

CHAPTER III

THEORY

1. Introduction to polyurethanes

Polyurethanes plays vital role in many industries-from ship building to footwear; construction to cars. They appear in an astonishing variety of forms, a variety that is continuously increasing. The properties of polyurethane can be varied over a very wide range by selecting the raw materials, their relative proportions and processing conditions, and the apparent density of the product. [Wirpsza, 1993]

Polyurethanes can be manufactured in an extremely wide range of grades, in densities form 6 kg/m^3 to 1220 kg/m^3 and polymer stiffness from very flexible elastomers to rigid, hard plastics. [Wood, 1987]

1.1 Types of polyurethanes.

A consideration of particular properties of certain grades of polyurethanes and the way in which these are used will serve to demonstrate their versatility. It can be classified to three types as follows. [Wood, 1987]

1.1.1.Foams

By itself, the polymerization reaction produces a solid polyurethane. Foams are made by forming gas bubbles in the polymerizing mixture. This is called "blowing".

Foam manufacture can be carried out continuously, to produce continuous laminates or slabstock, or discontinuously, to produce moulded items or free-rise blocks.

In quantity terms, there are three particularly significant types: low density flexible foams, low density rigid foams and high density flexible foams. [Wood, 1987]

1.1.2.Solid polyurethanes.

1.1.2.1 Solid polyurethanes elastomers. Most polyurethane elastomers have excellent abrasion resistance with good resistance to oil, petrol and many common non-polar solvents. They may be tailored to meet the needs of specific applications, as they may be soft or hard, of high or low resilience, solid or cellular form etc.

1.1.2.2 Adhesive, binders, coatings and paints. Polyurethanes are also used in flexible coatings for textiles and adhesives for films and fabric laminates. Polyurethane paints and coatings give the highest wear resistance to surfaces such as floors and the outer skin of aircraft. They are also becoming widely used for high quality finishes on automobiles.

1.2. Definitions

A urethane is essentially an ester of carbamic acid or substituted acid with the general formula: [Olding & Chem, 1987]

Figure 3.1 Polyurethane structure



Those urethanes, that find application in surface coatings, are all polyurethanes, which are obtained by reacting a polyisocyanate with a polyol. The properties of polymer are varied from hard to soft depending upon the selection of precursors and on the employed ratio. Polyurethanes contain other molecular species obtained by means of side reaction.

Polyurethanes are produced by the reaction of a di-isocyanate with a polyhydric alcohol on the lines of the mono-molecular reaction illustrated below:

Figure 3.2 Polyurethane reaction



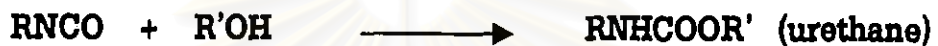
This reaction is exothermic. The rate of the polymerization reaction depends on the structures of both the isocyanate and the polyol. Aliphatic polyols with primary hydroxyl end-groups are the most reactive compared with other polyols.

1.3. Reactions of isocyanates

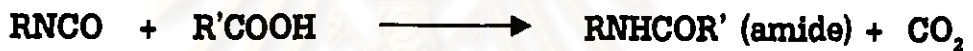
The isocyanate group (-NCO) can react with any compounds containing in active hydrogen atoms and diisocyanates may therefore be used to modify many other products. [Olding & Chem, 1987]

Figure 3.3 Reaction of isocyanate

Reaction with an alcohol yields urethane:



Reaction with a carboxylic acid yields an amide:



Reaction with an amine yields a urea:



Reaction with water produces a carbamic acid:

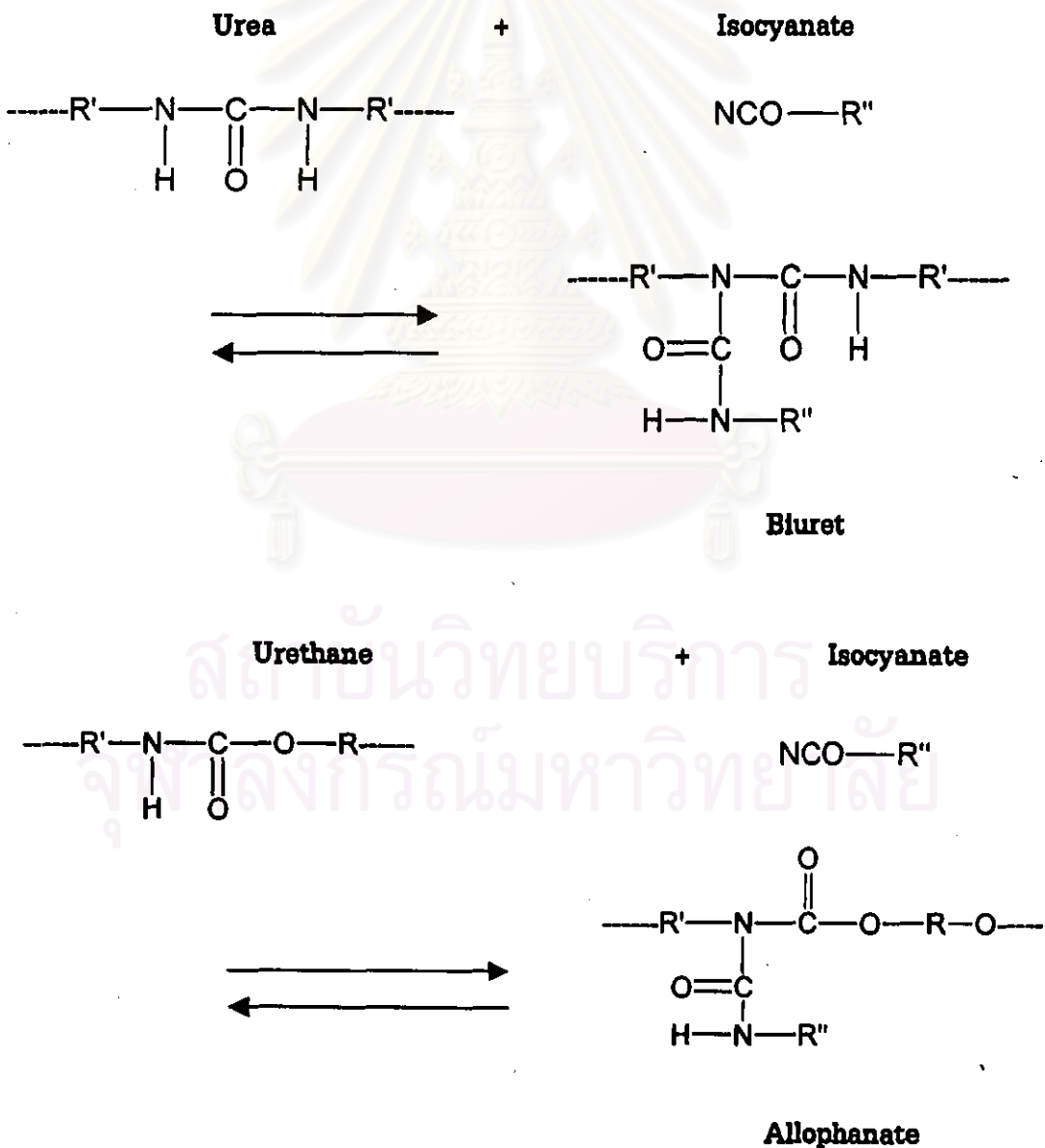


The unstable carbamic acid breaks down into an amine and carbon dioxide. The amines react with a further molecule of isocyanate to form urea. This last reaction is one way of introducing gas to form foams but it is a reaction to be avoided in surface coatings.

1.4 Secondary reactions of isocyanates.

Isocyanates may react, under suitable conditions, with the active hydrogen atoms of the urethane and urea linkages to form biuret and allophanate linkages, respectively. Both reactions are crosslinking reactions. The reaction of isocyanates with urea groups is significantly faster and occurs at a lower temperature than that with urethane groups. [Wood, 1987]

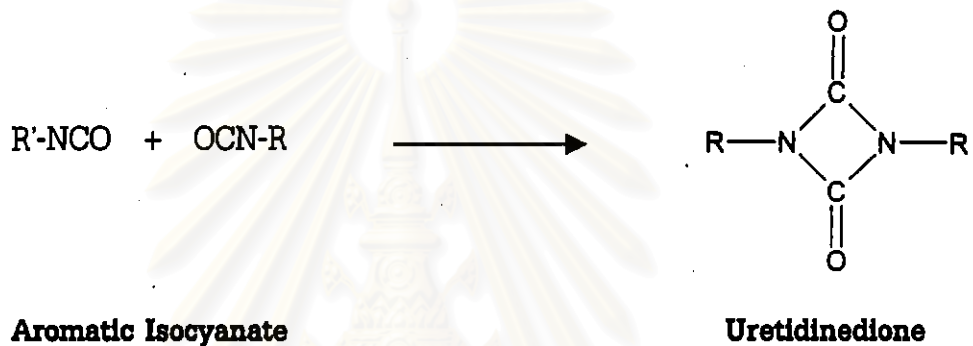
Figure 3.4 Secondary reaction of isocyanate



1.5 Isocyanate polymerization reactions

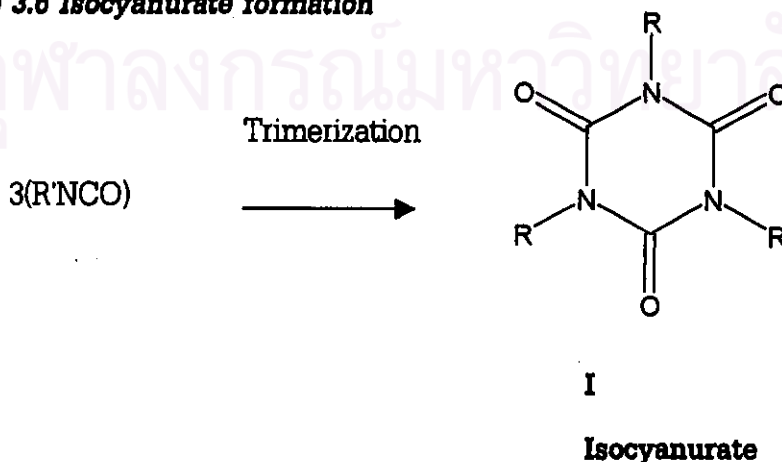
Isocyanates form oligomers, especially in the presence of basic catalysts, giving uretidinediones (commonly called dimers), and isocyanurates (commonly called trimers). Dimer formation arises only from aromatic isocyanates and it is inhibited by ortho substituents. [Wood, 1987]

Figure 3.5 Uretidinedione formation



Isocyanates are formed on heating both aliphatic or aromatic isocyanates. The reaction is accelerated by basic catalysts. Isocyanurate formation in polyurethane manufacture gives very stable branch point as, unlike the uretidenedione, biuret, allophanate and urethane linkages, the reaction is not easily reversed.

Figure 3.6 Isocyanurate formation





2. Polyurethane Coatings

In manufacturing of the polyurethane coatings, it needs to be consisted of two main parts, diisocyanate and polyol.

2.1. Diisocyanate

2.1.1. Aliphatic Diisocyanates

Aliphatic diisocyanates are used in the manufacture of color-stable polyurethanes for coatings and elastomer applications. Aliphatic diisocyanates afford polyurethane coating with outstanding weatherability. HDI and IPDI, are mainly used for rigid crosslinking coatings. Some types of aliphatic isocyanate are demonstrated here. [Ulrich, 1996]

2.1.1.1 Hexamethylene Diisocyanate (HDI)

Hexamethylene diisocyanate (HDI) is the classical aliphatic diisocyanate developed by Bayer prior to World war II. The major commercial products derived from HDI are biurets and isocyanurates. [Ulrich, 1996]

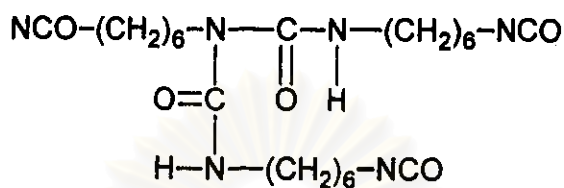
Figure 3.7 Structure of HDI



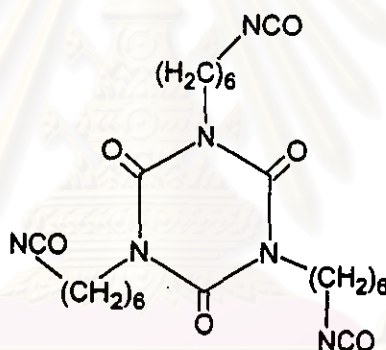
Because of its high vapor pressure, HDI is converted into derivatives, such as biurets or triisocyanurates, prior to its usage in coating applications. The

structure of HDI biuret shown below. These polyfunctional isocyanates give coatings with good color retention and weather resistance.

Figure 3.8 HDI-Biuret and HDI-Isocyanurate



HDI-Biuret



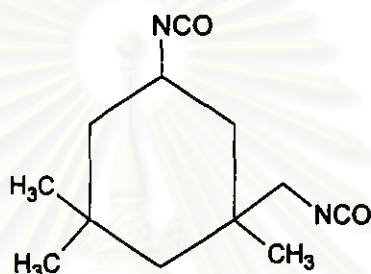
HDI-Isocyanurate

HDI, hexamethylene diisocyanate, being aliphatic, does not produce the same degree of yellowing comparing with TDI and MDI, but it is less reactive and the urethanes made from it are not as hard as those produced from aromatic isocyanates.

2.1.1.2 Isophorone Diisocyanate (IPDI)

The other major aliphatic diisocyanate for coating applications is isophorone diisocyanate (IPDI). The isophorone chemistry of IPDI chemistry is developed by chemische Werke Huls in Germany. [Ulrich, 1996]

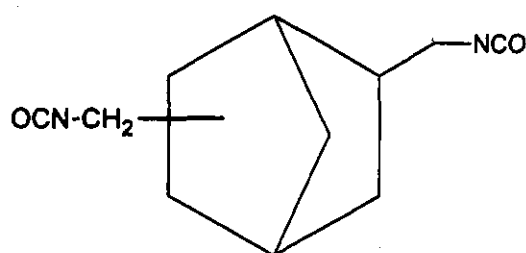
Figure 3.9 Structure of IPDI



IPDI has a primary and a secondary isocyanate group which facilitates derivative formation. Under certain conditions the primary isocyanate group will react faster than the secondary group.

2.1.1.2 Norbornanediisocyanate (NBDI)

Norbornanediisocyanate (NBDI) produced by Mitsui Chemical Inc. is a new cycloaliphatic diisocyanate, and is a suitable raw material for the production of light stable and weather resistance polyurethanes. It is low viscous, clear colorless to slightly pale yellow liquid with a weak specific odor.

Figure 3.10 Structure of NBDI

The reactivity of the two isocyanate groups is equal. It is similar to Hexamethylene diisocyanate (HDI), and is higher than Isophorone diisocyanate (IPDI).

As NBDI has a stiff norbornane structure, it would be expected that the polymers based on NBDI show higher thermal stability and hardness than ones based on isocyanates with a linear chain structure such as HDI.

NBDI can be used as the raw material for the production of non-yellowing polyurethane, polyurea, or polyisocyanurate resins. NBDI is used in the form of adducts with alcohols, blocked isocyanates, or tris-isocyanato-isocyanurates. The main fields of application are paintings and coatings.

2.1.2. Aromatic Diisocyanates

More than 90 % of the total world production of isocyanates is accounted for polymeric MDI (PMDI), its coproduct 4,4'-biphenyl-methane diisocyanate (MDI) and toluene diisocyanate (TDI). The major applications for TDI include flexible polyurethane foams, cast elastomers and surface coatings, while PMDI is used in

the manufacture of rigid polyurethane foam. MDI is mainly used in the manufacture of polyurethane elastomers. [Ulrich, 1996]

2.2 Polyols

The other component in the production of a polyurethane is a polyol. A wide range of polyols is used in polyurethane manufacture. The molecular weight and functionality of the polyol are the main factors, but the structure of the polyol chains is also important.

The *hydroxyl value* is used to measure the concentration of isocyanate-reactive hydroxyl groups per unit weight of the polyol and is expressed as mg KOH/g. Polyols sold for use in polyurethanes are invariably characterized by hydroxyl value as this is convenient for calculation of the stoichiometric formulation. The measured hydroxyl value of a polyol is related to its molecular weight and functionality:

$$\text{Hydroxyl Value} = \frac{56.1 \times \text{functionality} \times 1000}{\text{molecular weight}} \quad (3-1)$$

(mg KOH/g)

2.1.2 Polyester Polyols

The most commonly employed polyols are hydroxyl terminated polyesters based in straight chain aliphatic dibasic acids such as adipic, plus special polymeric polyols. Both types of polyols produce very tough polyurethane films under the proper curing conditions, but it is essential to ensure the complete

freedom from water contamination, not only in the primary reactants but also in other components that may be added, such as pigments. Any water which does enter the reaction will form carbon dioxide with the isocyanate groups and this carbon dioxide is unlikely to escape but rather it will remain trapped. These remarks apply to two systems, they are not appropriate to one part, moisture cured urethanes.

2.2.2 Polyether Polyols

Polyether polyols produced by treating polyhydric initiators with ethylene or propylene oxide are less costly than polyesters and they have the advantage of being less susceptible to hydrolytic degradation. However, despite their popularity in polyurethane foam systems they are less popular in the surface coatings.

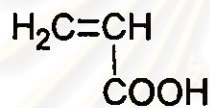
2.2.3 Acrylic polyols

The most popular in two pack surface coatings are the hydroxy functional acrylics and acrylics modified polyesters. These polyols offer good colour stability and a reasonably broad range of physical properties. They possess good solubility in ester solvents while aromatics such as xylene may be used as diluents. The colour stability is best when using aliphatic isocyanates or their adducts, but it is often acceptable to use TDI adducts in the less critical applications. Acrylic polyol can be classified into many different types. Only thermosetting acrylic polyol is mentioned here.

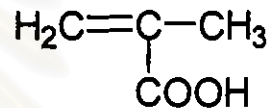
3. Synthesis acrylic polyol [Oldring and Chem, 1987]

There are two series of related monomers derived from acrylic acid and methacrylic acid. These monomers are termed acrylates and methacrylate respectively and polymers derived from either species are known collectively as acrylic resins. Typical acrylate and methacrylate monomers are shown below:
[Oldring & Chem]

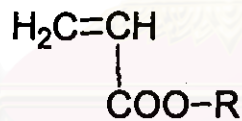
Figure 3.11 Acrylic monomer



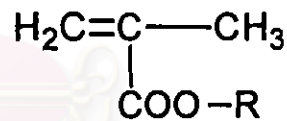
Acrylic acid



Methacrylic acid



Acrylic ester



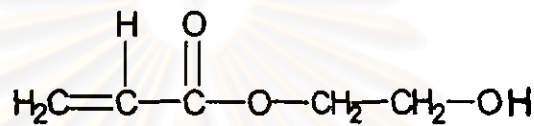
Methacrylate ester

Various types of functionality can be built into acrylic or methacrylic monomers and thus they are introduced into the final acrylic resin. The functional groups of acrylic monomers which are commercially available and used to give a cross-linking capacity are hydroxyl, carboxyl, amide and epoxy. At this point, hydroxyl functional acrylic polyol is interesting.

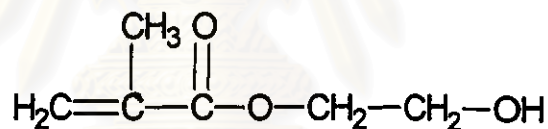
3.1 Hydroxyl monomer

Hydroxyl functionality is usually provided by hydroxy acrylates, or alternatively methacrylates which combine a double bond and a reactive hydroxyl group in the same molecule.

Figure 3.12 Hydroxyl acrylic monomer



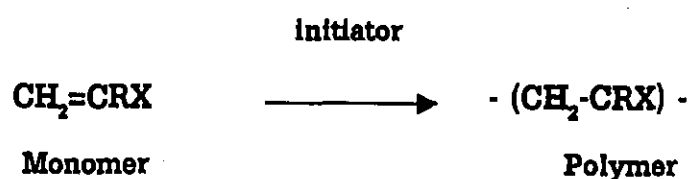
2-hydroxy ethyl acrylate (HEA)



2-hydroxy ethyl methacrylate (HEMA)

3.2 Mechanism of polymerization

Vinyl and acrylic monomers undergo addition polymerization to form long chains.:



Unlike condensation polymerization, addition polymerization leads to the production of high molecular weight polymers. There is also no release of water or other small molecules characteristic of condensation reactions. Polymerization can be considered to occur in three distinct and separate stages.

1. **Initiation** : Start of growth of the polymer chain by the attack of an initiation species on the double bond of the vinyl compound.
2. **Propagation** : Growth of the polymer chain by successive additions of monomer units.
3. **Termination** : Deactivation of the polymer chain terminating the further addition of monomer units.

3.3 Solution polymerization

This technique involves the polymerization of monomer in the presence of an organic solvent. In order for this technique to be effective both monomer and polymer must be soluble in the chosen solvent. A mixture of monomer, initiator, solvent (and chain transfer agent when low molecular weight is required) are heated together up to the reaction temperature, which is usually the reflux temperature of the solvent, or solvent mixture. Polymerization of the monomer takes place to give a solution of polymer in the solvent. The polymer solution can be used directly in surface coating systems either on thermoset, thermoplastic types, or in conjunction with other resins as co-cure systems

3.3.1. One shot process

This involves charging all the reactants together with solvent, initiator and modifier into the reactor and heating to the optimum breakdown temperature of the initiator employed. As propagation occurs, the temperature of the reactants is allowed to rise to the reflux temperature of the solvent present.

The reactants are then held at this temperature under reflux using the latent heat of vaporization of the solvent and reactor water cooling to remove excess heat of reaction.

The course of the reaction is monitored by viscosity and non-volatile content measurements, and when conversion of the monomer is complete the reactor is cooled. A wide molecular weight distribution is obtained using this technique. Since the concentration of initiator and modifier fall as the reaction proceeds, polymer chains produced later in the process are not subjected to the same frequency of termination reactions and are thus much higher in molecular weight than polymer produced earlier in the process.

3.3.2. Drip feed process (Continuous monomer addition)

This involves 'drip-feeding' a premixed charge of monomer, modifier and initiator into solvent has been preheated to reaction temperature. Ideally as the premix droplet comes in contact with the hot solvent the initiator decomposes to free radicals which immediately initiate propagation of the monomer. The polymer formed is dissolved in the solvent and is dispersed. In practice reaction does not occur immediately when the monomer contacts the hot surface and there is a slight build up initially of unreacted monomer. However, this can be

maintained at a relatively low concentration by correct choice of reaction conditions. The addition of a small amount of extra initiator after the premix addition is completed, is sufficient, normally, to complete the conversion of all the monomer present.

At any time during the polymerization the relative amounts of monomer, initiator, modifier and solvent are all reasonably constant. As a result polymers with a narrow molecular weight distribution are formed.

The premix feed rates are the critical factor in producing poly-dispersed material without the building up of unreacted monomers which could lead to an uncontrollable exothermic reaction and certainly to the wide spread of molecular weight. Therefore, the feed rates have to be carefully determined during laboratory process development. The commercial feed rates vary between two and ten hours, depending on the monomer type and the reaction conditions. Where the highly reactive monomers or the initiators with very short $t_{1/2}$ are employed, it is usual to keep the initiator separate from the monomer premix and add it separately at a predetermined rate throughout the monomer addition. This prevents the possibility of initiation occurring in the premix tank.

The usage of the drip feed process allows more latitude in the preparation of constant composition copolymers. By constantly varying the composition of the monomer feed during addition, the differences in reactivity between monomer types can be partly countered to produce copolymers approaching constant composition.

In practice, for the surface coating polymers, constant copolymer composition is not required. Since most copolymers are manufactured by the batch process, the overall compositions of the final solution are constant and it is

of little consequence that individual polymer chains may not have exactly the same monomer unit compositions.

The differences between wide and narrow molecular weight distribution (i.e. polydispersed and monodispersed) polymer solutions are generally evident in their rheology and in the film performance characteristics. In general, polydispersed systems are more flexible and have lower solution viscosity. However, since these properties are also influenced by other factors such as copolymer composition, solvent type and overall molecular weight. Solution polymers made by either process are acceptable, although the drip-feed process allows the stricter control on process conditions to be exercised and this is often desirable when dealing with highly exothermic chemical reactions and when consistency product is required.



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4.Type of Polyurethane Coatings

Isocyanates are used in many different ways in coatings. Essentially, any coating in which an isocyanate is used is called a urethane or polyurethane coating even though in some cases the primary cross-links are urea or other linkages rather than urethane groups. [Wick, Jones and Pappas, 1992]

Polyurethane coating can be classified in many ways. In this manner, there are three types which are presented as follow.

4.1. One pack polyurethane coatings

4.1.1 Uralkyds (Urethane alkyds)

Uralkyds are also called "urethane alkyds" or "urethane oils." In effect, they are alkyd resins in which a diisocyanate, usually TDI, has fully or partly replaced the PA usually used in the preparation of alkyds. Analogously to alkyds, uralkyds dry faster than the drying oil from which they were made since they have a higher average functionality.

Two principal advantages of uralkyd over alkyd coatings are superior abrasion resistance and resistance to hydrolysis. Disadvantages are inferior color retention (when TDI is used) of the films, higher viscosity of resin solutions at the same percent solids, and somewhat higher cost than alkyds.

The largest use of uralkyds is in architectural coatings. Most so-called varnishes sold to the consumer today are based on uralkyds; they are not really varnishes in the original sense of the word. Uralkyd varnishes are used as transparent coatings for furniture, woodwork, and floors, applications where good

abrasion resistance is important.

4.1.2 Moisture Curing Polyurethane Coatings

Another important class of polyurethanes is moisture curing coatings, which crosslink under ambient conditions by reaction of isocyanate groups with atmospheric water. The resins used as binders have multiple isocyanate groups per molecule. The coatings are stable when stored in the absence of water but cross-link after application because of the reaction of the isocyanate groups with water to form amines which then, in turn, react with another isocyanate to form substituted urea linkages.

Moisture cure urethane coatings are used in applications such as floor coatings where exceptional abrasion resistance and hydrolytic stability are important. Since the urea groups also can form intermolecular hydrogen bonds, presumably they can affect resistance to mechanical stress similarly to urethane groups.

Moisture cure coatings have the advantage that they are less susceptible to errors in application than the two-package coatings, where there is a chance of wrong ratios of packages affecting the stoichiometric ratios. A disadvantage is that the solvents, pigments, and other coatings components must be essentially water-free. The use of moisture cure coatings is primarily in clear, gloss coatings since it is very costly to remove adsorbed water from commercial pigments.

4.1.3 Blocked Isocyanates (baked type) polyurethane.

It was recognized in early work on utilizing isocyanates in coatings that there would be major advantages to developing systems that could be supplied as one-package coatings having minimal toxic hazard. These objectives led to work on "blocked isocyanates," an approach taking advantage of the fact that many of the addition reactions that isocyanates undergo are reversible. In this approach a di- or polyisocyanate is reacted with certain monofunctional active hydrogen compounds and the adduct (a blocked isocyanate) is formulated in to a coating with a polyfunctional hydroxy-substituted resin. The coating is stable at ambient temperature, but when it is baked the monofunctional reactant is released (and usually volatilized), and the polyfunctional resin reacts with the polyisocyanate to form cross-links. Aminefunctional resins, which are more reactive than hydroxy-functional resins, are also used in certain applications.

Synthesis of a blocked isocyanate may be accomplished as shown, where B-H represents the blocking group:

Figure 3.13 Unblocked reaction



Many blocked isocyanates are sufficiently stable in the presence of water at storage temperatures that they can be used in water-borne coatings. However, the usage of blocked isocyanates has at least two drawbacks: relatively high temperatures are required for cross-linking with polyol reactants, negating one of the major advantages of isocyanate cross-linked coatings, and, in some cases, release of the blocking agent causes a pollution problem.

4.2. Two-Package (2K) Polyurethane Coatings

The largest volume of urethane coatings is two-package (2K) coatings that are mixed just before application. One of the packages contains the polyol, pigments, solvents, catalyst(s), and additives; the other contains the polyisocyanate and moisture free solvents. Sometimes the catalyst is in a separate third package so that cure rate can be adjusted for variations in ambient conditions.

Virtually any class of polyhydroxy-functional resin can be used. Hydroxy-terminated polyester and hydroxy-substituted acrylic resins are the most common coreactants. In general terms, polyesters permit higher solids, greater solvent resistance, and better adhesion to metals while acrylics provide faster dry, lower cost (since the equivalent weight is usually higher than that of polyesters resulting in the need for less of the more expensive isocyanate), and better exterior durability resulting from superior hydrolytic and photochemical stability.

A variety of other coreactants can be cross-linked with isocyanates. Since all alkyd resins have unreacted hydroxyl groups, their rate of dry can be accelerated by adding a polyisocyanate like the isocyanurate trimer of IPDI just before application. Nitrocellulose (shipped wet with xylene instead of ethyl or isopropyl alcohol) is used in formulating cross-linking furniture lacquers. While hydroxy-terminated polyethers are widely used in urethane foams, they are not widely used in coatings applications since the resulting coatings show high moisture vapor permeability, relatively poor exterior durability, and are soft as a result of the low T_g of the polyethers. Bisphenol A epoxy resins are used; the cross-linking reaction is between the hydroxyl groups and the isocyanate. Ketimine derivatives of polyamines can be used in moisture cure coatings, but

they afford better properties in baking coatings, possibly due to the formation of cyclic ureas.

Polyisocyanate-polyol coatings for maintenance paint applications are generally cured at ambient temperatures, while those for automobile refinishing and aircraft applications are cured at ambient or modestly elevated temperatures. Since one wishes in many cases to have coatings with a T_g somewhat above the curing temperature, selection of the combination of polyisocyanate and polyol that will provide the appropriate final T_g becomes critical. If a polyisocyanate with relatively flexible aliphatic chains such as the isocyanurate of HDI is used, it should be used with a relatively high T_g acrylic or polyester. On the other hand, if a polyisocyanate that yields relatively rigid cross-linked sections is used, such as the trimethylolpropane-TMXDI prepolymer, a significantly lower T_g acrylic or polyester is required.

If the T_g of the partially reacted system is near the temperature at which the cross-linking must occur, the rate of urethane formation will become mobility controlled and the cure rate may be very slow. If the T_g of the fully reacted system is somewhat above the cure temperature, the reaction will virtually stop before the cross-linking reaction has gone to completion. This problem is, of course, reduced or eliminated by baking at temperatures above the ultimate T_g of the fully reacted coating.

An important variable in formulating two-package polyisocyanate-polyol coatings is the ratio of $N=C=O/OH$ used. In ambient cure systems, it is often found that a ratio of the order of 1.1:1 gives better film performance than a 1:1 ratio. A probable reason is that part of the $N=C=O$ groups react with water from the solvent, pigment, or air to give urea cross-links. To the extent that this happens, two hydroxyl groups would be left unreacted for each water molecule if

the ratio were exactly 1:1; the use of excess $\text{N}=\text{C}=\text{O}$ minimizes residual unreacted hydroxyl groups. Pot life can also be affected by the reactant ratios.

In the case of aircraft finishes it is common to use $\text{N}=\text{C}=\text{O}/\text{OH}$ ratios as high as 2:1. The resulting reduced hydroxyl concentration gives a longer pot life. It is also possible that the high mobility of water and the high reactivity of the amine groups resulting from the water-isocyanate reaction favors faster reaction rates at higher T_g values than occurs with only the hydroxyl-isocyanate reaction.

There is always a compromise between pot life and curing time because reaction rates are governed by the laws of chemical kinetics. Several formulating variables are available to increase pot life with little, or at least small, effect on cure time. The concentrations of reactive groups should be kept as low as possible. Of course, this becomes more difficult as one formulates to higher and higher solids. As noted in the preceding paragraph, using mixed hydroxyl-moisture curing systems will help.

Since isocyanate-alcohol reactions proceed slowest in media with high levels of hydrogen-bond accepting groups, solvents should be selected to the extent possible, which are strong hydrogen-bond acceptors and resins should be designed, if possible, with low levels of hydrogen-bond accepting groups. After application, as the solvent evaporates, the medium will become less hydrogen-bond accepting and the reaction rate will increase accordingly. This strategy serves the purpose of both extending the pot life and promoting reactivity after application.

Assuming the system is to be catalyzed, organotin catalysts are generally preferable. As discussed, reaction rates are reported to be dependent on alcohol concentration to the one-half power with organotin catalysts and to the first

power with amine catalysts, which tends to reduce the pot life and extend the cure time in the latter case. Furthermore, since the effectiveness of tin catalysts is reduced by the presence of carboxylic acids, one can add a volatile acid such as acetic acid to the formula. It will inhibit the reaction during the pot life stage but will evaporate during application, and the inhibiting effect will disappear. Although carboxylic acids reduce the effectiveness of tin catalysts, they do catalyze the reaction of aliphatic isocyanates with alcohols.

If very fast cure at relatively low temperature is needed, reactive coreactants and/or high catalyst levels are used, and pot life will be short. Such formulations can be applied using special spray equipment in which the two packages are fed to the spray gun by separate pumps and mixed inside the gun just before they are sprayed. Care is required to assure that the proper ratios are fed and thoroughly mixed, and, of course, such spray equipment is expensive.

4.3. Other types

4.3.1 Linear Thermoplastic Polyurethanes

Thermoplastic polyurethanes are made by polymerization of oligomeric diols and diisocyanates to form high molecular weight, linear polymers. They are used as lacquers without cross-linking. Typical uses are abrasion-resistant coatings for flexible, heat-sensitive substrates (e.g., vinyl fabrics, leather, elastomers, textiles, and foams). The combination of high molecular weight and strong intermolecular hydrogen bonding gives good film properties but also means that large amounts of hydrogen-bond acceptor solvents are needed to achieve application viscosity; as a result the coatings have to be applied at very low solids. Dispersions of thermoplastic polyurethanes in water have been developed to permit reduction in VOC emission.

4.3.2 Hydroxy-Terminated Polyurethanes

Diisocyanates can be reacted with diols and triols at an $N=C=O/OH$ ratio of less than 1 to make hydroxy-terminated polyurethanes, which can then be cross-linked with MF resins. Compared to hydroxy-functional acrylic resins, they offer the advantage of abrasion resistance and the possibility of using lower molecular weight resins, at least partly offsetting the viscosity disadvantage of urethanes. Molecular weight reduction of acrylic resins made by conventional free radical initiated polymerization is limited by the problem of ensuring that at least two hydroxyl groups are present on each oligomer molecule. In the case of hydroxy-terminated polyurethanes (as with polyesters), all of the molecules will have two (or more) terminal hydroxyl groups even at very low molecular weight.

4.3.3 Water-Borne Urethane Systems

As with all other resin systems used in coatings, increasingly stringent VOC emission control regulations have motivated development of water-borne polyurethane systems.

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5. Tensile properties [Rosato, 1991]

The tensile test is the experimental stress-strain test method most widely employed to characterize the mechanical properties of materials like plastics, metals and woods. From any complete test record one can obtain important information concerning a material's elastic properties, the character and extent of its plastic deformation, and its yield and tensile strengths and toughness.

The standard ASTM D638 explains the internationally accepted method of conducting tensile test and defines the terms generally used throughout the industry. The tensile test according to ASTM D638 is mostly performed on the dumb-bell specimen. ASTM D882 is also used as a standard procedure for tensile testing of materials in the film or sheet form.

A tensile test involves pulling or stretching a test specimen at a uniform rate of extension and measuring the corresponding load applied. The tensile force is recorded as function of the elongation. Figure 3.14 (a) shows a typical plot of tensile force versus tensile elongation. Sometimes such plot is normalized with respect to specimen dimensions as in Figure 3.14 (b). Various tensile stress-strain curves are also shown in Figure 3.15. Explanation of the terminology used in tensile testing is as follows:

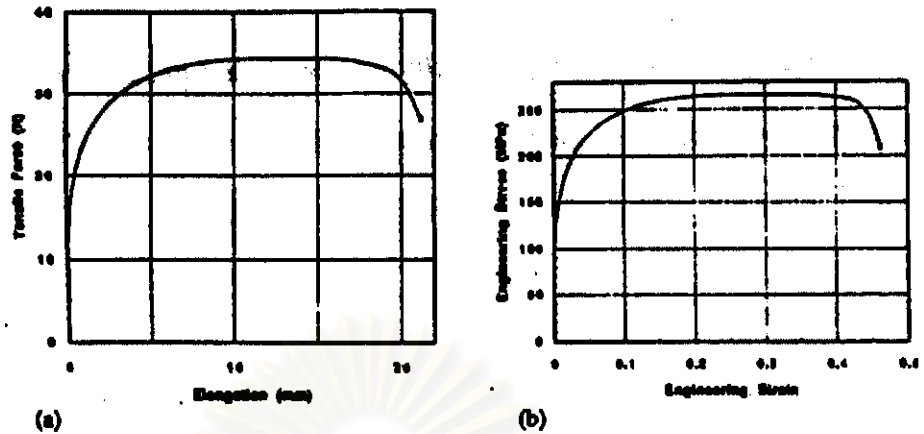


Figure 3.14 (a) Load-elongation curve from a tensile test and (b) corresponding engineering stress-strain curve [Han, 1992]

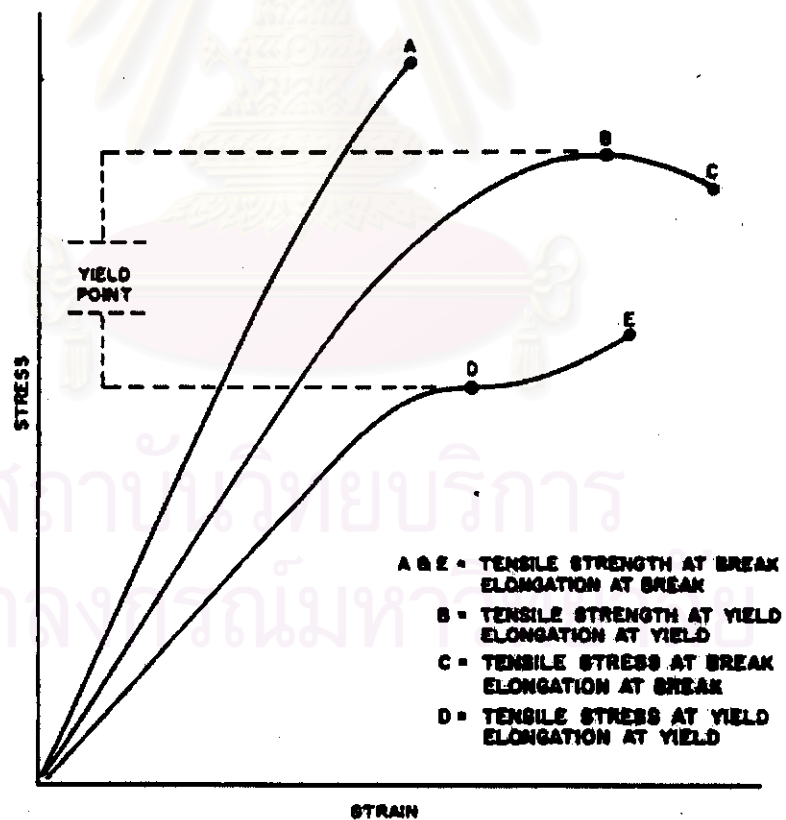


Figure 3.15 Tensile designations according to ASTM D638

5.1 Stress

Stress is the tensile load applied per unit of the original cross-sectional area at a given moment of the specimen. The standard unit of measure in Pa (Pascal) or pound per square inch (psi).

5.2 Strain

Strain is the ratio of elongation or deformation to the gauge length of the test specimen, that is, the change in length per unit of original length. It is expressed as a dimensionless ratio; mm/mm (in/in). As the strain is increased beyond the material's proportional limit, the specimen's elastic limit is reached.

However, below the elastic limit the material's behavior is elastic; that is, once it is unloaded, its recovery from deformation is essentially complete and instantaneous. Stressing the specimen above its elastic limit results in a degree of permanent set. This nonrecoverable stressing is called plastic strain. This strain is usually associated with plastics, but it is also seen in metals and other materials.

5.3 Elongation

The increase in the length of a test specimen that is expressed as a percentage of its extensometer gauge length is called its percentage of elongation.

5.4 Yield

The first point on a stress-strain curve at which an increase in strain occurs without any yield. The yield strength is generally established by constructing a line to the curve where stress and strain is proportional at a specific offset strain, usually at 0.2 percent. The stress at the point of intersection of the line with the stress-strain curve is yield strength at 0.2 percent offset. The example of the yield strength at 0.2 percent offset is shown in Figure 3.16.

5.5 Proportional Limit

A material's proportional limit is the greatest stress at which it is capable of sustaining an applied load without deviating from the proportionality of stress to strain. The proportional limit is shown in Figure 3.16.

5.6 Elastic Limit

The elastic limit of a material is the greatest stress at which it is capable of sustaining an applied load without any permanent strain remaining, once stress is completely released.

5.7 Tensile Strength

The maximum tensile stress sustained by a specimen during a tension test is its tensile strength. Again it is expressed either in Pa (Pascal) or Pound per square inch (psi). Tensile strength is shown in Figure 3.16.

When a material's maximum stress occurs at its yield point this is designated its tensile strength at yield. When the maximum stress occurs at a break, the designation is its tensile strength at break. In practice these differences are frequently ignored, often resulting in confusion in designs as to whether or not, for example, work hardening or cold drawing occurs before failure.

5.8 Modulus of elasticity

Most materials, including plastics and metals, have deformation proportional to their loads below the proportional limit. Since stress is proportional to load and strain to deformation, this implies that stress is proportional to strain. Hooke's law, developed in 1676, follows that this straight line in figure 3.16 of proportionally is calculated as.

$$\frac{\text{Stress}}{\text{Strain}} = \text{Constant}$$

The constant is called the modulus of elasticity (E) or Young's modulus, the elastic modulus, or just the modulus. This modulus is the slope of the initial portion of the stress-strain curve, normally expressed in terms such as MPa or Gpa (10^6 psi or Msi).

The modulus of elasticity is applied to describe the stiffness or rigidity of a plastic where its stress-strain characteristics depend on such factors as the stress or strain rate, and the temperature.



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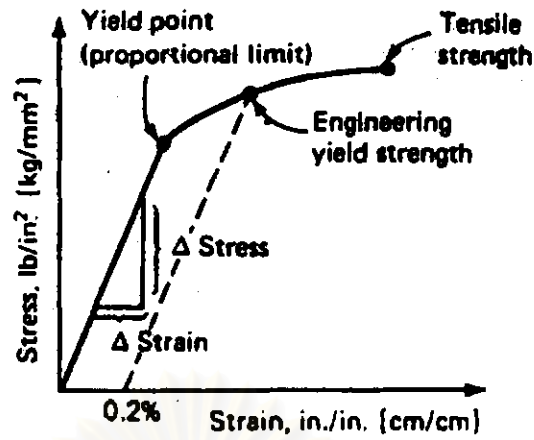


Figure 3.16 An example of the modulus of elasticity determined on the initial straight portion of the stress-strain diagram. [Rosato, 1991]

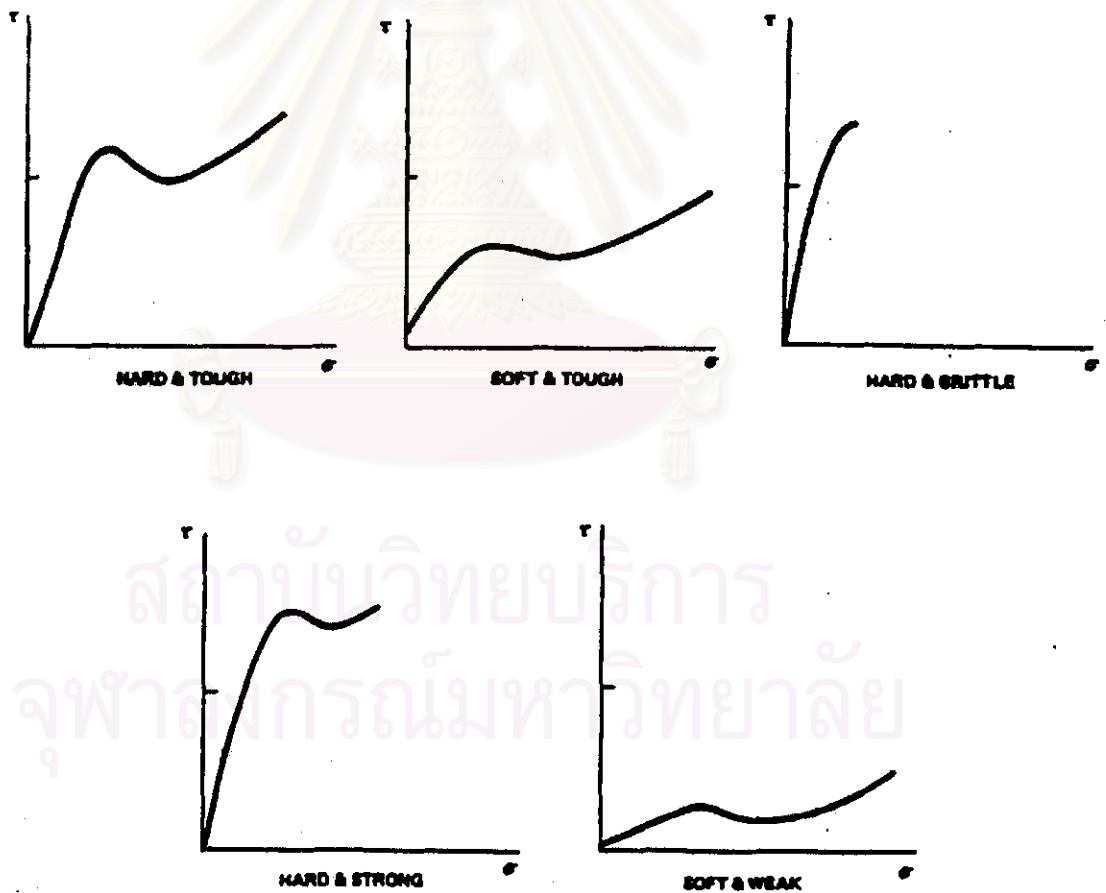


Figure 3.17 Tensile stress-strain curves for different plastics that relate the area under the curve to their toughness or physical properties [Rosato, 1991]

5.9 Area under the curve.

Generally, the area under the stress-strain curve is proportional to the energy required to break the plastic. It is thus sometimes referred to as the toughness of the plastic (Figure 3.17). However, there are types of behavior of plastics that are hard, strong, and tough.

5.10 Test Rates

The test rate or cross-head rate is the speed at which the moveable cross-member of a testing machine moves in relation to the fixed cross-member. The speed of such test is typically reported in cm/min, mm/min or in/min.

An increase in strain rate typically results in an increasing yield point and ultimate strength as shown in Figure 3.18 (a) and (b). For most rigid plastics the modulus does not change significantly with the strain rate. For softer thermoplastics, the theoretical elastic or initial tangent modulus is usually independent of the strain rate.

The elastic modulus and strength of both the rigid and the softer plastics each decrease with an increase in temperature as shown in Figure 3.18 (c). While in many respects the effects of a change in temperature are similar to those resulting from a change in the strain rate, the effects of temperature are relatively much greater.

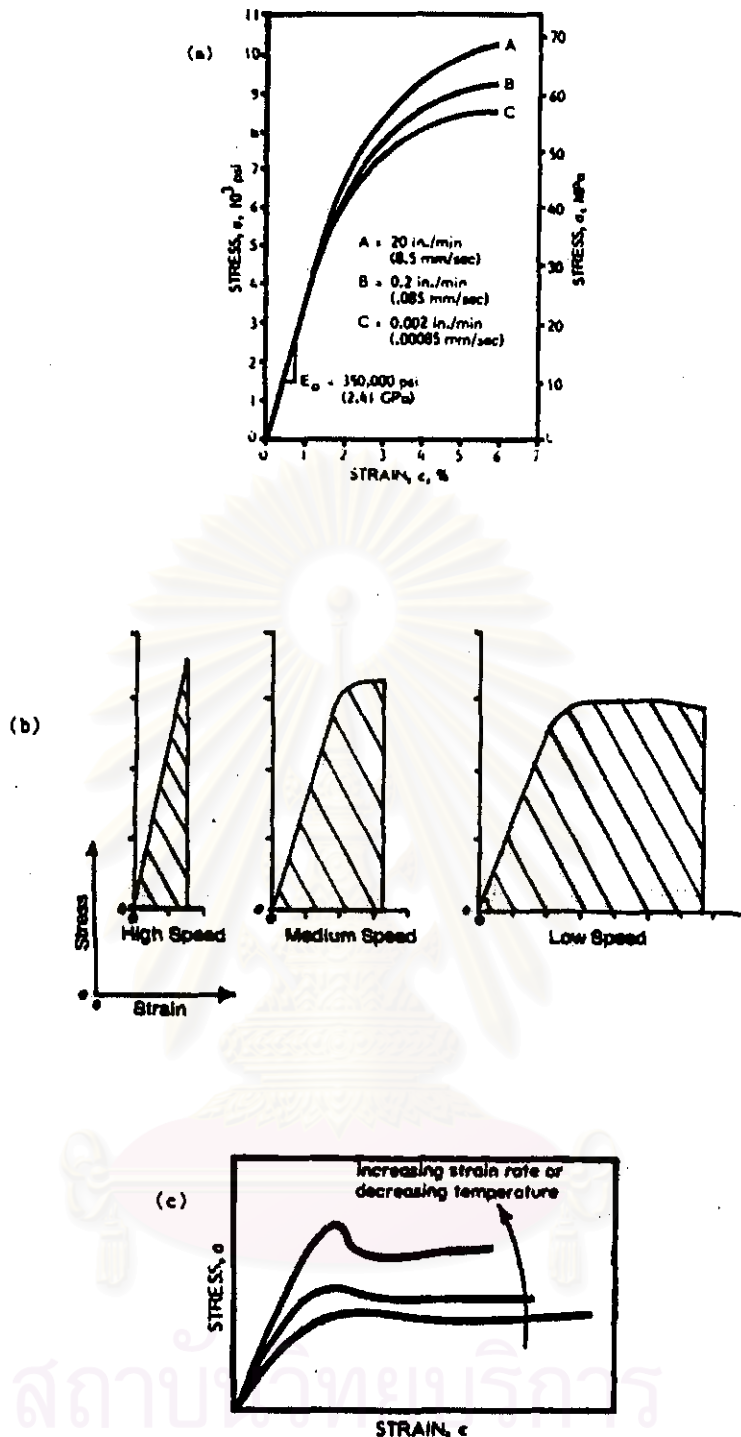


Figure 3.18 Example of the influence of different test rates and temperatures on basic stress-strain behaviors of plastics: (a) different testing rates as shown for polycarbonate, (b) effects of tensile speeds on the shapes of stress-strain diagrams, (c) a simplified version of the effects on curves of changes in test rates and temperatures. [Rosato, 1991]

5.11 Stress-strain behavior of coatings.

Coating, prepared for various end uses, exhibits a wide range of stress-strain behavior. It is not possible to give optimum property values for coatings in general because each end use has different property requirements. For example, a floor paint must be abrasion resistant. An automotive topcoat must be very resistant to loss of gloss and must withstand rapid impact of gravel without cracking. [Hill, 1987]

Structure of the binder can not be optimized for physical properties alone. The effect of binder structure on paint application and film formation must also be considered.

Modulus value of non-crystalline, unoriented glassy polymer do not vary over a wide range. A typical value is 2×10^{10} dynes/cm². Coatings that have T_g value well above room temperature will yield stress-strain slopes corresponding to approximately this value. All polymeric materials give modulus vs temperature plot at least somewhat similar to the one in figure 3.19. [Hill, 1987]

Crosslinks, even at low levels, eliminate the rubbery flow region because crosslinks prevent the long range, independent translational movement of polymer chains that are required for flow. As crosslink density increases, the rubbery plateau is shifted upwards because the average length of chain segments between junction points in the polymer network decreases. When the chain between the junction points are shorter, more force is required to elongate the sample. An increase in crosslink density has much smaller effect on modulus values in the glassy region than in the rubbery plateau region because the short range cohesive force that oppose elongation of glassy materials do not depend on the length of chain segment between junction point. [Hill, 1987]

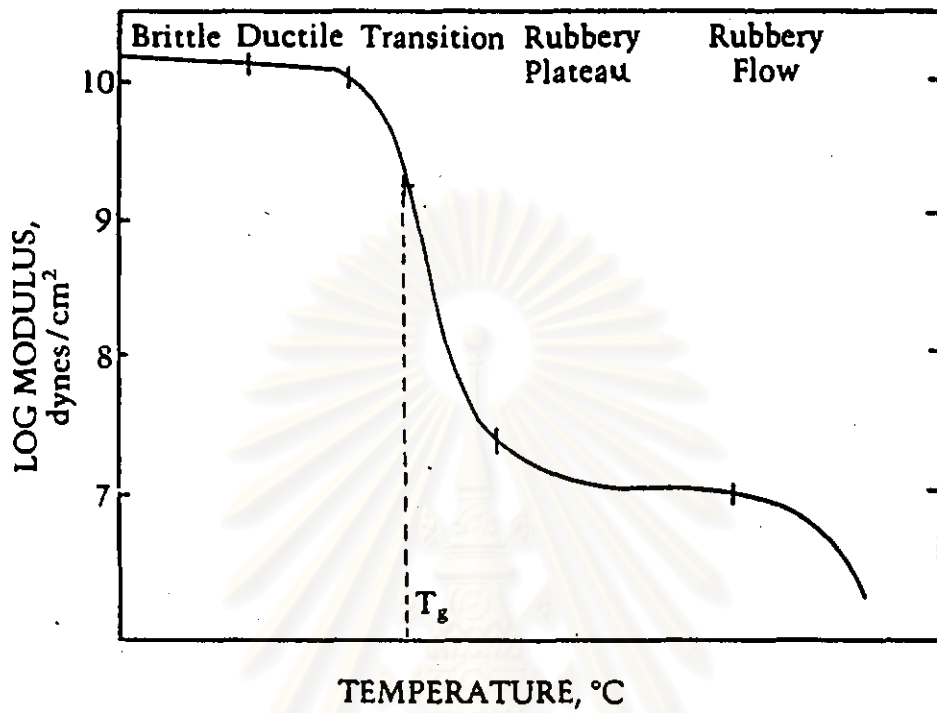


Figure 3.19 Dependence of modulus on temperature.

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6. Viscoelasticity [Hill, 1987]

The term "viscoelasticity" is made up of two parts. "Visco" comes from viscosity, a characteristic of liquids. Elasticity is a characteristic of solids. Viscoelastic materials exhibit some of the properties of liquids and some of the properties of solids. If there is sufficient force to cause response, the response will be either flow or deformation. A liquid undergoes flow and a solid undergoes deformation. In an ideal (Newtonian) liquid, the ratio of the force that opposes flow to the rate of flow is constant. The flow and deformation behavior of these ideal materials is very simple. Materials that are close to the Newtonian liquid side of the continuum in figure 3.20 can be called viscoelastic liquids. Many paints before and immediately after application fall into this category. Materials that are close to the Hookean solid side of the continuum can be called viscoelastic solids. The curing or film forming process consists of a shift along the continuum from left to right. Furthermore, properties observed for a given material can shift along the continuum depending on the manner in which a mechanical property determination is carried out. A rapid application of force will make the sample appear to be more solid-like. A slow application of force will make the sample appear to be more liquid-like.

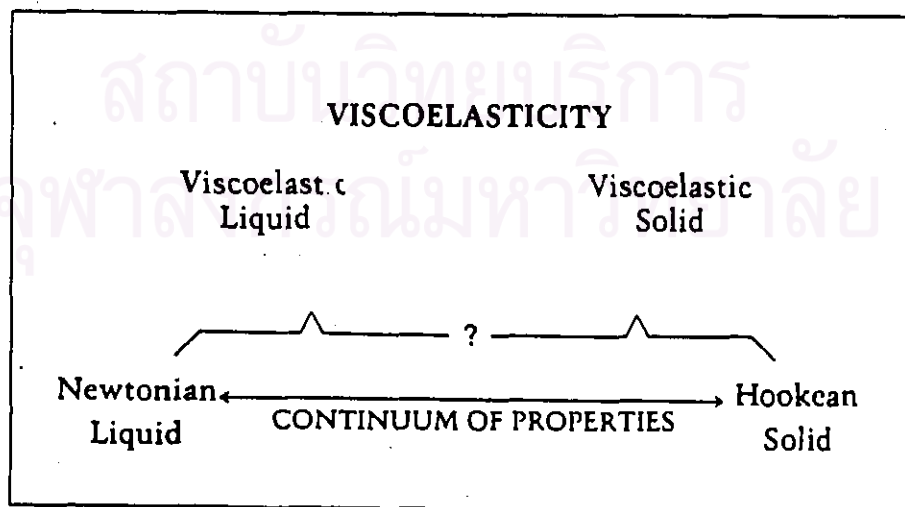


Figure 3.20 Viscoelastic material have properties somewhere on a continuum.

Dynamic Property Determinations.

The use of dynamic mechanical analysis (DMA) for characterization of cured coatings and for following the progress of curing reactions is increasing rapidly. The common feature of dynamic property determination is oscillatory stress and strain. Variable features are forced vs free oscillation and tensile vs shear deformation. In some cases, oscillatory strain is imposed and stress is measured while in other cases oscillatory stress is imposed and strain is measured. Plots of sinusoidal strain and stress are shown for a tensile determination in figure 3.21. Stress lags behind strain by an amount, δ , which can be expressed as an angle. For an ideal elastic solid, $\delta = 0^\circ$. For an Newtonian liquid, $\delta = 90^\circ$. For a viscoelastic solid, δ is between 0° and 90° . Dynamic properties can be defined in term of maximum strain (ϵ_0), maximum stress (σ_0), and the phase lag, δ . Storage modulus (E') is the elastic part of the response. Loss modulus (E'') is the viscous part of the response. When δ is zero, $\sin \delta$ is also zero. Then, as shown in the equation, $E'' = 0$. There is no viscous response when the two sine curves are exactly in phase.

$$\text{Storage modulus} = E' = \frac{\sigma_0 \cos \delta}{\epsilon_0}$$

$$\text{Loss tangent} = \frac{E''}{E'} = \tan \delta$$

$$\text{Loss modulus} = E'' = \frac{\sigma_0 \sin \delta}{\epsilon_0}$$

An example of DMA results is shown in Figure 3.22. The sample was a cured thermoset free film. Values of either E' or E , taken in rubbery plateau region, can be used to calculate crosslink density of unpigmented coating. The dashed horizontal line labeled E' (min) in figure 3.22. is drawn from the minimum on the storage modulus plot to the left axis which gives a value related to crosslink density. Common uses of loss modulus and $\tan \delta$ plots are to determine T_g and other aspects of extent of cure. Usually T_g is taken as the temperature of the maximum in the $\tan \delta$ plot as shown by the dashed vertical line in figure 3.22 [Hill, 1987]

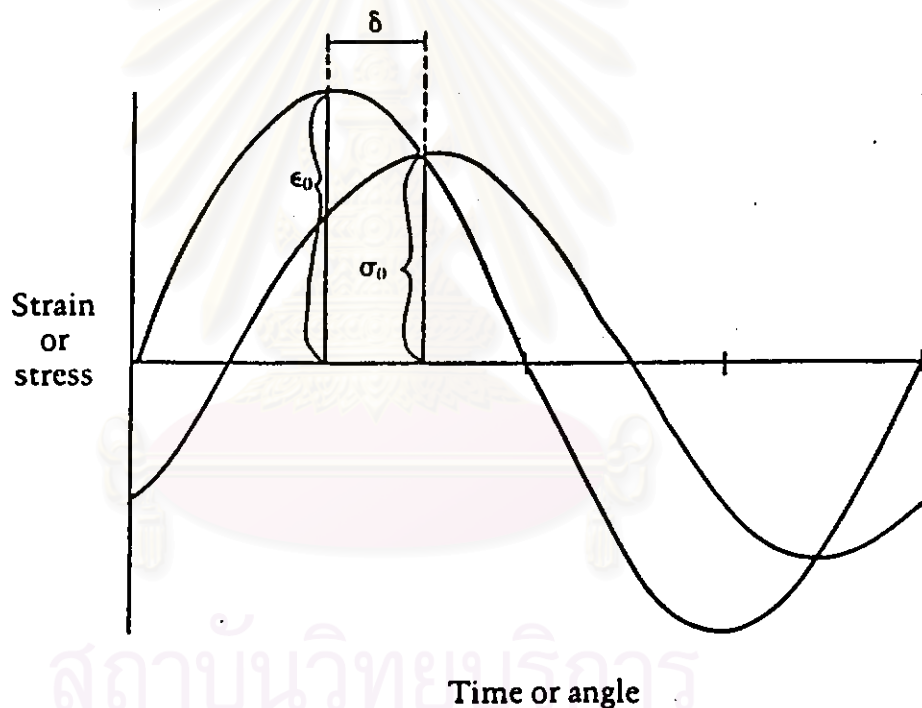


Figure 3.21 Sinusoidal strain and stress curve.

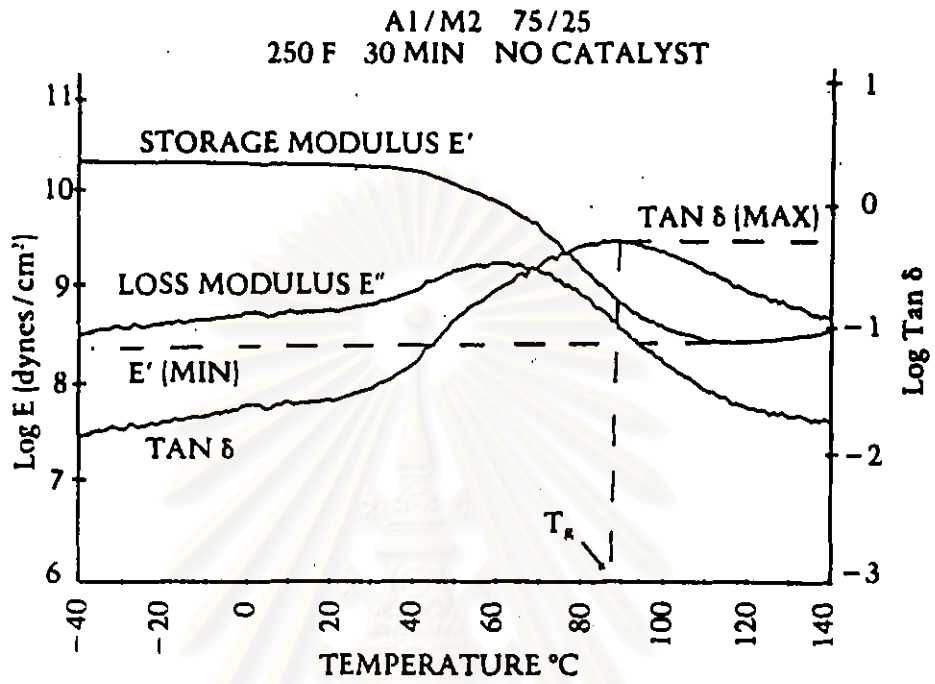


Figure 3.22 Dynamic properties vs temperature for a crosslinked acrylic film

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7. Experimental Design [Schmidt and Launsby, 1994]

Experimental design consists of purposeful changes of the inputs (factors) to a process (or activities) in order to observe the corresponding changes in the outputs (responses). The process (or activity) is defined as some combination of machines, materials, methods, people, environment, and measurement which, when used together, perform a service, produce a product, or complete a task. Thus, experimental design is a scientific approach which allows the researcher to gain knowledge in order to better understand a process and to determine how the inputs affect the response.

Figure 3.23 Experimental design concept



7.1 Experimental design procedure [Schmidt and Launsby, 1994]

Step 1. Statement of the problem

Step 2. Objective of the experiment

The objectives of the experiment are to determine the way to increase process capabilities. To achieve these objectives, they are necessary to characterize the process determining which are the important factors and what are their relations.

Step 3. Time period

Step 4. Select the response

The response or quality characteristic to be used in the experiments should be measurable and related to the customer's need and expectations.

Step 5. Select the factors.

Although numerous factors can be tested in the process the most effective effect should be select for the first

Step 6. Determine the number of resources for experimentation.

This step is limited by time and cost for experimentation.

Step 7. Which experimental designs and analysis strategies are appropriate

A wide variety of design types and analysis strategies are available. Some of the design types are 2 levels full factorial, 3 levels full factorial, central composite design. Numerous data analysis approaches are also available, simple graph, analysis of variance (ANOVA), regression modeling etc.

Step 8. Select the best type and analysis strategy to suit your needs.

Step 9. Randomization of the runs in the design matrix.

The run order should be conducted randomly to compensate for the effects of potential uncontrolled factors which were left out of the experiment.

Step 10. Conducting the experiment and recording the data.

Step 11. Analyze data, draw conclusions, make predictions, and do confirmatory test.

Step 12. Assess results, make decisions, and if necessary, conduct more experimentation

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7.2 Full factorial designs.

At here, two levels three factors will be discussed. For this type there are seven possible effects listed in the table 3.1.

Table 3.1 List of all possible effects for a full factorial design for 3 factors (A, B and C), each at 2 levels(-1 and +1).

Main effects	2-Way Interactions	3-Way Interactions
A	AB	ABC
B	AC	
C	BC	

The number of combinations or runs (n) for a full factorial design of k factors will be $n = 2^k$. The number of orthogonal columns representing all possible effects will be $n - 1$. In this example, the total of 7 effects can be analyzed in 8 runs. The design matrix is displayed in Table 3.2. Remember that the experimenter will use the actual setting values for columns A, B, and C when running the experiment. The remaining columns are obtained by multiplying the associated coded settings in each of the factor columns and they are used only in the analysis phase of the experiment.

Table 3.2 Coded design matrix for a full factorial of 3 factors (A, B and C) each at 2 level (-1 and +1).

Run	A	B	C	AB	AC	BC	ABC
1	-1	-1	-1	+1	+1	+1	-1
2	-1	-1	+1	+1	-1	-1	+1
3	-1	+1	-1	-1	+1	-1	+1
4	-1	+1	+1	-1	-1	+1	-1
5	+1	-1	-1	-1	-1	+1	+1
6	+1	-1	+1	-1	+1	-1	-1
7	+1	+1	-1	+1	-1	-1	-1
8	+1	+1	+1	+1	+1	+1	+1

7.3 Analysis of Variance (ANOVA)

Average response for each run

$$\bar{y}_r = \frac{\sum_{i=1}^{n_r} y_i}{n_r}$$

y_i = response of process

n_r = number of run

Variance for each run

$$S_r^2 = \frac{\sum_{i=1}^{n_r} (y_i - \bar{y}_r)^2}{(n_r - 1)}$$

The variance from each run (S_r^2) could be used to estimate σ^2 ; however, a better estimate will be obtained by pooling all the S_r^2 values. This pooled

estimate of run variances is referred to as the mean square error (MSE) and mean square between (MSB) and is calculated as shown.

$$MSE = \frac{\sum (n_r - 1)(S_r^2)}{\sum (n_r - 1)}$$

N = the total number of response values obtained in the entire experimental matrix

$$MSB = \frac{N}{4} (\Delta)^2$$

Δ = difference between low and high response y_+ - y_- .

Analysis procedure

Step 1 Define the hypothesis

$H_0 : \mu_{(+)} = \mu_{(-)}$ unimportant factor

$H_1 : \mu_{(+)} \neq \mu_{(-)}$ important factor

Step 2 Select an appropriate α (error)

Note : For industrial experiment it usually set α at 0.05 or 0.01.

Step 3 Compute MSB, MSE and $F_0 = MSB/MSE$. The degrees of freedom for MSB, df_b , is the number of levels minus 1, i.e., $df_b = 1$ for 2-levels designs. The degrees of freedom for MSE, $df_g = \sum (n_i - 1)$. These degrees of freedom are used to determine a critical F value, F_c , which is compared with F_0 .

Step 4 In an F table, look up $F(1-\alpha, df_b, df_g) = F_c$.

Step 5 Compare the ratio $F_0 = MSB/MSE$ to F_c from step 4.

If $F_0 \leq F_c$, fail to reject H_0 .

If $F_0 > F_c$, reject H_0 in favor of H_1 , with at least $(1-\alpha)$ 100% confidence of being correct.

Example of three factors ANOVA

From table 3.2, eight runs have to be conducted.

Table 3.3 Experimental results

Run	y_1	y_2	y_3	\bar{y}_r	S_r^2	df_r
1	5	7	6	6.00	1.00	2
2	20	21	23	21.33	2.33	2
3	6	4	5	5.00	1.00	2
4	23	19	18	20.00	7.00	2
5	21	21	20	20.67	0.33	2
6	4	5	6	5.00	1.00	2
7	24	21	19	21.33	6.33	2
8	5	8	7	6.67	2.33	2

Result	A	B	C	AB	AC	BC	ABC
$\bar{y}_{(-)}$	13.08	13.25	13.25	12.67	20.83	13.16	13.08
$\bar{y}_{(+)}$	13.42	13.25	13.25	13.83	5.67	13.33	13.42
$\Delta = \bar{y}_{(+)} - \bar{y}_{(-)}$	0.34	0	0	1.16	-15.16	0.17	0.34
MSB	0.6936	0	0	8.0736	1378.95	0.1734	0.6936
$F_0 = MSB/MSE$	0.26	0	0	3.029	517.43	0.065	0.260

$$MSE = \frac{2*1 + 2*2.33 + 2*1 + 2*7 + 2*0.33 + 2*1 + 2*6.33 + 2*2.33}{2 + 2 + 2 + 2 + 2 + 2 + 2 + 2} = 2.665$$

$$F_c = F(0.95, 1, 16) = 4.49$$

$$\text{Grad mean} = \frac{6+21.33+5+20+20.67+5+21.33+6.67}{8} = 13.25$$

Example of calculation

Only A factor will be presented here. The other can be calculated at the same procedure.

From the table 3.3

Run number 1, 2, 3 and 4 is result for low level of A factor

$$\bar{y}_{A(-)} = (6+21.33+5+20)/4 = 13.08$$

$$\bar{y}_{A(+)} = (20.67+5+21.33+6.67)/4 = 13.42$$

$$\Delta = 13.42 - 13.08 = 0.34$$

$$MSB_A = N/4 (\Delta)^2 = 24/4 * 034^2 = 0.6936$$

$$F_A = (MSB_A)/(MSE) = (0.6936)/2.665 = 0.260$$

Compare F_A with F_c , you can see that F_A is less than F_c , so the factor A is unimportant factor in prediction equation.

From the table 9.3, most of the effects are not significant. The only significant terms for the prediction equation are the grand mean and the AC interaction effect. Therefore the prediction equation becomes:

$$Y = 13.25 + 0.17(A) + 0(C) - 7.585(AxC)$$

In order to use this equation to predict the response for various factor setting, you must ensure the levels for A and C are in the coded form, i.e., somewhere between -1 and +1.

From the predicted equation, if your objective is to minimize or maximize the response, you can determine the optimum setting by using the prediction equation. For example, consider minimizing the average predicted response, Y . Since the coefficient for A is positive, setting A at (-1) will move the Y in the minimum direction. The negative coefficient of $A \times C$ and the previously determined negative setting for A will dictate that factor C be set to -1 . The resulting predicted average response will be:

$$Y = 13.25 + .17(-1) - 7.585(-1)(-1) = 5.495$$



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