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Polyblending an Epoxy Polymer Adhesive  
with Kraft Lignin

Marwan Khoury

A Thesis

in

The Centre for Building Studies

---

Presented in Partial Fulfillment of the Requirements  
for the Degree of Master of Engineering at  
Concordia University  
Montréal, Québec, Canada

August 1987

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## ABSTRACT

### Polyblending an Epoxy Polymer Adhesive with Kraft Lignin

Marwan Khoury

A bisphenol-A based epoxy polymer adhesive was modified by polyblending with Kraft lignin. Lignin, with amounts between 10% and 20% by weight improved the adhesive tensile strength of the epoxy polymer, but did not much affect its adhesive shear strength (by tension loading), or its weatherability.

The effect of post curing temperature on the adhesive shear strength of the epoxy polymer and polyblends was also determined. A 4 hour post cure at 75 C best improved this strength (by about 75%). The temperature dependence of the epoxy polymer and polyblends' adhesive joint strength was typical of epoxy adhesives.

The glass transition temperatures of the polyblends, as measured by Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA), were very close to that of the epoxy polymer adhesive. The variations of tensile moduli of the polyblends and the epoxy adhesive, as determined by DMA, were also similar, and lignin appears to mix well with the epoxy system. Infrared analysis showed that lignin apparently does not interact with the epoxy polymer system during curing.

In short, polyblending with Kraft lignin between 5 and 20% by weight would reduce the cost of the epoxy adhesive formulation with no detrimental effects and certain improvements in some properties, especially with heat curing.

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## LIST OF SYMBOLS

### Symbol

- ASTM : The American Society for Testing and Materials
- AW : Accelerated Weathering
- CGSB : The Canadian Government Standards Board
- CP : centiPoise
- DBP : Dibutyl Phthalate
- DGEBA : Diglycidyl Ether of Bisphenol-A
- DMA : Dynamic Mechanical Analysis
- DSC : Differential Scanning Calorimetry
- DTA : Diethylenetriamine
- DTA : Differential Thermal Analysis
- EP : Epoxy Polymer
- EP-L5 : Epoxy/ 5% Lignin Polyblend
- EP-L10 : Epoxy/ 10% Lignin Polyblend
- EP-L15 : Epoxy/ 15% Lignin Polyblend
- EP-L20 : Epoxy/ 20% Lignin Polyblend
- MMA : Methylmethacrylate
- NW : Natural Weathering
- PDS : Poly (Dimethyl Siloxane)
- PVA : Poly (Vinyl Acetate)
- PVC : Poly (Vinyl Chloride)
- TMA : Thermal Mechanical Analysis
- R, R', R'' : Alkyl or Aryl Group

## INTRODUCTION

In an increasingly competitive market for building and construction adhesives, epoxy polymer systems exhibit excellent strength, versatility and durability especially for structural uses. However, their moderate to high prices make them less competitive in other building applications, and in need of modification to decrease their cost while maintaining or improving their performance properties. Mechanical polymer blending is increasingly becoming one of the more feasible and economical methods for achieving this goal, especially when the epoxy polymer is blended with another cheap and abundant polymer.

In this research, a bisphenol-A based epoxy polymer system was polyblended with Kraft lignin, a byproduct of the pulp and paper industry, and a cheap, natural and abundant polymer. The effect of this polyblending on mechanical and thermal properties was determined.

The mechanical properties investigated were adhesive tensile strength and adhesive shear strength (by tension loading). The effect of temperature on curing of the epoxy adhesive and polyblends (as reflected by their adhesive shear strength) and their elevated temperature performance were also studied. This was due to the fact that, in the past, insufficient emphasis has been given to temperature effects on the properties of construction adhesives.

Thermal properties as the glass transition temperature and the variation of tensile modulus with temperature were determined by Differential Scanning Calorimetry and Dynamic Mechanical Analysis.

Lastly, the effect of Kraft lignin on the curing of the epoxy adhesive and possible lignin-epoxy interaction were investigated by Infrared Spectroscopy.

The following two introductory chapters discuss in general epoxy polymer systems and polyblends, with emphasis on consumption and use in the building sector. The other parts deal with the experimental work, and present and discuss the results pertaining to properties studied. A general conclusive chapter evaluates the achievements of the research and presents certain recommendations for future work.



## EPOXY POLYMER SYSTEMS

### INTRODUCTION

Epoxy polymer systems provide excellent strength, toughness, chemical resistance, adhesive and electrical properties. This combination of superior properties, coupled with the variety and breadth of applications, have made these systems superior to many other polymeric materials. Their applications vary from electronic encapsulation to protective coatings, structural plastics and adhesives.

In the building and construction industry, epoxy systems find a variety of applications as adhesives, mortars, injection resins, composite materials and coatings. Although today epoxy adhesives represent a relatively small part of the total adhesive market for building and construction, they are one of the best structural adhesives available where high strength and durability are critical. The main hindrance is their high price, and there are continuous efforts to make them more competitive in a yet widening market.

This chapter discusses in general the development, chemistry and characteristics of epoxy polymer systems, with emphasis on the role and applications of epoxy adhesives in the building sector.

## DEVELOPMENT

### Brief history

Although epoxy resin technology was initiated in Europe and the United States in the 1920's and early 1930's, the beginning of the modern epoxy resin technology is considered to be the patent of Schlack of I.G. Farben (1,2,3). In 1934, Schlack mentioned the polyglycidyl ethers of polyphenols that were later acknowledged as resins by Moss in 1937 (4).

In 1936, P. Castan developed a low-melting resin that produced a thermosetting compound when reacted with phthalic anhydride. His patents of 1938 and 1943 describe the production of diglycidyl ethers and esters, and the polymerization of these resins with acid anhydrides, and organic and inorganic bases. These resins included one based on bisphenol-A and epichlorohydrin (1,2). In 1946, CIBA of Basel introduced this epoxy resin adhesive (Araldite I) at the Swiss Industries Fair (1,5).

Meanwhile in 1939, J.O. Greenlee of Devoe-Reynolds of the United States developed new coating resins through the bisphenol-A and epichlorohydrin synthesis (2,3). Shell Chemicals Corporation, after obtaining licenses to Devoe-Reynolds' patents, started marketing a number of liquid and solid epoxy resins. Production of bisphenol-A type resins in the USA rose from a zero base in 1948 to 170 million pounds in 1965 (2,3).

By the late 1960's, at least 25 types of resins were commercially available, including polyfunctional and cycloaliphatic resins, and resins for flame retardancy and flexible coatings (1,2,5). Since then, there has been a rapid increase in the world production of epoxy resins, mainly due to the development of certain application fields including adhesives, composites and electronics (2,5).

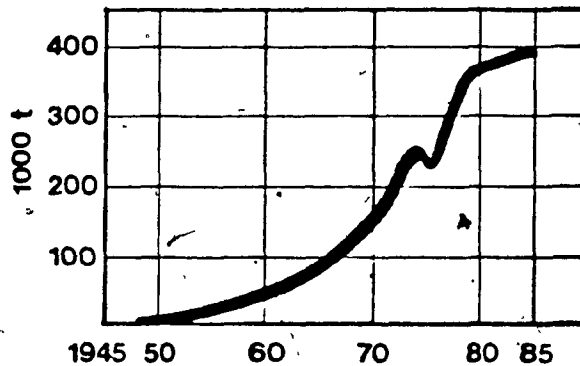


Fig. 1 World production of epoxy resins (5)

#### Building and Construction Market

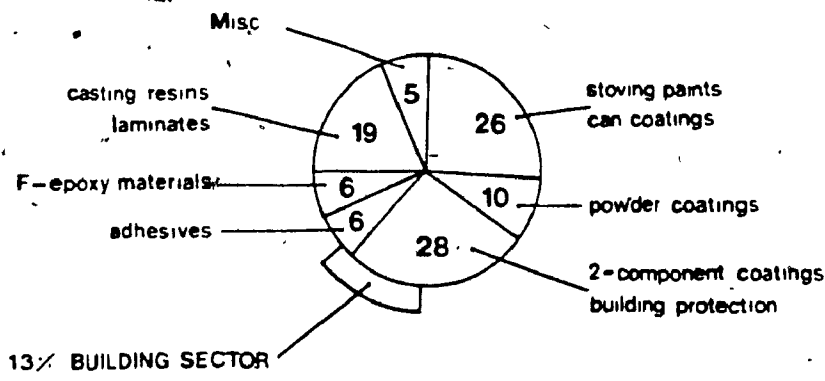
Epoxy adhesives represent a relatively small share of the total epoxy resin consumption. Table 1 shows the pattern of epoxy resin consumption in the USA and Canada in the years 1979-1984 (5), where bonding adhesives constitute around 5% of the total consumption.

**Table 1** Pattern of epoxy resin consumption in USA/Canada 1979-1984 (5)

Application Field	approx. wt. %
Protective coatings	50
Reinforced uses	25
Tooling, Casting, Molding	10
Bonding adhesives	5
Flooring, Paving	5
Others	5

The Canadian import market for epoxy resins showed an average annual growth rate of 10% between 1982 and 1985, of which adhesives constituted 5% on the average (6).

In Western Europe, epoxy adhesives constituted 6% of the total epoxy resin consumption in 1983 as shown in figure 2 (7).



**Fig. 2** Pattern of consumption of about 120,000 t of epoxy resins in Western Europe in 1983 (7).

In the structural-engineering area, epoxy adhesives constituted 7% of the total synthetic engineering adhesives and sealant consumption in the USA (1982). This accounted to a value of 33 million pounds with an expected annual increase of 3.1% between 1982 and 1995 (8).

In Western Europe, the building sector shared in 1983 13% (16,000 t) of the total epoxy resin market in a variety of applications including epoxy adhesives, injection resins, mortars and concrete (7). In the USA, the construction market accounted to 33% of epoxy resin formulations for structural applications in 1980 (9). Table 2 shows the construction market for epoxy resins (USA) based on a formulated product basis (9).

Table 2 Construction market for epoxy resins in the USA, 1980

Construction Market for Epoxy Resins (Formulated product basis) USA 1980				
Application Field	ER Vol, MM lb	Conversion Factor	Formulated Product	
			MM lb	\$ MM
Flooring	11	3	33	85
Paving	3	3	9	25
Other	6	3	18	50
Total	20		60	160

In 1982, the US wood and construction industry shared 22% of the total adhesives and sealants consumption, with epoxy adhesives constituting 3% of this market share i.e. 60 million pounds.

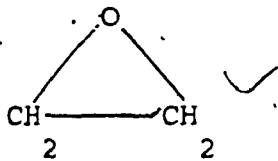
# CHEMISTRY

## Epoxy Polymers

Epoxy prepolymers are low-molecular-weight (MW = 400 to 5000) linear polymers containing the epoxy (also known as the epoxide, oxirane or ethoxyline group) in their molecular structure. On average, two epoxy groups are present per molecule of resin, and are the center of reactivity of the molecule (1,2).

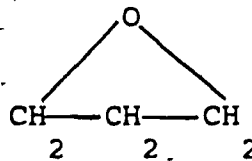
The epoxy is defined as a chemical group consisting of an oxygen atom bonded with two carbon atoms already united in some other way (2). The three types of epoxy groups are the following:

$\alpha$ -epoxy (1,2-epoxy)



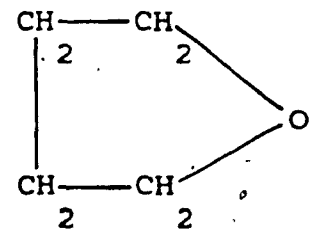
ethylene oxide

1,3-epoxy



trimethylene oxide

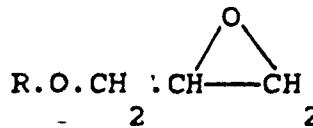
1,4-epoxy



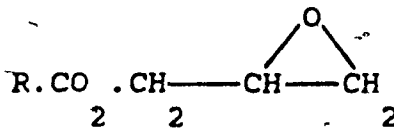
tetrahydrofuran

Most of the common epoxy polymers contain the 1,2-epoxy groups. These 'parent' polymers can be classified into five chemical groups (1,2):

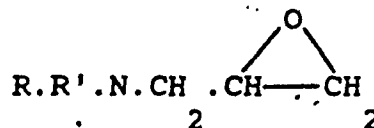
1) Glycidyl ethers



2) Glycidyl esters



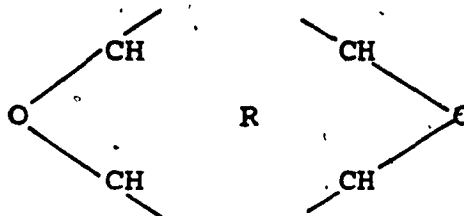
3) Glycidyl amines



4) Linear aliphatic



5) Cycloaliphatic



Epoxy resins are either liquid or solid thermoplastics which on the addition of a curing agent (hardener) polymerize to form thermosets. In the thermoset form, the polymer resin becomes a tough, infusible three-dimensional network due to crosslinking of its molecules by strong covalent bonds (1,2,10,11). It is in this state that most epoxy polymers are useful, although certain high molecular weight resins are used as thermoplastics in coatings (2,10). The most common and widely used epoxy resins are based on the diglycidyl ethers of bisphenol-A (DGEBA); (diphenylolpropane) (1,2,11,12). These epoxy resins are produced by the process shown in figure 3.

The glycidyl esters and amines, and the aliphatic polyepoxides are of limited use. The cycloaliphatic diepoxides are mainly utilized in specialized applications where a certain property is to be outstandingly good (1,10,11).

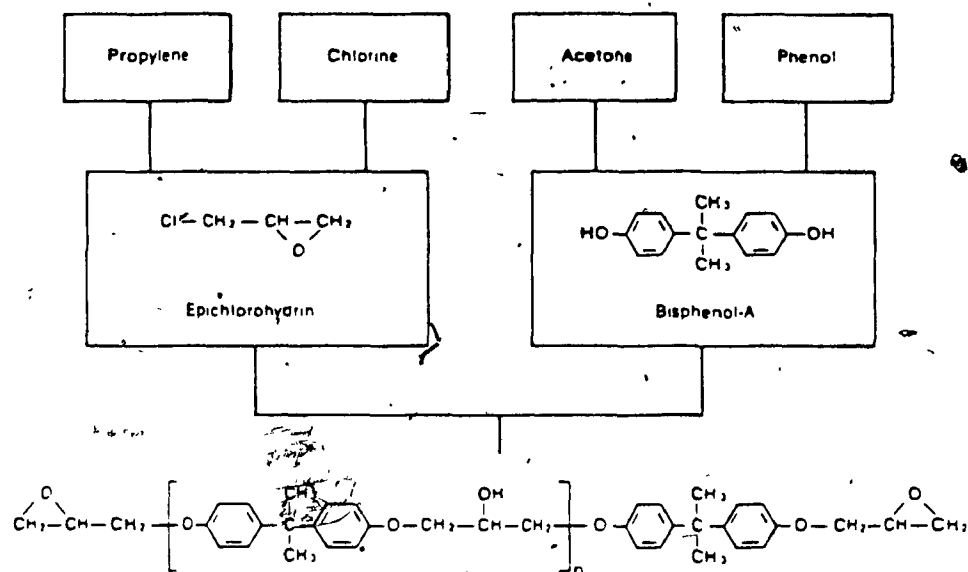


Fig. 3 Manufacturing process for bisphenol-A based epoxy polymers. (DOW Chemicals of Canada Ltd.)

### Curing

As noted earlier, epoxy polymers are rarely used alone, but are converted from a liquid or a brittle solid into a hard and infusible crosslinked polymer. This conversion is commonly called curing and is achieved by the addition of a curing agent.

### Curing Agents

There are numerous curing agents for epoxy polymers, and a proper selection will depend, among other variables, on application techniques, pot-life required, cure conditions and properties required. Curing agents determine both the type of chemical bonds formed and the degree of crosslinking that occurs, thus affecting the properties of the final product.

Potter (1,4) classifies curing agents into two groups, catalytic and polyfunctional. The catalytic curing agents act as initiators for homopolymerization i.e. the crosslinking is achieved through the epoxy resin's own reactive sites (1,4,13).



The polyfunctional curing agents act as reactants or comonomers in the polyaddition reaction, forming bonds between two resin chains. The most common curing agents for bisphenol-A based epoxy adhesives are polyamines and dicyanodiamide (14). Appendix A lists major curing agent types, their advantages, disadvantages and applications.

The curing process is divided into two stages (1,2): conversion and crosslinking. During conversion, the epoxy groups react at different points of the reactive mass leading to an increase in the resin's molecular weight. The second stage is mainly the occurrence of crosslinking leading to the formation of a thermoset. The amount of initial conversion, the distance between the crosslinking centers and the properties of the curing agent will determine the degree of cure.

The curing rate differs depending on temperature and the reactivity between the epoxy polymer and curing agent. Although this rate could be slowed down (several hours) or speeded up (less than a minute), it is difficult to precisely predict it and the degree of curing (1,2,12).

In practice, curing is achieved by mixing the epoxy polymer and curing agent in stoichiometric or near stoichiometric ratios: one gram equivalent of epoxy reacts with the quantity of amine containing the equivalence of one active hydrogen.

### Curing Temperature

Although curing can occur at or below room temperature, heat is required in certain cases. The curing reaction itself is exothermic and the system's temperature may reach up to 200 °C (4). This temperature depends upon the system's components, their temperature and that of the surroundings.

An increase in the curing temperature increases the reaction rate, and decreases the system's viscosity allowing a greater number of epoxy groups to react. This produces better crosslinking and results in toughness and improved chemical resistance of the final product (1,2). However, the increase in temperature could considerably reduce the system's pot-life (2,4). There is also a risk of thermal shrinkage as cooling occurs. Excessive temperature may cause bubbling, leading to inhomogeneities, cracking and complete degradation in extreme cases. Finally, a very low reaction temperature could prevent complete curing, leading to unadequate results.

### Diluents

Diluents are low viscosity compounds mainly used to reduce the viscosity of an epoxy system. They may also be selected to produce minor changes in cured properties, pot-life and exotherm (2,11,15). There are three main classes of diluents:

- 1) Non-reactive diluents that may be trapped within the cured system leading to degradation (2), and include dibutyl phthalate, butyl alcohol and coal tar (2,11).

2) Reactive epoxy-containing diluents, either monoepoxy molecules or low-molecular-weight epoxy polymers (2,15). The latter is preferred because it may be used at high concentrations without much affecting the cured properties (2,15):

3) Reactive non-epoxy-containing diluents, such as active-hydrogen containing molecules and compounds capable of reacting with the curing agent. Examples include nonyl phenol and furfuryl alcohol (11,15).

### **Modifiers**

#### Flexibilisers

Flexibilisers are used to reduce the generic brittleness of epoxy systems, and are divided into two main groups:

1) Reactive flexibilisers, such as a flexible epoxy polymer (polyglycol diepoxides), that lead to the incorporation of long flexible molecular chains in the system's network (2,4,11).

2) Non-reactive plasticisers, that lead to unreacted long-chain molecules within the cured system (2,14,15).

#### Resinous Modifiers

Thermoplastics, thermosets and elastomers have been used to modify the properties of epoxy systems. Many modifying polymer resins often react chemically with the epoxy polymers forming copolymers, or polymer alloys. These include nylon, vinyl, polyester, polyurethane, butadiene-acrylonitrile rubbers and phenolic resins (4,11,14). Other polymers such as coal-tar pitch and petroleum-derived bitumens are used to alter certain properties and cheapen the epoxy system. These do not react chemically with the epoxy polymers and result in polyblends.

## Fillers and Other Additives

Inert fillers and reinforcements are used to enhance or obtain specific desired properties in an epoxy system, and to reduce material cost. These additives may increase viscosity (imparting thixotropy), surface hardness, impact strength, thermal conductivity (metallic fillers) and specific gravity. They may also decrease the coefficient of thermal expansion, and reduce exotherm and shrinkage. Certain fillers could change the electrical and chemical properties. Appendix B lists typical effects of such additives on properties.

Other additives include cure accelerators (phenol to epoxy polymer and aliphatic amine), fire retardants (halogenated resins) and antioxidants.

## CHARACTERISTICS

### Advantages

#### Versatility

Due to the many possible combinations of epoxy polymers, curing agents, diluents and modifiers, epoxy systems may be considered the most versatile of the polymeric materials. The final properties could be varied according to the end application and use environment.

#### Adhesion

Epoxy systems exhibit excellent adhesion to most materials.

This is due to the following reasons:

- 1) The presence of a variety of functional groups including the epoxy, hydroxyl, amine and other polar groups. This results in high specific adhesion to many materials (2,11).
- 2) The high surface contact between adherends and the epoxy systems due to low shrinkage during curing (1,2).
- 3) The ability to reduce the system's viscosity with diluents and modifiers, resulting in better spreading and wetting of the adherends (14).

#### Low Shrinkage

Since no water or volatile byproducts evolve during curing, epoxy systems exhibit very low shrinkage. This is in the order of 4% for a DGEBA epoxy with diethylenetriamine (DTA) as curing agent, as compared to 20% for Methylmethacrylate (MMA) (16). This

could be further reduced to a fraction of 1% by the addition of silica and other inorganic fillers (11). In the case of epoxy adhesives, low shrinkage results in less stress into the bond line and leads to stronger bonds.

#### Curing Conditions

Epoxy systems could cure rapidly or slowly at practically any temperature from 0 to 200 °C, depending on formulations and especially on the type of curing agent (2,4). This facilitates their use in the building sector where cold cure is usually required.

#### Physical and Mechanical Properties

When properly formulated, epoxy systems have very good physical and mechanical properties. Their good properties at normal and high temperatures and their high resistivity make them excellent electrical insulators (2,10). When used in adhesive applications, failure under stress usually occurs in the adherends, due to the high cohesive and adhesive strength of the epoxy systems.

#### Thermal Properties

Epoxy systems are generally characterized by low thermal conductivities, and high coefficients of thermal expansion, about ten times that of metals. Their maximum use temperature may vary between 90 and 180 °C, and depends on the kind of main components and degree of crosslinking. The thermal stability of the system increases with the increasing degree of crosslinking (4,16).

## Chemical Resistance

Cured epoxy systems are characterized by their resistance to a wide range of chemicals. This resistance can be selective and mainly depends on the curing agent used (2,4). In general, most epoxy systems are extremely resistant to caustics and have good to excellent resistance to acids. They are also resistive to moisture and common atmospheric pollutants, an important feature for outside construction applications.

## **Disadvantages**

### Price

Epoxy systems are not cheap but have moderate to high prices on the market. Modifiers, especially fillers, can reduce the cost of epoxy formulations, allowing them to be competitive in applications where cost otherwise would make them prohibitive.

### Disadvantages in Adhesive Bonding

In adhesive bonding, careful surface preparation and good joint design are required for optimum results. In general, epoxy adhesives have low peel, cleavage and impact strength (1,2,14), which should be considered in the design of joints. Other disadvantages include short pot-life and the need for mixing shortly before use.

### Toxicity

While the cured epoxy systems are toxicologically inert, certain epoxy polymers and diluents may cause dermatitis, and aliphatic amine-type curing agents are toxic. Unpleasant fumes may be given off with heat curing. In all cases handling precautions should be observed.

## APPLICATIONS FOR BUILDING

### Segmental Concrete Construction

One of the first structures where precast concrete units (slender cruciform columns) were bonded with an epoxy adhesive system was at Coventry Cathedral, Britain, 1960-62 (17). Other early examples include the Sydney Opera House (shell roof), 1963-67 (17), the Sugar Terminal in Durban (precast concrete arches), 1965 (18), and the Olympic Stadium (console cantilever arm and anchoring 'banana' beam) and the Velodrome roof (Y-shaped ribs) constructed for the 1976 olympic games in Montreal (19).

In bridge construction, this technique has been successfully used since 1962 in many parts of the world including North America (7,17,20). It is practicable, and reduces construction time and overall cost.

### Composite Construction

Reinforcing of structures through epoxy-bonding of steel plates to concrete beams dates back to the mid 1960's. Between 1965 and 1967, three buildings in South Africa were strengthened using this technique (18), while laboratory tests in France were carried out on simply supported beams reinforced by steel plates from beneath (21). Since then, this technique has been widely used in strengthening of existing buildings and road bridges using steel plates, beams and angles (7,17,19,20).



Another example of composite construction pioneered in South Africa in the early 1960's was the epoxy-glueing of brick panels into the reinforced concrete frames of buildings (18). This resulted in composite action of the frames, enhancing the strength at an economical overall cost.

#### Material Bonding

Epoxy adhesive systems have the ability to bond similar materials as well as the advantage to bond different ones. Composite units (concrete-steel and concrete-aluminum) as well as sandwich assemblies from similar construction materials were studied since the early 1960's (22,23). Today, epoxy adhesive systems are extensively used in concrete-concrete and metal-concrete bonding due to their excellent adhesion characteristics (17,20,24,25). Such systems also perform well in bonding glass to ceramics. An early example is the lantern of the Cathedral of Christ the King, Liverpool, 1968, where glass-concrete panels are bonded with an epoxy adhesive (17).

Prefabricated panels with stone veneers, brickslips, metal and ceramic tiles, wood and certain plastic laminates bonded to concrete backings with epoxy adhesives are common in buildings today (24,25,26). These adhesives are also used for bonding of exterior claddings and interior finishes to brick, concrete and concrete-block walls (24,26). Building surfaces are at times finished through setting of stone aggregates in an epoxy mastic (25). Certain facade panels consist of a rigid plastic insulating core sandwiched between epoxy mortar panels (7).

### Other Uses

Epoxy adhesive systems are also used in polymer (epoxy) concrete, and in mortars for industrial and heavy-traffic flooring, floor coating compounds and bonding of most floor tiles (1,7,24,26). Epoxy adhesives are extensively used in crack injection for structural repairs of bridges, roads, tunnels, dams and historic stone and brick structures. Other uses include grouting foundations for heavy machine installation, pile bonding and clay-pipe bonding (19,27). Epoxy adhesives are sometimes used for resilient floor coverings where high strength and water resistance are required (26). They are also used in the bonding of rubber, and some plastics to ceramic, new plaster to old plaster in a high-humidity environment, and certain ceiling finishes such as glassfiber mat panels (24,26). Lastly, epoxy adhesive systems have been successfully utilized in stone consolidation and preservation (28).

## POLYBLEND

### INTRODUCTION

Since the early 1970's, there has been an increasing concern with the future supply of energy and materials. The cost of most materials, including synthetic polymers, usually rise with rising energy costs. However, the cost-effectiveness of synthetic polymers is less affected by energy cost rise. This is partly due to the corrosion-resistance of such materials, and the fact that the production of petrochemicals, including the supply for monomers, is less than 10% of all petroleum production (29).

Today, polymer blending (polyblending) has become one of the most commercially important and inexpensive ways to developing new materials from readily available base polymers. The main aim of polyblending is the production of good-performance materials at a reduced cost. This is achieved through the infinite blending possibilities, the ability to use existing or more flexible processing equipment, and the capacity to combine expensive polymers with cheap and abundant ones.

### DEFINITION

Polyblends (alloys) are intimate physical mixtures of two polymers, with no covalent bonds between them (30,31,32). In polyblends, as in interpenetrating polymer networks (IPN's), the components are in different macromolecular compounds, which differentiates them from block and graft copolymers (30,31).

## COMPATIBILITY AND MIXING

Polyblends are grouped into incompatible (immiscible, heterogenous), † semicompatible, or compatible (miscible, homogenous) blends (31,32). Due to the inherent incompatibility of different polymer chains, polyblends do not usually form true solid solutions. When two distinct phases remain upon mixing, the polyblend is considered incompatible (31,32). In semicompatible polyblends one of the components will be dispersed in a continuous matrix of the other. In compatible blends, and due to mutual solubility, a mono-phase system is formed (30,31,33). However, true compatibility is rare (31,34).

In the thermodynamic definition, miscibility depends on the free energy of mixing ( $\Delta F_m$ ), that may be written as:

$$\Delta F_m = \Delta H_m - T \Delta S_m$$

where ( $\Delta H_m$ ) is the heat and ( $\Delta S_m$ ) the entropy of mixing (31,34). When small molecules of different liquids are mixed, the increase in randomness and entropy is very high and outweighs the endothermic heat of mixing. The result is negative free energy and thus miscibility. When macromolecules are mixed, thousands of atoms in each molecule remain together, decreasing the mixing randomness and resulting in lower entropy gain (34). This in turn lowers the possibility to outweigh the endothermic heat of mixing, making true mixing and miscibility more difficult.

In practice, the degree of compatibility is defined with respect to the resulting properties of the polyblend. Blends with satisfactory properties are considered compatible and vice versa (34). Figure 4 shows such a system for evaluating compatibility.

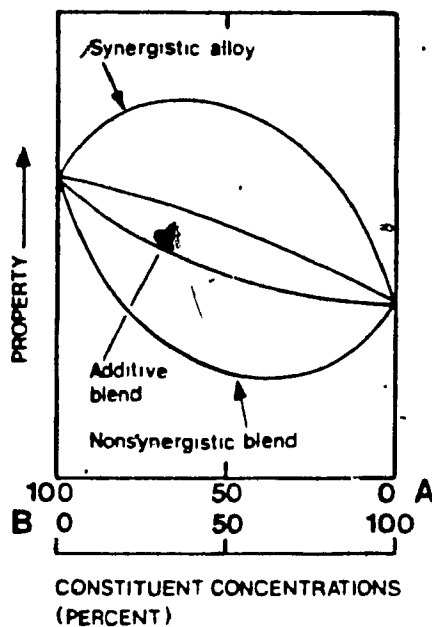


Fig. 4 Compatibility graph for polyblends (35)

A property of the polyblend, of value  $P$ , is described by the following equation:

$$P = P_1C_1 + P_2C_2 + IP_1P_2$$

where  $P_1$  and  $P_2$  are property values for constituent polymers, and  $C_1$  and  $C_2$  their respective concentrations. The number 'I' defines the level of synergism created by polyblending. When 'I' is positive, the blend properties exceed the expected arithmetic averages of those of the components (synergistic blend). For a negative 'I', the blend properties are below the predicted values (nonsynergistic blend) (35). While synergistic blends are usually termed alloys, polyblends with properties corresponding closely to the predicted values ( $I=0$ ) are sometimes called additive blends.

## PROPERTIES

The properties of polyblends depend, apart from the properties of the constituent polymers, upon the morphology of the blend (36). The size, shape, distribution and degree of separation of the dispersed and continuous phases will in turn depend upon the following (32,36,37):

- 1) Rheological and interfacial adhesion properties of the polymers.
- 2) Volume ratio of the components.
- 3) Composition of constituent polymers.
- 4) Molecular weight and structure of each polymer.
- 5) Blending conditions including temperature and pressure.
- 6) Method of blend preparation i.e. mixing, open-rolls blending, extrusion.

In general, compatible polyblends exhibit optical clarity, a single sharp glass transition temperature, and homogeneity at a submicroscopic level (50-100 Angstroms) (31,32,36). The mechanical properties of such blends are usually superior to those of incompatible ones. Incompatible polyblends have two  $T_g$ 's which belong to each component, are usually opaque and show true two-phasic behavior (31,32,33). In most cases, polyblends are semicompatible and their behavior is neither true two-phasic heterogeneous nor mono-phasic homogeneous. The glass transition is broadened over that observed in homogeneous systems, and is shifted from the pure-component values (33). The weathering behavior of polyblends is quite complicated due to different aging rates and continuous interaction between the two components.

Experimental techniques used to determine compatibility in polyblends include electron microscopy, differential scanning calorimetry, small-angle X-ray diffraction, light scattering, thermal analysis and dynamic mechanical analysis.

## POLYBLENDING OF EPOXY ADHESIVES

Polymers used in blends with epoxy polymers are many, and in most cases have functional groups capable of reacting with the epoxy. Polyblending with nylon is one example, and where epoxy-nylon adhesives show high shear strength as well as high peel strength (14,38). Studies concerned with rubber-epoxy polyblends are numerous. They include determining the effect, among others, of butadiene-acrylonitrile and n-butylacrylate/acrylic acid copolymer on the morphology and mechanical and thermal properties of such polyblends (39,40,41,42,43,44,45).

Other polymers used in blends with epoxy systems include poly (vinyl formal) and poly (vinyl butyral) (14), polyethylene (46), polyurethane (14), phenolic resins (14), poly (vinyl chloride) and poly (vinyl acetate) (47,48), and coal-tar pitch and petroleum-derived bitumens (4).

Of special concern to this research is the lignin-epoxy adhesive patented by Shiraishi et al (49) in 1986 and published after this study was started. The adhesive obtained by these authors is based on a completely different method than ours. It is a result of a catalyzed chemical reaction between lignin and phenolics at temperatures under 240°C. In our case, we obtained a physical mixture, at room temperature, between lignin and an epoxy polymer. The 'Shiraishi' adhesive has a tensile shear adhesion of 3.1-3.4 MPa and 1.7-2.1 MPa before and after immersion in boiling water.



Another study done at the Center for Building studies (Concordia University, Montreal) dealt with polyblending a similar epoxy polymer with DBP, PVC and PVA (48). While DBP increased the ultimate adhesive tensile strength, PVC and PVA had generally a detrimental effect. Epoxy/DBP blends also had better resistance to natural weathering than the other polyblends and the unblended epoxy adhesive.

## LIGNIN IN POLYBLEND S

### Lignin: a Definition

Lignin is a natural polymer acting as a cementing agent of cellulose fibers in the woody structure of higher plants (50). Lignin, after cellulose, is the principal constituent of wood (around 25%) and the second most abundant natural polymer (50,51).

The exact chemical structure of natural lignin is not known, but analysis indicates it having an aromatic nature (50). Functional groups such as hydroxyl (OH), methoxyl (OCH<sub>3</sub>) and carbonyl (C=O) are contained within all kinds of lignins (separated from different species).

### Kraft Lignin

Kraft (alkali) lignin is a technical lignin which is a byproduct of the pulp and paper industry, the principal source of commercial lignins. It is produced by acidulation of the spent black liquor from the Kraft process (50).

In 1980, 20 million tons of Kraft lignin were generated from the pulping process in the US pulp and paper industry alone. Only around 35 thousand tons were consumed worldwide in numerous applications, of which their use as macromolecules in material systems is relatively small (52). This includes uses as thermosetting resins, as antioxidants and reinforcements in rubber, and as components in polyblends (53).

## Examples of Applications

Many of the applications of lignin in polyblends involve its presence as a dispersed phase (particle applications) or possibly as an associate of macromolecules.

As early as 1958, Nicholas (54) employed Kraft lignin as a reinforcing agent and antioxidant in elastomeric compositions. He concluded that modified lignin could be incorporated into the matrix of polymers due to functionalization. In 1963, Feldman (55) utilized alkali hydrotropic and hydrolytic lignins in the manufacturing of phenoplasts. Later in 1967, Montgomery (56) improved the strength of poly (vinyl chloride) through blending with a mixture of lignin and butadiene-styrene copolymer.

More recent examples include the work by Fuhrmann (57), 1980, in which lignin was used as a component in adhesives for plywood, particle board and fiberboard. Genov (58), 1983, improved the bonding strength of plywood (with sulfur modified phenol-formaldehyde) through the addition of lignin. In 1986, Chodak et al (59) increased the thermal oxidative stability of polypropylene through blending with Kraft lignin. Yoshida et al (60) used Kraft lignin as a chemical component in the production of polyurethanes having good mechanical properties and high thermal stability. Also, Shiraishi et al (49) patented a chemically synthesized Kraft lignin/epoxy adhesive having good strength and water resistance.

At the Center for Building Studies (Concordia University), Beznaczk (61) showed that Kraft lignin improves the mechanical performance of a silicone sealant (PDS)/10% PVC polyblend. Lacasse (62,63) showed that Kraft lignin improves the tensile properties of polyurethane, acrylic and butyl based sealants.

## EXPERIMENTAL RESEARCH

### OBJECTIVES AND PROGRAM

The objectives of the research were to determine the effect on properties and cost of a bisphenol-A type epoxy polymer adhesive through mechanical polyblending with Kraft lignin, a byproduct from pulpmills.

The epoxy polymer system and the polyblends were tested for their adhesive strength in tension and in lap-shear by tension loading, their response to natural and accelerated weathering and to different curing conditions, and their elevated temperature performance.

The thermal properties of the epoxy adhesive and the polyblends, such as the glass transition temperature and tensile modulus variation with temperature, were determined by Differential Scanning Calorimetry and Dynamic Mechanical Analysis.

Infrared Spectroscopy was used to investigate possible interaction of lignin with the epoxy system during the curing of the adhesive.

## **MATERIALS**

### **Epoxy Prepolymer**

The basic epoxy prepolymer is a commercial accelerated diglycidyl ether of bisphenol-A (CIBA-Geigy, 1200 CA resin), with the basic chemical formula previously shown in figure 3.

### **Curing Agent**

The curing agent is a commercial accelerated aliphatic polyamine (CIBA-Geigy, 1200 CA hardener). In all the experiments the ratio between the epoxy prepolymer and curing agent was 3.3:1 by weight.

### **Kraft Lignin**

The second polymer, Kraft lignin, is a commercial lignin (Tomlinite-Domtar), extracted from a mixture of hardwoods (maple, beech, elm), and precipitated from the black liquor with sulfuric acid, with the pH adjusted to a level of 6 to 7 with carbon dioxide (52).

### **Polyblends**

The amounts of Kraft lignin used in the polyblends were 5, 10, 15 and 20 percent by weight, and are designated in the text as EP-L5, EP-L10, EP-L15 and EP-L20 respectively. In all the experiments, the polyblends were compared with the unmodified epoxy adhesive system, designated EP.

### Mixing of Polymers

The polyblends were prepared directly prior to use: The components were manually mixed together with a stirring glass rod for five minutes, at room temperature. The batches used at a time were kept between 4.5 and 6 grams as to ensure close mixing conditions. The gel time for the epoxy adhesive and the polyblends varied between 21 to 25 minutes after initial mixing.

### Substrates: Material and Preparation

The substrate material used in the adhesive joints was an aluminum alloy. Prior to use, the substrates were cleaned with pure acetone, followed by a thorough cleaning with a detergent solution and a final rinse with distilled water. They were then air-dried at lab conditions (approx. temp. of 23°C; R.H. 35-50%) for 24 hours prior to the preparation of test joints.

In cases where a primer was used, it was applied to the adherend and allowed to air-dry for one hour before joint preparation. The primer used was DOW Corning's 1200 prime coat, a dilute solution of reactive materials with a room temperature viscosity of 1 cP.

## ADHESIVE STRENGTH IN TENSION

Due to the fact that the tensile strength of adhesives are relatively low when compared with those of metals, they are usually employed in joint designs that load them in other modes, and where their tensile strength is not critical (64,65). However, tensile tests are very common for evaluation and quality control of adhesives because they yield fundamental strain, modulus and strength data.

### Joint Design

A simple butt joint, consisting of an adhesive bead (50.8x12.7x12.7 mm) cast between two prismatic pieces of aluminum substrates (76.2x25.4x12.7 mm), was used for testing the adhesive strength in tension (adapted from ASTM C719-79 and CGSB CAN2-19.0-M77). The joint would be loaded in tension alone, although certain cleavage stresses may exist due to the rigid aluminum substrates.



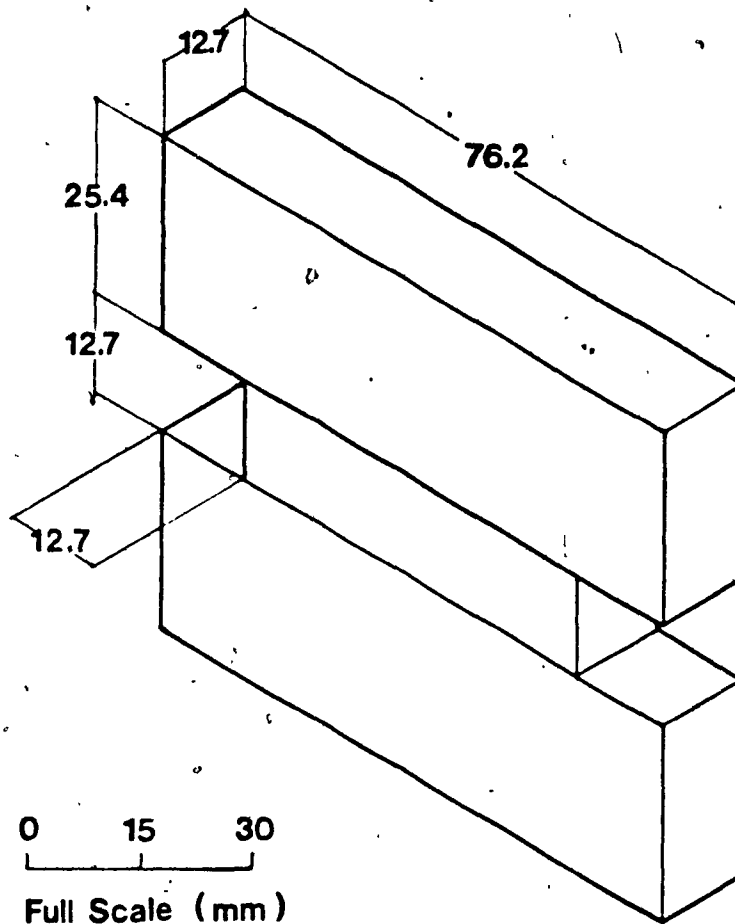


Fig. 5 Tensile butt joint

#### Casting of Specimens

The specimens were cast in wooden molds similar to the one shown in figure 6. Wooden spacers (12.7 mm cubes) were placed between the substrates to ensure a uniform adhesive bead size. Cellophane tape on the spacers and wax paper below the specimens prevented their adherence to the mold or spacers. The specimens were tightly fitted as to prevent leakage of the adhesives below the substrates, and to ensure proper bonding.

The unmodified epoxy adhesive and the polyblends were of a relatively low viscosity, and were therefore poured into the molds. They were self-levelling and no visible air bubbles were observed during the curing reaction of all mixtures.

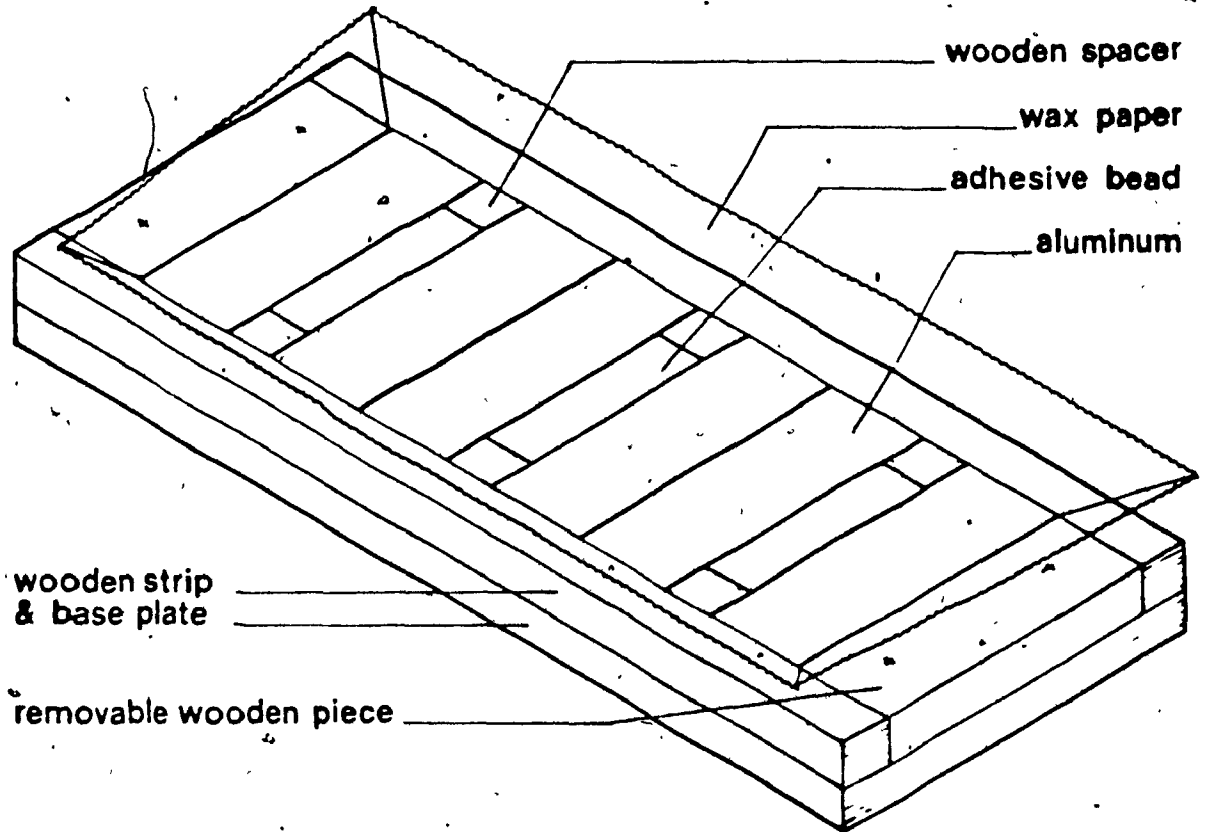


Fig. 6. Wooden molds for casting of butt joint specimens

## Specimen Conditioning

After curing for 24 hours at room temperature, the specimens were subjected to the following conditions:

### Lab Conditions

Four sets (each set consisting of 5 to 10 specimens) with EP, EP-L5, EP-L10 and EP-L20 were kept for 125 days at a temperature of 23°C and a relative humidity between 35 and 50%.

### Natural Weathering

Four sets, similar to the above, were kept outside in downtown Montreal, in a relatively polluted area, for varying periods till failure.

The sets with EP, EP-L5 and EP-L20 failed after 30 days (between February 19 and March 20, 1987). The average temperature during this period was -6°C. The lowest temperature was -20°C and the highest 8°C.

The set with EP-L10 failed after 64 days (between February 19 and April 23). The average temperature during this period was 7.5°C, the lowest -20°C and the highest 22°C.

Two additional sets with EP and EP-L10 were prepared using a surface primer (DOW Corning 1200 prime coat) and exposed to natural weathering. They failed after 23 days (between March 29 and April 20). The average temperature was 8°C with a minimum of -8°C and a maximum of 27°C.

### Accelerated Weathering

Another four sets (no primer) with EP, EP-L5, EP-L10 and EP-L20 were kept in a dark environmental chamber (without u.v. light) and subjected to 52 temperature cycles (2 cycles/24 h) in the temperature range  $-30^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ .

Two other sets. (with primer) and with EP and EP-L10 were subjected under the same conditions to 84 cycles (4 cycles/24 h) in the temperature range  $-30^{\circ}\text{C}$  to  $35^{\circ}\text{C}$ .

### Test Procedure

The specimens were tested on the Instron 1125 Universal Testing Machine. The test grips designed for this type of test are schematically shown in figure 7. The load is applied perpendicular to, and away from, the bond area. As the specimen elongate, its resistance increases and is detected by a load cell. This load value is recorded by the instrument on a moving chart. Elongation continues until failure in the bond, adhesive, or substrate occurs.

The crosshead speed (relative rate of motion of the grips) used was 2 mm/min with a chart drive of 20 mm/min and the testing temperature was  $23^{\circ}\text{C}$ .

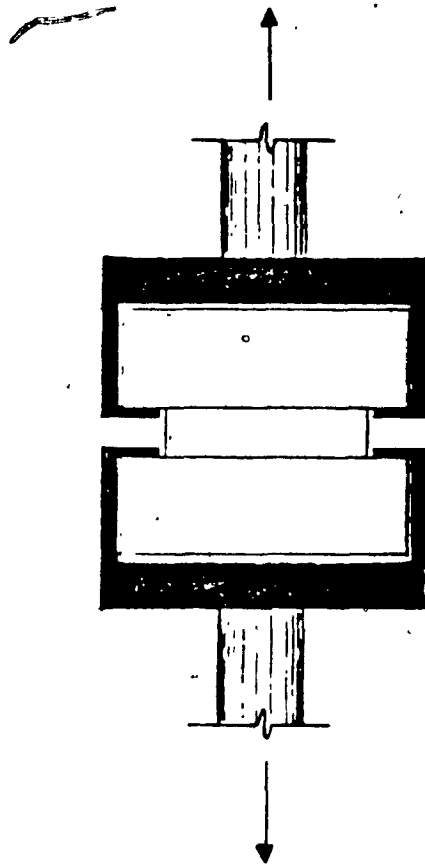


Fig. 7 Test grips for tensile testing

### Results and Discussion

#### Lab Conditions

The results of tensile testing of the four sets kept at lab conditions are shown in figure 8. Values to plot stress-strain curves are average of 5 to 10 successful tests. Conclusions are drawn taking into consideration the maximum error of estimate (90% confidence with a degree of freedom  $n-1$ ,  $n$  being the number of specimens in a set). In all tests, the standard deviation was  $\pm 0.2$  MPa; less than the accepted ten percent variation in practice.

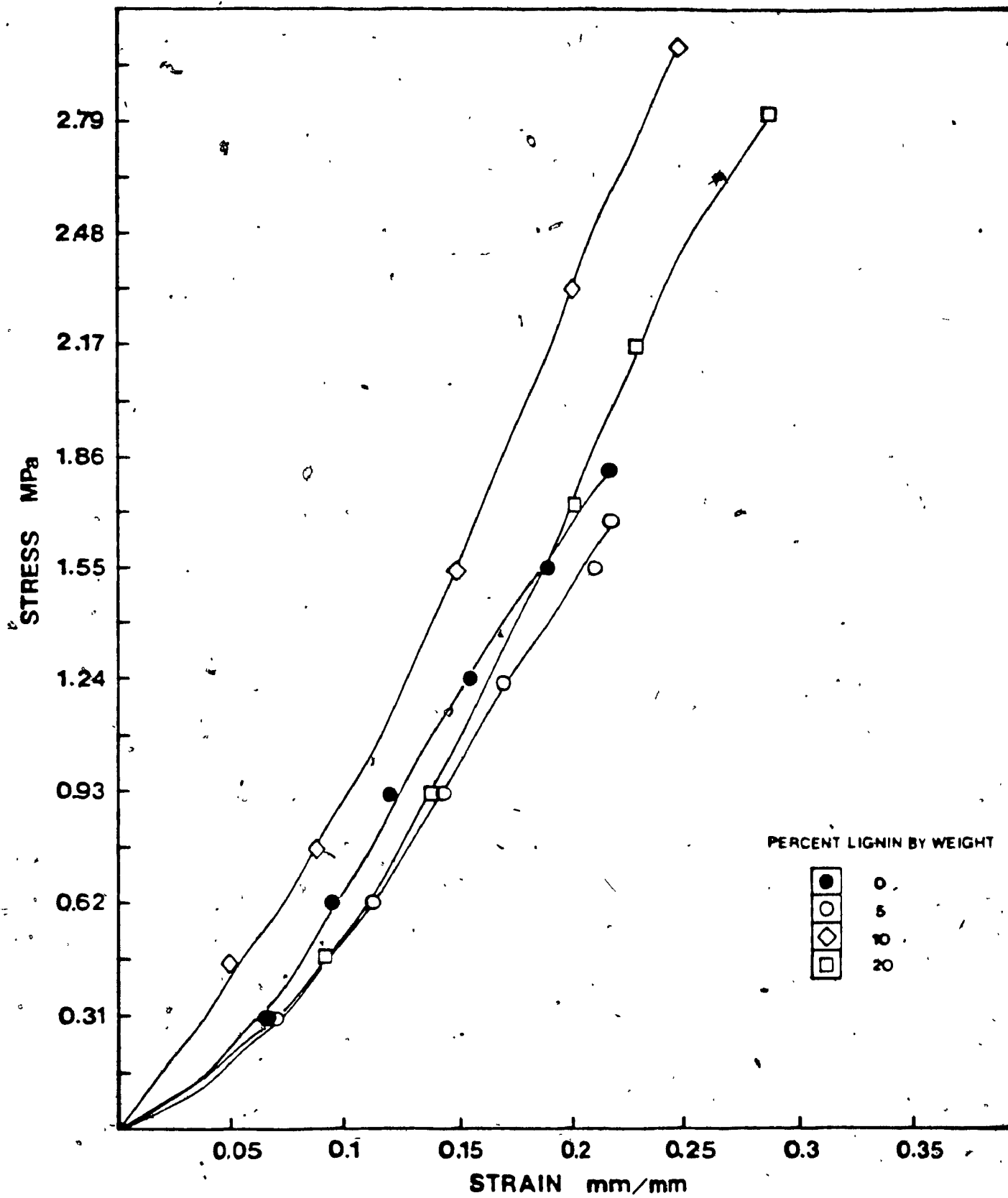


Fig. 8 Tensile strength properties of adhesives; specimens aged for 125 days at 23°C and 35-50% R.H.; aluminum substrates; test temperature = 23°C; crosshead speed = 2 mm/min.

All joints failed in adhesion (failure in the bond line), and the results are presented below:

- 1) The adhesive tensile strength of the polyblend with 5% lignin did not vary much from that of the epoxy adhesive.
- 2) There was a considerable increase (approx. 50%) in the adhesive tensile strength of the polyblends with 10 and 20% lignin, over that of the epoxy adhesive.
- 3) EP-L20 showed the highest strain.

Figure 9 shows the variation of the adhesive tensile strength with lignin. Similar variation of strength properties with other additives are presented in a recent review by Moloney et al (66) on filled epoxy polymer systems.

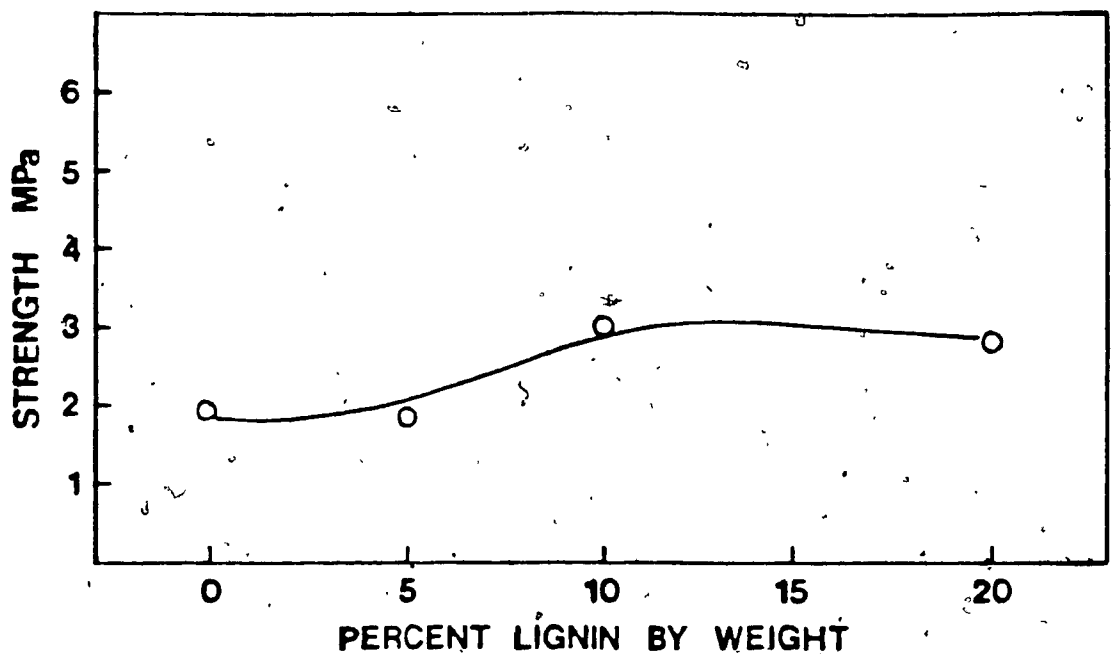


Fig. 9 Variation of the adhesive tensile strength of the epoxy polymer system with lignin.

A number of factors could have contributed to the increase in adhesive tensile strength. Feldman and Banu (67) have shown that Kraft lignin slightly decreases the peak exotherm-temperature during curing of the same epoxy polymer. This exotherm moderation, due to lignin replacing part of the epoxy polymer as an inert component not undergoing irreversible change on heating, leads to a reduction in shrinkage upon cure. Reduced shrinkage results in smaller residual stresses in the bond line and the formation of a stronger bond. The slight increase in viscosity with the addition of lignin does not significantly affect the wetting and spreading capabilities of the adhesives. It is possible to conclude that polyblending with lignin (10 to 20 percent by weight) increases the adhesive tensile strength of the epoxy polymer system.

#### Natural Weathering

Under the conditions described in the section on specimen conditioning, all samples failed by separation of the adhesive bead from the aluminum substrate. The longest duration to failure was obtained with the EP-L10 polyblend, where the period of exposure was double that of the epoxy adhesive and the other polyblends. The use of primer in this case did not affect the durability of epoxy adhesive joints and relatively reduced that of EP-L10.



One of the main factors in joint durability is the adhesive/adherend interface (68), which in turn depends on the surface pretreatment used, surface chemistry and topography (68,69). In adhesion of metals, the interactions of organic macromolecules with the surface oxide layer are essential (69,70,71). However, water absorption associated with epoxides, combined with the possibility of certain curing agents to hydrolyze, may rupture the oxide layer critical for adhesion (70,72). In the case of epoxy bonded aluminum joints, special primers are needed to reach high stability of adhesion against humidity and corrosion, with an anodizing process resulting in the highest durability (69,71). In the polyblend EP-L10, a possibility of stabilization of the oxide layer through interaction with lignin could have contributed to the slight improvement in joint durability.

#### Accelerated Weathering

All the joints, including those with EP-L10, failed after the 52 cycles described earlier. The primer had no significant improvement on the behavior of joints with EP and EP-L10, with failure occurring after 84 cycles.

In artificial weathering, the effect of thermal shock, due to cycling, is apparently the main cause of failure in all the joints. The relatively lower thermal expansion coefficients that could have resulted from polyblending with lignin have not improved the performance through the reduction of strain on the bond line. In both the accelerated and natural weathering, the relatively large size of the adhesive bead may have contributed to higher stress on the bond line with temperature variation. From the results obtained so far, it is possible to say that lignin does not improve the weatherability of the epoxy polymer adhesive.

## ADHESIVE STRENGTH IN SHEAR (BY TENSION LOADING)

Shear tests are very common and useful in the adhesive industry because they are simple and economical to conduct, and they duplicate the geometry and type of loading for many structural adhesives (65,73). In shear joints, stress distribution is not uniform, especially with rigid adhesives, and is concentrated at joint edges with the center portion of the adhesive contributing little to the total strength (64). Consequently, the mean load at which a joint specimen fails is considerably below the true strength of the adhesive.

### Joint Design

A single-lap shear joint with aluminum substrates (101.6x25.4x1.6 mm) was used for evaluating the adhesive shear strength by tension loading (ASTM D-1002), with an overlap length of 12.7 mm, as shown in figure 10.

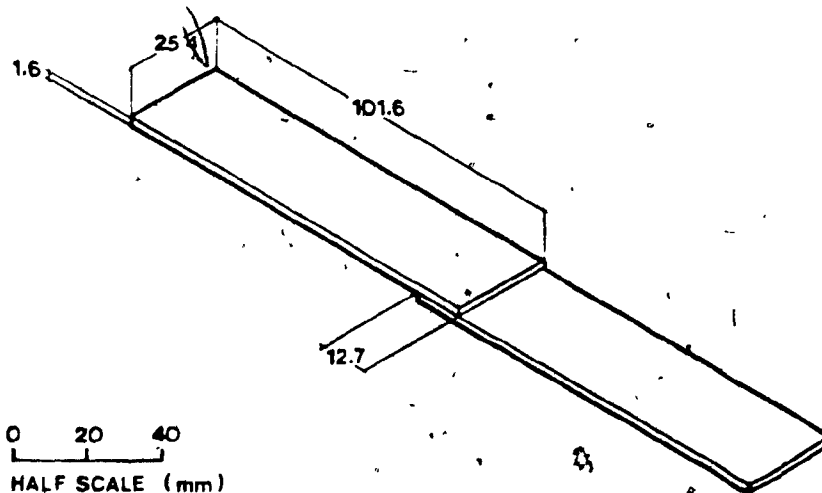


Fig. 10 Single-lap shear joint

The strength of a single-lap shear joint is directly proportional to the width of the joint, and also increases (though not linearly) with the length of overlap, and the thickness and stiffness of the adherends (64,65,73).

### Casting of Specimens

In all the following experiments, no primer was used on substrates' surfaces. The adhesives were applied across both sides of the overlap area, and to a sufficient length across this area (approx. 6 mm). The specimens were held rigidly by tape on wooden base plates, while wooden strips allowed the length of the overlap to be controlled. Two threads were placed across the bonded area (between the substrates) to ensure a uniform adhesive thickness in all specimens. This setting is shown in figure 11. After curing, excess adhesive outside the bonded area was sawn off.

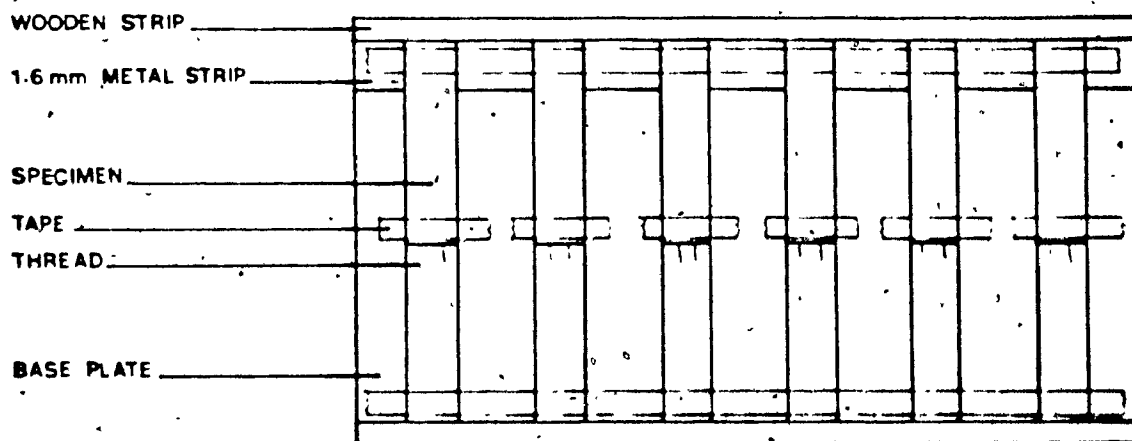


Fig. 11 Casting of single-lap shear specimens.

## **Specimen Conditioning**

After curing for 24 hours at room temperature, the specimens were subjected to the following conditions:

### 3-Days Curing (Series A)

Five sets (5 to 10 specimens each) prepared with EP, EP-L5, EP-L10, EP-L15 and EP-L20, were cured for 3 days at room temperature before testing.

### Lab Conditions (Series L)

Five similar sets were kept for 115 days at a temperature of 23°C and relative humidity between 35 and 50%.

### Natural Weathering (Series NW)

Another five sets were kept outside for 115 days (between February 19 and June 9). The average temperature during this period was 10°C. The lowest recorded temperature was -20°C and the highest 30°C.

### Accelerated Weathering (Series AW)

Five sets were exposed to temperature cycling in the environmental chamber for 108 days. The total number of cycles was 366, including 66 at 2 cycles/24 h and 300 at 4 cycles/24 h. In all cycles, the temperature range was between -30°C and 35°C.

## **Test Procedure**

After conditioning, the specimens were tested on the Instron 1125, with test grips shown in figure 12. The loading was in tension, with a crosshead speed of 1 mm/min, a chart drive of 20 mm/min and a testing temperature of 23°C.



Fig. 12 Set-up for shear testing by tension loading (74)

#### Results and Discussion

Results of shear testing of the four series are summarized in figure 13. As mentioned earlier, mean values are determined from 5 to 10 successful tests, and conclusions drawn here and in the remaining tests take into consideration estimation errors within a 90% confidence interval. In all the tests, failure was in adhesion.

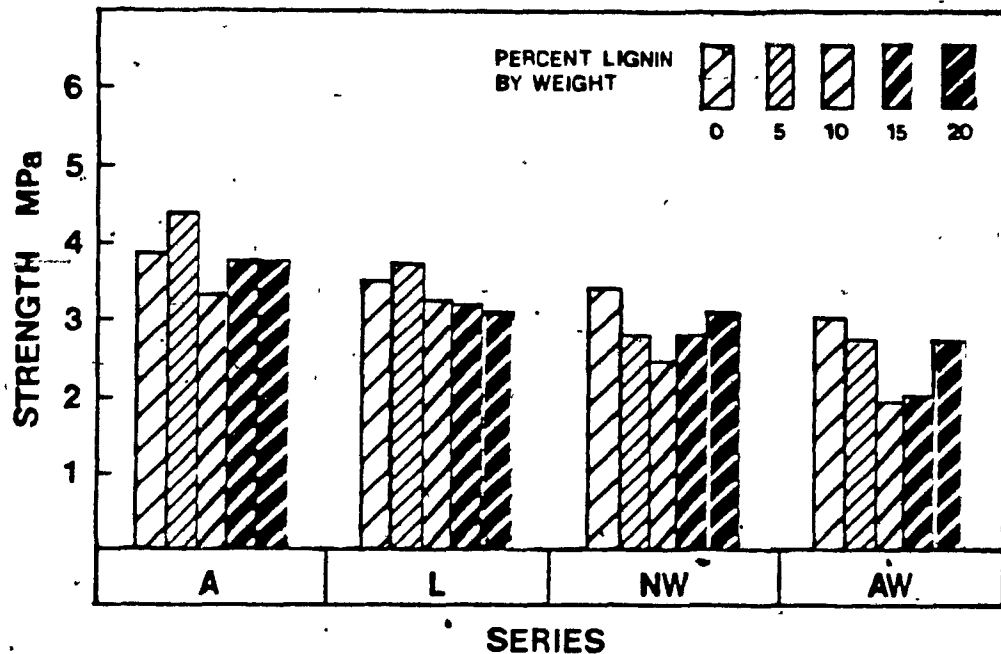


Fig. 13 Adhesive strength in shear by tension loading.  
 Series A: 3-days curing at room temperature.  
 Series L: 115 days at lab conditions, 23°C, 35-50% R.H.  
 Series NW: 115 days of natural weathering, Feb. 14-June 9,  
 Series Aw: 108 days of accelerated weathering, 366 cycles

3-Day Curing (Series A)

The adhesive shear strength of the epoxy adhesive and the polyblends were relatively close, as shown in figure 14. The two polymers are apparently compatible and lignin does not much affect the adhesive shear strength of the epoxy system. It is possible to say that polyblending with lignin up to 20% by weight could reduce the cost of the epoxy adhesive without much altering its shear strength.

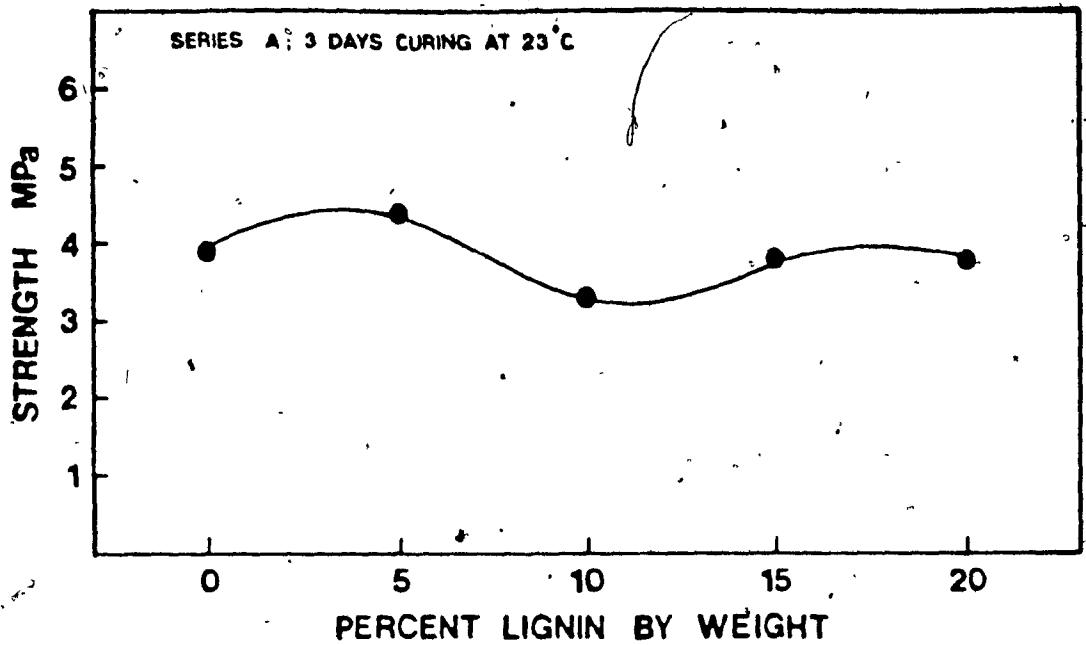


Fig. 14 Variation of adhesive shear strength of the epoxy adhesive with lignin. Series A.

Lab Conditions (Series L)

Testing of Series L after 115 days at lab conditions resulted in overall lower values, with an average decrease in adhesive shear strength of 12%, as compared to Series A.

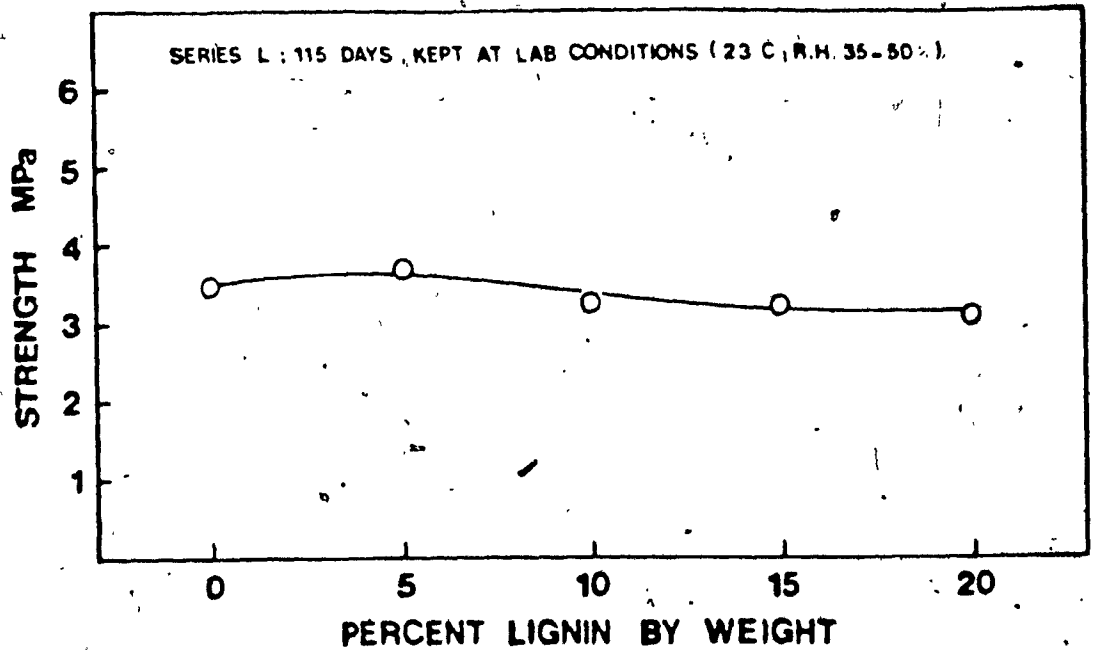


Fig. 15 Variation of adhesive shear strength of the epoxy adhesive with lignin. Series L.



The variation in adhesive shear strength with lignin was very small as shown in figure 15. It is possible that full cure at room temperature was not achieved, and resulted in the slight drop in shear strength of the epoxy adhesive and the polyblends (see figure 13). In a study by Brett (75), full cure of a DGEBA epoxy polymer with a polyamine was only achieved at temperatures above 80 C. In delaying full cure by storing lap-shear joints at 25 C for various times before heat curing, the load fell rapidly to about 60% of its potential value as shown in figure 16.

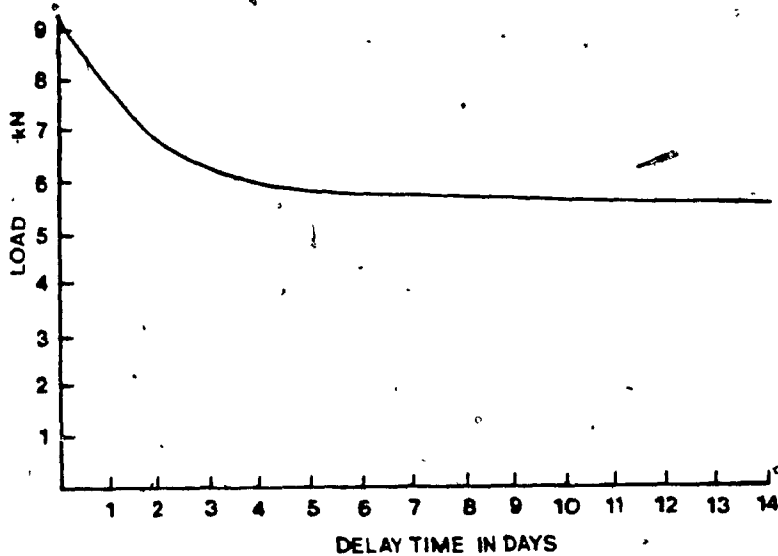


Fig. 16 Effect of delayed cure (75)

### Natural Weathering (Series NW)

Due to 115 days of natural weathering, the shear strength of the epoxy adhesive and the polyblends decreased, the slightest decrease occurring with EP and EP-L20, as shown below in figure 17. This may be attributed to cryolysis (mechano-chemical degradation process due to freeze-thaw cycles) (76). Furthermore, the often highly polluted and acidic nature of the rain (pH approx. 4) may also play a part in reducing the mechanical properties of the specimens in Series NW.

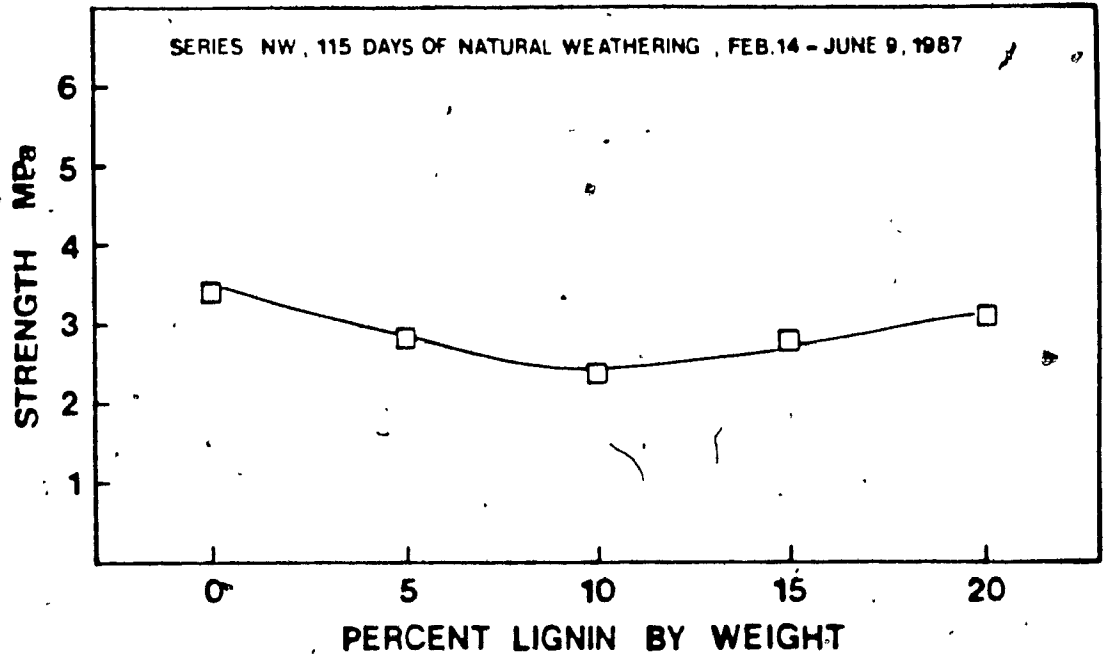


Fig. 17 Variation of adhesive shear strength of the epoxy adhesive with lignin. Series NW.

### Accelerated Weathering (Series AW)

The test results of Series AW are shown below in figure 18.

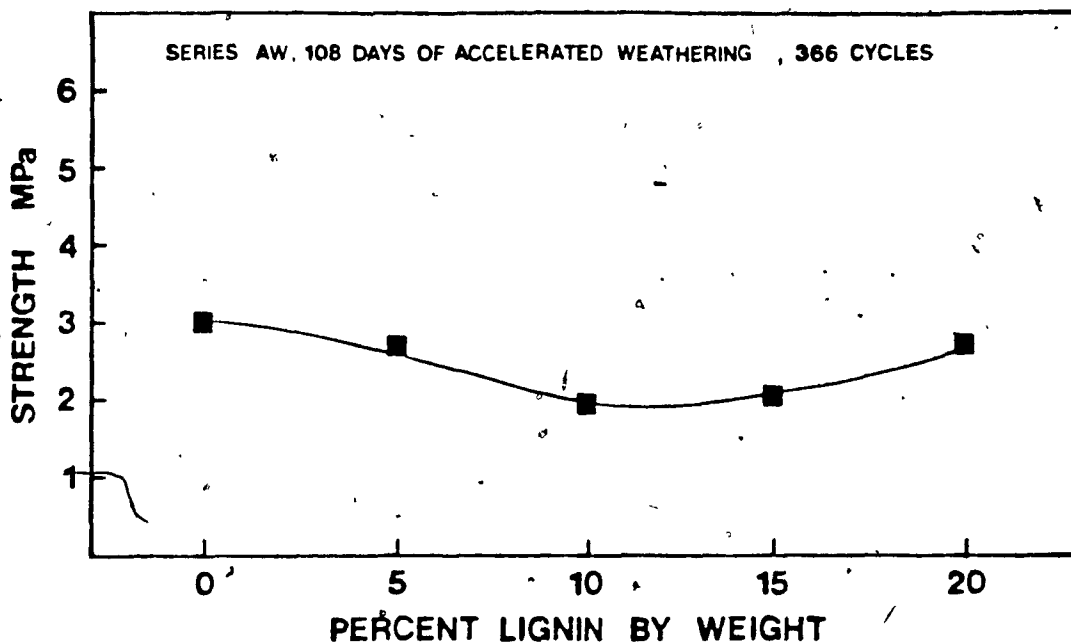


Fig. 18 Variation of adhesive shear strength of the epoxy adhesive with lignin. Series AW.

Accelerated weathering led to higher degradation than natural weathering. This can be attributed to the effect of thermal shock which was more severe in this case.

Figures 19 and 20 show the comparative behavior of the epoxy adhesive and the respective polyblends under the different conditions discussed. This behavior was more or less similar, where accelerated weathering resulted in the lowest values in all cases. The pure epoxy adhesive and the polyblend with 20% lignin appear to be slightly better resistive to weathering than the others. In conclusion, polyblending with lignin up to 20% by weight could reduce formulation cost without adversely affecting the epoxy polymer's adhesive shear strength and weatherability.

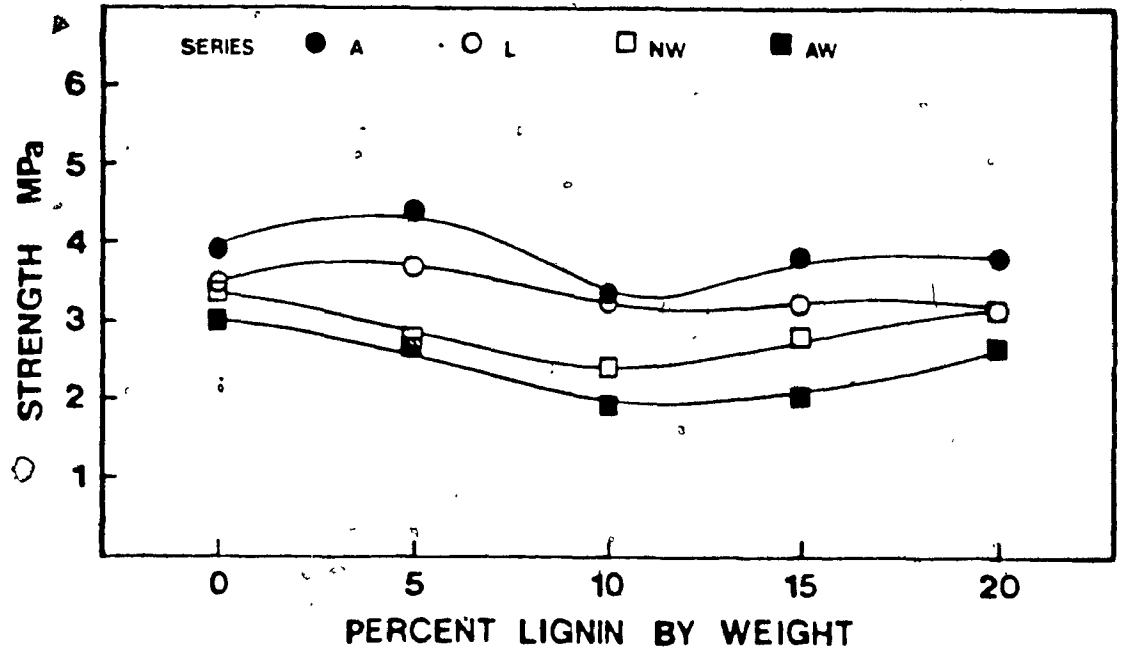


Fig. 19 Variation of adhesive shear strength of the epoxy adhesive depending on lignin and weathering conditions.

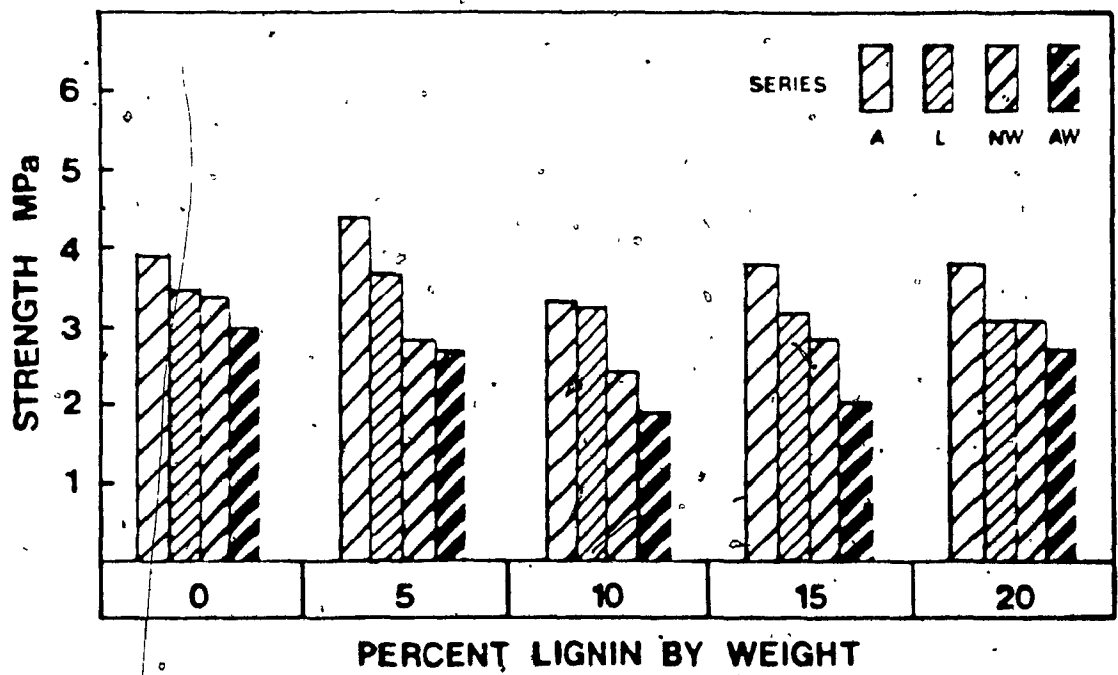


Fig. 20 Comparative behavior of the epoxy adhesive and polyblends in response to weathering conditions.

## EFFECT OF TEMPERATURE ON CURING AND ADHESIVE SHEAR STRENGTH

The first purpose of this part of the research was to study the effect of temperature on the curing process, as reflected by the adhesive shear strength of the epoxy polymer and polyblends. The second, was to determine the temperature dependence of this strength, relating it to the rheological states of the adhesives.

### Cure Schedule

There are no theoretical methods for calculating optimum cure conditions, and the usual process is to determine the degree of cure experimentally in terms of optimizing the desired properties (2). In practice, a thoroughly cured epoxy polymer is one which provides best properties for a certain application.

The following cure schedule was followed in this work. After curing the single-lap shear specimens for 24 hours at room temperature, they were post cured for 4 hours at higher temperatures. The post curing temperatures were 50, 60, 75 and 100 °C. All specimens were tested 3 days after preparation, including those not subjected to heat curing, (considered in the following discussion to be 'post cured' at 23 °C).

For each post curing temperature, five sets (5 to 10 specimens each) were prepared with the epoxy adhesive and the four respective polyblends. The specimens were tested for adhesive shear strength by tension loading, with a crosshead speed of 1 mm/min and a testing temperature of 23 °C (Room Temperature Testing).

### Elevated Temperature Testing

Elevated temperature performance of similar sets, post cured at '23', 50, 60, 75, and 100 °C was determined. Testing temperatures were 23, 50, 75 and 100 °C for the sets post cured at '23', 50 and 60 °C; and 23, 40, 50, 60, 75 and 100 °C for the sets post cured at 75 and 100 °C.

The adhesive shear strength at elevated temperatures was determined according to ASTM D-2295. Each specimen was heated inside an environmental test chamber (figure 21) for 25 minutes before testing. Values to plot the following graphs are averages of 5 to 10 successful tests.



Fig. 21 Environmental test chamber for temperature testing  
(74)

### Results and Discussion (Room Temperature Testing)

The results of room temperature testing are summarized in figure 22. In all the tests, the failure was in adhesion. The highest adhesive shear strengths were due to a post curing temperature of 75°C, with an average increase of 75% for the epoxy system and the polyblends. The highest strengths were those of EP-L15 and EP-L20.

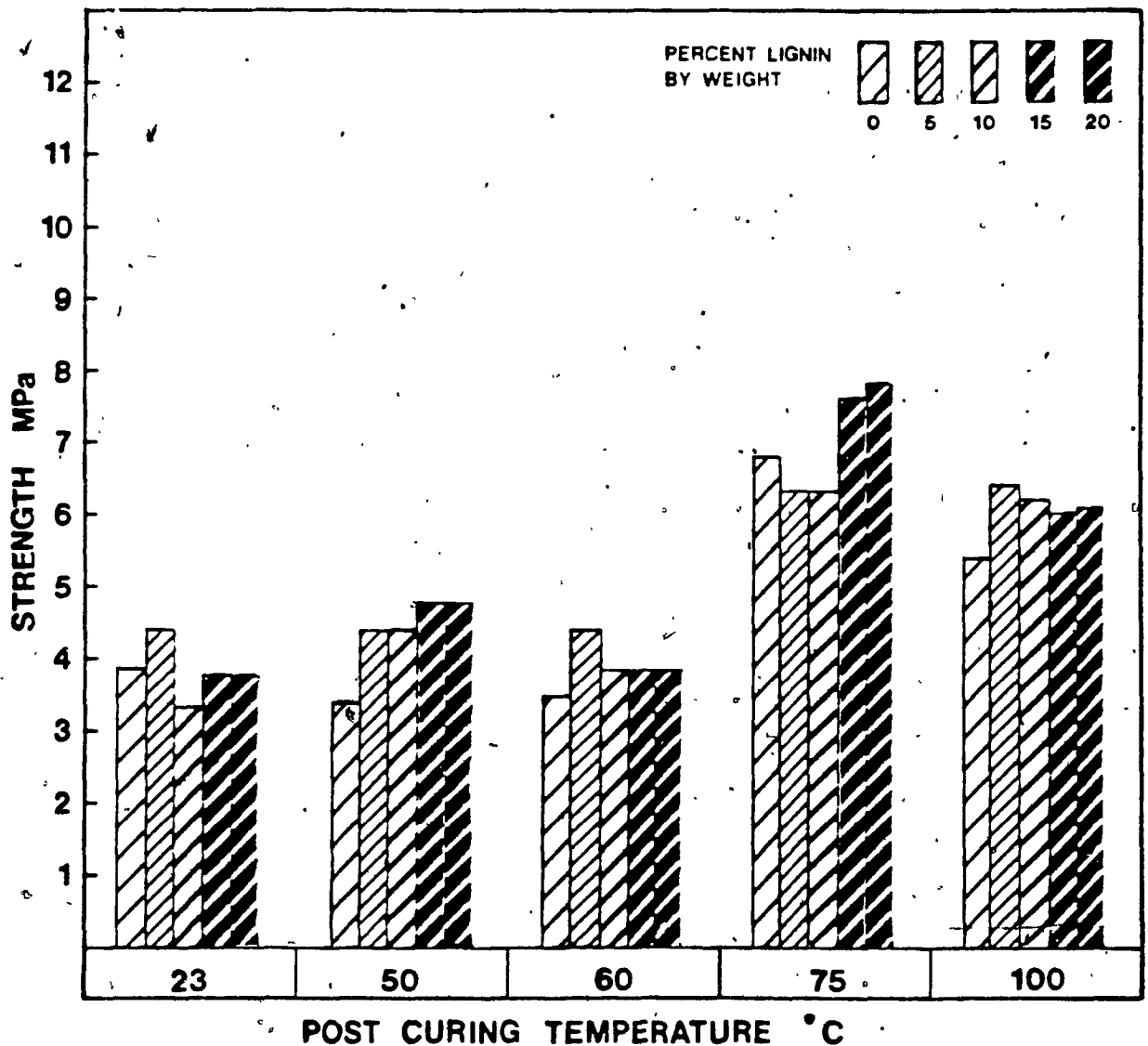


Fig. 22 Variation of adhesive shear strength of the epoxy polymer and polyblends, depending on the post curing temperature.

Figures 23 to 27 show the variation of adhesive shear strength of the epoxy polymer system and the respective four polyblends, depending on the post curing temperature.

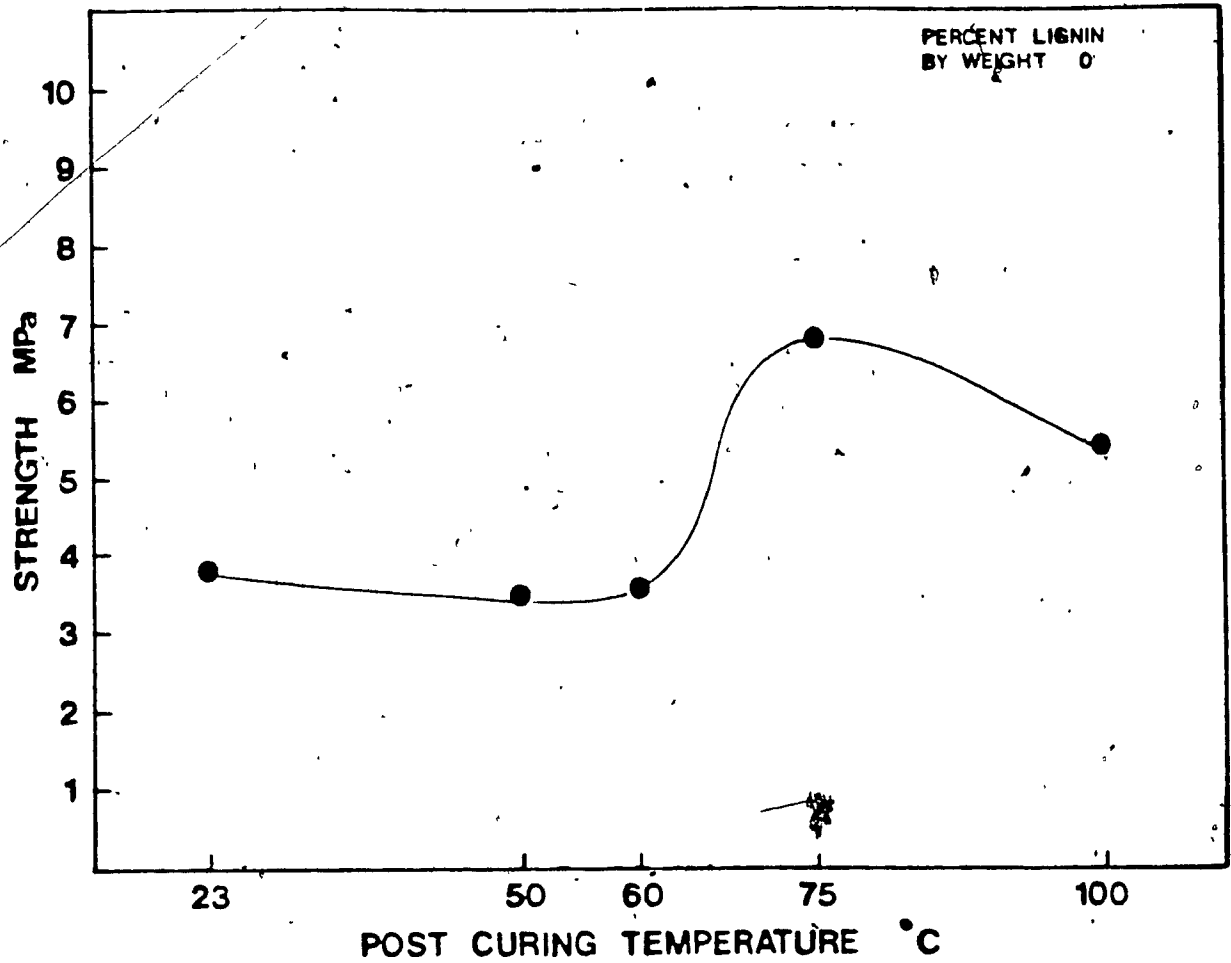


Fig. 23 Variation of adhesive shear strength of the epoxy polymer system (EP), depending on the post curing temperature.



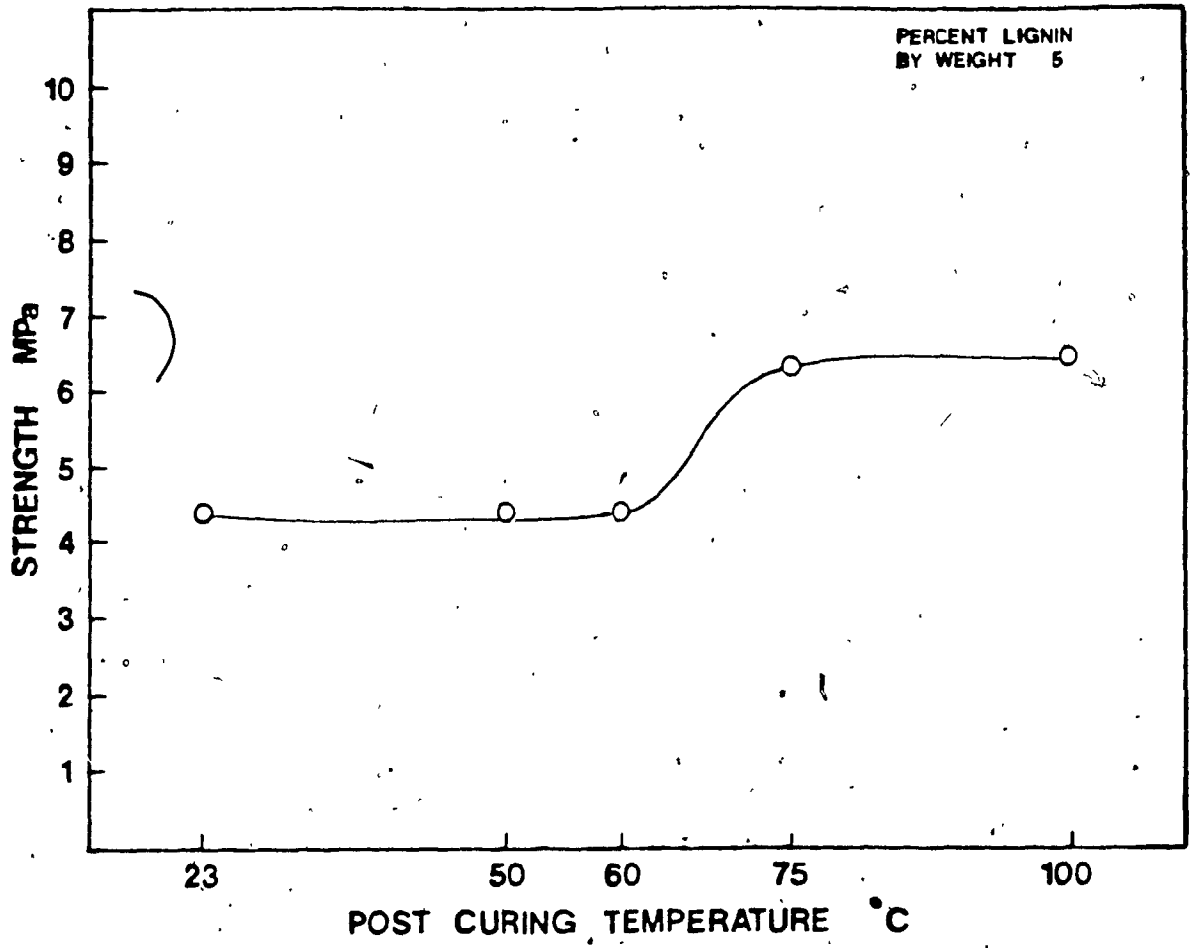


Fig. 24 Variation of adhesive shear strength of the polyblend (EP-L5) depending on the post curing temperature.

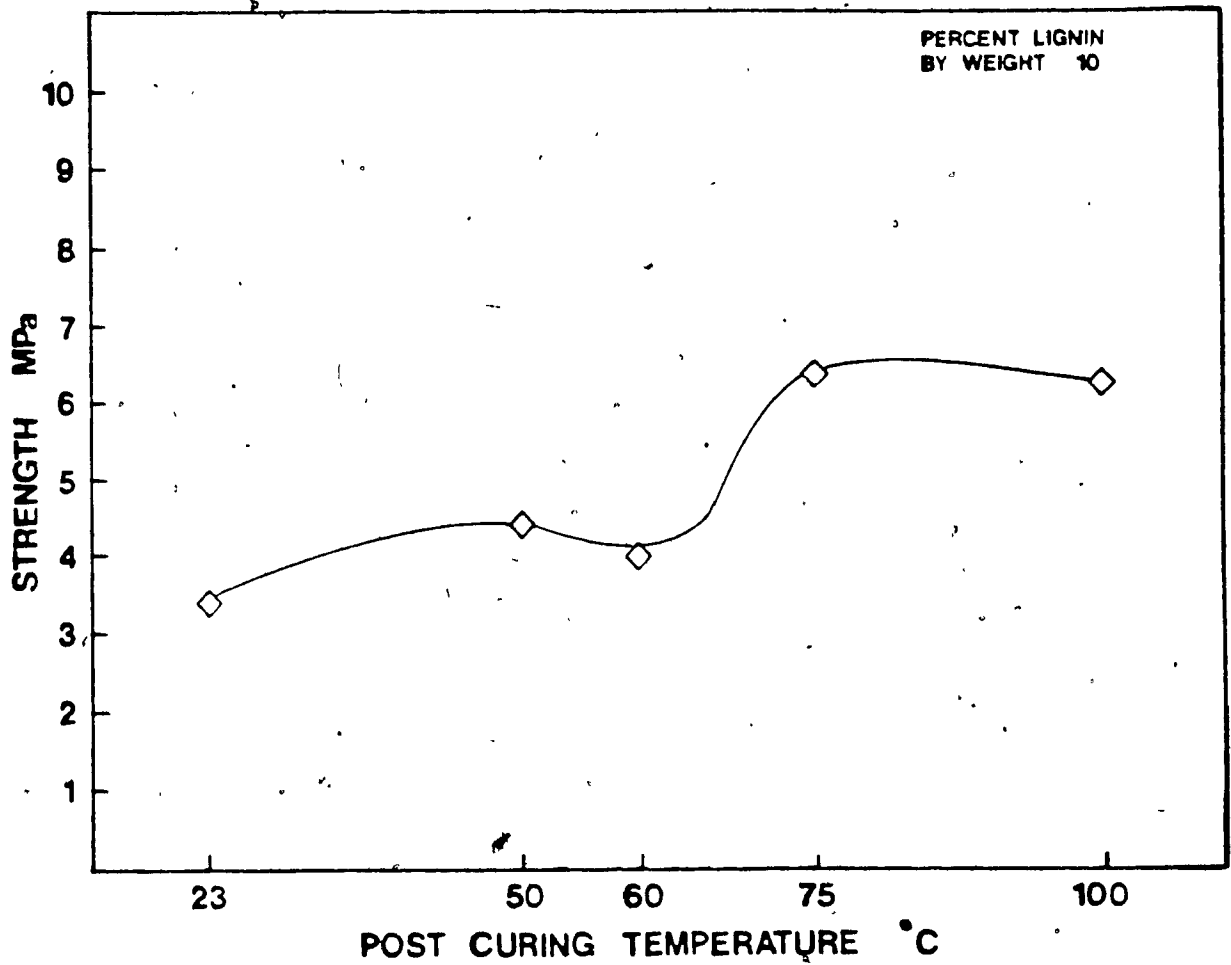


Fig. 25 Variation of adhesive shear strength of the polyblend (EP-L10) depending on the post curing temperature.

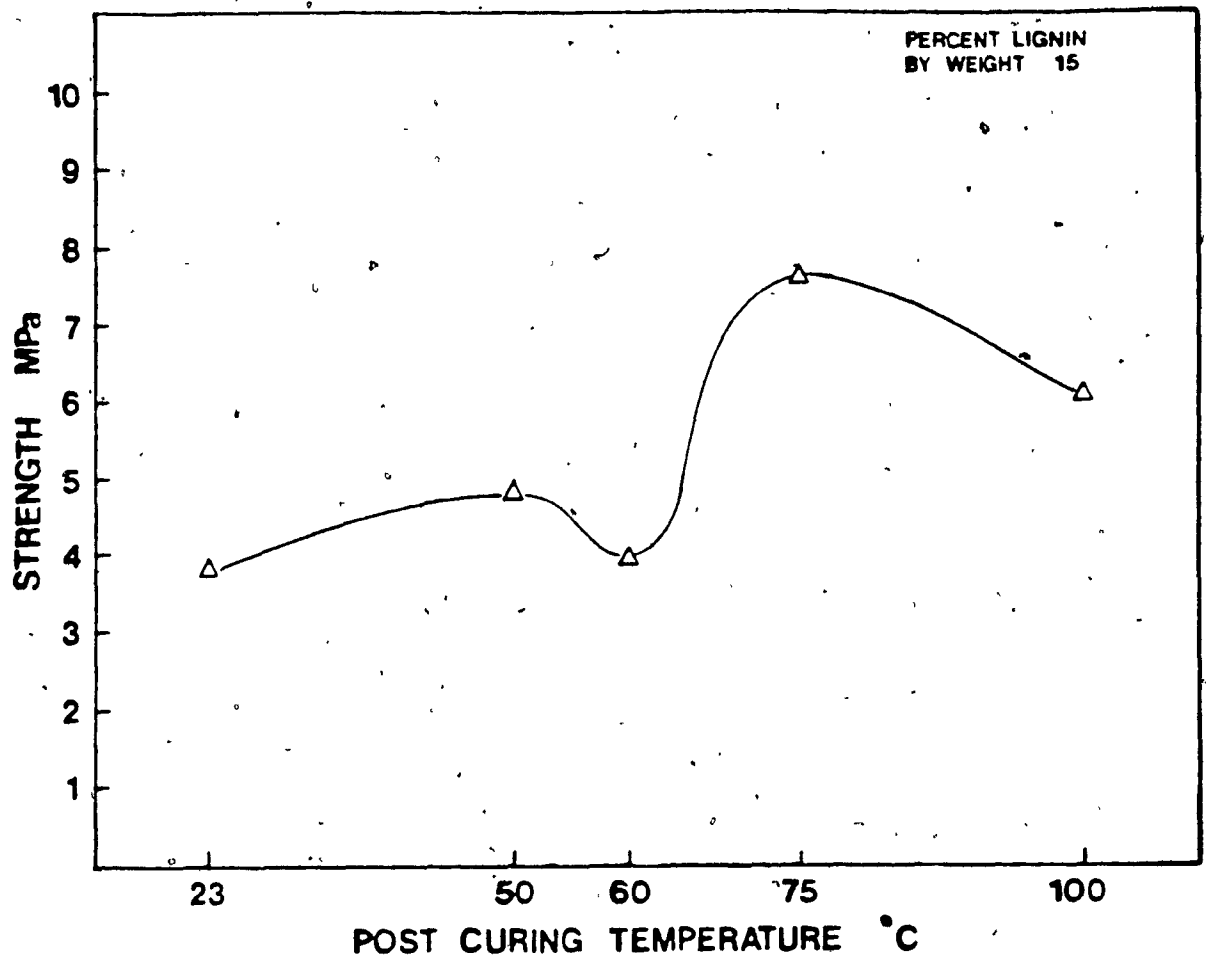


Fig. 26 Variation of adhesive shear strength of the polyblend (EP-L15) depending on the post curing temperature.

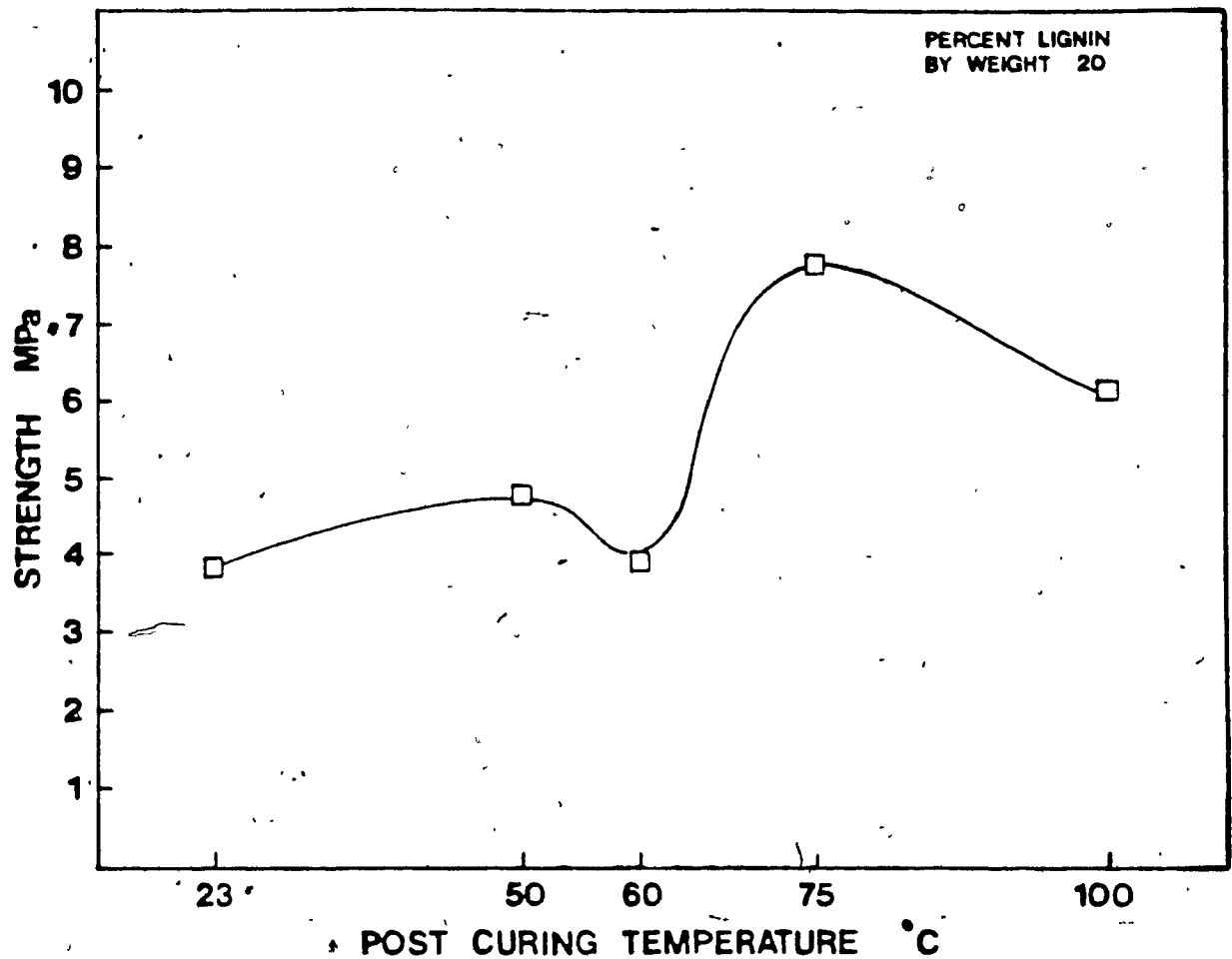


Fig. 27 Variation of adhesive shear strength of the polyblend (EP-L20) depending on the post curing temperature.

As shown in the previous five figures, post curing at 50 and 60°C did not have much effect on the adhesive strength in shear, while the 100°C post cure resulted in improvements, though generally lower than those due to the 75°C post curing temperature.

The pattern of adhesive shear strength variation with post curing is similar for the epoxy polymer and the polyblends, as shown in figure 28.

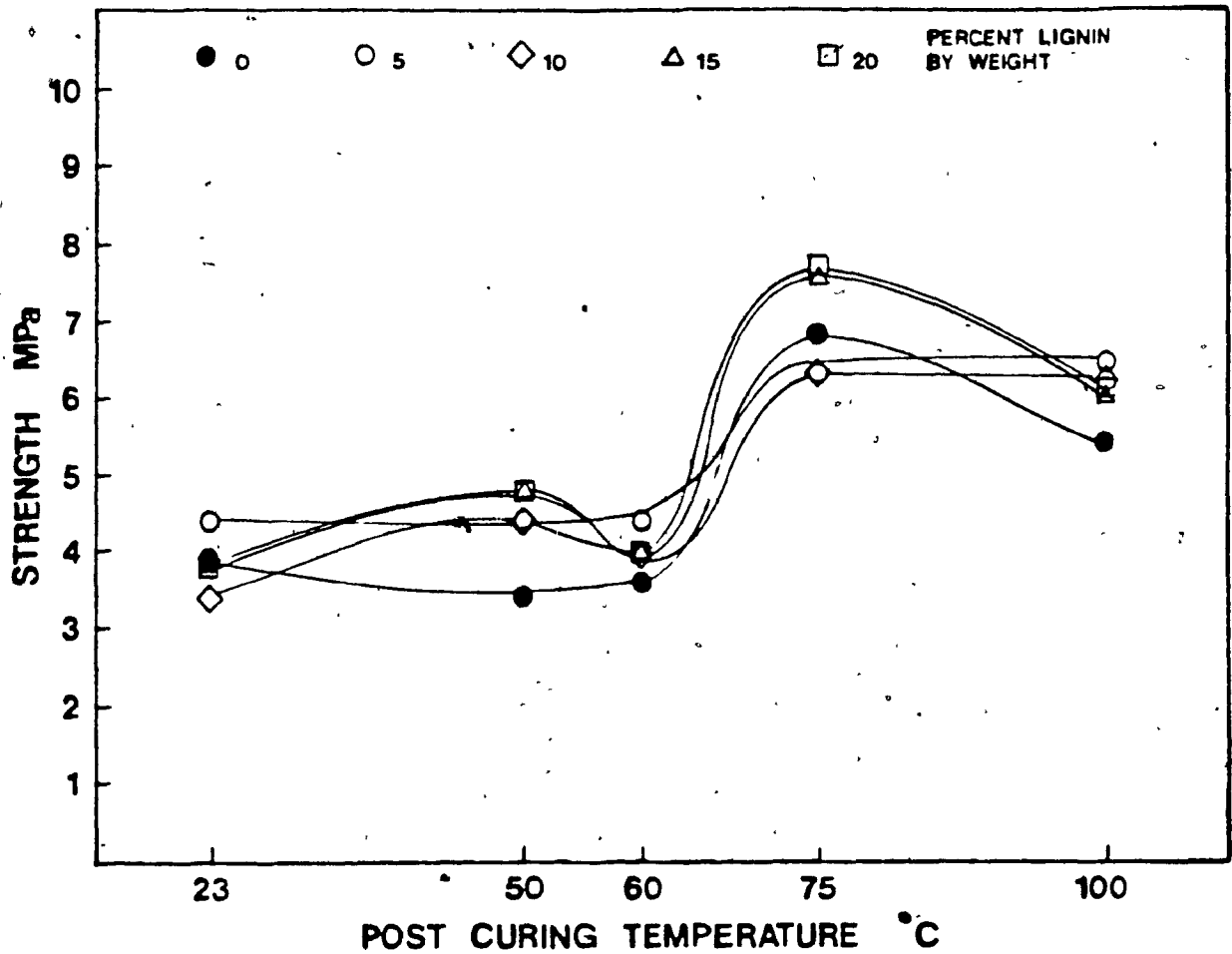


Fig. 28 Pattern of variation of adhesive shear strength for the epoxy polymer and polyblends, depending on the post curing temperature.

In general, post curing at higher temperatures than that of the initial cure will improve the strength properties of epoxy polymers in proportion to the degree of cure. During initial curing, and as the molecules polymerize, their rotational and translational motion is reduced, resulting in reduced chances for covalent bonds to be formed with adjacent molecules (2). With post curing, increased thermal agitation allows more sterically hindered epoxy groups to react, leading to higher crosslinking and better strength properties (2,77). Better cohesive properties of the adhesives lead in turn to better adhesive joints (1,14).

Potter (1), suggests a post curing temperature above the glass transition temperature of an epoxy polymer system for maximization of crosslinking. In this case, the 75°C post curing temperature was above the Tg's of both the epoxy adhesive and the polyblends, and higher strengths were partly a result of the adhesives attaining a critical degree of crosslinking. At 100°C post curing (approx. 30°C above the Tg's), the bulk strength properties slightly decreased and resulted in lower adhesive strength values.

Besides the bulk strength of the adhesive, the strength of adhesive joints depends on the interfacial state of adhesion (14). With post curing, this state is improved due to the following factors:

- 1) The decrease in viscosity of the adhesive at higher temperatures, leading to better interfacial contact (78).
- 2) The dissolution or displacement of remaining contaminants on the adherend, which might have been insoluble in the adhesive at lower temperatures (78,79).
- 3) The relaxation of interfacial stress that might have existed upon initial curing (78).

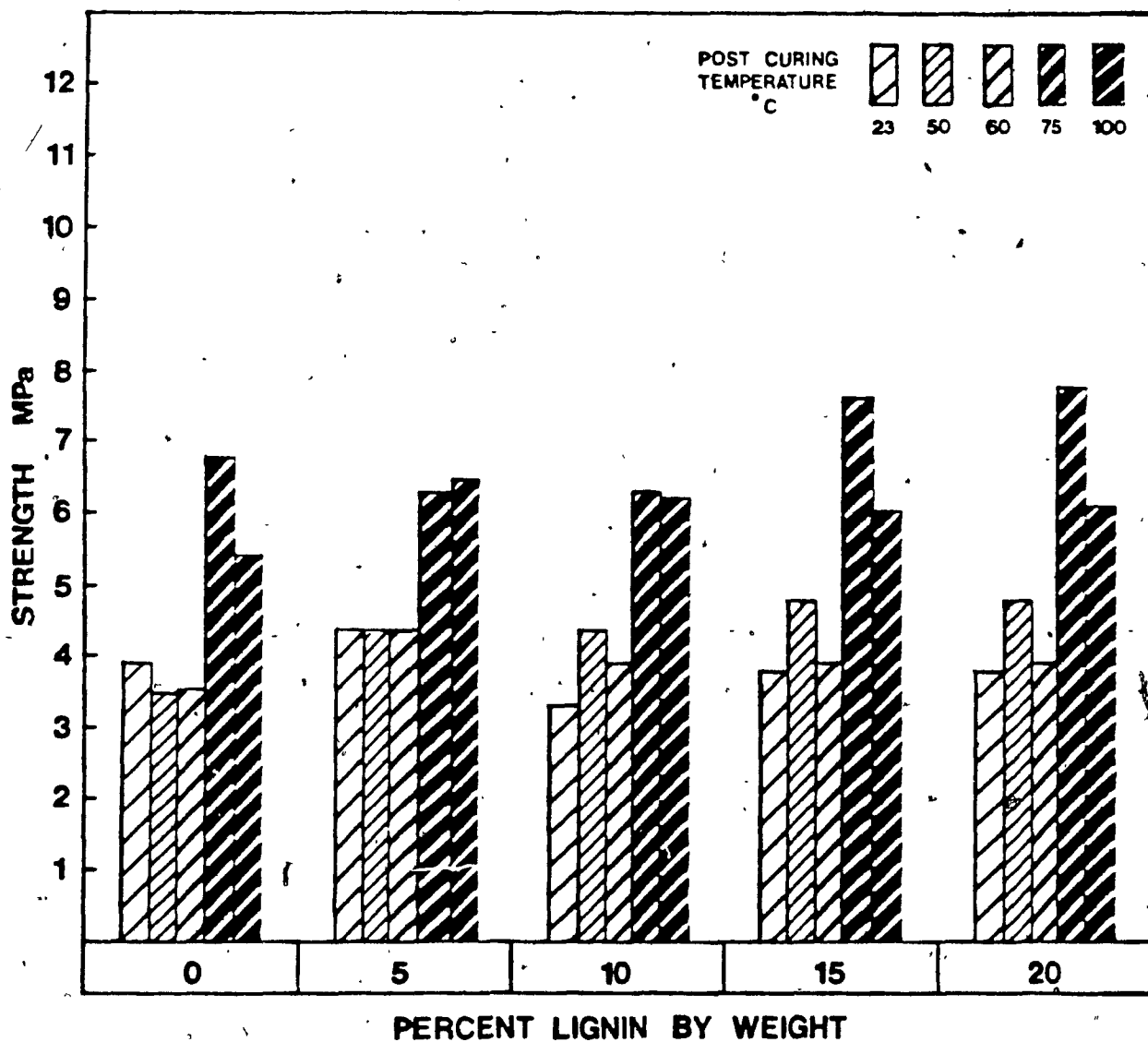


Fig. 29 Variation of adhesive shear strength of the epoxy polymer with lignin depending on the post curing temperature.

The higher adhesive shear strength of EP-L15 and EP-L20 could be attributed to lignin providing a certain resistance to flow during heat curing (80). As shown in figure 29, the increase of strength with post curing could show that originally insufficient exotherm occurred in the thin glue line to assure full cure. Lastly, the relation between the results obtained with EP-L15 and EP-L20 is consistent with post curing.

Figures 30 to 34 show the variation of adhesive shear strength of the epoxy polymer with lignin and how it is influenced by the post curing temperature.

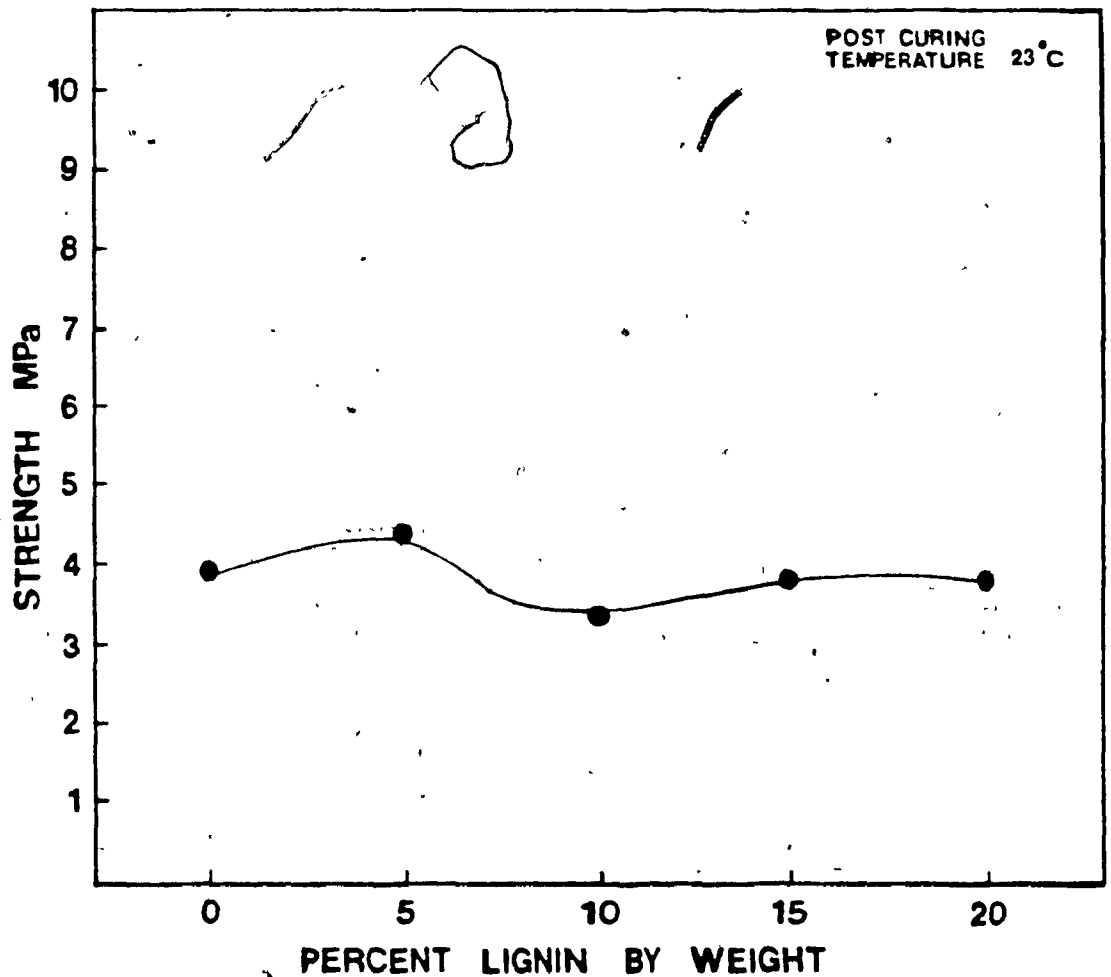


Fig. 30 Variation of adhesive shear strength of the epoxy polymer with lignin. Post curing temperature = 23°C.



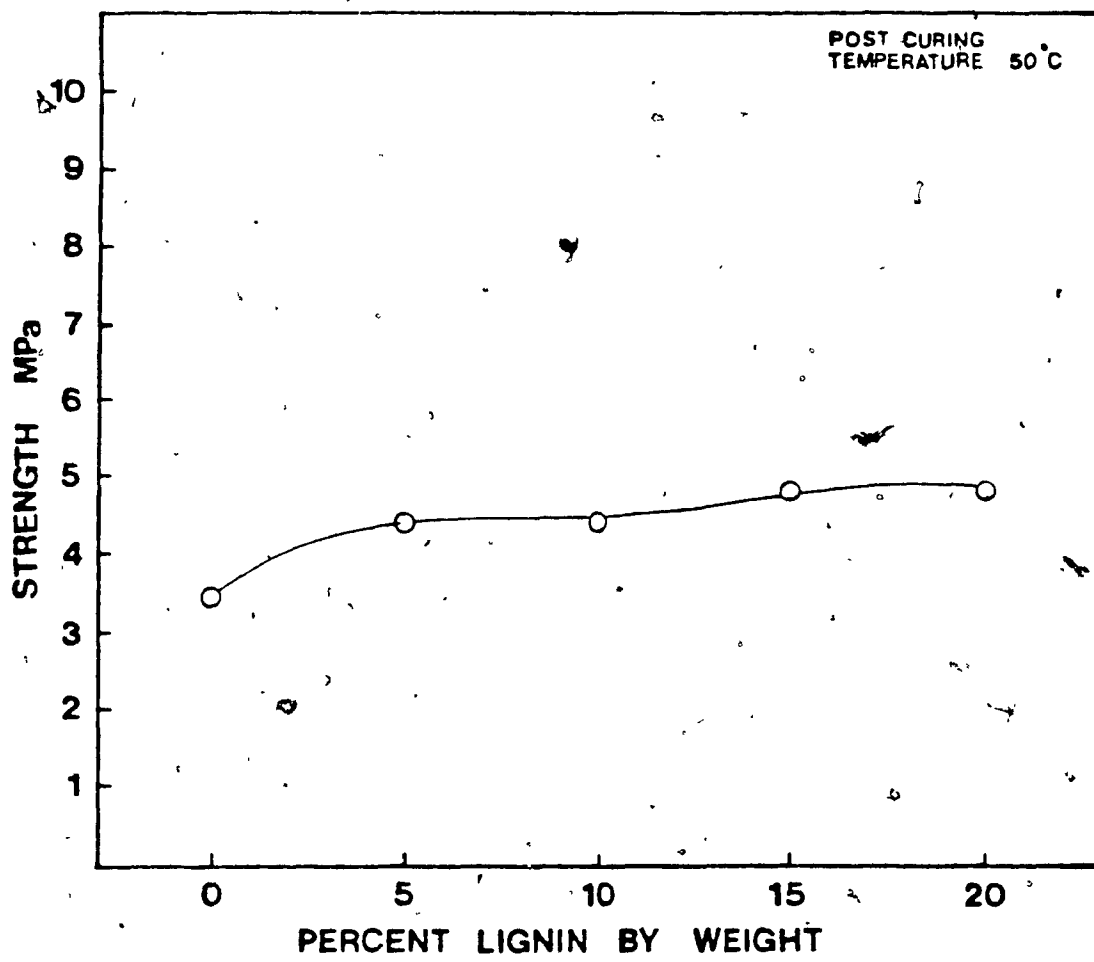


Fig. 31 Variation of adhesive shear strength of the epoxy polymer with lignin. Post curing temperature = 50°C.

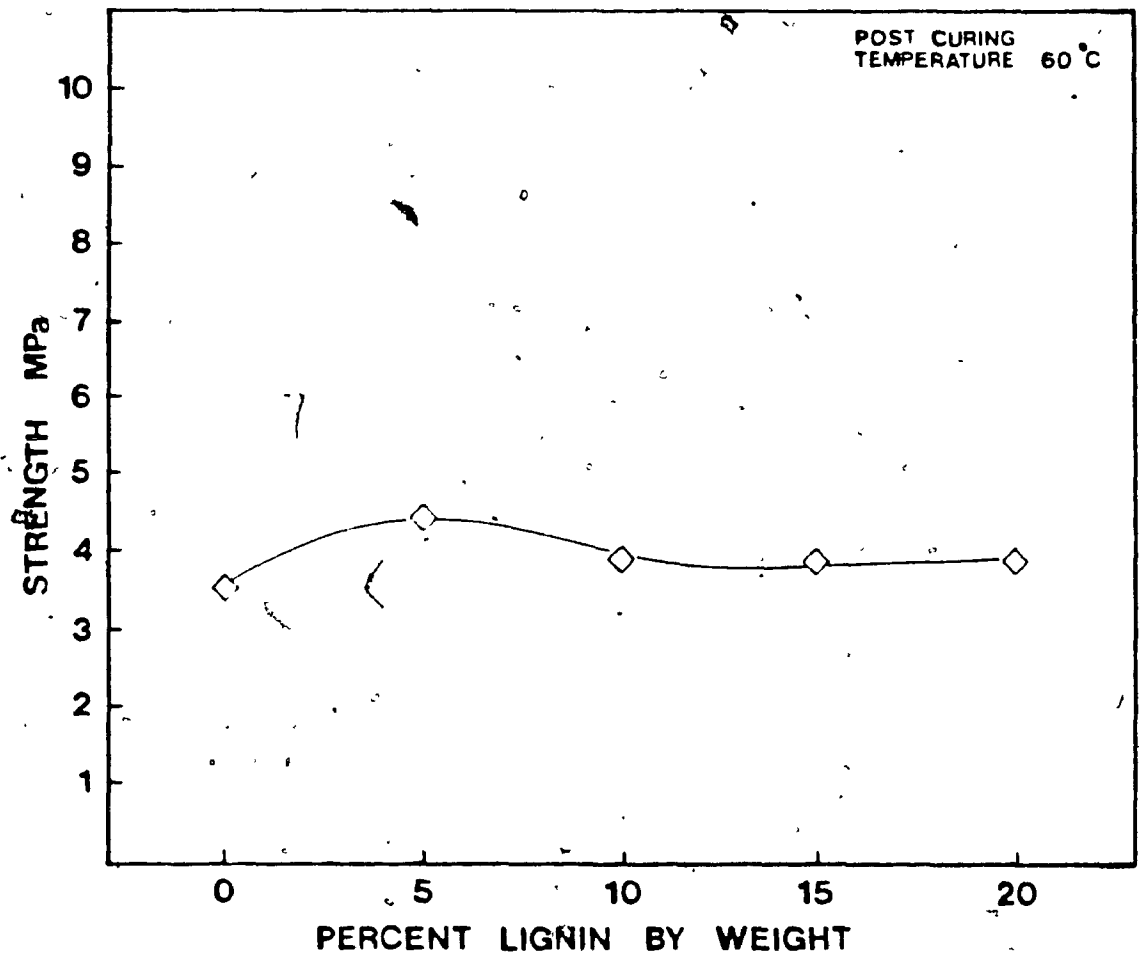


Fig. 32 Variation of adhesive shear strength of the epoxy polymer with lignin. Post curing temperature = 60°C.

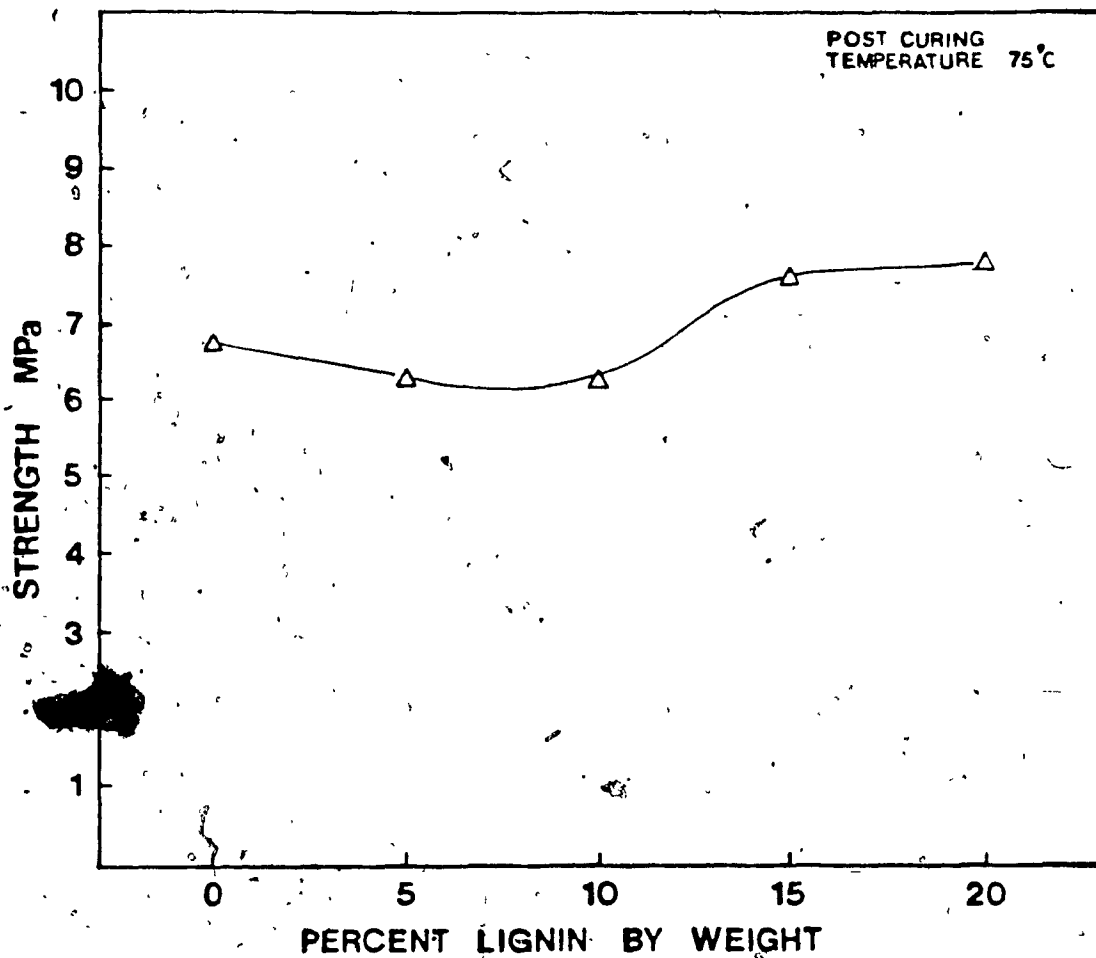


Fig. 33 Variation of adhesive shear strength of the epoxy polymer with lignin. Post curing temperature, = 75°C.

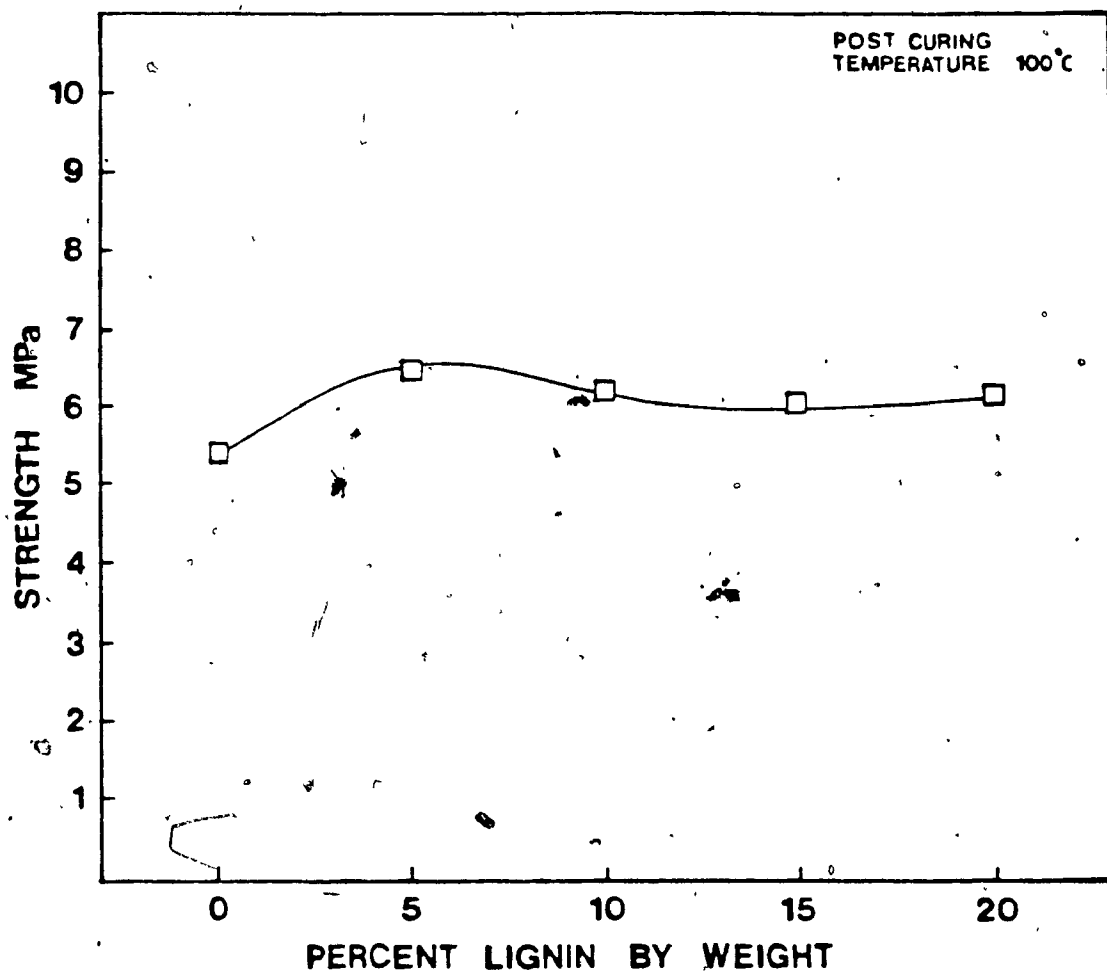


Fig. 34 Variation of adhesive shear strength of the epoxy polymer with lignin. Post curing temperature = 100°C.

As shown from the previous figures, post curing at 50 and 60°C did not improve the strength of the epoxy adhesive or the polyblends. However, and as shown below in figure 35, there was a marked shift in strength with post curing temperatures above the Tg's of the adhesives. Above Tg, the motion of macromolecular chains becomes possible; so, as a result of the attraction between them, new intermolecular forces appear and lead to the increase of mechanical strength (reflected upon the adhesive strength) within certain temperature limits.

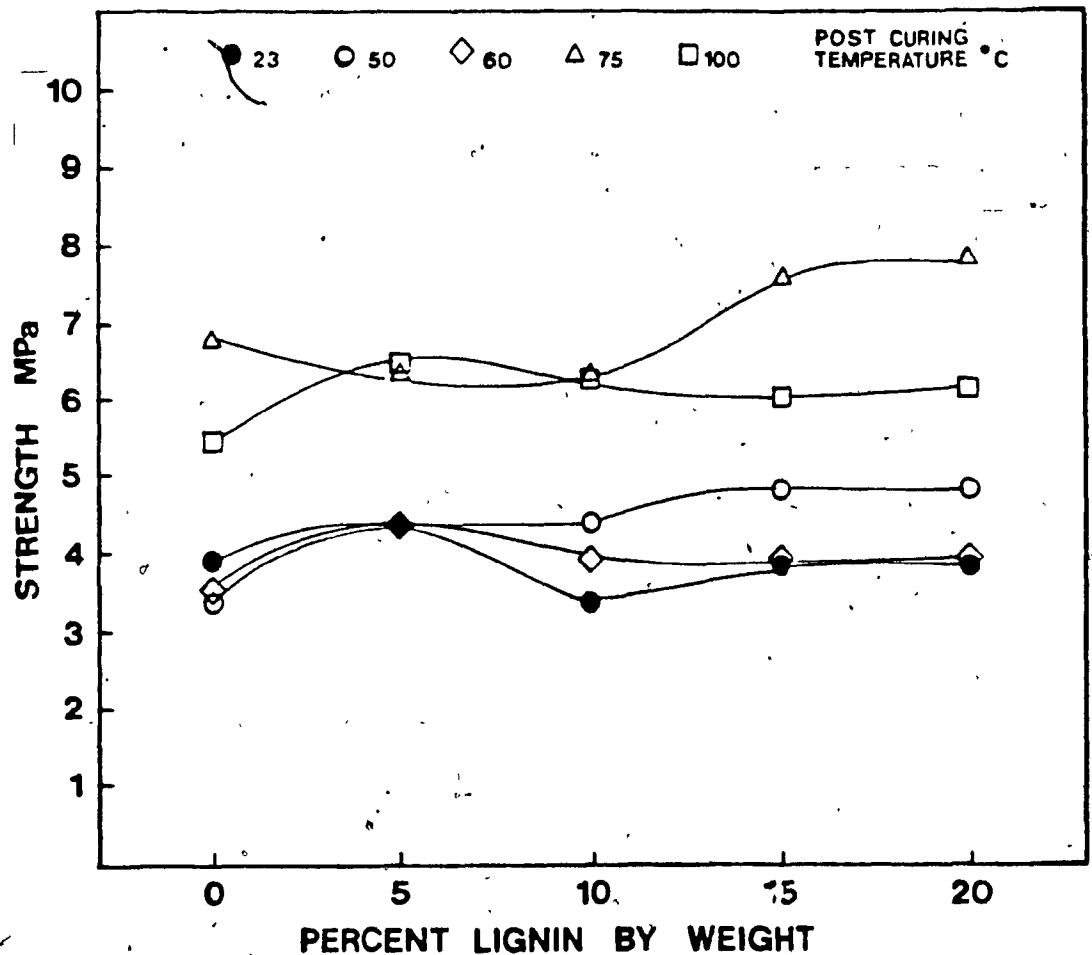


Fig. 35 Pattern of variation of adhesive shear strength of the epoxy polymer with lignin, depending on post curing temperature.

## Results and Discussion (Elevated Temperature Testing)

The temperature dependence of adhesive shear strength of the epoxy polymer and the polyblends is shown in figure 36. The variations of this dependence with the different post curing temperatures are shown in figures 37 to 40.

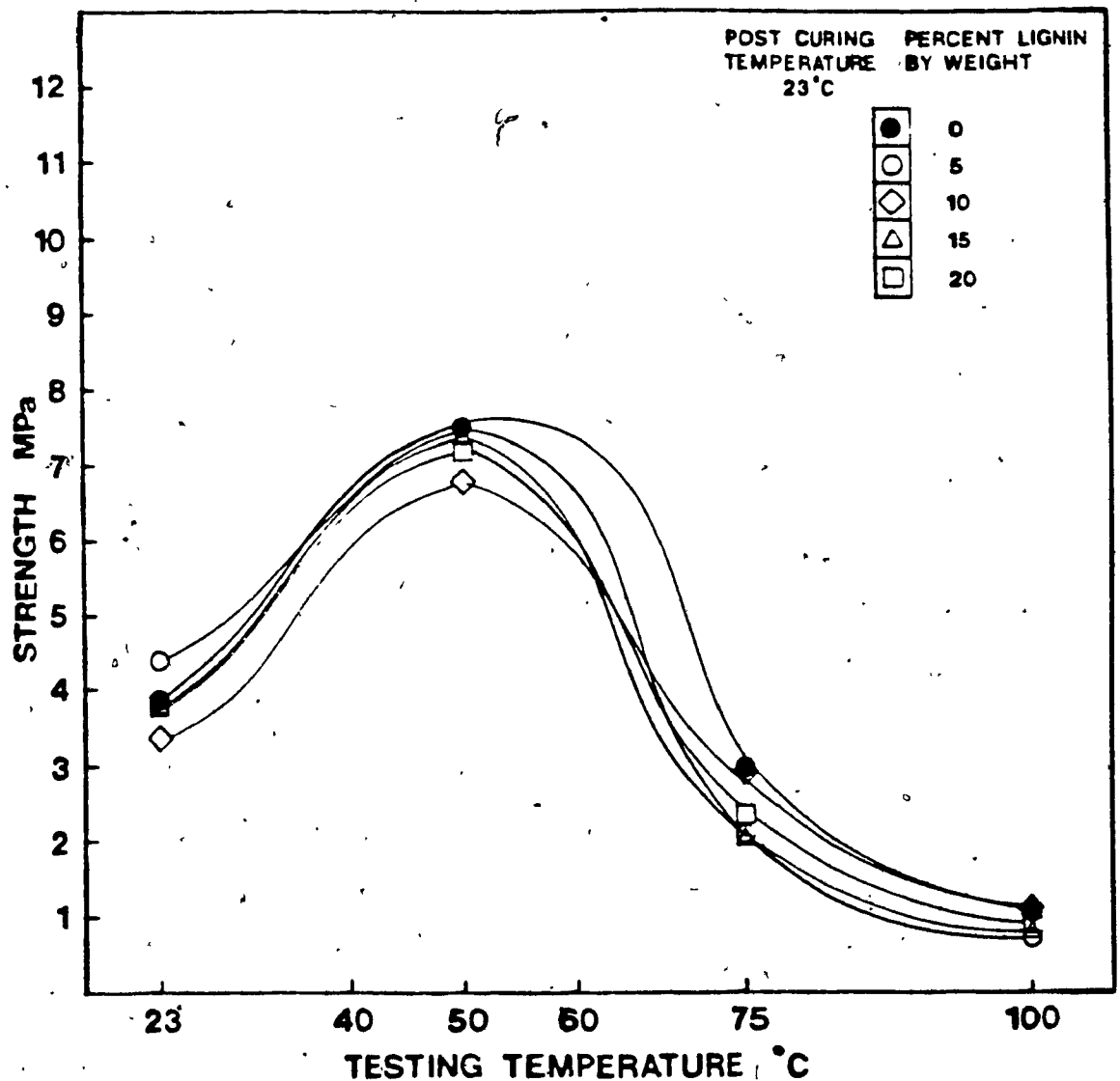


Fig. 36 Temperature dependence of the adhesive shear strength of the epoxy polymer and polyblends. Curing temperature = 23°C.

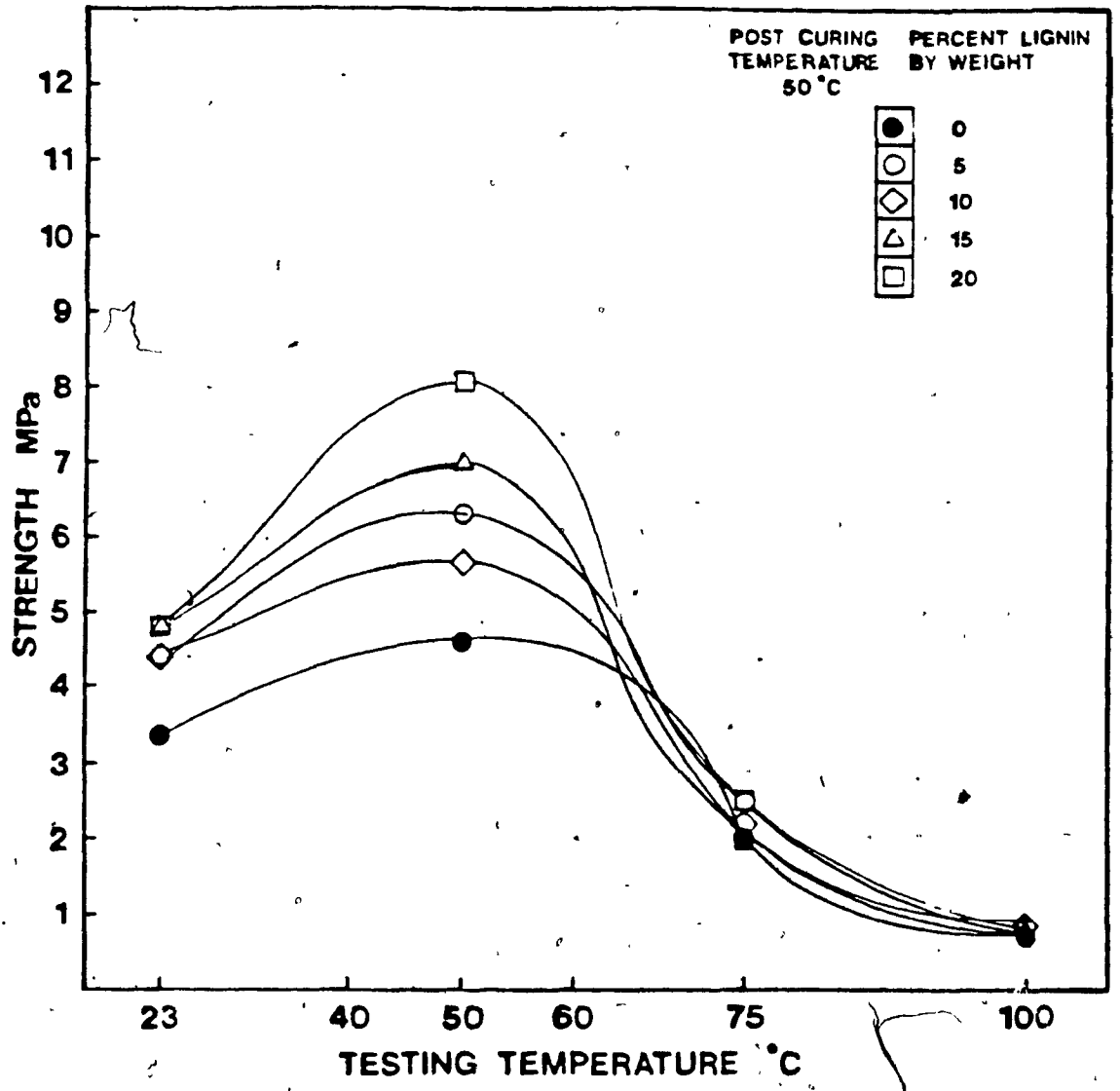


Fig. 37 Temperature dependence of the adhesive shear strength of the epoxy polymer and polyblends. Post curing temperature = 50°C.

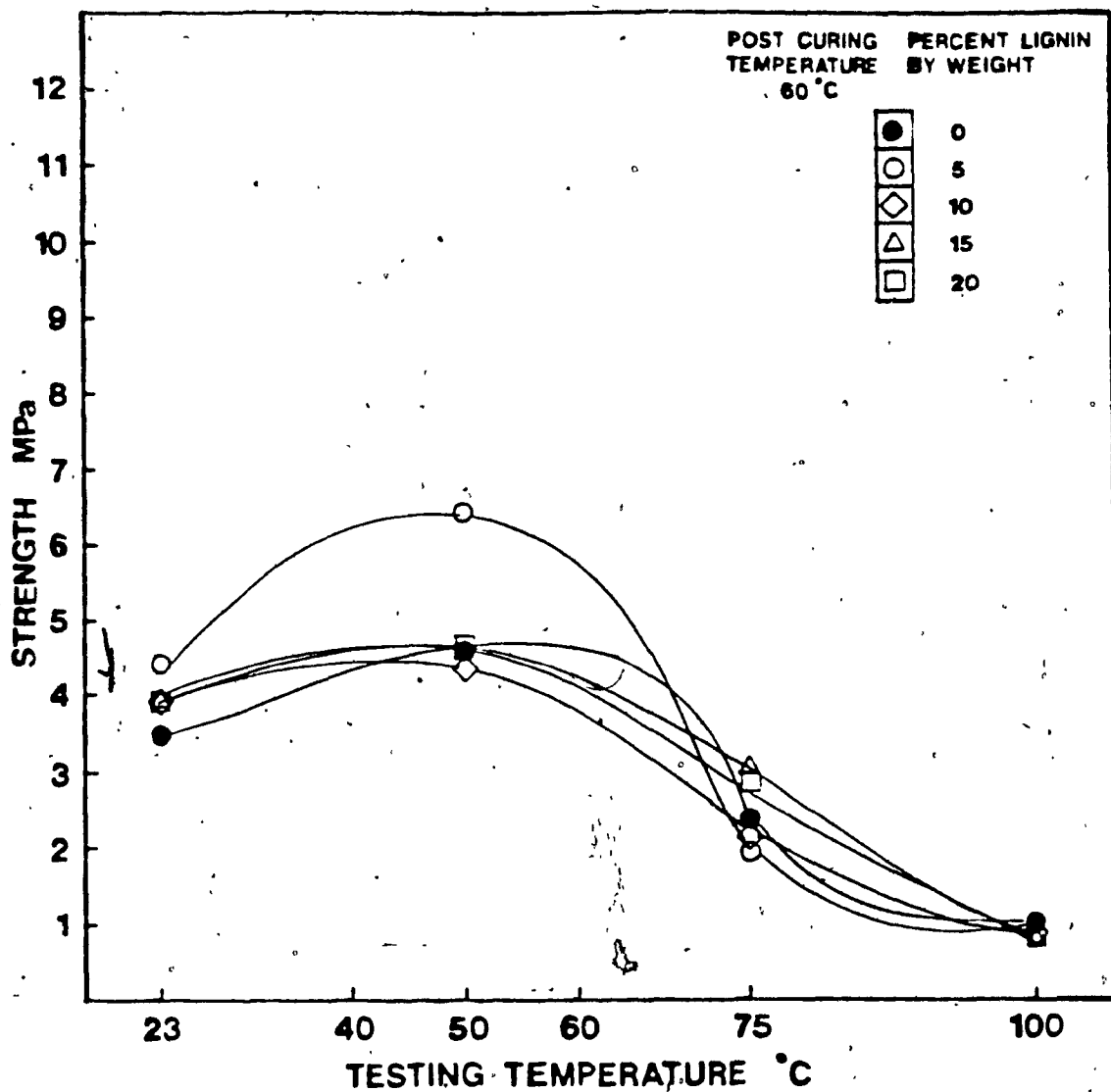


Fig. 38 Temperature dependence of the adhesive shear strength of the epoxy polymer and polyblends. Post curing temperature = 60 °C.



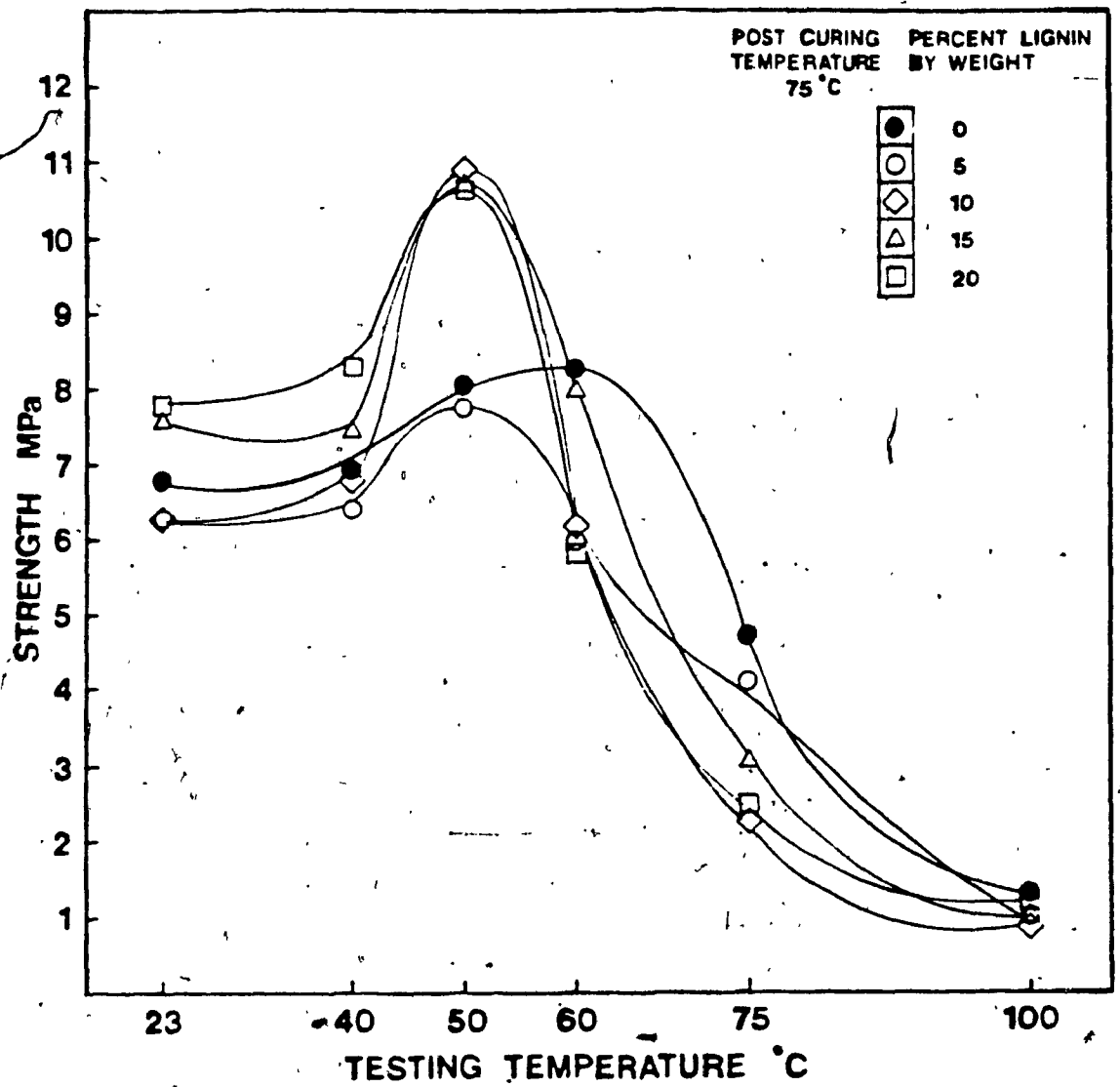


Fig. 39 Temperature dependence of the adhesive shear strength of the epoxy polymer and polyblends. Post curing temperature = 75 °C.

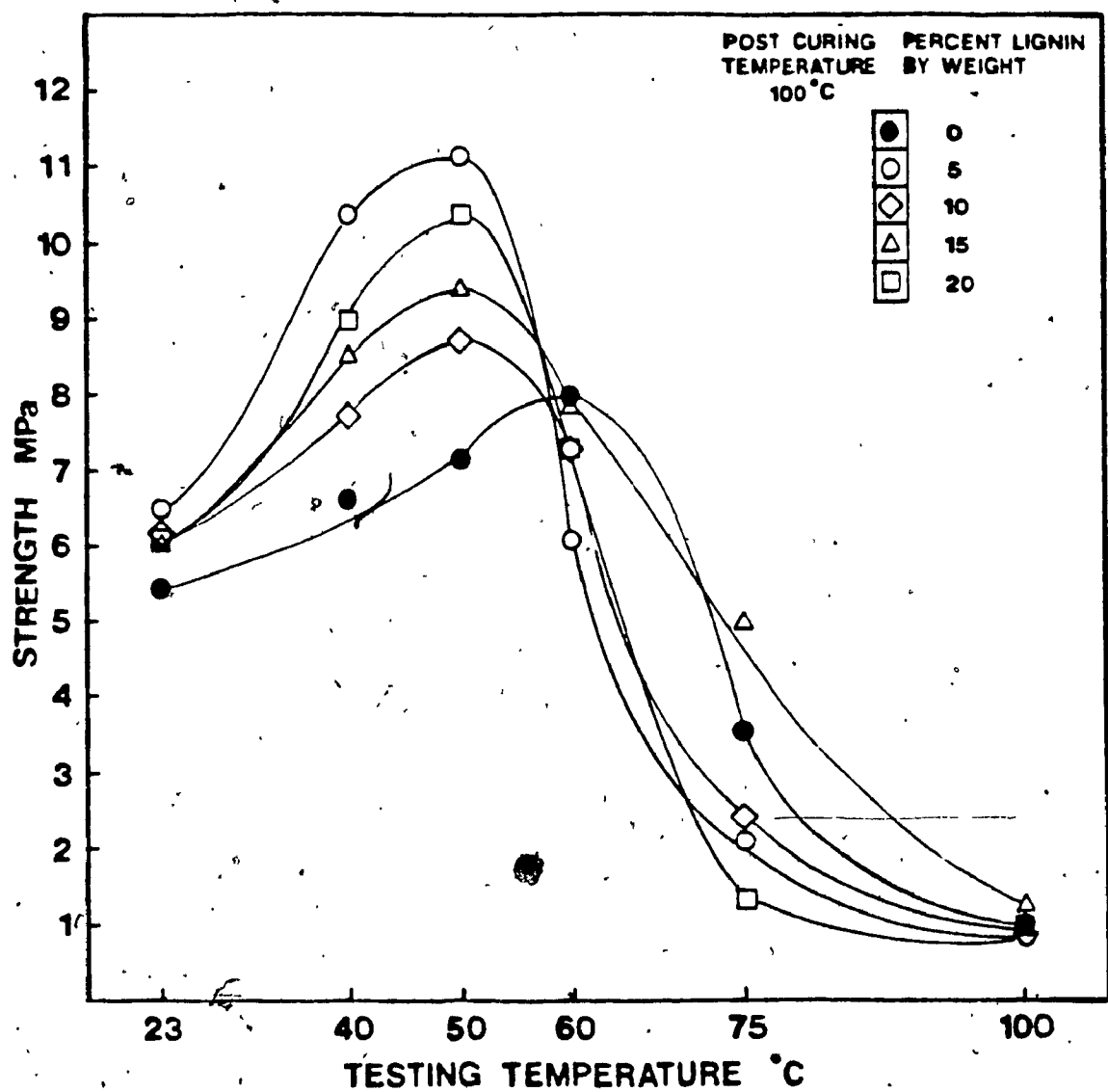


Fig. 40 Temperature dependence of the adhesive shear strength of the epoxy polymer and polyblends. Post curing temperature = 100°C

These patterns are usual for epoxy adhesive lap-shear joints (14.81,82,83). Figure 41 shows similar patterns for bisphenol-A and bisphenol-F based epoxy adhesives (steel/adhesive lap-shear strengths ) (82).

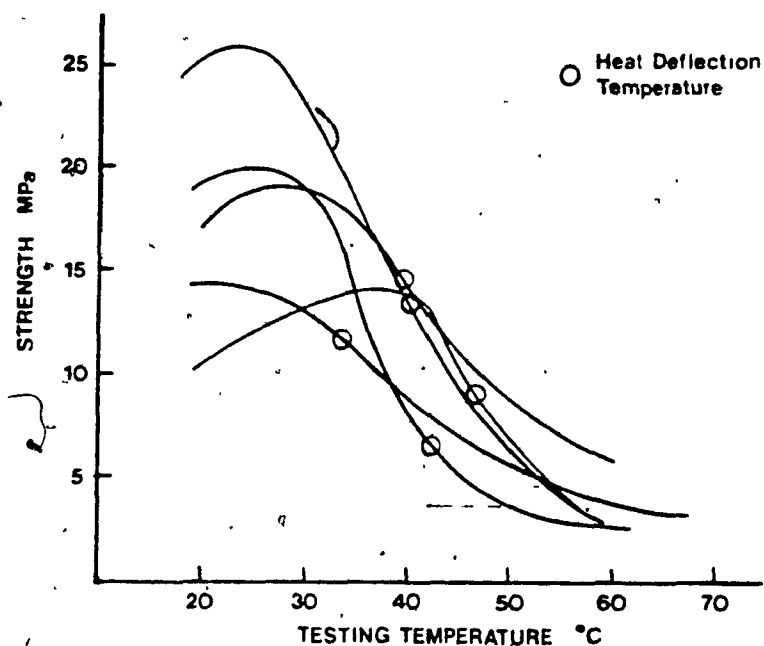


Fig. 41 Temperature dependence of steel/adhesive lap-shear strengths (82).

It is also well recognized that the strength behavior of polymers depend on the rheological state, which in turn affects the strength of adhesive joints in the generalized manner shown in figure 42.

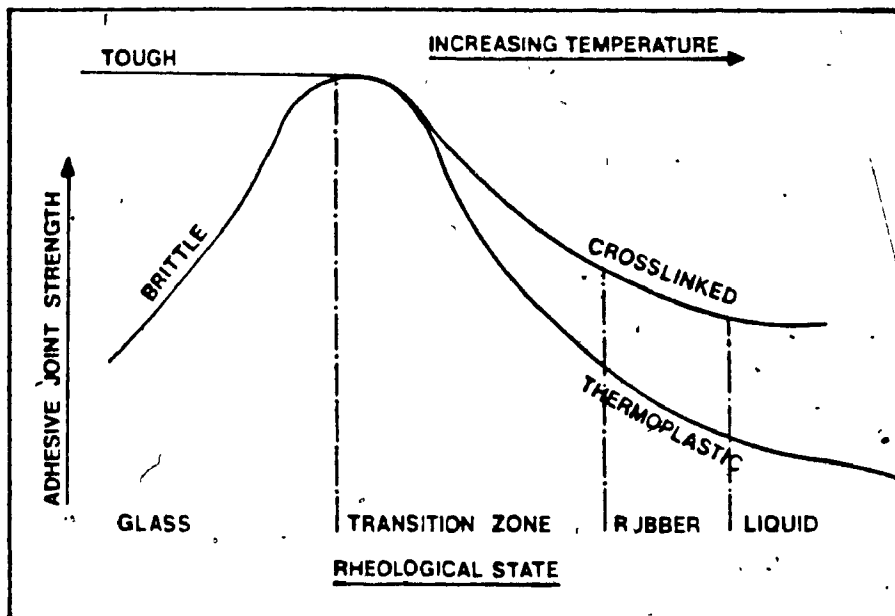


Fig. 42 Schematic diagram of the effect of the rheological state on adhesive lap-shear strength (14).

At low temperatures below the transition zone, the strength, extensibility and toughness of epoxy polymer adhesives depend on the short segment motion existing in the glass state (77). Failure is usually in adhesion (as was the case in this study), since the ultimate strength of the adhesive is high and the weakest point is at the interface (78).

As mentioned earlier, increasing the temperature agitates the molecular motion affecting the rheological state which in turn changes the failure stress in the adhesive joint.

The broad maxima in the adhesive shear strength may be attributed to the following factors:

- 1) A result of the general strength/temperature relationship (degree of cure) affecting the bulk shear strength of the adhesive.
- 2) The relaxation of the adhesive at higher temperatures, and the resulting modification of stresses at the edges of the bonded area (80,82).
- 3) Other reasons include the formation of stronger interfacial contact due to decreased viscosity and dissolution of contaminants.

In proper joints, the adhesive shear strength is usually maximized in the vicinity of  $T_g$  (14,84). In the transition zone, a combination of a decrease in bulk strength, a viscoelastic response of the adhesive and an increase in its coefficient of thermal expansion, cause a decline in the adhesive shear strength (1,78).

Figures 43 to 47 show that the patterns are in agreement with the  $T_g$ 's determined for the epoxy adhesive and polyblends and discussed later. Another observation is the strength retention of the epoxy adhesive and polyblends up to around  $60^\circ\text{C}$ , after which a rapid decrease occurs. In all cases, better elevated temperature performance resulted from post curing at  $75$  and  $100^\circ\text{C}$ .

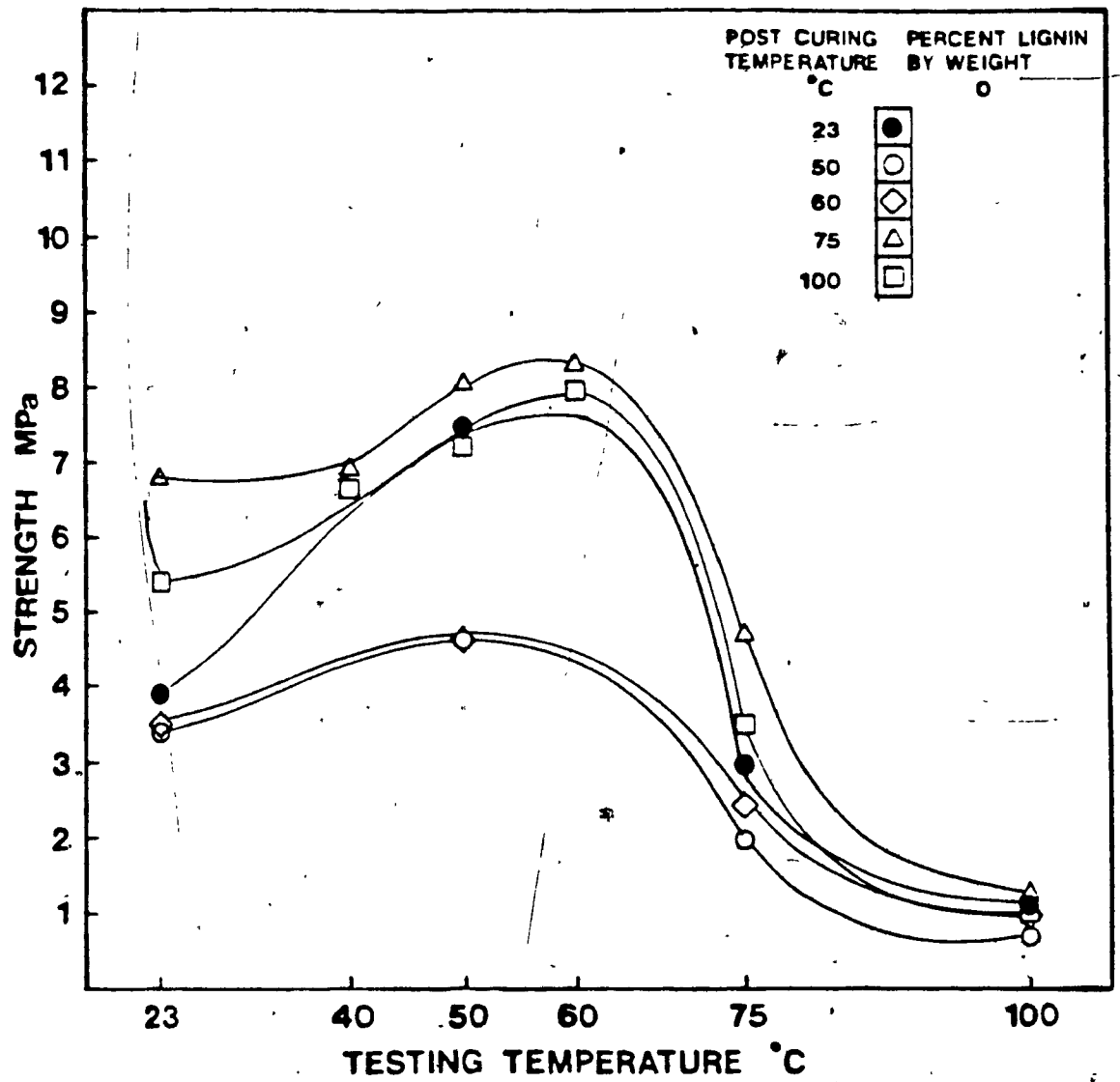


Fig. 43 Temperature dependence of adhesive shear strength of the epoxy polymer. Variation with post curing temperature.

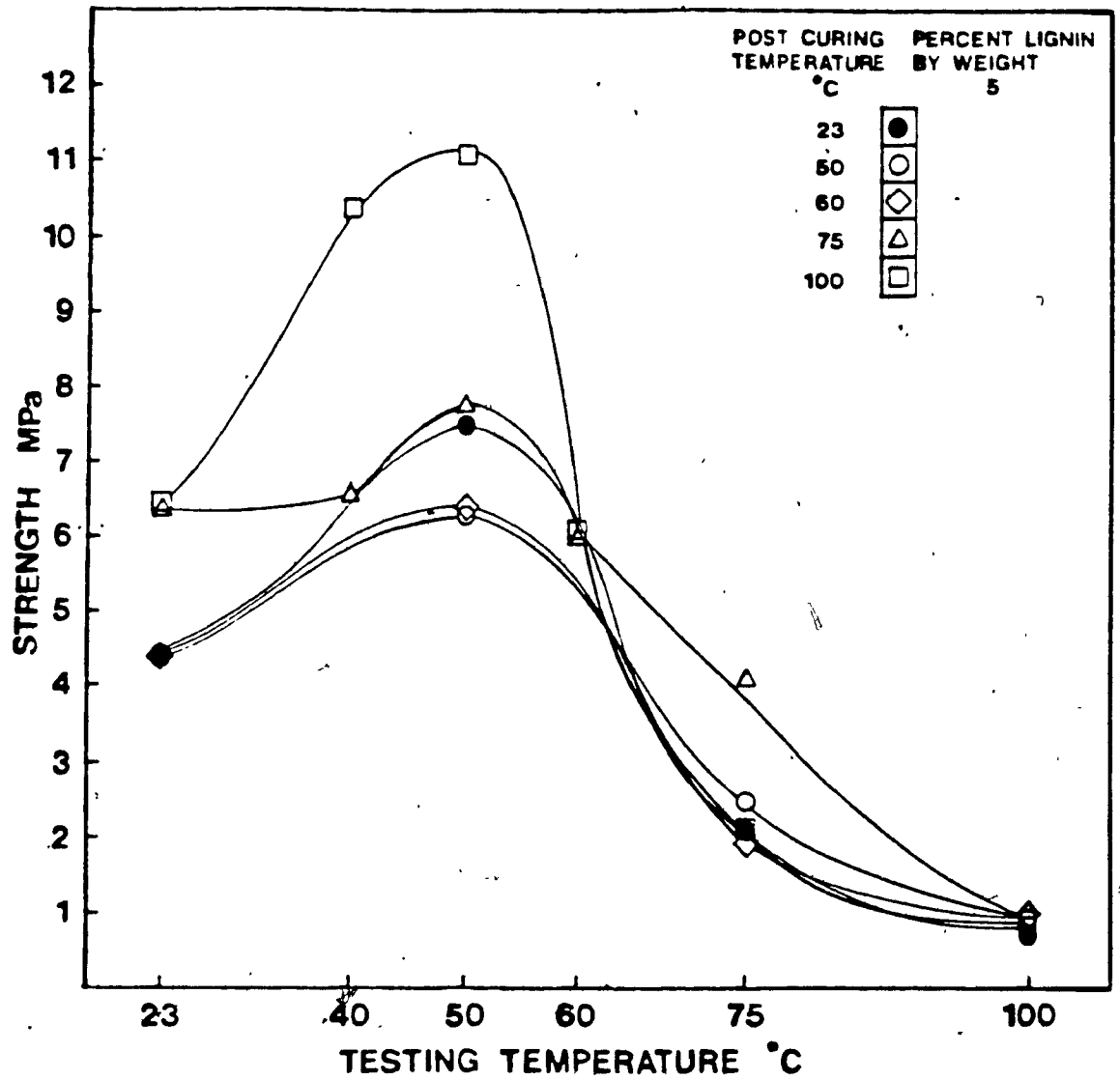


Fig. 44 Temperature dependence of adhesive shear strength of the polyblend EP-L5. Variation with post curing temperature.

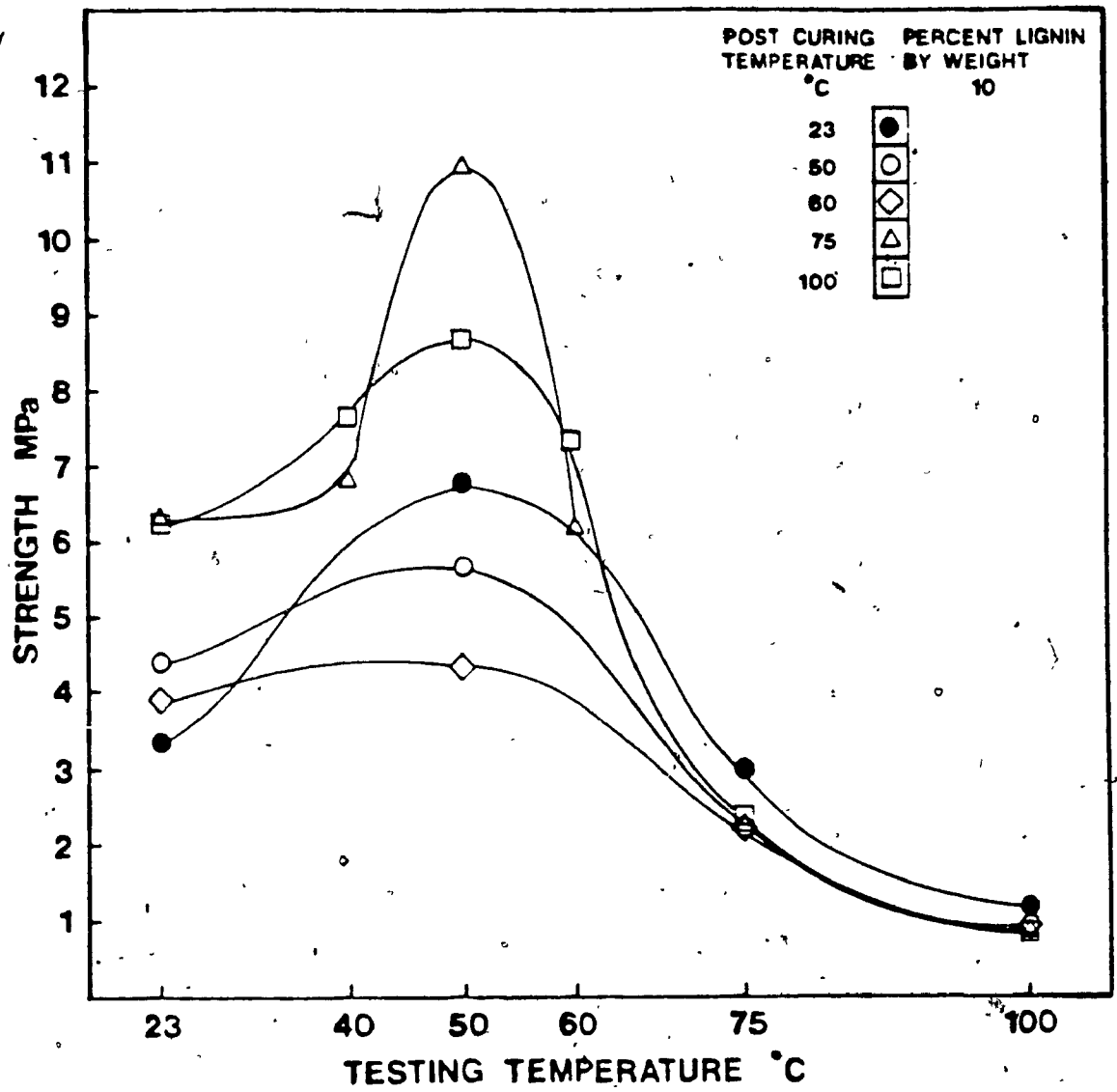


Fig. 45 Temperature dependence of adhesive shear strength of the polyblend EP-L10. Variation with post curing temperature.



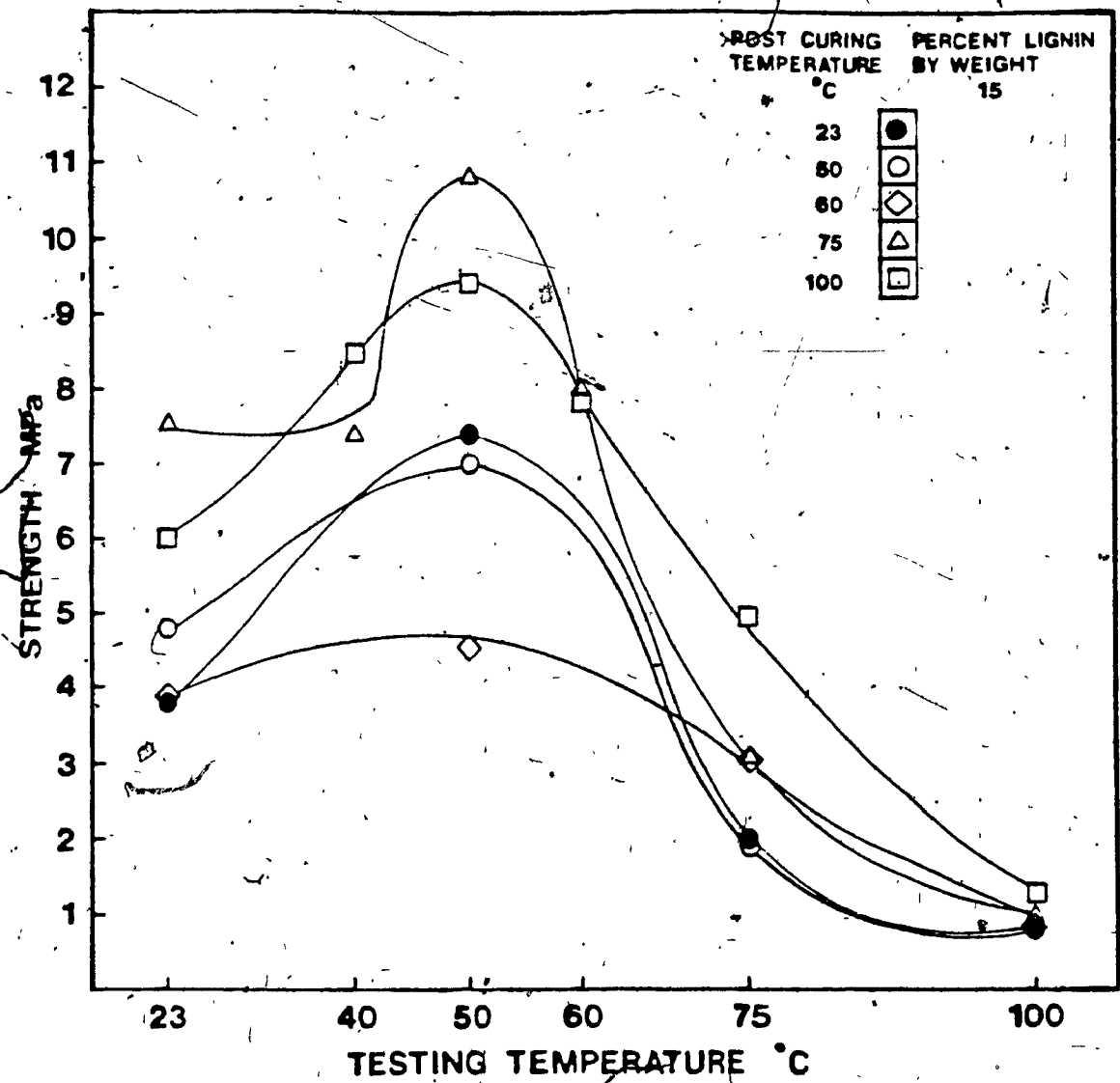


Fig. 46 Temperature dependence of adhesive shear strength of the polyblend EP-L15. Variation with post curing temperature.

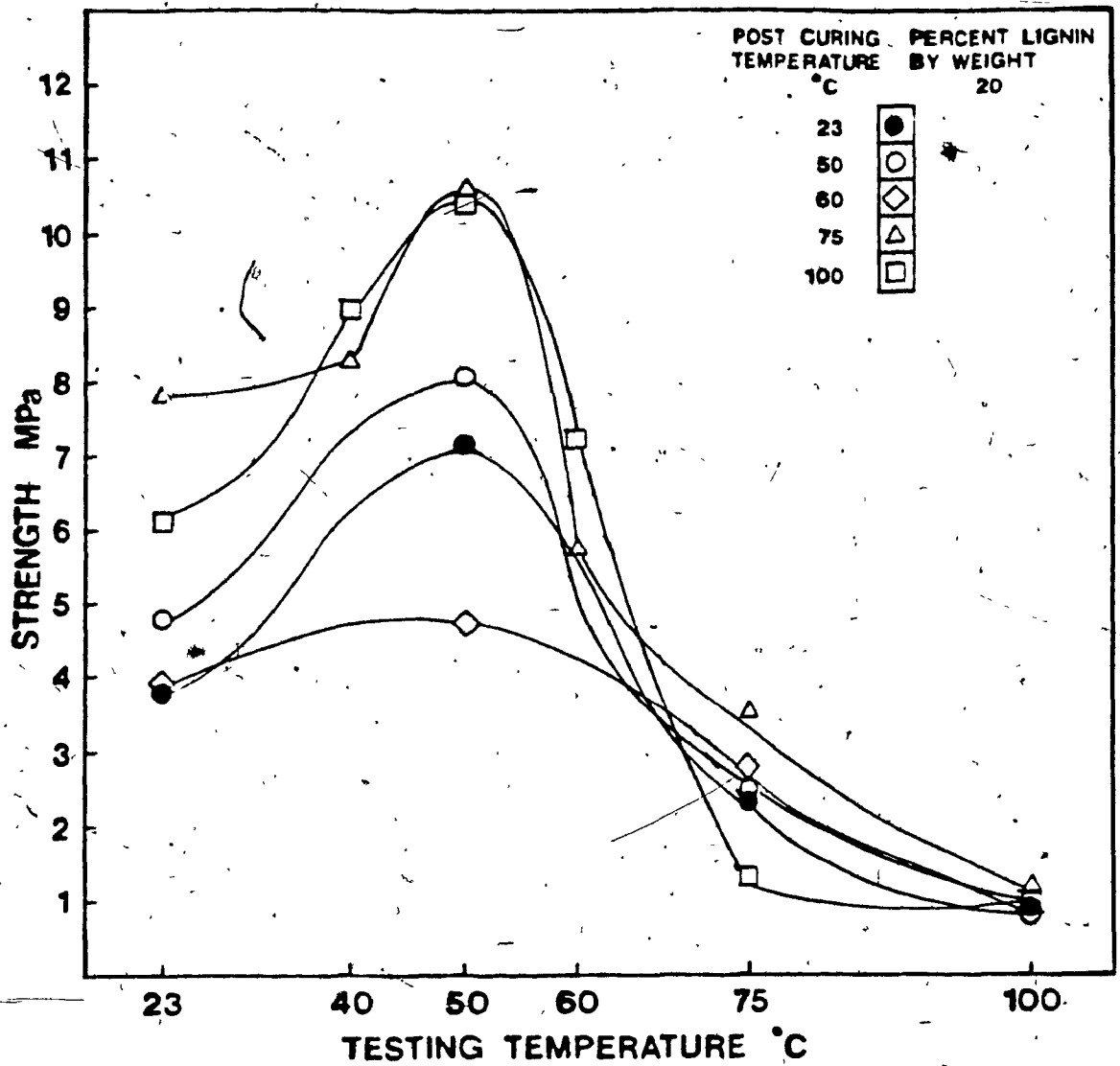


Fig. 47 Temperature dependence of adhesive shear strength of the polyblend EP-L20. Variation with post curing temperature.

In conclusion, post curing for 4 hours at 75°C best improves the adhesive shear strength and elevated temperature performance of the epoxy adhesive and the polyblends with Kraft lignin. The behavior of both the epoxy adhesive and polyblends is typical of epoxy adhesives, where the rheological state controls the strength of the joint. This in turn shows that the polyblends have resulted in a satisfactory interfacial state of adhesion similar to that of the epoxy adhesive.

### **Practical Applications in Buildings**

Although heat curing is not yet standard practice in the building sector, examples, especially in extreme conditions, are common. One example is the construction of Montreal's Olympic Stadium where air temperatures of -18°C necessitated heat curing by banks of infrared heaters. Another example is the use of hot-air blowers in the construction of the Marron Bridge in the UK. Other more sophisticated techniques include electrically heated joint surfaces, and are considered feasible, economical and able to provide controlled curing conditions (81).

With respect to elevated temperature performance, many of the epoxy adhesives currently used in building exhibit a marked reduction in strength at temperatures above 40°C, limiting their use where fire resistancy is critical (20). Recent research on this issue has been mostly concentrated on the behavior of epoxy-repaired structures (85).

In our case, 50°C could be considered as a safe service temperature for the epoxy adhesive and the polyblends, although more information is necessary for long term exposure. Also, with post curing for 4 hours at 75°C, the adhesive shear strength could be increased by 75% allowing a wider application range for both the epoxy adhesive and the polyblends, at a reduced material cost in the latter case.

## **THERMAL TESTING (DIFFERENTIAL SCANNING CALORIMETRY)**

Differential Scanning Calorimetry (DSC) is a thermal analysis technique that measures the quantity of energy absorbed (endothermic process) or evolved (exothermic process) by a material as its temperature is changed.

This is achieved by heating a sample of the material and an inert reference material at a controlled rate in a controlled atmosphere. The difference in temperature between sample and reference, due to heat induced changes, is directly related to the differential heat flow between them. This differential heat flow is quantitatively measured and stored. Such a technique can measure, among others, boiling and melting points, heat of reactions, and polymer cure and glass transition.

### **Glass Transition Temperature**

The glass transition temperature ( $T_g$ ) can be defined as the temperature below which an amorphous polymer (or an amorphous region of a semi-crystalline polymer) is rigid and brittle and above which is rubbery and soft (16).  $T_g$  is a very important characteristic of such polymers, especially in relation to application temperatures, since it has a strong influence on mechanical properties such as modulus (16,32,77). In adhesive applications of polymers,  $T_g$  can affect the strength of the bulk adhesive, which reflects on the adhesive joint performance at different temperatures (14,78). Fischer and Schmid (86), measured differences in  $T_g$  in bulk adhesives and predicted, with considerable accuracy, the adhesive shear strength (by torsion).

With respect to polyblends, Tg can give information about compatibility of the polymers (34). In our case, Tg could be indicative of possible reaction of lignin with the epoxy polymer system, since Tg of epoxy systems is affected by the degree of crosslinking (87).

#### Test Procedure

DSC was used to determine the Tg's of the epoxy adhesive and the four respective polyblends. The sample and the reference (empty cell pan) were placed in the sample chamber of the DuPont 910 Differential Scanning Calorimeter, and heated at a constant rate of 10 C/min, from 20 to 150 C under a nitrogen atmosphere. In all tests, a preliminary thermal cycle (first run) was performed to erase previous thermal history (ASTM D-3418). Measurements of energy differential against temperature were recorded and later plotted on a DuPont 1090 Thermal Analysis System. In the following two diagrams, the heat flow curves were edited for comparison purposes. No values were indicated on the heat flow axis as they would not have necessarily showed experimental values.

## Results and Discussion

Figure 48 shows the preliminary thermal cycles for the epoxy adhesive and the polyblends. The endotherms observed for all samples are due to volume relaxation caused by short range ordering of the amorphous polymers (43).

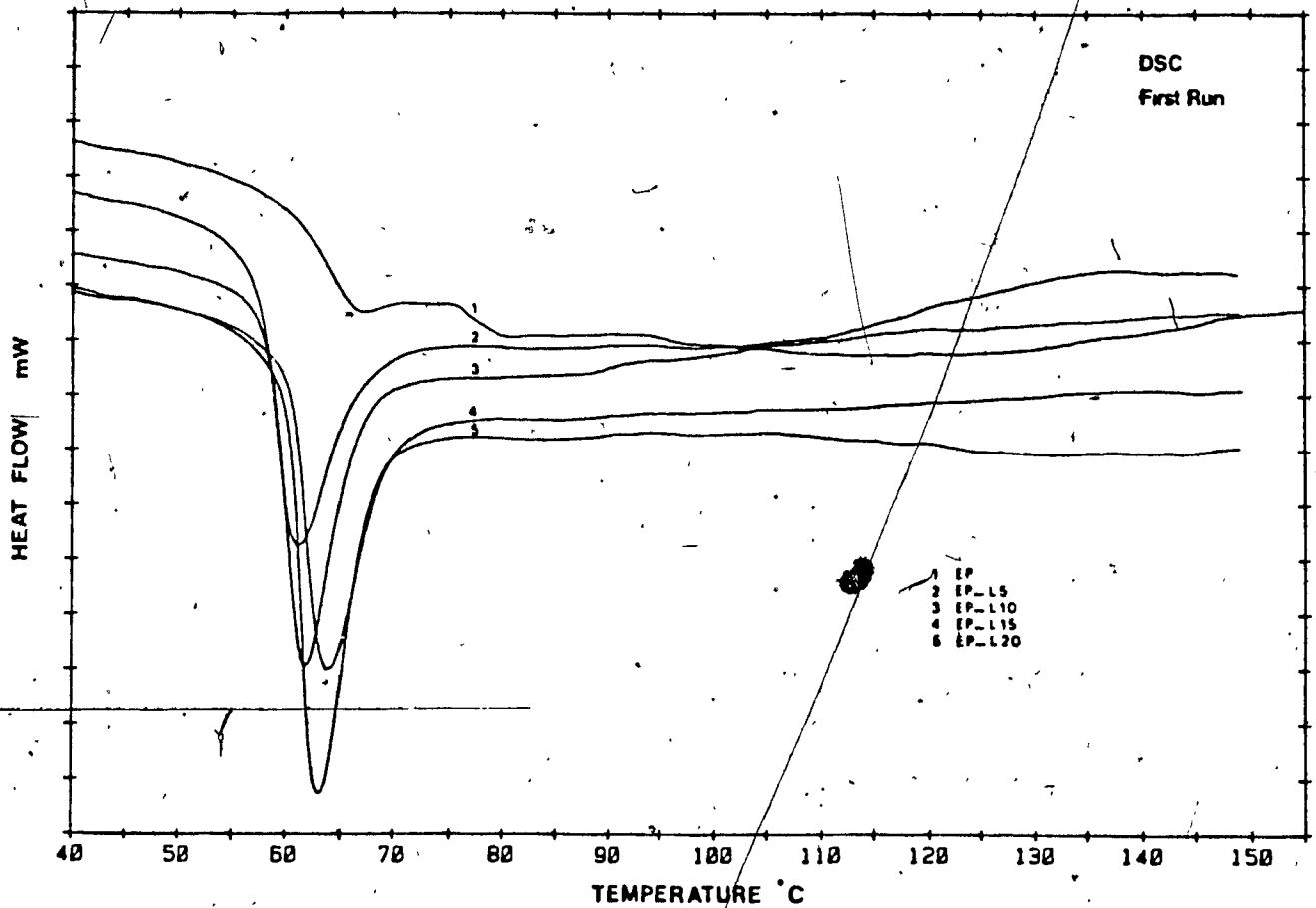


Fig. 48 Preliminary thermal cycles (DSC first run) for the epoxy adhesive and polyblends.

Figure 49 below shows the DSC diagrams for the epoxy adhesive and polyblends. Tg was determined as the first inflection in the heat flow curve.

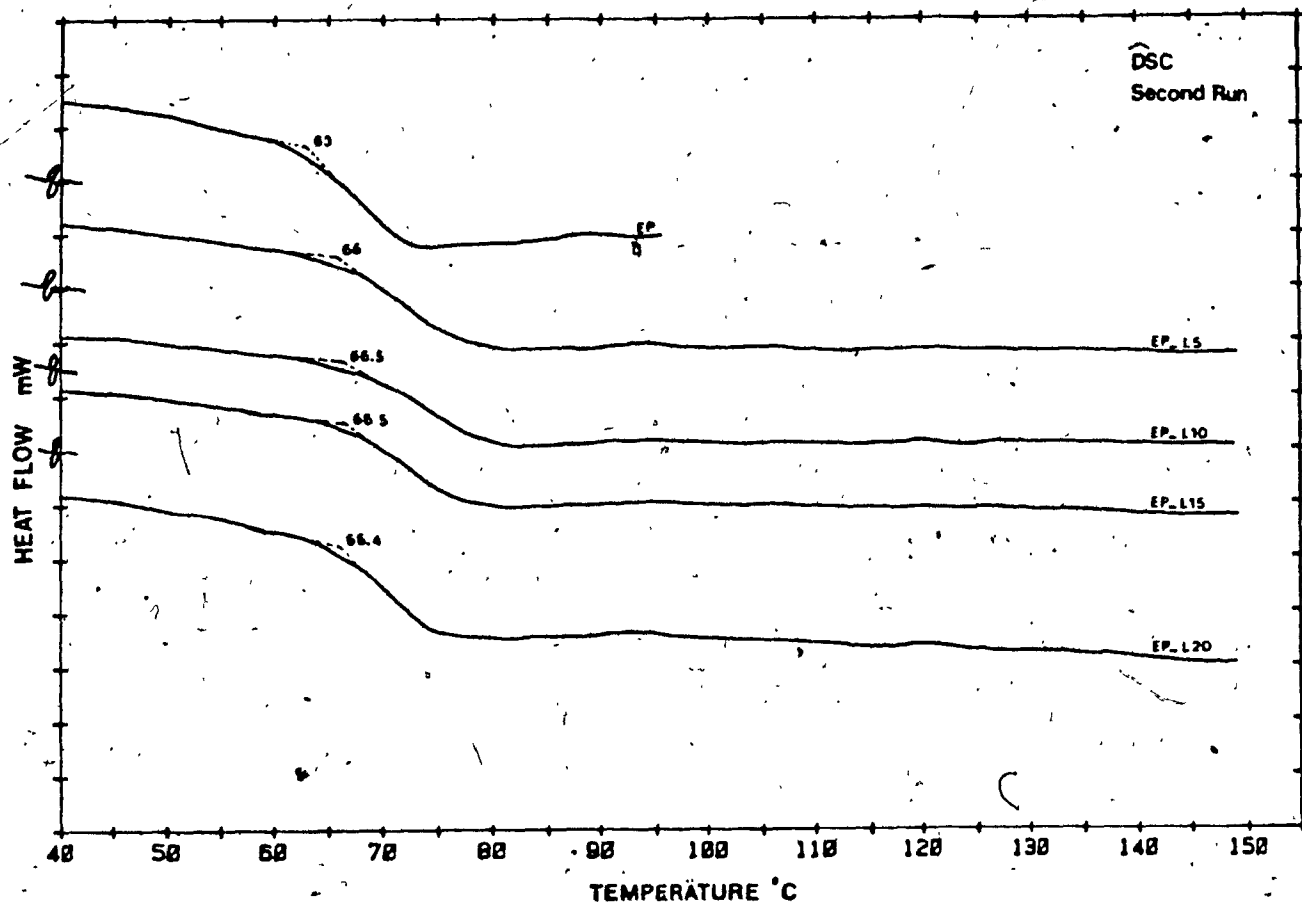


Fig. 49 DSC diagrams of the epoxy adhesive and polyblends.



Three observations could be made from the above results:

- 1) The polyblends exhibited a single Tg characteristic of monophasic systems.
- 2) The Tg's of the polyblends were very close, though slightly higher than that of the epoxy adhesive.
- 3) The slope (or sharpness) of the transition is fairly similar in all cases.

The above are essential criteria for determining the miscibility of two polymers (33). It should be noted here that Tg determined for pure Kraft lignin varied between 128.5 and 135 C. If these values and the ones obtained for the epoxy adhesive and polyblends are applied to the compatibility formula discussed on page 23, the value of 'I' obtained is very close to zero and the polyblends do not exhibit synergism (with up to 20% lignin) and could be considered as additive blends.

In conclusion, polyblending with Kraft lignin in this case does not much vary the Tg of the epoxy adhesive and thus does not apparently interact with the epoxy polymer system. It is also possible to conclude that the two polymers mix well with each other.

## **THERMAL TESTING (DYNAMIC MECHANICAL ANALYSIS)**

Dynamic Mechanical Analysis (DMA) is another thermal analysis technique that quantitatively measures stored and dissipated energy by a material with temperature change. Due to viscoelastic properties of polymeric materials, the stored energy represents an elastic modulus or stiffness of the material, while the dissipated energy represents modulus loss or mechanical damping.

The method is based on oscillating a sample/mount system at a constant amplitude, and detecting changes in the system's resonant frequency due to viscoelastic properties' variation with temperature or time. Electrical energy is used to maintain a constant amplitude throughout the test. The frequency of oscillation is a measure of modulus while the electrical energy is a measure of mechanical damping of the material. DMA is used to determine glass transition, gelation point, and general variation of the mechanical properties with temperature or frequency (time) in terms of modulus, loss modulus and loss tangent.

### **DMA Characterization of Adhesives and Polyblends**

Two factors contribute to the performance and endurance of adhesive joints at elevated temperatures; the thermal stability of the bulk adhesive, and this stability of the adhesive in the boundary layer (14). The former factor and the fact that modulus and strength difference between adhesive and adherend affect the stress concentrations in joints, makes it important to understand the behavior of the adhesive with temperature variation. DMA is one method of obtaining such information (77).

Furthermore, with DMA results, it is possible to compare the decrease of bulk modulus with increasing temperature, to the adhesive strength versus temperature (86), and to relate the bulk properties and bonding abilities of adhesives (82,86). With respect to polyblends, and in addition to the preceding reasons, DMA provides information about compatibility and interfacial adhesion of the constituent polymers (88,89).

#### **Test Procedure**

DMA was used to measure the Tg's, and the variation of modulus and damping with temperature, of the epoxy adhesive and the polyblends. The cured samples used in this study were prismatic pieces of approximate dimensions (60x11x3 mm). Each sample was clamped between two parallel arms of a DuPont 982 Dynamic Mechanical Analyzer (clamped length = 24 mm), and set into oscillation at a constant amplitude of 0.2 mm. The sample was then heated at a constant rate of 5°C/min from 20 to 100°C under a nitrogen atmosphere (ASTM D-4065). All measurements were stored and later plotted on the DuPont 1090 Thermal Analysis System.

#### **Results and Discussion**

The variation in tensile modulus with temperature for the epoxy adhesive and polyblends are shown in figures 50 to 54 respectively. The Tg's were determined from the peak values in the loss modulus profile (ASTM D-4065).

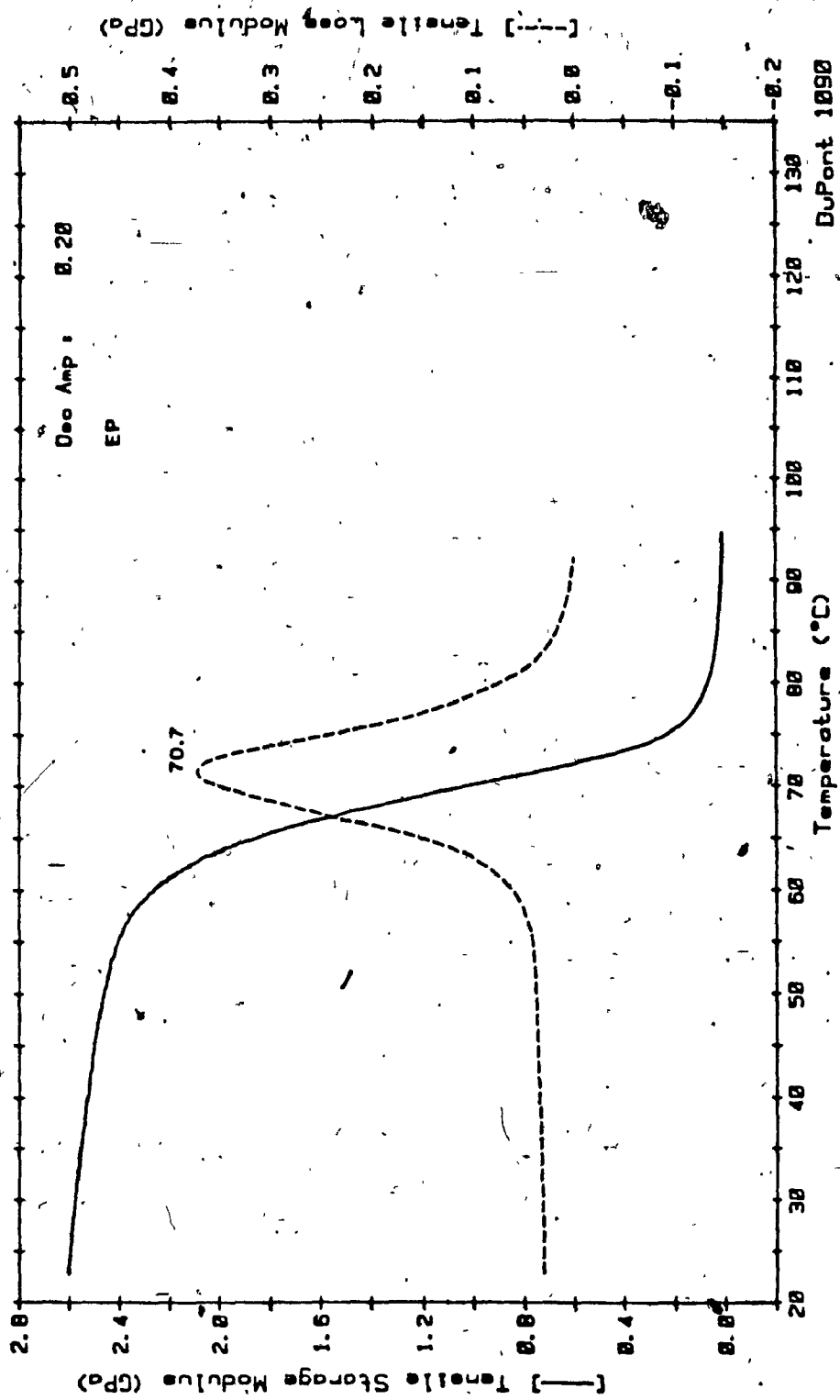


Fig. 50 Tensile modulus/tensile loss modulus variation with temperature. EP:  $T_g = 70.7^\circ\text{C}$

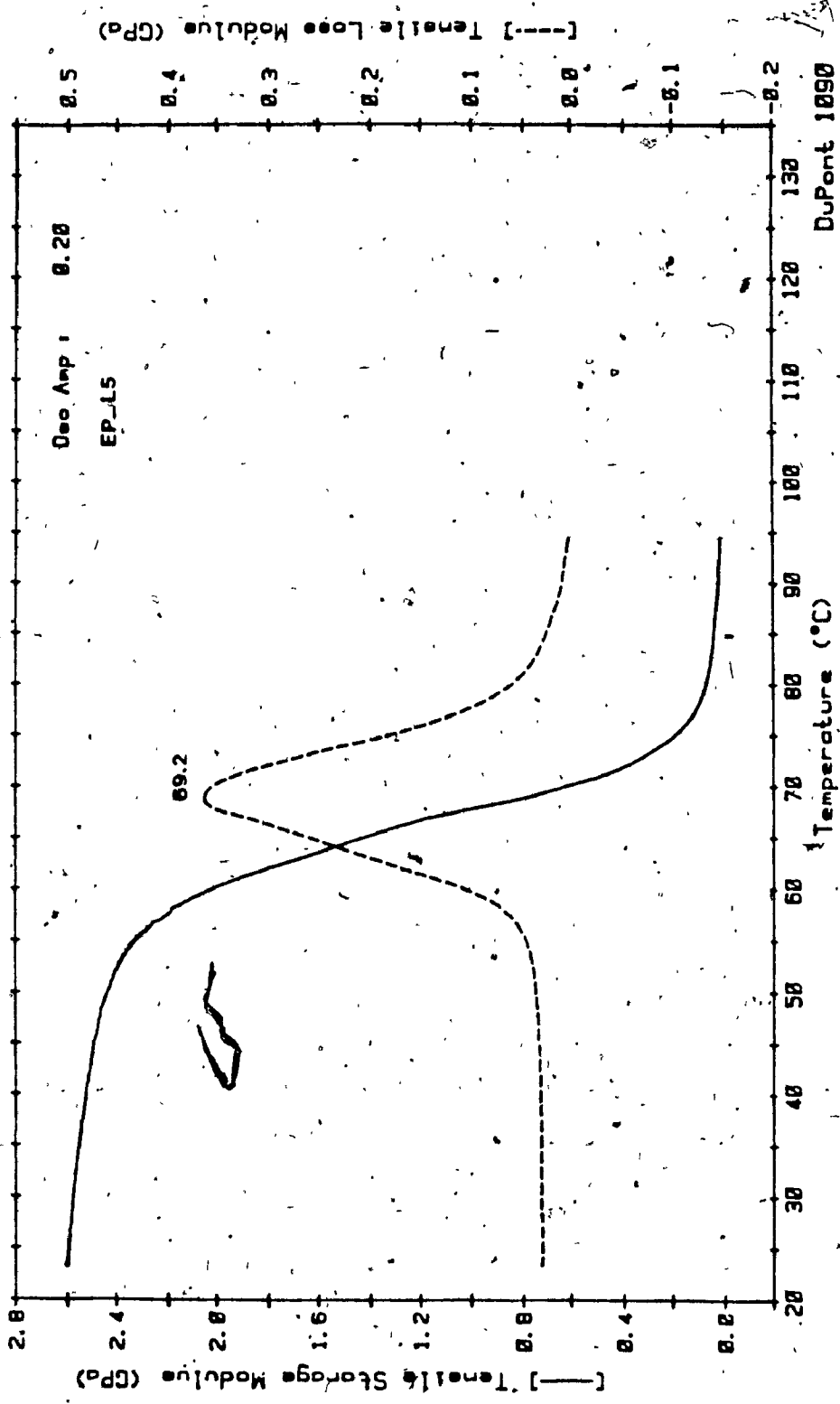


Fig. 51. Tensile modulus/tensile loss modulus variation with temperature. EP-L5:  $T_g = 69.2^\circ\text{C}$

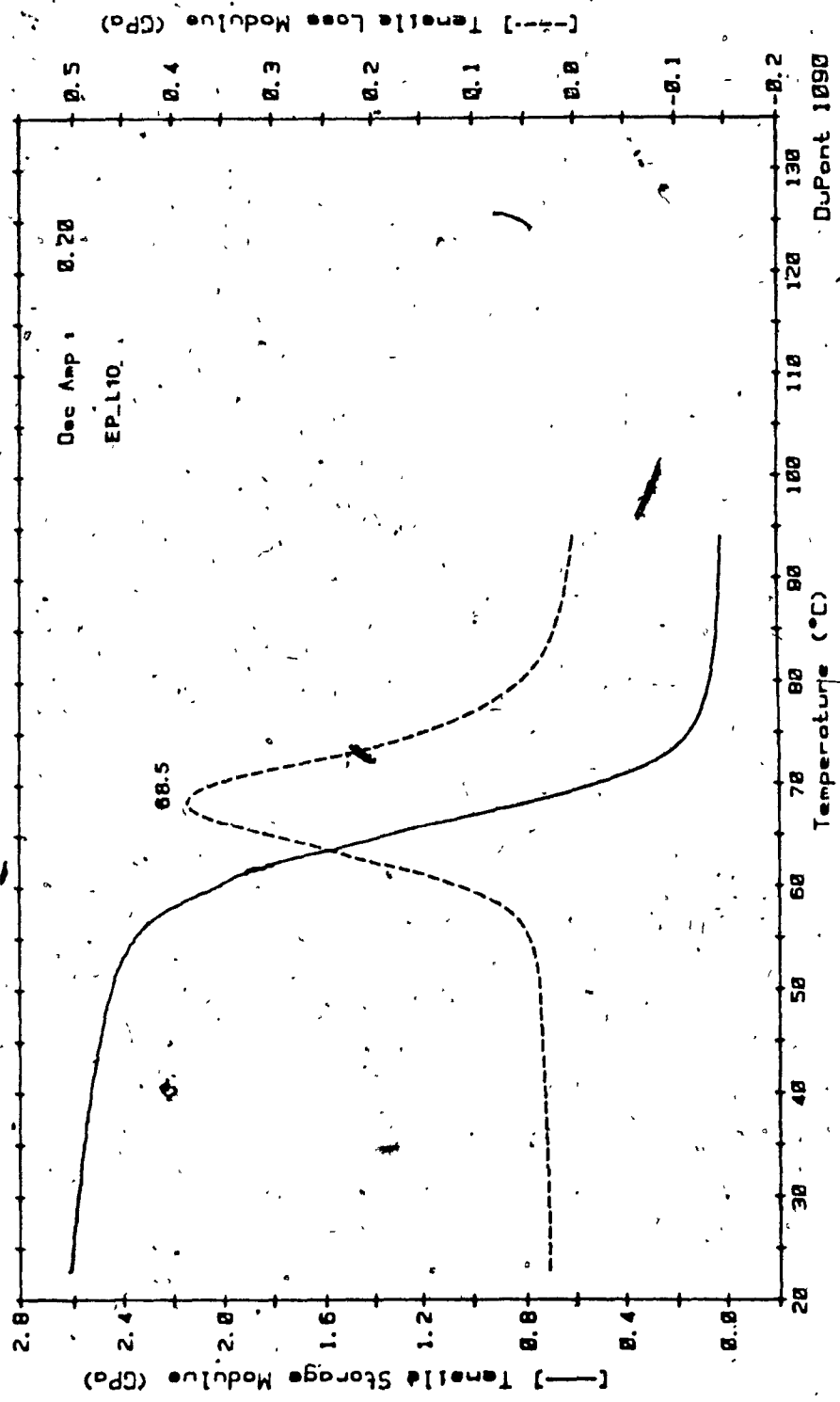


Fig. 52 Tensile modulus/tensile loss modulus variation with temperature. EP-L10:  $T_g = 68.5^\circ\text{C}$

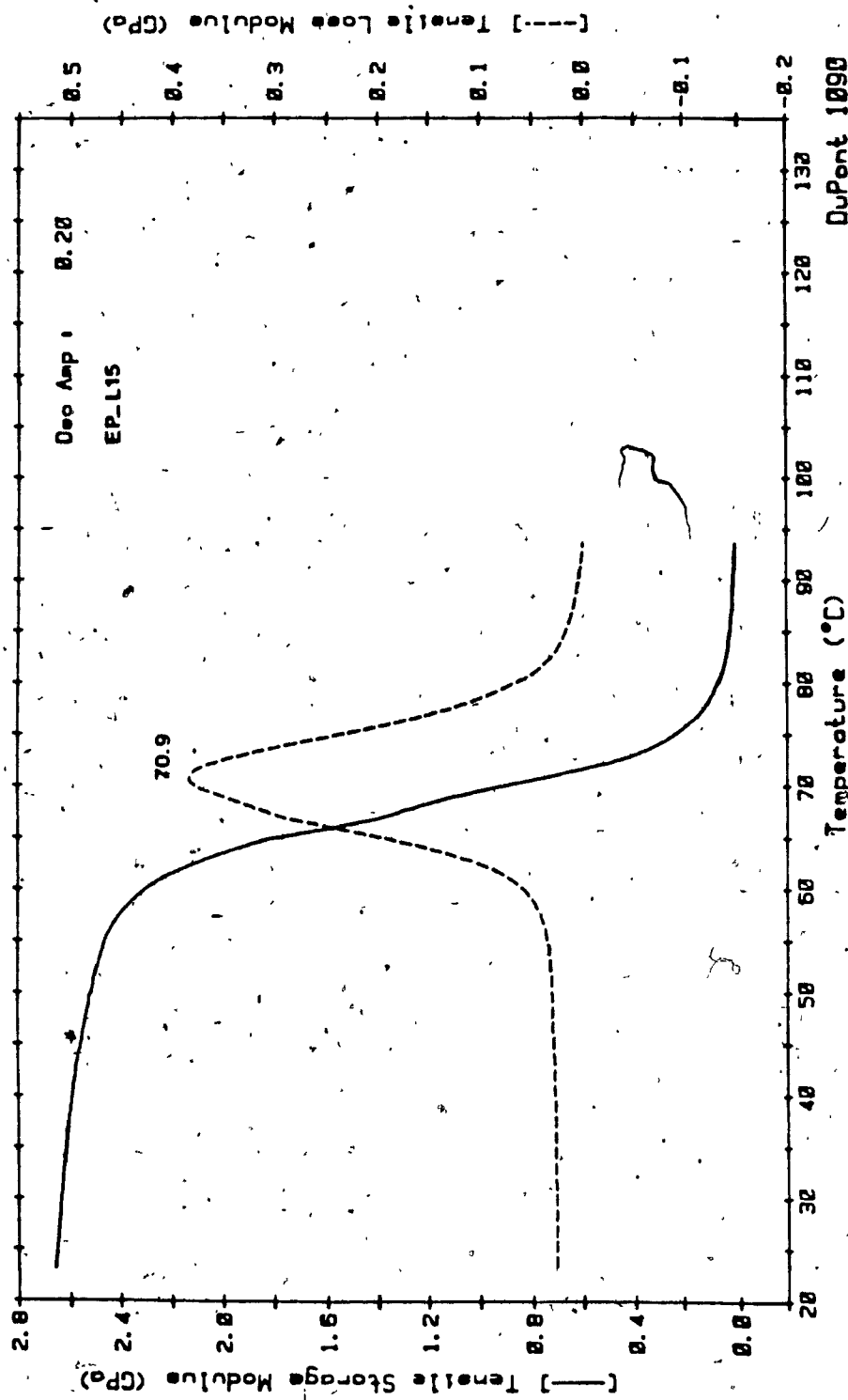


Fig. 53 Tensile modulus/tensile loss modulus variation with temperature. EP-L15:  $T_g = 70.9^\circ\text{C}$

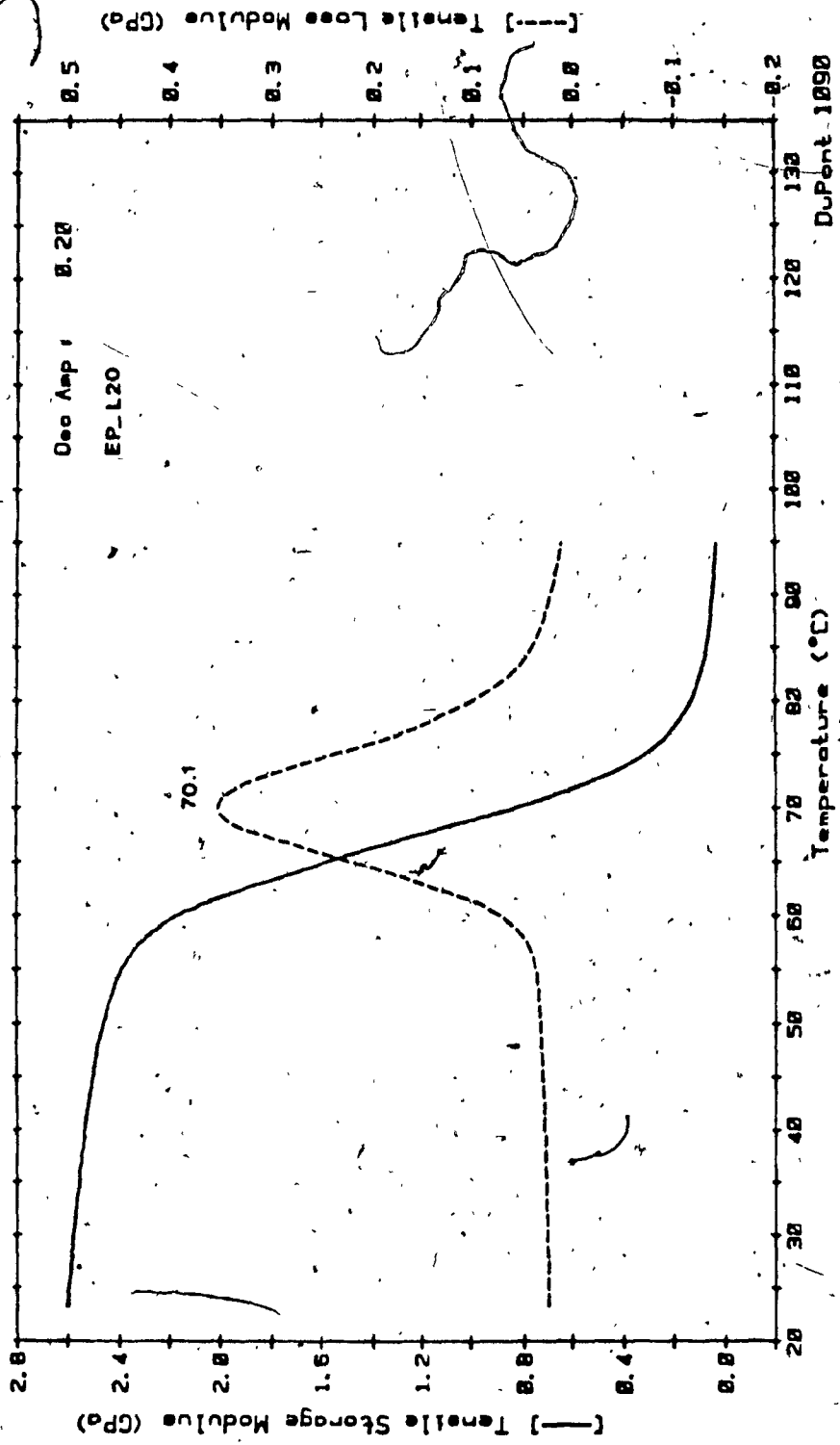


Fig. 54 Tensile modulus/tensile loss modulus variation with temperature. EP-L20:  $T_g = 70.1^\circ\text{C}$



DMA is very sensitive in detecting all changes in the state of molecular motion with temperature, and is more accurate in determining Tg than DSC, DTA (Differential Thermal Analysis) or TMA (Thermal Mechanical Analysis) (1,77,88,90). The Tg's of the polyblends are very close to that of the epoxy adhesive. The two sets of values for Tg, obtained by DSC and DMA are compared in figure 55 below.

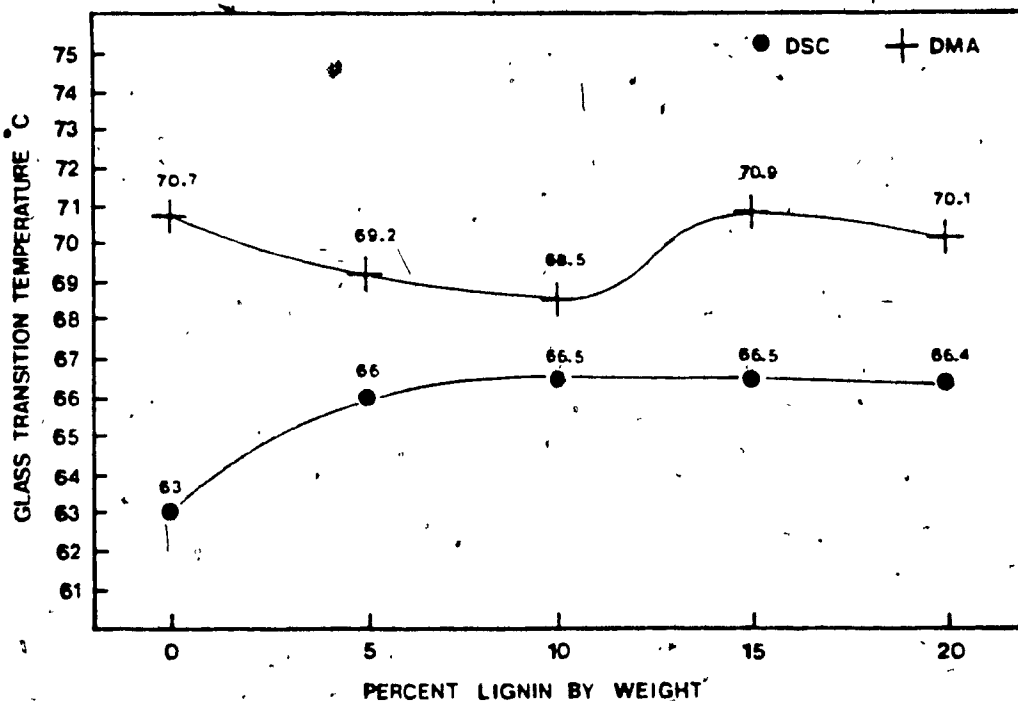


Fig. 55 Variation of the glass transition temperature with lignin as determined by DMA and DSC.

Furthermore, figures 49 to 53 show a one-step 'tensile storage modulus vs. temperature' curve, and a related one-peak 'tensile loss modulus vs. temperature' curve, characteristic of amorphous polymers and compatible polyblends (34,77).

In all cases, the values of tensile moduli were similar (approx. 2.6 GPa at room temp.), as were the variations of these moduli with temperature. The more rapid loss was apparent starting from the temperature range 50 to 60°C; and although these are not shear moduli, they could still be compared to the loss in adhesive shear strength in the same temperature range and discussed previously.

Figure 55 shows the loss tangent ( $\tan \delta$ ) for the five cases.

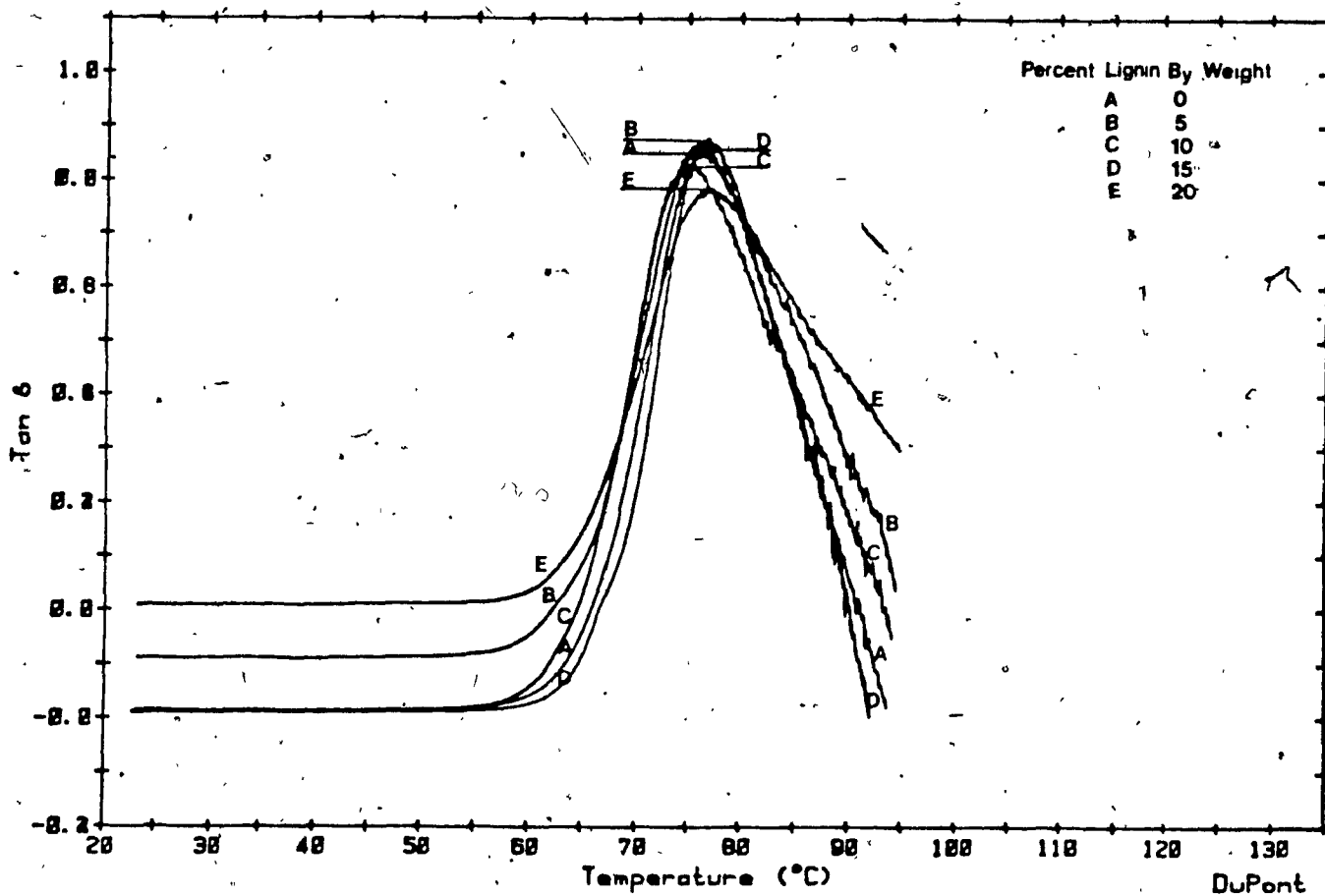


Fig. 55 Loss tangent of the epoxy adhesive and polyblends depending on temperature.

The loss tangent is the ratio of loss modulus ( $E''$ ) to the storage modulus ( $E'$ ) (i.e.  $\tan \delta = E''/E'$ ). The peak height of  $\tan(\delta)$  was not much affected by the presence of Kraft lignin up to 15% by weight. However, the peak slightly decreased and the curve ( $E$  in Fig. 55) broadened, probably due to increased stiffness (88,89). This also shows that even at 20% lignin by weight, the polymer/polymer adhesion is sufficient to prevent separation.

## CURING AND LIGNIN-EPOXY INTERACTION

In a previous study done at Concordia University (67), the kinetics of curing of the same epoxy polymer system in the presence of Kraft lignin was investigated. It was established that lignin increases the conversion time, slows the overall curing process and slightly decreases the heat of reaction. It was also established that lignin has the potential of reacting with the aliphatic amine curing agent.

In this part of the research, infrared spectroscopy was used to investigate the effect of polyblending with lignin on the curing of the epoxy polymer system. In this analysis, an infrared spectrophotometer directs infrared radiation on a thin layer of specimen and measures and records the relative amount of energy absorbed by the specimen as a function of wavelength of infrared variation (74). The spectra chart is compared with charts of known substances to identify different chemical groups.

### Test Procedure

Each specimen (EP and respective polyblends) was prepared by dispersing 6 mg of solid ground sample in 1000 mg of potassium bromide and sintering 300 mg of this mixture in a disc. In the case of the epoxy prepolymer, 6 mg of the viscous liquid on a 300 mg potassium bromide disc was used. The spectra were investigated with an Infrared Spectrophotometer (Beckman Model 4240).

## Results and Discussion

The infrared spectra for the epoxy prepolymer are shown in figure 56, and are governed by the following absorption bands:

### 1) Bisphenol-A Units:

$\text{>C=C<}$  aromatic at 1610, 1580, 1510, & 1460  $1/\text{cm}$ .

$\text{>C-H}$  aromatic at 1185 & 1010  $1/\text{cm}$ .

$\text{>C-H}$  aromatic in para substituted benzene at 830  $1/\text{cm}$

CH<sub>3</sub>

-C- 'geminate' methyl groups at 1385 & 1365  $1/\text{cm}$ .

CH<sub>3</sub>

### 2) Ether units:

$\text{>C-O-C<}$  saturated at 1160 & 1140  $1/\text{cm}$ .

$\text{>C-O-C<}$  branched at 1120 & 1070  $1/\text{cm}$ .

$\text{>C-O-aryl}$  aromatic at 1250  $1/\text{cm}$

### 3) Epoxy Ring:



at 920, 870 & 760  $1/\text{cm}$ .

$\text{>C-H}$  (in epoxy ring) at 3060, 3005, 1410 & 1345  $1/\text{cm}$ .

### 4) -OH groups: broad band at approximately 3500 $1/\text{cm}$ .

The infrared spectra of the cured epoxy polymer without lignin is also shown in figure 56. The most visible changes in the spectra are those due to the epoxy ring (920, 870, 760  $1/\text{cm}$ ); (see also figure 58). The  $\text{>C-H}$  in the epoxy ring (3060, 3005, 1410, 1345  $1/\text{cm}$ ) are also less intense. Changes are also observed in the bands of saturated ether (1160, 1140  $1/\text{cm}$ ).

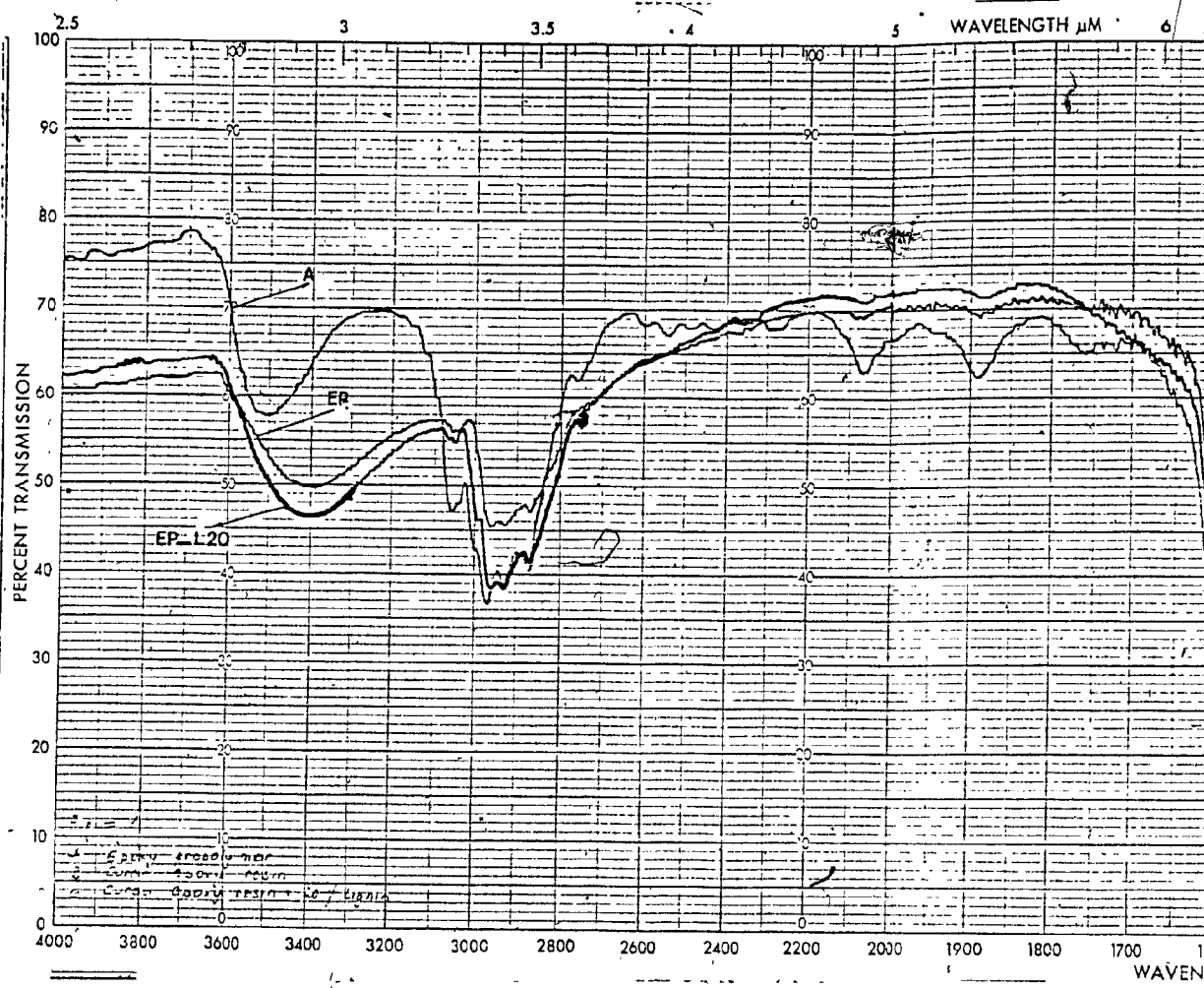


Fig. 56 Infrared analysis for: A (epoxy prepolymer), EP & EP-L20

The band for the OH group broadens and shifts to 3410  $1/cm$ , due to increase in hydroxyl concentration (1). For an epoxy polymer based on bisphenol-A and cured with an aliphatic polyamine, the hydroxyl band shifts from 3326  $1/cm$  to 3106  $1/cm$  (2). It should be noted that for the majority of bisphenol-A based epoxy polymers, the characteristic band for the OH group is at around 3400  $1/cm$  (91,92).

6 7 8 9 10 11 12 13 14 15 16 17 18 20 22 25 30

WHEN RECEIVING SPECIFY CHEMIST AND NUMBER  
BELL & HOWELL INSTRUMENTS INC TELEPHONE EAST U.S.A.

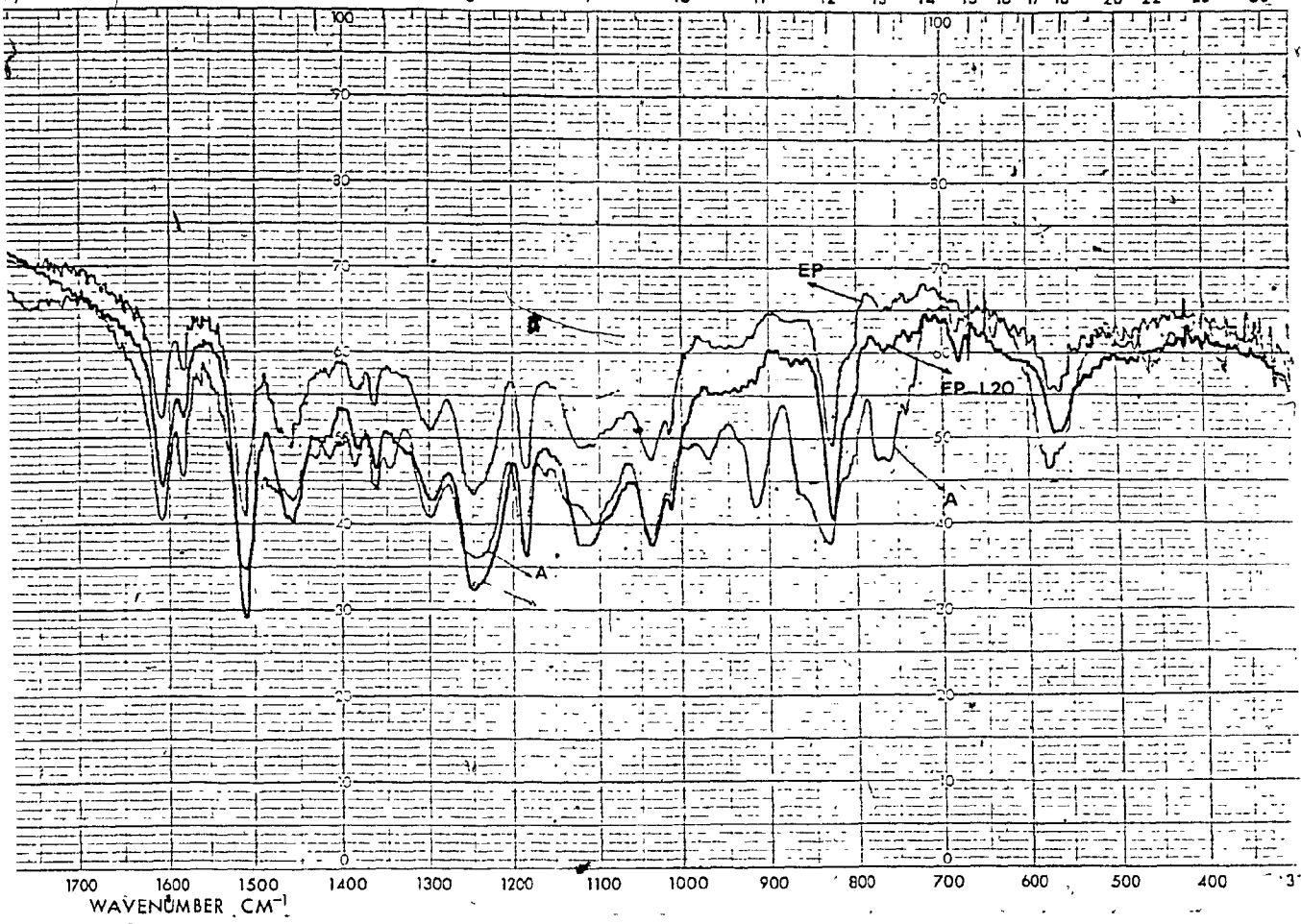


Figure 57 shows the spectra for the polyblends EP-L5 and EP-L20. The changes are similar for these two polyblends, as well as for the remaining two (not shown due to similarity), and are in turn comparable to the spectra of the epoxy adhesive with respect to changes for the epoxy ring, saturated ether and OH bands.

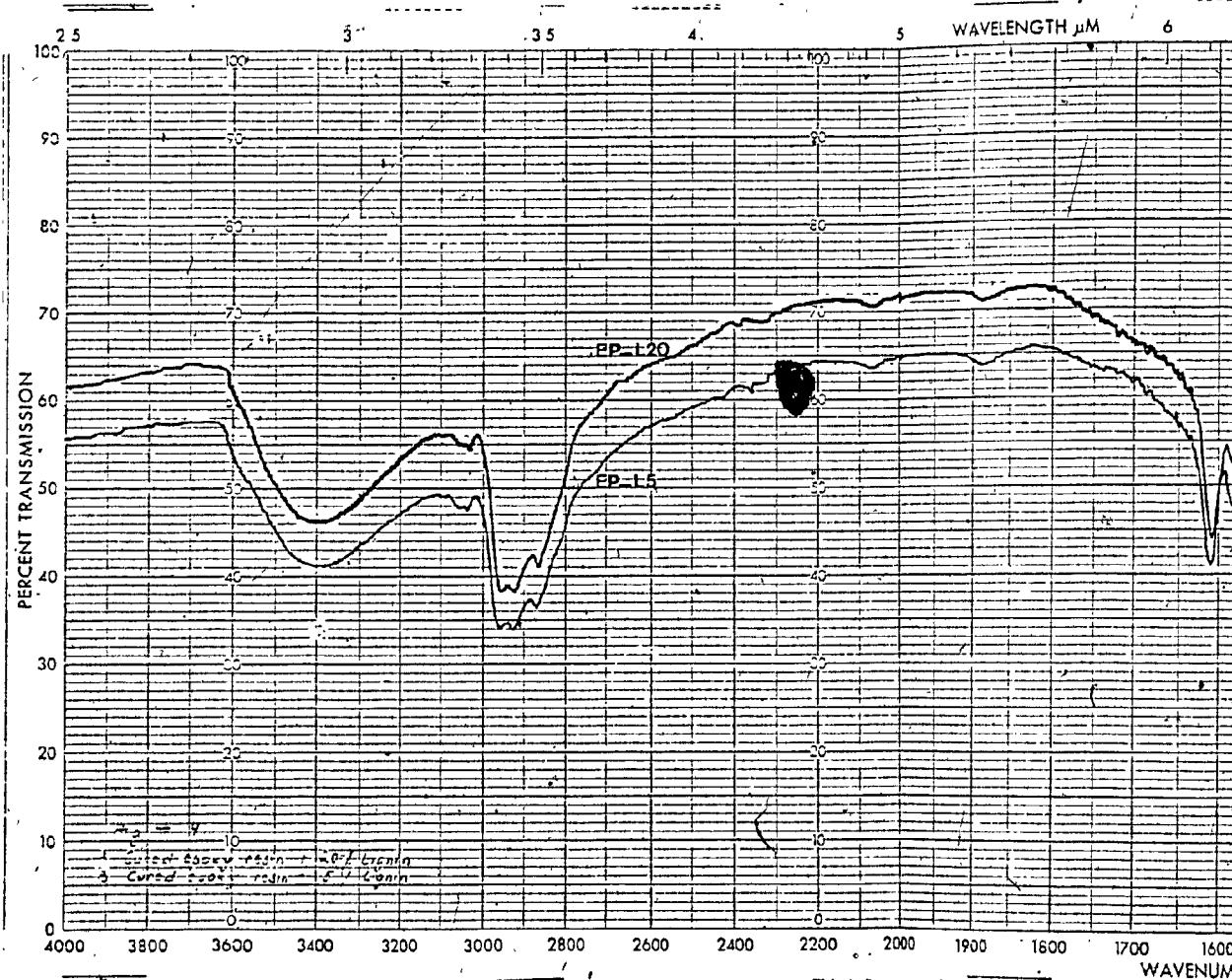


Fig. 57 Infrared analysis for EP-L5 & EP-L20



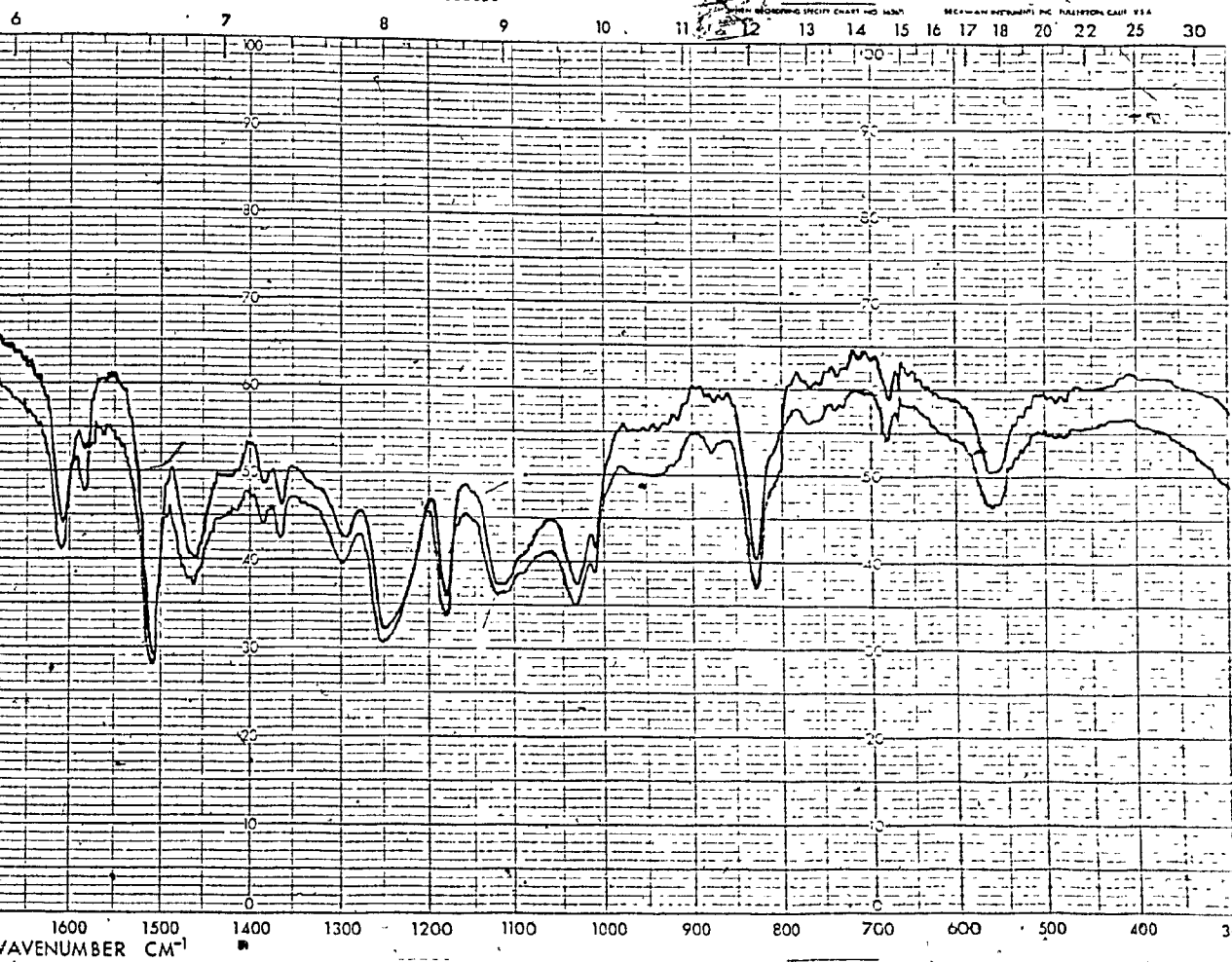


Figure 58 shows the changes due to the epoxy ring (920,870,760  $1/cm$ ), where the changes are similar for EP and EP-L20 (as for the other polyblends). One can conclude that Kraft lignin apparently does not participate in the curing process of the epoxy polymer.

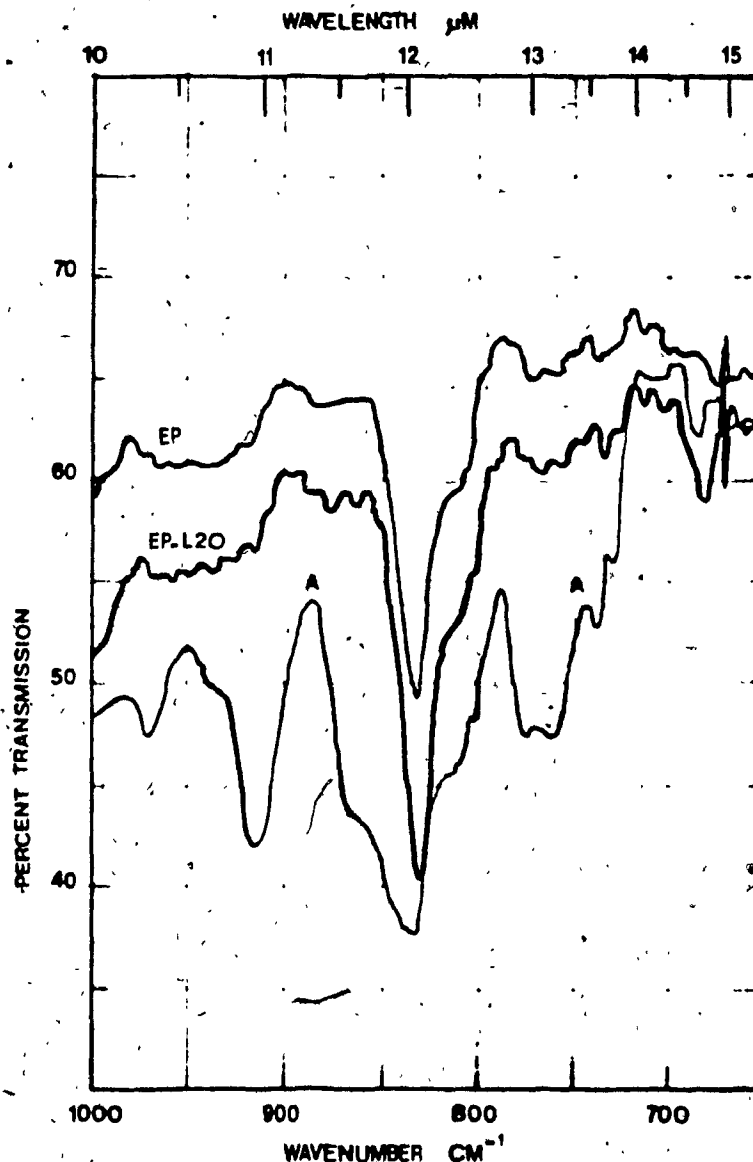


Fig. 58 Infrared analysis: changes due to the epoxy ring.

## CONCLUSION

The major findings of the research, under the conditions previously described, are listed below:

- 1) Polyblending with Kraft lignin (10 to 20% by weight) improves the adhesive tensile strength of the epoxy polymer system.
- 2) The adhesive shear strength (by tension loading) of the epoxy system is not affected by polyblending with lignin.
- 3) Lignin does not necessarily improve the durability of the epoxy adhesive strength.
- 4) Post curing for 4 hours at 75°C improves the adhesive shear strength and the elevated temperature performance of both the epoxy adhesive and the polyblends.
- 5) The epoxy/lignin polyblends' behavior at elevated temperatures is typical of that of epoxy adhesives in proper joints.
- 6) The glass transition temperatures of the polyblends are close to that of the epoxy adhesive.
- 7) Polyblending with lignin does not change the temperature dependence of the tensile storage and loss moduli as determined by Dynamic Mechanical Analysis.
- 8) Kraft lignin appears to be miscible with the epoxy polymer system.
- 9) Kraft lignin apparently does not participate in the curing process of the epoxy polymer.

10) The adhesive shear strengths of the polyblends, before and after weathering, are better than those obtained by Shiraishi et al (49) (see p. 26); and the polyblends are a result of a simpler and cheaper method of preparation.

In short, polyblending of a bisphenol-A based epoxy polymer adhesive with Kraft lignin is an effective, feasible and economical method of reducing the cost and modifying the epoxy polymer formulation. This statement is supported by the above findings and the facts that the price of Kraft lignin is about 10 cents per kg (vs. \$5 - \$12 per kg for the epoxy system) and the possibility to use it in this case in amounts up to 20% by weight.

This research has also proven the potential presented by a renewable resource, lignin, as a component in polyblends. In the case of polyblending with the bisphenol-A type epoxy adhesive, the following recommendations for future study are presented:

- 1) Increasing the percent of Kraft lignin up to 45%, where manual mixing at room temperature is still possible, and determining the effect on adhesive strength and other properties.
- 2) Determining the performance of polyblends in adhesive joints at cold testing temperatures.
- 3) Optimizing the adhesive strength of the polyblends, and the epoxy adhesive, through a combination of post curing schedules and adherend surface treatments.
- 4) Studying the flammability of the adhesive and polyblends, and how it is affected by fire retardants.
- 5) Determining any possible health risks that may result from the preparation and use of the adhesive or polyblends.

## REFERENCES

- 1) W.G. Potter, Epoxide Resins, Plastics Institute, London, 1970.
- 2) H. Lee & K. Neville, Handbook of Epoxy Resins, McGraw Hill, New York, 1967.
- 3) C.A. May, "Introduction to Epoxy Resins", in C.A. May & Y. Tanaka (Eds), Epoxy Resins: Chemistry and Technology, Marcel Dekker, New York, 1973, pp 1-7.
- 4) W.G. Potter, Uses of Epoxy Resins, Chemical Publishing Co., New York, 1976.
- 5) F. Lohse, Epoxy Resins: New Results and Developments, Makromol. Chem., Macromol. Symp., 7, 1987, pp 1-16.
- 6) Anon., Market Opportunities Catalogue: Imports Trends, Market Development Branch, Dept. of Regional Industrial Expansion, Ottawa, Dec. 1986.
- 7) B. Neffgen, Epoxy Resins in the Building Industry - 25 Years of Experience, The Int'l J. of Cement Composites & Lightweight Concrete, V.7, No.4, Nov. 1985, pp 253-260.
- 8) A. Barker, Adhesive Consumption May Rise 60% by Volume by 1995, Adhesives Age, V.27, No.1, 1984, pp 32-36.
- 9) R.E. Brown & R.W. McCrea, Competition Chances for Growth for Epoxy Adhesive Markets, Adhesives Age, V.25, No.2, 1982, pp 21-26.
- 10) J. Puglisi, "Epoxy", in: Modern Plastics Encyclopedia, 1985-86, pp 21-23.
- 11) M. Savla, "Epoxy Resin Adhesives", in: I. Skeist (Ed), Handbook of Adhesives, 2nd ed., Van Nostrand Reinhold, New York, 1977, pp 434-445.
- 12) R.T. Dowd, "General Chemistry of Bisphenol-A Based Epoxy Resins", in: P.F. Bruins (Ed), Epoxy Resin Technology, Interscience Publishers, New York, 1968, pp 1-10.
- 13) Y. Tanaka & T.F. Mika, "Epoxide Curing Reactions", in: May & Tanaka (Eds), Epoxy Resin: Chemistry and Technology, (ref.3), pp 135-225.
- 14) A.F. Lewis & R. Saxon, "Epoxy Resin Adhesives", in: May & Tanaka (Eds), Epoxy Resins: Chemistry and Technology, (ref.3), pp 373-450.

- 15) T.F. Mika, "Curing Agents and Modifiers", in: May & Tanaka (Eds), Epoxy Resins: Chemistry and Technology, (ref.3), pp 240-306.
- 16) G.R. Moore & D.E. Kline, Properties and Processing of Polymers for Engineers, Society of Plastics Engineers, Prentice Hall, New Jersey, 1984.
- 17) P.C. Hewlett & J.D.N. Shaw, "Structural Adhesives Used in Civil Engineering", in: W.C. Wake (Ed), Developments in Adhesives, V.1, Applied Science Publishers Ltd., London, 1977, pp 25-72.
- 18) C.J. Fleming & G.E.M. King, "The Development of Structural Adhesives for Three Original Uses in South Africa", International Union of Testing & Research Labs for Materials & Structures, RILEM, Int'l Symp., Paris, Dec. 1967, pp 241-251.
- 19) Anon., Araldite Adhesives for the Construction Industry, CIBA-Geigy, Pub. No. M31c, April 1979.
- 20) G.C. Mays, Structural Applications of Adhesives in Civil Engineering, Materials Science & Technology, V.1, Nov. 1985, pp 937-943.
- 21) R. L'Hermite & J. Bresson, "Synthetic Resins in Building Construction", RILEM (ref.18), pp 175-203.
- 22) R. Cirrode, "Techniques d'Assemblage par Collage", RILEM (ref.18), pp 253-261.
- 23) R. L'Hermite, Les Resines Synthetiques dans les Structures, L'Architecture d'Aujourd'hui, No.141, 1968-69, pp 105-108.
- 24) J.R. Panek & J.P. Cook, Construction Sealants and Adhesives, 2nd ed., John Wiley & Sons, New York, 1984, pp 262-317.
- 25) P. Maslow, Chemical Materials for Construction, Structures Publishing Co., Farmington, Michigan, 1974, pp 286-319.
- 26) Anon., Adhesives: Applications, AJ, V.169, No.18, London, 2 May 1979, pp 923-936.
- 27) J. Delmonte, "Adhesives for the Construction Industry", in: C.V. Cagle (Ed), Handbook of Adhesive Bonding, McGraw Hill, New York, 1973, pp 25.1-25.9.
- 28) D. Feldman & M. Khoury, "Epoxy Polymer Systems as Stone Preservatives", Paper submitted for publication, Concordia University, Montreal, 1986.

- 29) J. Guillet (Ed), *Polymers and Ecological Problems*, Plenum Press, New York, 1973, Introduction.
- 30) J.R. Kenney, "An Approach to New Polymeric Materials via Blocks Grafts and Blends", in: D. Klempner & K.C. Frisch (Eds), *Polymer Alloys (Blends, Blocks, Grafts & Interpenetrating Networks)*, Polym. Sc. & Tech., V.10, Plenum Press, New York, 1977, pp 21-22.
- 31) J.A. Manson & L.H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976.
- 32) D.J. Williams, *Polymer Science and Engineering*, Prentice Hall Inc., New Jersey, 1971.
- 33) O. Olabisi, L.M. Robeson & M.T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
- 34) R.D. Deanin et al, "Practical Properties of Multi-Phase Polymer Systems", in: L.H. Sperling (Ed), *Recent Advances in Polymer Blends Grafts and Blocks*, Polym. Sc. & Tech., V.4, Plenum Press, New York, 1974, pp 63-91.
- 35) S.Y. Kienzle, *Alloys and Blends: Tying Properties to Markets*, *Plastics Engineering*, Feb. 1987, pp 41-43.
- 36) J.J. Elmendorf & R.J. Maalcke, "Some Microrheological Aspects of Polymer Blending", in: J.C.S. Seferis & P.S. Theocaris (Eds), *Interrelations between Processing Structure and Properties of Polymeric Materials*, Elsevier Science Publishers, Amsterdam, 1984, pp 219-227.
- 37) M.T. Shaw & R.H. Somani, "Phase Equilibria in Polymer Melts by Melt Titration", in: C.D. Han (Ed), *Polymer Blends and Composites in Multiple Systems*, American Chemical Society, Washington D.C., 1984.
- 38) Y.Y. Wang & S.A. Chem, *Polymer Compatibility: Nylon-Epoxy Resin Blends*, *Polym. Eng. Sci.*, V.20, 1980, pp 823-829.
- 39) L.T. Manzione et al, *Rubber-Modified Epoxies II. Morphology and Mechanical Properties*, *J. Appl. Polym. Sci.*, V.26, 1981, pp 907-932.
- 40) S.C. Kunz & P.W.R. Beaumont, *Low-Temperature Behaviour of Epoxy-Rubber Particulate Composites*, *J. Mater. Sci.*, v.16, 1981, pp 3141-3152.
- 41) J. Daly et al, *Rubber-Modified Epoxy Resin: Equilibrium Physical Properties*, *Polymer*, V.22, 1981, pp 2391-2401.
- 42) T.T. Wang & M.M. Supko, *Phase Separation of Rubber-Modified Epoxies*, *J. Appl. Polym. Sci.*, V.26, 1981, pp 2391-2401.

- 43) Z.H. Ophir et al, Tg Annealing Studies of Rubber-Modified and Unmodified Epoxy Systems, J. Appl. Phys., V.49, 1978, pp 5032-5038.
- 44) Y. Lee et al, Liquid-Rubber-Modified Epoxy Adhesives Cured with Dicyandiamide.I.Preparation and Characterization, J. Appl. Polym. Sci., V.32, 1986, pp 6317-6327.
- 45) Y. Lee et al, Liquid-Rubber-Modified Epoxy Adhesives Cured with Dicyandiamide.II. Morphology and Adhesion Strengths, J. Appl. Polym. Sci., V.32, 1986, pp 6329-6338.
- 46) R.R. Galluci & R.C. Going, Preparation and Reactions of Epoxy-Modified Polyethylene, J. Appl. Polym. Sci., V.27, 1982, pp 425-437.
- 47) A.M. Usmani, J. Elastom. Plast., V.13, 1981, p 170.
- 48) D. Feldman et al, Modification of Epoxy Polymer by Plasticizing Blending Or Reinforcing, J. Appl. Polym. Sci., V.29, 1984, pp 515-531.
- 49) N. Shiraishi et al, JP 61 215 610 [86,215,610], 1986.
- 50) D.W. Goheen & C.H. Hoyt, "Lignin", in: Encyclopedia of Chemical Technology, 3rd ed., V.14, 1981, pp 294-311.
- 51) L.H. Sperling & C.E. Carraher, "Renewable Resource Monomers and Polymers", in: Sperling & Carraher (Eds), Polymer Applications of Renewable-Resource Materials, Polym. Sci. & Tech., V.17, Plenum Press, New York, 1981, pp 6-7.
- 52) S.Y. Lin, "Lignin Utilization: Potential and Challenge", in: D.A. Tillman & E.C. Jahn (Eds), Progress in Biomass Conversion, V.4, Academic Press, New York, 1983, pp 32-78.
- 53) K. Kringstad, "The Challenge of Lignin", in: L.E. St.Pierre & G.R. Brown (Eds), Future Sources of Organic Raw Materials, CHEMRAWN I, Pergamon Press, New York, 1980, pp 627-636.
- 54) R.F. Nicholas, US Patent, 2 854 422, 1958.
- 55) D. Feldman, Phenoplasts from Lignin, Celluloza Hirtie (Bucharest), V.12 (8-9), 1963, pp 275-280.
- 56) C.W. Montgomery, US Patent, 3 330 788, 1967.
- 57) A. Fuhrmann, in: Proceedings of the 5th Int'l Congr. of Scandanavian Chemical Engineers, Bellacent, Copenhagen, 1980, pp 526-535.
- 58) I. Genov, DMP, V.26, No.5, 1983, pp 1380-1390.
- 59) I. Chodak et al, Blends of Polypropylene with Lignin, Chem. Pap., V.40, No.4, 1986, pp 461-470.



- 60) Chem. Abst. V.106, No. 106:157402, 1987.
- 61) L.M. Beznacuk, Improving the Durability of Silicone Sealants through Polyblending, Masters Thesis, Center for Building Studies, Concordia University, Montreal, 1986.
- 62) M. Lacasse, Sealant Polyblends with Lignin, Masters Thesis, Center for Building Studies, Concordia University, Montreal, 1986.
- 63) D. Feldman, M. Lacasse & R. ST. J. Manly, "Contribution to the study of Lignin - Polyurethane & Lignin - Acrylic Polyblends", in: Adhesion 87, 2nd Int'l Conf., Plastics & Rubber Institute, London, 1987, pp H1 - H6.
- 64) S.Y. Elliot, "Techniques for Evaluation of Adhesives", in: Cagle (Ed), Handbook of Adhesive Bonding, (ref.27), pp 31.1-31.7.
- 65) A.H. Landrock, Adhesives Technology Handbook, Noyes Publication, Park Ridge, NJ, 1985, pp 287-289.
- 66) A.C. Moloney et al, Parameters Determining the Strength and Toughness of Particulate Filled Epoxide Resins, J. Mater. Sci., V.22, 1987, pp 381-393.
- 67) D. Feldman & D. Banu, Kinetic Data on the Curing of an Epoxy Polymer in the Presence of Lignin (Paper to be published in the J. Polym. Sci.), 1986.
- 68) A.J. Kinloch, Durability of Structural Adhesives, Applied Science Publishers, London, 1983, pp 1-35.
- 69) P.J. Hine et al, Adhesion of Microfibrous Surfaces on Steel and Copper to Epoxy Resins, J. Adhesion Sci. & Tech., V.1, No.1, 1987, pp 69-78.
- 70) A.J. Kinloch, "Predicting and Increasing the Durability of Structural Adhesive Joints", in: K.W. Allen (Ed), Adhesion, V.3, Applied Science Publishers, London, 1979, pp 1-12.
- 71) H. Kollék et al, "Some Aspects of Chemistry in Adhesion of Aluminum Joints", in: G. Bartelos & R.J. Schliekelmann (Eds), Progress in Advanced Materials and Processing, Elsevier, Amsterdam, Mater. Sci. Monograph No.29, 1985, pp 83-94.
- 72) J. Comyn et al, "The Effect of Water on Epoxide Resins and Joints", in: Allen (Ed), Adhesion, V.3, (ref.70), pp 13-29.
- 73) C.V. Cagle, "Bonding Various Substrates", in: Cagle (Ed), Handbook of Adhesive Bonding (ref.27), pp 11.14-11.21.
- 74) S. Vishu, Handbook of Plastics testing Technology, John Wiley & Sons, New York, 1984.

- 75) C.L. Brett, "The Effect of State of Cure on Bond Performance", in: Allen (Ed), Adhesion, V.3, (ref.70), pp 53-64.
- 76) D. Feldman, Natural and Accelerated Weathering of Some Polyblends, J. Appl. Polym. Sci., V.26, 1981, pp 3493-3501.
- 77) D.H. Kaelble, "Physical and Chemical Properties of Cured Resins", in: May & Tanaka (Eds), Epoxy Resins: Chemistry and Technology, (ref.3), pp 327-369.
- 78) G.W. Miller, "Adhesion and the Glassy State", in: R.L. Patrick (Ed), Treatise on Adhesion and Adhesives, Marcel Dekker Inc., New York, 1973, pp 127-158.
- 79) E.W. Garnish & C.G. Haskins, "The Effect of Surface Conditions when Bonding with Epoxy Adhesives", in: D.J. Alner (Ed), Aspects of Adhesion, University of London Press, 1969, pp 259-278.
- 80) J.C. Bolger, "Structural Adhesives for Metal Bonding" in: Patrick (Ed), Treatise on Adhesion and Adhesives, (ref.78), pp 10-16.
- 81) P. Davies, Epoxy Structural Adhesives, Civil Engineering, Aug. 1976, pp 77-81.
- 82) R.J. Lark & G.C. Mays, "Epoxy Adhesive Formulation: Its Influence on Civil Engineering Performance", in K.W. Allen (Ed), Adhesion, V.9, Elsevier-Applied Science Publishers, London, 1985, pp 95-110.
- 83) C.L. Mahoney, Epoxide-Based Adhesives Offer Strength and Endurance, Adhesives Age, May 31, 1986, pp 309-313.
- 84) J.J. Bickerman, The Science of Adhesive Joints, 2nd ed., Academic Press, 1968, pp 309-313.
- 85) J.M. Plecnik et al, Temperature Effects on Epoxy Adhesives, ASCE, J. Structural Division, Jan. 1980, pp 99-113.
- 86) M. Fisher & R. Schmid, "Shear Strengths of Bonds and Bulk Properties of Adhesives", in: Allen (Ed), Adhesion, V.3, (ref.70), pp 31-52.
- 87) M. Cizmecioglu et al, Influence of Cure Conditions on Glass Transition Temperature and Density of an Epoxy Resin, J. Appl. Polym. Sci., V.36, 1986, pp 6177-6190.

88) R.E. Wetton, "Dynamic Mechanical Thermal Analysis of Polymers and Related Systems", in: Wetton et al (Eds), Dynamic Mechanical Thermal Analysis of Materials, J. Phys. Colloq., 1985, pp 179-221.

89) A.R. Greenberg, Influence of Filler Chemistry on the Glass Transition Behavior of a Polymer Matrix Composite Material, J. Mater. Sci. Letters, V.6, 1987, pp 78-80.

90) P.S. Gill, Thermal Analysis of Epoxy Prepreg Materials, Thermal Analysis Application Brief, DuPont Instruments Publication.

91) J. Haslam et al, Identification and Analysis of Plastics, Heiden, London, 1980, p 687.

92) Hummel-Scholl, Infrared Analysis of Polymers, Resins and Additives - an Atlas, Wiley Interscience Publishers, New York, 1969, spectrums 1029-1036.

## APPENDIX A

### Types of Curing Agents for Epoxy Polymers. (DOW Chemicals of Canada Ltd.)

Type	Advantage	Disadvantage	Application <sup>1</sup>
Polysulfides	Moisture insensitive Quick set time Flexible	Odor Poor elevated temperature performance	Adhesives, sealants
Aliphatic amines	Convenience Room temperature cure Low viscosity Low formulation cost	Critical mix ratios Strong skin irritant High vapor pressure Blushes	Civil engineering, adhesives, grouts, castings and electrical encapsulation
Polyamides	Convenience Room temperature cure Low toxicity Good flexibility or resilience Good toughness	Higher formulation cost High viscosity Low heat resistance Low vapor pressure	Civil engineering, adhesives, grouts, castings, coatings
Amidoamines	Reduced volatility Convenient mix ratios Good toughness	Poor elevated temperature performance Some incompatibility with epoxy resin	Construction adhesives, concrete bonding, troweling compounds
Aromatic amines	Moderate heat resistance Good chemical resistance	Solids at room temperature Long elevated temperature cure schedules	Filament wound pipe, electrical encapsulation, adhesives
Dicyandiamide	Latent cure Good elevated temperature properties Good electrical properties	Long elevated temperature cure Insoluble in resin	Powder coatings, electrical laminates, one-component adhesives
Catalytic	Extremely long pot life High heat resistance	Long elevated temperature cure schedules Poor moisture resistance	Adhesives, electrical, encapsulation, powder coatings, electric laminates
Anhydrides	Good heat resistance Good chemical resistance	Long elevated temperature cure schedules Critical mix ratios	Filament wound pipe, electrical encapsulation and adhesives
Melamine formaldehyde	Good hardness and flexibility One-package stability Solvent-free systems	Elevated temperature cure	Waterborne coatings, container and deco finishes
Urea formaldehyde	Good film color One-package stability Good intercoat adhesion	Elevated temperature cure	Fast bake enamels, primers and topcoats
Phenol formaldehyde	Good elevated temperature properties Good chemical resistance Good hardness and flexibility	Solid Poor weatherability	Powder coatings, molding compounds

<sup>1</sup>Applications listed for the various types of curing agents are general guidelines only and are not intended to be restrictive. Certain types of epoxy curing agents have broad use in a range of applications.

## APPENDIX B

### Typical Effects of Fillers on Properties of Epoxy Polymer Systems (DOW Chemicals Canada Ltd.)

Desired Effects	Improved Thermal Conductivity	Improved Machinability	Improved Abrasion Resistance	Improved Impact Strength	Improved Electrical Conductivity	Improved Thixotropic Response
Additives	calcium carbonate, calcium silicate, powdered aluminum, or copper	alumina, flint powder, carborundum, silica or molybdenum disulfide	chopped glass	mica, silica powdered or flaked glass	metallic fillers, or alumina	colloidal silica, Bentonite clay
Cost	D	D	N	D	D	I
Exotherm	D	D	D	D	D	D
Thermal Conductivity	I	I	I	I	I	D
Heat Deflection Temp	I	I	I	I	I	N
Machinability	I	D	D	D	I	I
Abrasion Resistance	N	I	I	I	D	D
Impact Strength	D	D	I	D	D	N
Tensile Strength	D	N	I	D	N	N
Flexural Strength	D	N	I	D	N	N
Compress Strength	D	N	I	D	N	N
Dielectric Constant	I	I	I	I	I	N
Thixotropy	N	N	N	N	N	I

D — Decrease  
I — Increase  
N — Essentially no effect