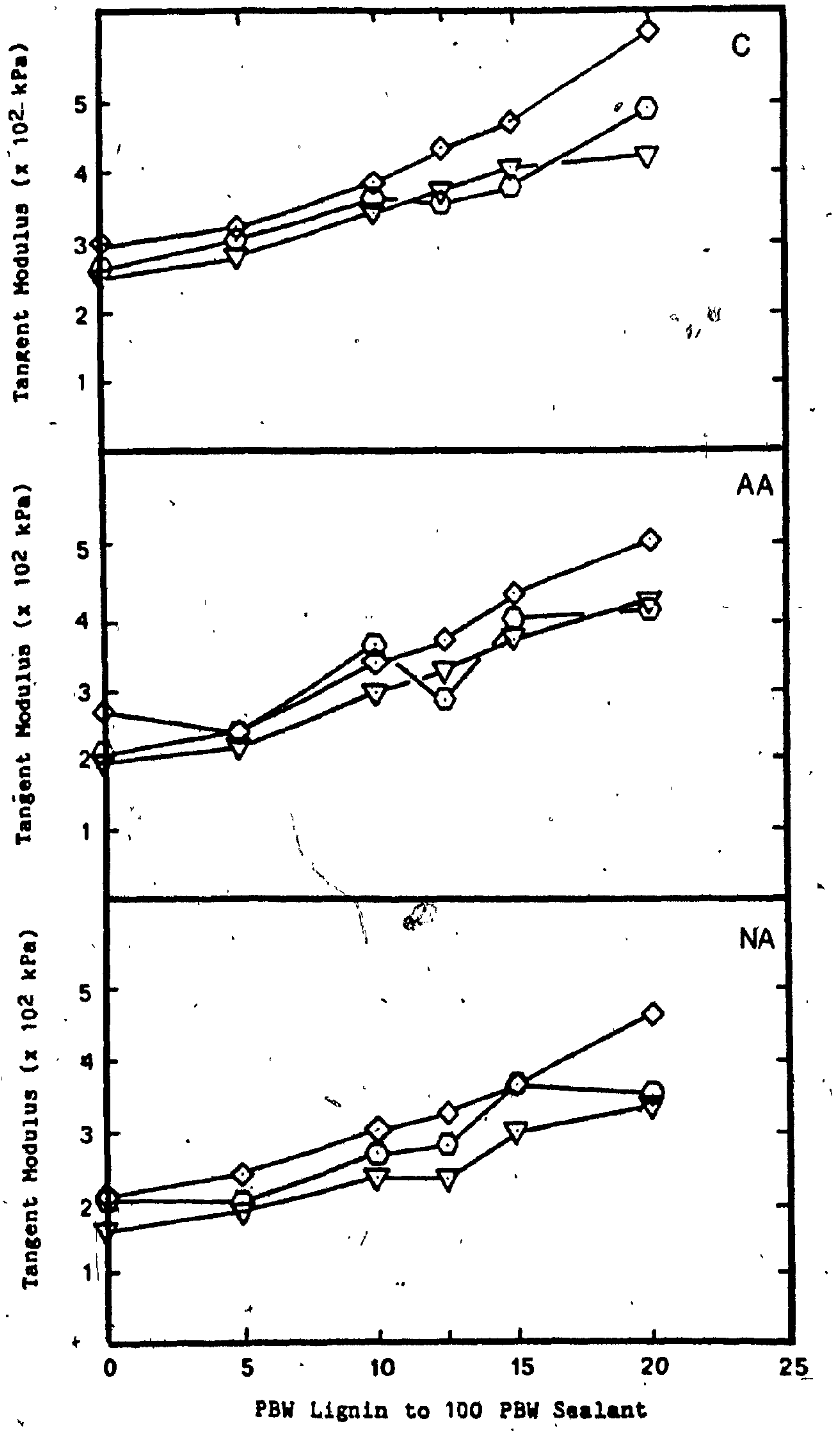

Figure 74 - Tangent modulus of L-PU polyblends as a function of L loading in: C, AA, and NA conditions. Substrates: ▽ - wood; ○ - mortar; ◇ - aluminum

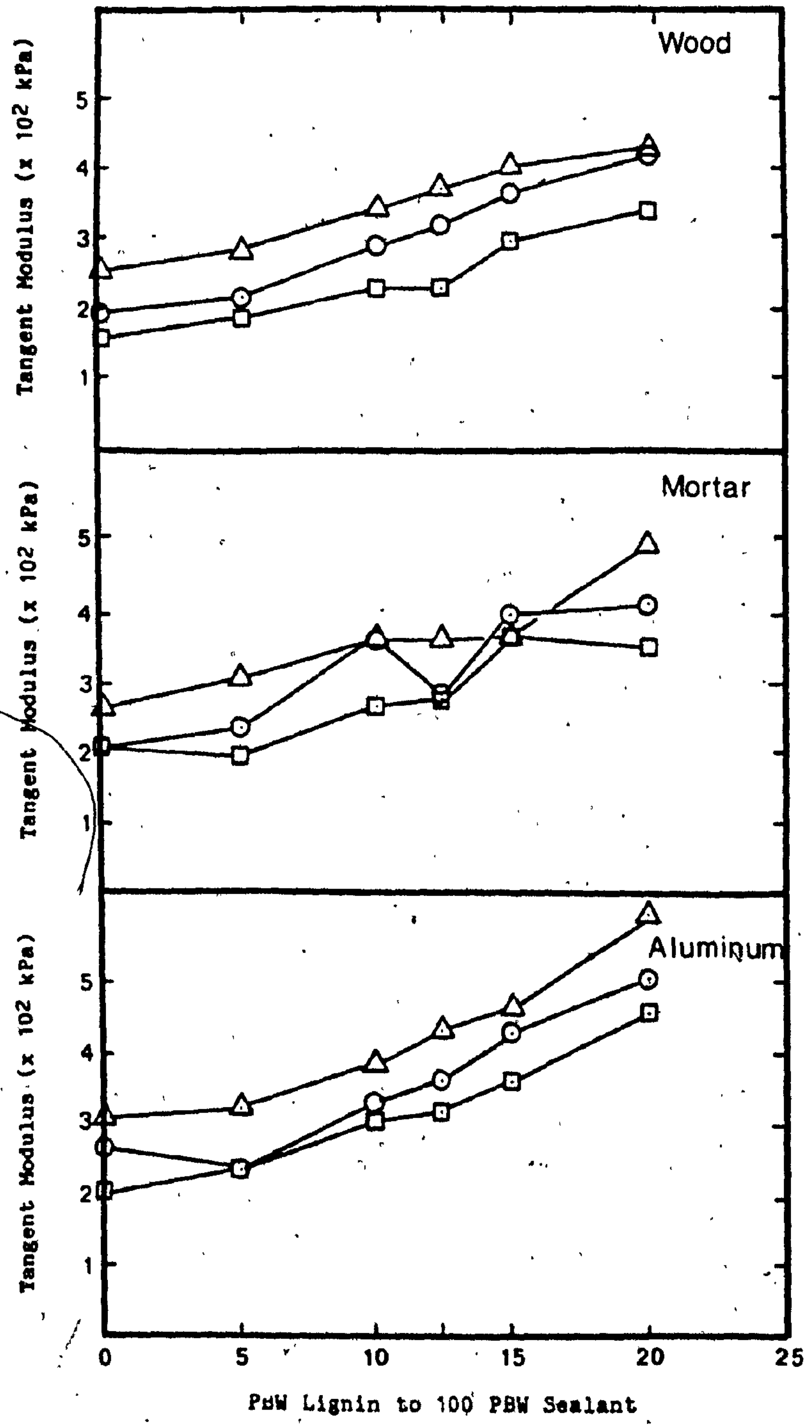

Figure 75 - Tangent modulus of L-PU polyblends as a function of L loading on: wood, mortar, and aluminum. Aging conditions: △ - C; ○ - AA; □ - NA

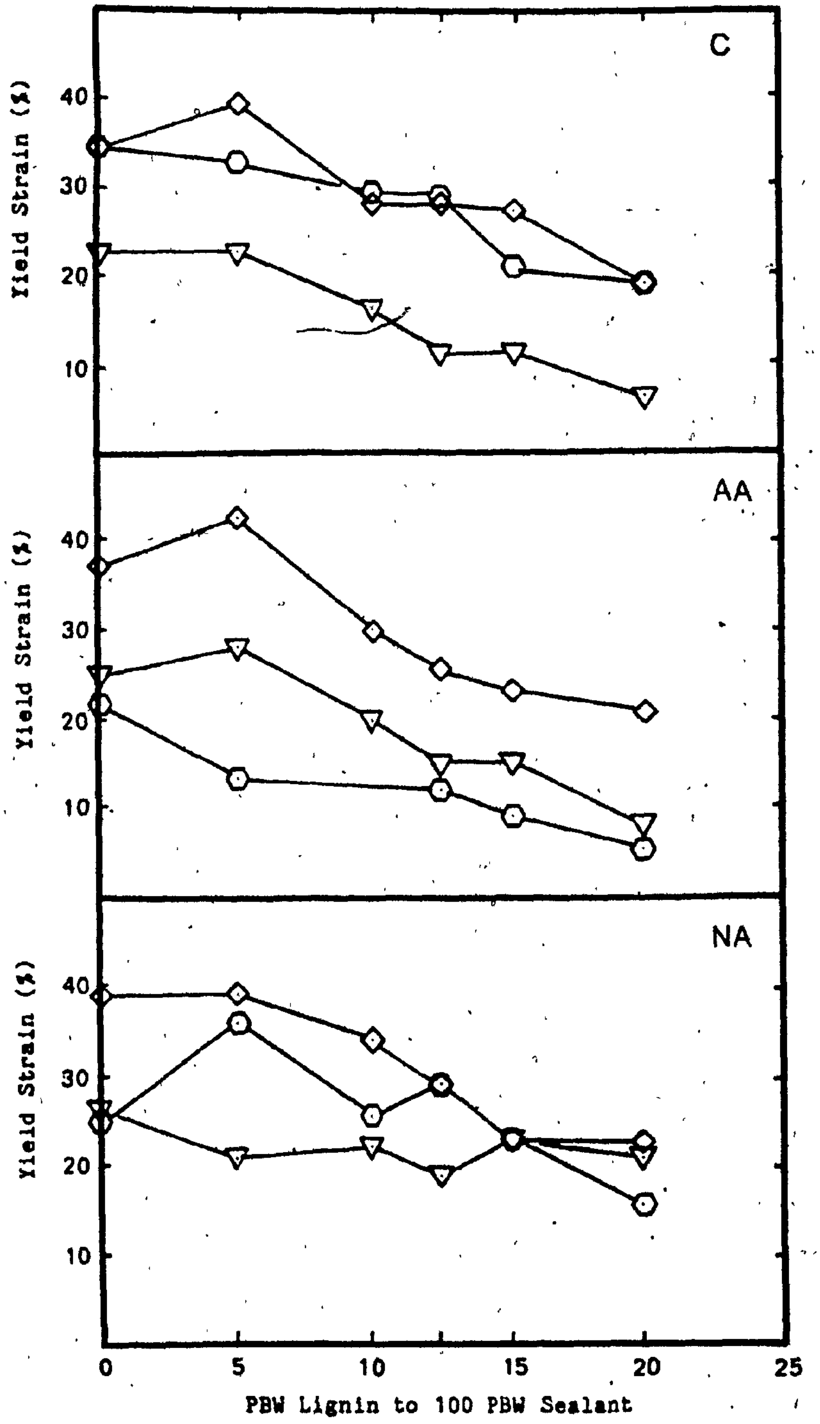

Figure 76 - Yield strain of L-PU polyblends as a function of L loading in: C, AA, and NA conditions. Substrate: ▽ - wood; ⬡ - mortar; ◇ - aluminum

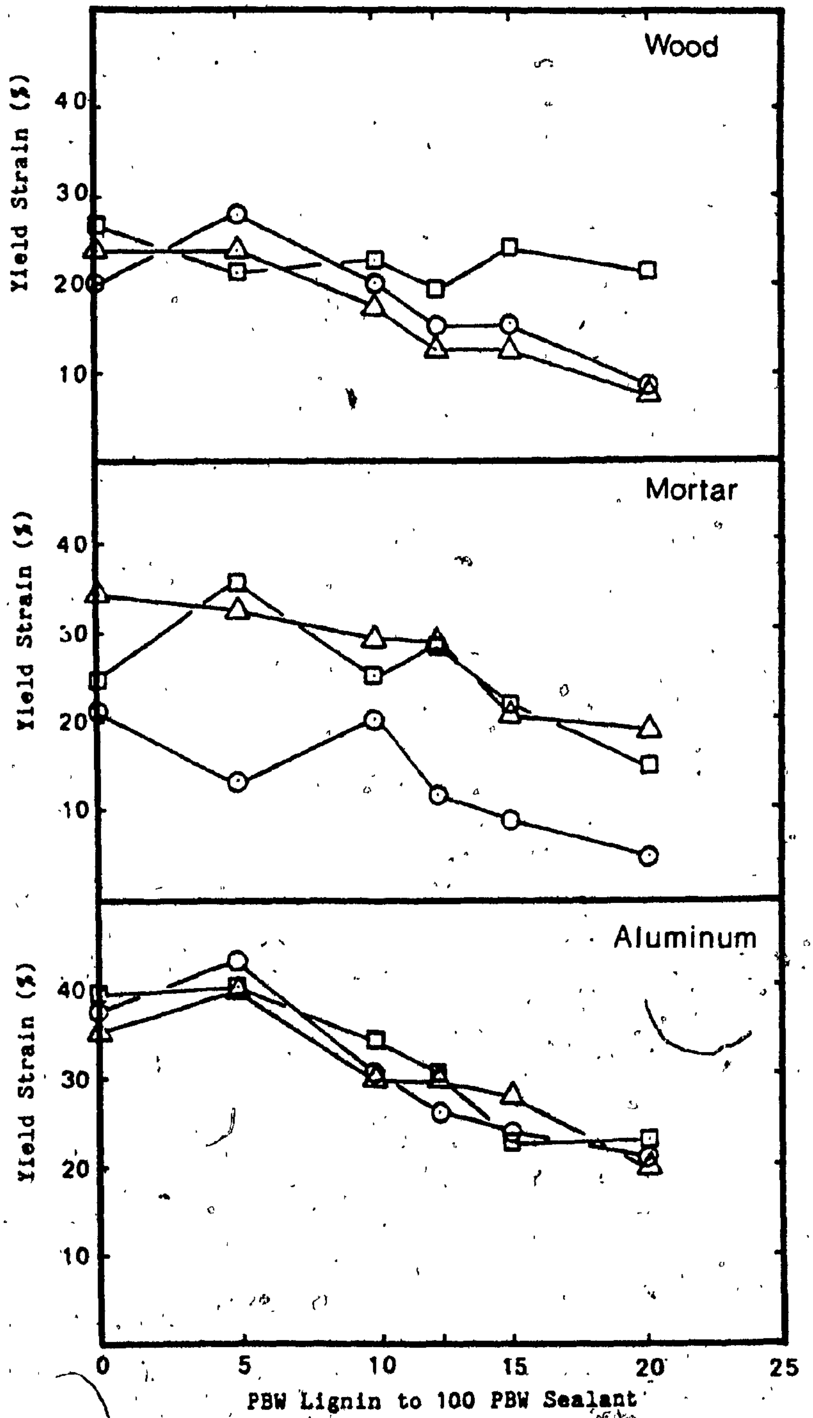

Figure 77 - Yield strain of L-PU polyblends as a function of L loading on: wood, mortar, and aluminum. Aging conditions: △ - C; ○ - AA; □ - NA

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1. The addition of lignin, in varying proportions, to a polymeric based sealant, in certain cases increases the tensile toughness, modulus, and stress and strain at yield.
2. The degree to which the mechanical properties are increased depends on the amount of lignin present in the polymer matrix, the type of polymer being blended, and the nature of the substrate to which the sealant polyblend is adhered.
3. The addition of lignin to butyl-based sealants is not considered beneficial since the higher modulus matrix does not possess sufficient adhesive strength to withstand minor joint deformations. Adhesive failure is seen to occur at areas of high stress concentration located at the edges of the sealant- substrate interface.
4. The excellent adhesive properties of acrylic-based sealants provide sufficient strength such that cohesive failure occurs with the addition of up to 15 parts lignin in 100 parts sealant. Thereafter, any additional lignin is seen to render the matrix so stiff as to cause adhesive failure along the sealant-substrate interface.
5. Lignin-polyurethane sealant blends are enhanced with the

addition of lignin. The adhesive tenacity of PU to all the substrates enables the continued reinforcement of PU sealant with the addition of lignin. The strength of the sealant blend varies according to the type of substrate to which it is adhered.

Lignin is considered to act as a reinforcing filler in a two-phase, polymer-particulate system. Among other considerations, the mechanical properties are dependent on the interfacial interaction between each phase. Evidence of two phase behavior is obtained from LM, SEM, and DSC analysis. SEM photomicrographs clearly depict the differences between the morphology of lignin particles and PU. The color contrast shown in photomicroprints of L-PU blends also shows the existence of two distinct phases. Finally, the similarity between thermographs of neat and blended sealants obtained from DSC thermal analysis is indicative of two-phase behavior, since single phase behavior would have shown a shift or change in the Tg of the neat sealant in relation to the Tg of lignin.

6. The curing mode of L-PU sealants is modified with the addition of lignin. The initial setting time is reduced with the addition of lignin, but the rate of curing remains constant, indicating that the matrix is hardened in direct proportion to the amount of lignin present in the blend. However, the rate of cure is the same for all blend ratios, which suggests that the lignin does not

affect the chemical curing process.

7. The durability of the blended sealants, as measured by the change in mechanical properties of specimens subject to natural and accelerated aging programs, is generally neither hindered nor improved with the addition of lignin.

6.2 Recommendations

In contrast to L-B sealants, L-A sealant polyblends showed considerable improvements in strength with the addition of lignin. It would be useful to confirm the role of lignin in enhancing the mechanical properties of L-A blends, by conducting a series of tests to establish their phase behavior, their curing mode, and the effect of lignin concentration on their durability. Phase behavior would best be analysed using SEM in conjunction with DSC. The former method would confirm multi-phase behavior by illustrating the contrast between the morphologies of individual components of the blend. In the latter method, any divergence in the Tg of the polymeric matrix could be detected on a thermograph of the blended sealant. Sequence hardness testing could provide a means to study the curing mode of L-A sealants. The durability of these blends may be established by a tensile testing program similar to the one used in this report. In order to achieve more conclusive results, a greater number of samples would need to be tested, thereby increasing the reliability of the data.

In terms of L-PU sealant polyblends, a number of recommendations with regards to further study may be made.

A more practical approach to the development of a marketable sealant might include the following steps:

i) Selection of a base polymer formulation based on the manufacturer's recomendations.

i.e. weight % of: - base polymer;
- plasticizer;
- reinforcing agents;
- other additives as required.

ii)Repeated formulation of the sealant blend to verify the most suitable laboratory production methods and to establish reliability of the product blend.

i.e. test the curing and mechanical characteristics of the various sealant batches to insure the formulation is consistant with the manufacturer's recommendations.

iii) Modify the blend with the addition of lignin:

There may exist a relationship between the quantity of lignin (volume fraction) or the size of the lignin particles (specific surface area) and the corresponding change in mechanical properties of the blended sealant. An analysis of the elastic modulus, tensile strength, or other mechanical properties in relation to the volume fraction or specific surface area of lignin would be beneficial from the standpoint of providing optimum mechanical properties through proper sealant formulation.

The quantity of other additives in the blend would be varied to accomodate the inclusion of lignin; the weight ratios of additive to lignin would be monitered to assess their impact on the sealant formulation.

iv) Analyze the sealant formulation in terms of its':

- Morphology , using the light microscope (LM) and scanning electron microscope (SEM).
- Thermal behavior and glass transition temperature, using a differential scanning calorimeter (DSC).
- Mechanical spectrum, using a differential mechanical analyzer (DMA).
- Chemical interaction with lignin particles, using nuclear magnetic resonance (NMR).

v) Test the sealant to determine:

a) basic mechanical characteristics.

i.e.
- nominal adhesive, cohesive, and shear strength;
- elastic modulus;
- stress relaxation parameters;
- Poisson's ratio.

b) characteristic curves based on mechanical testing at various temperatures.

c) durability to natural and accelerated aging processes based on a method which simultaneously ages and stresses (tension or compression) the sealant: The Institute for Research in Construction, a division of the National Research Council of Canada, has constructed an outdoor weathering rack for sealants, which relies on the different thermal expansion coefficients between metals to cause sealant stresses (39). The rack is arranged such that, upon temperature change, the differential movement of dissimilar metal bars, provides the necessary expansion or contraction of the sealant bead. The length of the testing rack required to perform these tests is quite long. A more compact apparatus, based on a device suggested by K. Ka[illegible]pati (40), would be more advantageous, since AA and NA tests could be conducted using the same apparatus, possibly enabling the correlation of AA and NA test results. Such a device would be equipped to test numerous specimens in a single test series, providing a statistical basis from which a correlation program might be established. An electromechanical link could easily equate the temperature at the sealant surface to a predetermined extension of the sealant bead. Thus sealants would undergo thermal and mechanical cyclic testing simultaneously.

vi) Test the sealant to meet the required government standards.

The following list of sealant performance characteristics, based on ASTM standards, does not represent the entire range of tests required for government approval, however as a partial list, it does demonstrate the wide range of tests to which sealants must be subjected in order to meet required government standards.

a) staining and color change (C 510 - 71)
b) extrusion rate and application life (C 603 - 69)
c) rheological properties (C 639 - 69)
d) indentation hardness (C 661 - 70)
e) tack-free time (C 679 - 71)
f) low-temperature flexibility and tenacity (C 711 - 72)
g) bubbling (C 712 - 72)
h) UV - cold box exposure (C 718 - 72)
i) effects of heat aging on weight loss, cracking, and chalking (C 794 - 75)
j) adhesion-in-peel (C 794 - 75)
k) slump (C 2202 - 73)

vii) perform a production cost analysis of the the sealant formulation in consideration of the cost of lignin to that of the base polymer.

Although the above outline is quite general in nature it nonetheless provides a framework from which a more detailed program might be established. Of course a cost analysis need not be performed in the final stages of this program as it may be beneficial to establish earlier on, the cost effectiveness of blending lignin with various sealants.

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8. APPENDIX

8.1 APPENDIX 1

Tension. Specimen Casting, Curing and Testing Record

*	Polymer		Quantity of Samples				Event (Date)		Cure
	Type	Blend	Cast on Substrate Type				Casting	Testing	£ of
		(%)	Al	M	W	Total			Days
P	PVAc	0	2	2	2	6	30.01.85	04.02.85	5
	"	10	2	2	2	6	"	"	"
	"	0	2	2	2	6	"	"	"
	"	10	2	2	2	6	"	"	"
P	A	0	-	4	-	4	18.02.85	11.03.85	21
	"	0	3	-	3	6	"	30.04.85	71
	"	10	3	-	3	6	"	"	"
	"	10	-	4	-	4	"	"	"
P	B	0	-	-	3	3	18.02.85	11.03.85	21
	"	0	-	-	2	2	"	29.04.85	70
	"	0	2	-	-	2	"	"	"
	"	0	-	4	-	4	"	"	"
	"	10	3	-	3	6	"	"	"
	"	10	-	4	-	4	"	"	"

* Test Designation: P-preliminary; AC-accelerated curing; AA-accelerated aging: NA-natural aging; C-control

*	Polymer Type	Polymer Blend (%)	Quantity of Samples Cast on Substrate Type Al	M	W	Total	Event (Date) Casting	Event (Date) Testing	Cure E of Days
P	PU	0	3	3	3	9	18.02.85	26.02.85	8
	"	10	3	3	3	9	"	"	"
P	S	0	3	3	3	9	18.02.85	26.02.85	8
	"	10	3	3	3	9	"	"	"
P	Ps	0	3	3	3	9	18.02.85	25.03.85	13
	"	10	3	3	3	9	"	"	"
P	PVAc	0	6	6	-	12	23.02.85	26.03.85	31
	"	2.5	-	6	-	6	"	"	46
	"	5	6	6	-	12	"	"	"
	"	7.5	6	6	-	12	"	"	"
	"	10	6	6	-	12	"	"	"
	"	2.5	-	-	6	6	"	14.04.85	51
	"	5	-	-	6	6	"	"	"
	"	7.5	-	-	6	6	"	"	"
	"	10	-	-	6	6	"	"	"
	"	2.5	6	-	-	6	01.03.85	26.03.85	25
	"	10	2	2	-	4	[illegible]	10.04.85	40
	"	0	-	-	6	6	"	15.04.85	45

* <u>Test Designation</u>: P-preliminary; AC-accelerated curing; AA-accelerated aging; NA-natural aging; C-control

*	Polymer Type	Blend (%)	Quantity of Samples Cast on Substrate Type Al	M	W	Total	Event (Date) Casting	Testing	Cure # of Days
P	PU	0	6	6	6	18	04.03.85	15.04.85	42
	"	2.5	6	6	6	18	"	"	"
	"	5	6	-	6	12	08.03.85	22.04.85	45
	"	5	-	6	-	6	"	"	"
	"	7.5	6	6	6	18	"	25.04.85	48
	"	10	6	6	6	18	"	26.04.85	49
P	PU	0	6	6	6	18	17.05.85	17.06.85	31
	"	5	6	6	6	18	"	"	"
	"	10	-	6	-	6	"	"	"
	"	10	6	-	6	12	"	18.06.85	32
	"	15	6	6	6	18	18.05.85	"	31
	"	20	6	6	6	18	"	"	"
	"	25	6	6	6	18	"	"	"
AC	PU	0	5	-	-	5	12.07.85	11.07.85	9
	"	0	5	-	-	5	"	"	"
	"	10	5	-	-	5	"	"	"
	"	10	5	-	-	5	"	"	"

* Test Designation: P-preliminary; AC-accelerated curing; AA-accelerated aging: NA-natural aging; C-control

*	Polymer		Quantity of Samples				Event (Date)		Cure
	Type	Blend	Cast on Substrate Type				Casting	Testing	E of
		(%)	Al	M	W	Total			Days
AA	PU	0	6	6	6	18	02.07.85	07.03.86	248
	"	5	6	6	6	18	"	10.03.86	251
	"	10	6	6	6	18	"	14.03.86	255
	"	12.5	6	6	6	18	"	17.03.86	258
	"	15	6	6	6	18	"	18.03.86	259
	"	20	6	6	6	18	"	19.03.86	260
NA	PU	0	6	6	6	18	03.07.85	07.04.86	278
	"	5	6	6	6	18	"	"	"
	"	10	6	6	6	18	"	"	"
	"	12.5	6	6	6	18	"	"	"
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"
NA	A	0	6	6	6	18	04.07.85	08.04.86	278
	"	5	6	6	6	18	"	"	"
	"	10	6	6	6	18	"	"	"
	"	12.5	6	6	6	18	"	"	"
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"

* <u>Test Designation</u>: P-preliminary; AC-accelerated curing; AA-accelerated aging: NA-natural aging; C-control

*	Polymer Type	Polymer Blend (%)	Quantity of Samples Cast on Substrate Type Al	M	W	Total	Event (Date) Casting	Event (Date) Testing	Cure E of Days
AA	B	0	6	6	6	18	08.07.85	26.03.86	261
	"	5	6	6	6	18	"	"	"
	"	10	6	6	6	18	"	"	"
	"	12.5	6	6	6	18	"	"	"
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"
NA	B	0	6	6	6	18	09.07.85	09.04.86	274
	"	5	6	6	6	18	"	"	"
	"	10	6	6	6	18	"	"	"
	"	12.5	6	6	6	18	"	"	"
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"
AA	A	0	6	6	6	18	12.07.85	20.03.86	251
	"	5	6	6	6	18	"	21.03.86	252
	"	10	6	6	6	18	"	24.03.86	255
	"	12.5	6	6	6	18	"	25.03.86	"
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"

* Test Designation: P-preliminary; AC-accelerated curing; AA-accelerated aging: NA-natural aging; C-control

*	Polymer		Quantity of Samples Cast on Substrate Type				Event (Date)		Cure
	Type	Blend (%)	Al	M	W	Total	Casting	Testing	E of Days
C	PU	0	6	6	6	18	17.07.85	07.03.86	233
	"	5	6	6	6	18	"	10.03.86	236
	"	10	6	6	6	18	"	14.03.86	240
	"	12.5	6	6	6	18	"	17.03.86	243
	"	15	6	6	6	18	"	18.03.86	244
	"	20	6	6	6	18	"	19.03.86	245
C	A	0	6	6	6	18	19.07.85	20.03.86	244
	"	5	6	6	6	18	"	21.03.86	245
	"	10	6	6	6	18	"	24.03.86	248
	"	12.5	6	6	6	18	"	25.03.86	249
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"
C	B	0	6	6	6	18	23.07.85	26.03.86	246
	"	5	6	6	6	18	"	"	"
	"	10	6	6	6	18	"	"	"
	"	12.5	6	6	6	18	"	"	"
	"	15	6	6	6	18	"	"	"
	"	20	6	6	6	18	"	"	"

* <u>Test Designation</u>: P-preliminary; AC-accelerated curing; AA-accelerated aging: NA-natural aging; C-control

#	Polymer Type	Blend (%)	Quantity of Samples Cast on Substrate Type Al	M	W	Total	Event (Date) Casting	Testing	Cure # of Days
AC	PU	0	10	-	-	10	31.07.85	15.08.85	15
	"	0	10	-	-	10	"	"	"
	"	10	10	-	-	10	"	"	"
	"	10	10	-	-	10	"	"	"
	"	15	10	-	-	10	"	"	"
	"	15	10	-	-	10	"	"	"
	"	5	10	-	-	10	01.08.85	16.08.85	"
	"	5	10	-	-	10	"	"	"
	"	12.5	10	-	-	10	"	"	"
	"	12.5	10	-	-	10	"	"	"
	"	20	10	-	-	10	"	"	"
	"	20	10	-	-	10	"	"	"

\# Test Designation: P-preliminary; AC-accelerated curing; AA-accelerated aging; NA-natural aging; C-control

Total Number of Specimens Cast: 1523

8.2 APPENDIX 2

Curing Test Sequence and Hardness Data for L-PU Blends

Polymer Type: L-PU; 0%

Casting Date: 23.07.85

From Casting	Average Durometer Hardness At Delay Time		
Hrs.	0s	10s	60s
25	6.2	1.7	0.2
48	20.0	15.1	12.9
72	34.5	30.0	27.3
144	44.5	39.3	36.3
185	46.8	41.3	40.2
216	49.1	41.5	38.7
405	46.5	39.2	37.1
911	50.0	42.8	40.7
1519	48.3	43.2	41.4
2853	58.8	55.4	52.8

Polymer Type: L-PU; 5%

Casting Date: 23.07.85

From Casting	Average Durometer Hardness At Delay Time		
Hrs.	0s	10s	60s
24	6.2	0.7	0.0
27	9.5	3.2	1.7
42	23.2	17.6	15.1
56	31.7	26.7	24.1
72	40.0	34.0	31.0
144	46.7	39.6	36.6
216	47.5	40.9	38.1
407	43.0	37.9	35.7
913	49.5	42.7	40.4
1517	53.0	47.7	44.9
2853	55.3	51.2	49.6

Polymer Type: L-PU; 10%

Casting Date: 22.07.85

From Casting	Average Durometer Hardness At Delay Time		
Hrs.	0s	10s	60s
22	8.0	0.7	0.0
25	13.3	5.1	3.0
32	21.2	13.9	11.0
48	37.5	28.8	25.5
72	39.5	35.2	32.3
168	50.0	43.6	40.8
216	50.2	45.1	42.2
408	52.0	47.0	44.0
936	54.8	47.5	44.4
1541	52.8	47.8	45.6
2950	57.3	54.2	52.3

Polymer Type: L-PU; 12.5%

Casting Date: 18.07.85

From Casting	Average Durometer Hardness At Delay Time		
Hrs.	0s	10s	60s
20	8.8	0.6	0.0
24	18.3	6.6	4.3
41	30.7	23.6	21.2
65	42.8	35.2	32.6
113	51.7	42.4	39.7
185	46.2	40.1	37.5
425	50.8	45.6	42.9
1033	53.2	47.4	45.3
1618	56.0	49.6	47.8
3048	58.8	56.1	54.3

Polymer Type: L-PU; 15%
Casting Date: 17.07.85

From Casting Hrs.	Average Durometer Hardness At Delay Time 0s	10s	60s
	-	-	-
20	10.6	1.9	-
24	20.3	8.1	5.8
40	39.5	28.1	24.7
64	51.2	38.1	35.2
112	53.7	44.8	43.7
208	53.7	46.9	44.1
376	56.0	49.4	46.4
784	55.8	47.9	45.7
1648	57.7	52.7	50.7
3069	56.7	53.5	52.0

Polymer Type: L-PU; 20%
Casting Date: 16.07.85

From Casting Hrs.	Average Durometer Hardness At Delay Time 0s	10s	60s
19	11.8	1.2	-
20	15.0	4.0	2.0
24	20.5	5.7	3.6
38	39.8	30.1	26.9
64	50.7	41.3	38.7
112	50.8	43.8	40.9
208	57.3	50.4	47.5
400	59.8	52.2	49.0
807	57.0	49.3	47.0
1672	54.8	50.2	48.5
3091	61.0	58.0	56.0