CHAPTER III

THEORY

3.1. Polyethylene

Polyethylene initially was a homopolymer of ethylene, but today most polyethylenes are copolymers of ethylene with Iso-organic to 10% of a-olefins, such as I-butene, 4-methylpentene, I-hexene, and I-octene. LDPE and some HDPE grades are ethylene homopolymers. LDPE is a branched polymer with only 40 to 60 % crystallinity. The other polyethylene grades are predominantly linear, with small amounts of branching caused by the comonomer. The linear polyethylenes are produced using Ziegler-Natta catalysts, or transition metal catalysts (chromium or titanium with alkylaluminum cocatalysts

Polyethylene is a partially amorphous and partially crystalline polymer. Side chain branching is the key property factor in controlling the degree of crystallinity. HDPE has up to 90 % crystallinity, while LDPE exhibits crystailinity as low as 50%. The higher density PE cause an increases in stiffness, tensile strength, hardness; heat and chemical resistance, opacity, and barrier properties, but reduce impact strength and stress crack resistance. A comparison of PE materials-is show in Table 3.1.1.

The trend in polyethylene production is toward the manufacture of more cost effective products with improved physical properties. Also HDPE consumption will increase because of growth of the high molecular weight (HMW and UHMW) polymers, which have superior properties over the regular HDPE polymers. [18]

Table 3.1.1 Types of Polyethylene

PE	Density (g/cm^3)	Crystallinity	Melting Point (0C)
ULDPE	0.880-0.915	Low	
LLDPE	0.918-0.940	High	130
LDPE	0.910-0.955	40-60 %	107-120
HDPE	0.941-0.954	High	130-138
HMW-HDPE	0.944-0.954	High	
UHMW-HDPE	0.955-0.957	High	-*

* Has no melting point.

3.2 Polypropylene

3.2.1 General features

A fast growth of PP production, in comparison to other thermoplastics, has been encouraged by significant advances in catalyst and process development and by the attractive combination of features which characterizes this polymer such as low density, heat distortion temperature above 100°C, extraordinary versatility in terms of properties, applications, and recycling in addition to a low cost [19]. PP is a vinyl polymer obtained, by means of organo-metallic catalysts [20], from propylene (CH_2-CH-CH_3) through the reaction:

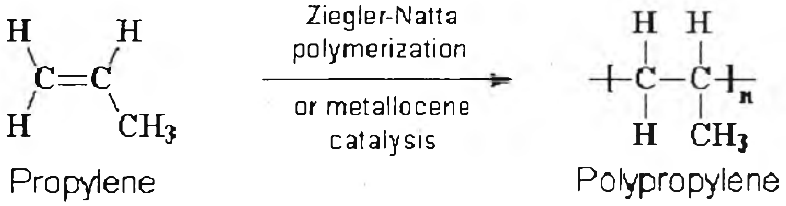


Fig 3.2.1 Polymerization of propylene

smaller crystalline PE can be resolved on TEM micrograph. Electron diffraction coupled with TEM imaging is used to elucidate the orientation of PE crystallites with respect to the interfaces of the microphase separated block copolymer lamellar domains. Fast quenching from microphase separated melt-state was found to result in confinement of PE crystallization within the microphase separated PE domains of the block copolymer morphology. The orientation of the PE crystallites thus formed was found to be random.

R. Strapasson, S.C. Amico, M.F.R. Pereira, T.H.D. Sydenstricker [15] made PP/LDPE blends (0/100, 25/75, 50/50, 75/25 and 100/0 w/w) via injection molding carried out under various injection temperatures and to evaluate their tensile and impact properties. The blends yielded tensile stress–strain curves very dependent on their composition, especially regarding elongation at break and the presence of necking. An irregular behavior for the 50/50 w/w blend is reported. Nevertheless, a linear variation of the yield strength and elastic modulus with the blend composition was observed. The behavior of the blend was also very dependent on processing temperature. Addition of 25% of LDPE to the PP may result in similar degradation of its mechanical properties to that caused by a 10 °C processing temperature increase. Statistical analyses proved valuable when reporting results concerning blends.

Lixiao Wang, Baotong Huang. [16] studied the structure and properties of presumed polypropylene(PP)-b-polyethylene(PE) block copolymers and the corresponding blends (PP/PE) investigated by wide-angle x-ray scattering (WAXS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), torsional pendulum apparatus, and other techniques measuring mechanical properties. Crystallinity, morphological structure, and mechanical properties of the block copolymer and blend vary with the PP and PE composition. Compared with PP homopolymers and PP/PE blends, PP and PE segments in PP-PE block copolymers have a reduced cystallinity, especially PE segments. An additional peak at about -40 °C is observed in dynamic relaxation spectra; substantially different morphology is revealed; and mechanical properties are greatly improved for the sequentially copolymerized PP-PE block copolymers, indicating the existence of PP-PE block structure.

Eleonora Vaccaro, Anthony T. Dibenedetto, Samuel J. Huang. [17] showed the compatibilization of low density polyethylene with polypropylene is accomplished through the addition of maleated polyethylene and maleated polypropylene. Prediction of the tensile properties of these blends is attempted, using a model based on continuity of phases in a two components mixture of thermoplastics

Depending on the organization of CH_3 groups along the backbone, three configurations can be distinguished: isotactic, syndiotactic and atactic. When all the groups are on the same side of the chain, PP is isotactic: in this case chains have a very regular arrangement; consequently they can pack easily together in a crystal structure. Thus, the higher the amount of isotactic phases in the polymer, the higher the degree of crystallinity in the solidified PP. In syndiotactic configuration, methyl groups are laid alternatively on either side of the carbon chain. This structure yields a highly flexible PP. No order at all is present in atactic PP: the side groups are randomly situated on either side of the backbone and therefore the polymer has a very low degree of crystallinity. Compared to isotactic PP, the syndiotactic isomer 'exhibits higher impact resistance and improved adhesion on organic surfaces or glass fillers' [21]. However, PP is semi-crystalline, which means it always has two phases, an amorphous and a crystalline one. When cooling is slow enough, molecular chains have time to arrange themselves in 'lamellar' fibrils. These structures grow out from a central nucleus in the three dimensions yielding an organization with a spherical symmetry. The whole assembly is called '*spherulite*' and is illustrated in Figure 3.2.2.

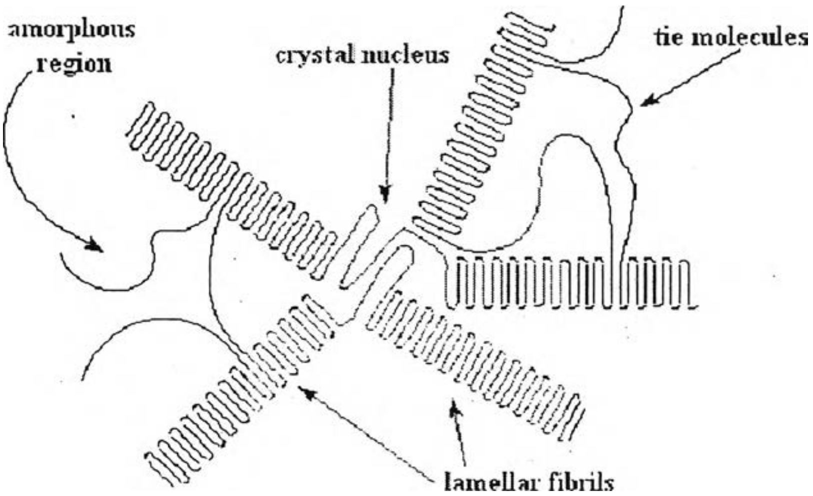


Figure 3.2.2 Schematic illustration of chains organization in PP spherulites

Thus it is possible to distinguish: spherulites on the largest scale, the lamellar structure on the intermediate level and the crystal structure on the smallest scale.

PP is a polymorphic material. This means its crystals can be arranged in several forms: monoclinic a, hexagonal. , triclinic or smectic. . The formation of acertain crystal form will depend on the crystallization conditions [22].

3.2.2. PP properties

The PP mechanical properties, as stiffness and ductility, are strongly affected by its crystallinity degree. The latter, though, does not depend only on tacticity but it is influenced by thermal history as well: for instance, quenching the polypropylene, the biggest part of polymer will be 'frozen' in an amorphous arrangement, more the few crystals formed will be small. Such a material will be less stiff than the slowly cooled one. [22]

The third largest sales volume polyolefin is polypropylene (PP), properties of which are included in Table 3.2.1. Polypropylene is a lightweight, moderately high Tm plastic that finds use in the manufacture of pipe, sheet, blow-molded containers, and as a textile fiber (i.e., olefin fiber). In general, α-olefins such as PP cannot be polymerized by either radical or ionic catalysts. While atactic PP can be produced by use of a Lewis acid or organometallic compound, the product is a branched, rubbery polymer (Tg = -20 at ambient temperature with no important commercial applications. In the 1950s, Natta showed that Ziegler-type catalysts could be used to produce stereoregular PP with high crystallinity; however, in contrast to the polymerization of HDPE, the coordination polymerization of α-olefins is slower and more critically dependent on the nature of the catalyst. The commercial plastic, first introduced in 1957, is highly isotactic (i.e., i-PP). High-molecular-weight (150,000 to

1,500,000) i-PP can be obtained by using a heterogeneous catalyst of a violet crystalline modified titanium (III) chloride with a cocatalyst or activator, usually an organoaluminum compound such as diethylaluminum chloride.

Table 3.2.1 Properties of Commodity Polyolefins

Property	**ASTM**	**LDPE**	**HDPE**	**PP**
Specific gravity	D792	0.91-0.93	0.94-0.97	0.90-0.91
Crystallinity, %	—	50 - 70	80-95	82
Melt temperature,^{0}C	—	98-120	127-135	165-171
Tensile strength, MPa[a]	D638	4.1-16	21-38	31-41
Tensile modulus,GPa[b]	0638	0.10-0.26	0.41-1.24	1.10-1.55
Elongation-to-break, %	0638	90-800	20-130	100-600
Impact strength, notched Izod, J m^{-1} [c]	0256	No break	27-1068	2 1-53
Heat-deflection temperature, at 455 kPa (66 psi)	D648	38-49	60-88	225-250

[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 1.45×10^5

[c] TO convert J m^{-1} to lbf in^{-1}, divide by 53.38

In comparison to HDPE, commercial grades of i-PP have a higher Tm, slightly lower crystallinity, and better crack resistance. Its higher Tm allows PP to be used in products that must be steam sterilized and the polymer retains high tensile strength at elevated temperatures. The low temperature impact strength of polypropylene is somewhat sensitive to fabrication and test conditions due to the restriction of molecular motion leading to brittle behavior take place not far below room temperature in polypropylene, but much lower temperature in polyethylene.

To overcome brittleness, widely usage polymers are made of both random and block copolymers of propylene with ethylene. The block copolymers are the most impact resistant, and are used in injection molding application. To retain transparency, random copolymers are use for film application, while the homopolymer is used almost exclusively filaments. One disadvantage of PP is the susceptibility of its methyl groups to thermooxidative degradation. [23]

3.3 Ziegler-Natta Catalyst

The Ziegler-Natta catalysts of today originated in 1953 when Karl Ziegler of the Max Planck Institute, Germany, found that nickel in combination with triethylaluminum (TEAL) dimerized olefins. This prompted a survey of the effect of other transition metals. It was discovered that Group IV metals, especially titanium, were effective polymerization catalysts for ethylene. Following Ziegler's successful preparation of linear polyethylene in 1953, Giulio Natta prepared and isolated isotactic (crystalline) polypropylene at the Milan Polytechnic Institute. This was immediately recognized for its practical importance. Ziegler and Natta shared the Nobel Prize in Chemistry in 1963.

A Ziegler-Natta catalyst is composed of at least two parts: a transition metal component and a main group metal alkyl compound. The transition metal component is usually either titanium or vanadium. The main group metal alkyl compound is usually an aluminum alkyl. In common practice, the titanium component is called "the catalyst' and the aluminum alkyl is called "the co-catalyst". However, it is really the combination of the two which form the active catalyst.

In some instances, especially for catalyzing the polymerization of propylene, a third component is used. This component is used to control stereoregularity and can either be incorporated into the catalyst during its synthesis (internal donor) or can be added to the polymerization reactor with the catalyst during the polymerization (external donor). Aromatic esters can be used as internal donors. Aromatic esters, alkoxysilanes and hindered amines can be used as external donors.

Ziegler and Natta's work to demonstrate that the stereoregular polymerization of polypropylene could be achieved opened the scientific floodgates. An explosion of new chemistry, processes, and new products engulfed the world, virtually overnight. While in 1950, no one had ever seen crystalline PP, there were by 1960 several commercial producers, delivering some 50,000 tons of PP into several rapidly expanding applications. Today, Ziegler-Natta catalysts are used worldwide to produce the classes of polymers from alpha olefins.

3.3.1 Stereospecificity

Stereochemical control is one of the most important attributes of the Ziegler-Natta catalyst.

3.3.1.1 Steric Isomerism and Tacticity

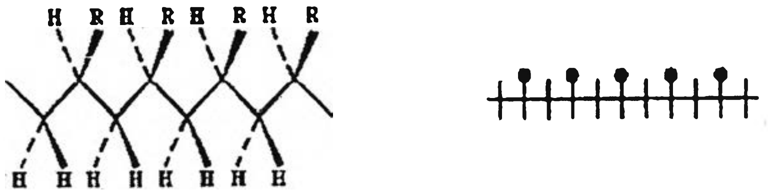
Steric isomerism is observed in the polymerization of alkenes whenever one of the carbon atoms of the double bond is at least monosubstituted. The polymerization of a monosubstituted ethylene, CH_2=CHR (where R is any substituent group), leads to polymers in which every other carbon atom in the polymer chain is a pseudochiral center. Each pseudochiral center is a site of steric isomerism in the polymerization of CHz=CHR. Considering the main carbon-carbon chain of the polymer -(CH,-CHR),- to be stretched out in its fully extended planar zigzag conformation, two different configurations are possible for each pseudochiral carbon since the R group may be situated on either side of the plane. The regularity in the configuration of successive pseudochiral centers determines the overall order of tacticity of the polymer chain. If the R groups on successive pseudochiral carbons are randomly distributed on the two sides of the planar zigzag polymer main chain, the polymer is termed atactic. An isotactic polymer structure occurs when the pseudochiral center in each repeating unit in the polymer chain has the same configuration, In this case, all the R groups will be located on one side of the plane of the carbon-carbon polymer chain. A syndiotactic polymer structure occurs when the configuration of the pseudochiral centers alternate from one repeating unit to the next with the R groups located alternately on the opposite sides of the polymer chain plane4 (see Figure 3.3.1). For polymerizations of 1,2-disubstituted ethylenes and dienes, steric isomerism is quite complicated.

3.3.1.2 Stereochemical Control by Ziegler-Natta Catalysts

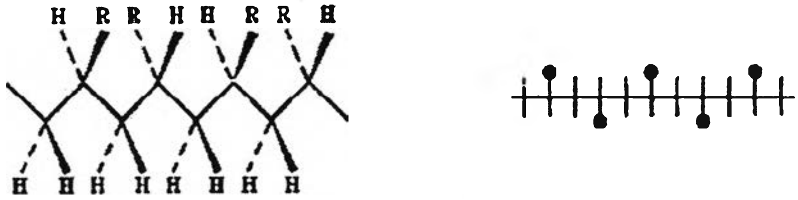
Ziegler-Natta catalysis provided for the first time stereochemical control of the polymerization process. By carefully selecting the combination of catalyst and cocatalyst, one is able to produce polymers with the desired steric structure.

The polyethylene produced in Ziegler-Natta polymerization is linear, which is characterized by the absence of long or short chain branching. For a-olefin polymerization, polyolefins of isotactic or syndiotactic structure can be obtained by using special Ziegler-Natta catalysts. There are even more choices in steric structures for polydienes; polydienes of the 1,4-cis, the 1,4-trans-, and the 1,2-structures, as well as the 3,4-structure in the case of substituted dienes, can be produced with proper Ziegler-Natta catalysts.

Isotactic



Syndiotactic



Atactic

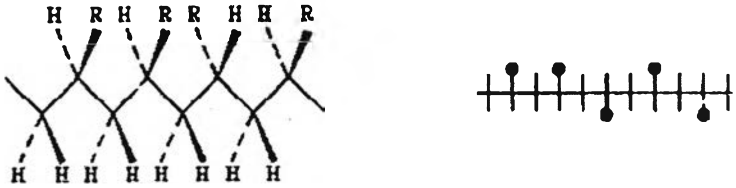


Fig. 3.3.1 The steric isomers of monosubstituted alkenes.

3.4 The molecular architecture of block copolymers [24]

Block copolymers are prepared by joining two or more chemically distinct polymer blocks together. The constituent polymers are often thermodynamically incompatible. As shown in Figure 3.4.1 although a nearly limitless number of molecular architectures based on two, three or more monomer types can be constructed, the block copolymers can be divided into two categories from the point of view of topology: linear and nonlinear. A linear AB diblock copolymer consists of a chain of monomers of type A attached at the end to a chain of type B monomers. Similarly, the chains of monomers A, B and C or more monomer types are joined together to form ABC triblock copolymer or multi block copolymers. When three or more different polymer chains are connected at one point, one of the types of nonlinear block copolymers, a multi-arm star copolymer is formed. Although innovative developments in polymer chemistry have stimulated the creation of many useful types of block copolymers, practical difficulties in copolymer synthesis still remain. In most polymer syntheses, normal chemical kinetics results in a distribution of molecular weights, and in block copolymers, this will produce compositional heterogeneity.

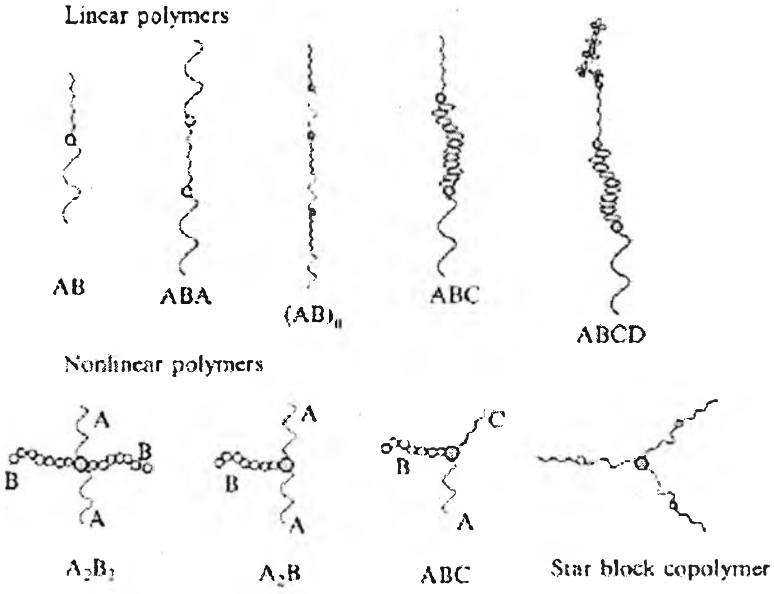


Figure 3.4.1 Molecular architecture of block copolymers

3.5 Polymer Blends

Polymer blends are the mixtures of at least two polymers or copolymers. The blending of two or more existing polymers may obtain the new properties that without synthesizing the new polymers. In the plastic industry, polymer blends are more advantageous than the synthesis of new polymers because of their lower production cost.

The majority of polymer-polymer mixtures is two-phase systems and is usually referred to as *immiscible* polymer blends [4]. However, single-phase or *miscible* blends are also possible. The physical properties and applications of blended polymers depend to a large extent on the degree of miscibility of the blend components. The mixing characteristics of two chemical components are governed by the Gibbs free energy change which occurs on their mixing (ΔGm), according to the following equation:

$$\Delta \mathrm{Gm} = \Delta Hm - T\Delta \mathrm{Sm} \qquad (3.1)$$

where T is the temperature, and ΔHm and ΔSm are the enthalpy and entropy of mixing, respectively. If ΔGm is negative, mixing may occur spontaneously and a solution will be produced as a result. In the case of low-molecular-weight compounds, ΔSm is highly positive, and hence - $T\Delta$Sm will be negative and mixing will be particularly favoured. Usually, ΔHm, which depends upon energetic interactions between the molecules, is positive and therefore not favourable for mixing. The positive ΔHm is often outweighed by a negative entropy term so that mixing will then occur. The more similar the chemical nature of the two components, then the lower is the value of ΔHm and the more likely mixing becomes. In summary, for two polymers to be miscible, the Gibbs free energy of mixing must be negative. Miscibility of polymers that are attracted to each other is thermodynamically favoured. Miscibility is also more likely in blends containing low-molecular-weight polymers.

The majority of polymer blends is immiscible and has the advantage that their properties may be more readily tailored. There are a number of phase morphologies exhibited by such blends. The different types of dispersions of polymers in the matrix of an immiscible polymer are illustrated in Figure 3.5.1. Blends may consist of one phase dispersed as simple spheres in a matrix of the other polymer. The dispersed phase may also take the form of platelets or fibrils. A morphology consisting of an interpenetrating network of phases is also feasible. An *interpenetrating polymer network* (IPN) consists of an assembly of at least two polymers in network form, one of which is prepared or cross-linked in the presence of the other. The properties of immiscible polymer blends can be improved by the addition of a *compatibilizer.* Compatibilization is the process of modification of .the interfacial properties of an immiscible polymer blend to improve the adhesion and blend properties. This process can involve the incorporation of block or graft copolymers which are identical to those in the respective phases.

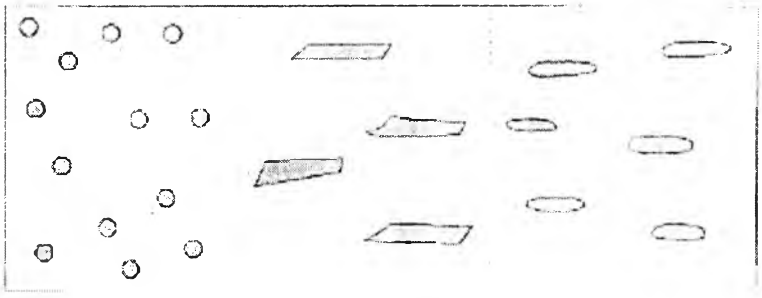

(a) (b) (c)

Figure 3.5.1 The different morphologies exhibited by immiscible blends of polymers: (a) spheres; (b) platelets (c) fibrils.

3.5.1 Blends of block copolymer with two homopolymers [24]

The addition of block or graft copolymers represents the most extensively researched approach to compatibilisation of blends. Block copolymers have been more frequently investigated than graft copolymers, and in particular block copolymers containing blocks chemically identical to the blend component polymers. It is perhaps not surprising that block and graft copolymers containing segments chemically identical to the blend components are obvious choices as compatibilizers, given that miscibility between the copolymer segments and the corresponding blend component is assured, provided the copolymer meets certain structural and molecular weight requirements, and that the copolymer locates preferentially at the blend interfaces. The classical view of how such copolymers locate at interfaces is shown in Figure 3.5.2, and experimental verification that this happens has been found for many systems; for example Barentsen *et al.* and Fayt *et al.* both for blends of low density polyethylene (LDPE) with polystyrene (PS), and Yang et al. for HDPE/polypropylene (PP) blends.

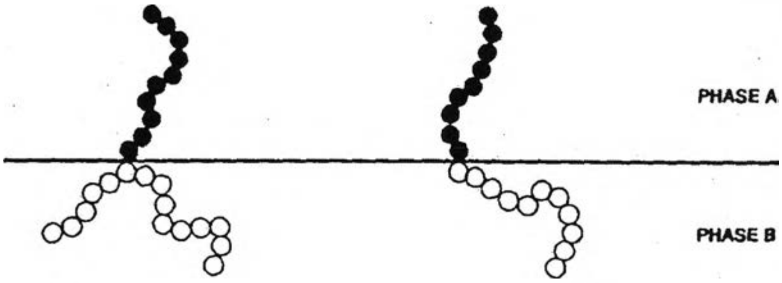


Figure 3.5.2 Schematic diagram showing location of block and graft copolymers at phase interfaces.

Theory suggests that compositional polydispersity is also important for effective compatibilization. It leads to a greater gradation in composition across the interface, and consequently lowers the configurational entropy of the homopolymers. In practice, polymers are compatibilized during melt processing. Then kinetic quantities such as the rate of diffusion of the copolymers to the interface and the shear rate are important. Macosko have shown that the coalescence of polymer droplets is inhibited by diffusion of block copolymers. The molar mass must be low enough so that diffusion occurs rapidly but not too low to prevent entanglements at the interface. On the other hand, copolymers with a molar mass that is too high get stuck in micelles.

Block copolymers act as compatibilizers by reducing the interfacial tension between homopolymers. Recent work shows that block copolymers can reduce the interfacial tension between homopolymers to the extent that polymeric microemulsions can be formed where the copolymer forms a continuous film between spatially continuous homopolymer domains. A bicontinuous microemulsion forms in the mixture composition range where mean-field theory predicts a Lifshitz point. A Lifshitz point is defined as the point along the line of critical phase transitions at which macro- and microphase branches meet. The observation of a microemulsion shows that mean-field theory breaks down due to the existence of thermal composition fluctuations. Although a theory for these composition fluctuations has not yet been developed, it has been shown that some properties of the microemulsion (elastic constants, composition profiles) can be modelled using an approach where the effective interaction between copolymer monolayers is computed.

3.2.2 Methods of blending [25]

3.5.2.1 Melt Mixing

Melt mixing of thermoplastics polymer is performed by mixing the polymers in the molten state under shear in various mixing equipments. The method is popular in the preparation of polymer blends on the large commercial scale because of its simplicity, speed of mixing and the advantage of being free from foreign components (e.g. solvents) in the resulted blends. A number of equipments are available for laboratory scale mixing such as internal mixer, electrically heated two roll mill, extruder and rotational rheometer.

The advantages of this method are the most similar to the industrial practice. The commercial compounding or adding additives into base polymers are applied by melt mixing. So the investigations of polymer blends by melt mixing method are the most practical methods in industrial applications.

3.5.2.2 Solvent Casting

This method group is performed by dissolving polymers in the same solvent. The solution is then cast on a glass plate into thin films and the removal of solvent from the films is performed by evaporating the solvent out at ambient or elevated temperature.

The most severe problem with solvent casting is the influence of the solvent on the resulted product especially the shift of the phase diagram. In spite of the fact that most of the solvent can be removed from a cast film, the nature of the film depends strongly on the types of solvents and casting conditions.

3.5.2.3 Freeze Drying

In the freeze drying processes, the solution of the two polymers is quenched down immediately to a very low temperature and the solution is frozen. Solvent is then removed from the frozen solution by sublimation at a very low temperature and pressure. Dilute solutions must be used and the solution volume must have as large surface area as possible for good heat and mass transfer.

3.5.2.4 Emulsions

The advantages of the emulsion polymer mixing are the easy handing and all the other advantages as the solvent casting. The mixing or casting of the film requires neither expensive equipment nor high temperature. However, emulsions of polymers are an advance technique and not always applicable to all monomers.

3.5.2.5 Reactive Blend

Co-crosslinking and interpenetrating polymer networks (IPN) formations are the special methods for forming blends. The idea of these methods is to enforce degree of miscibility by reactions between the polymer chains. Other methods involve the polymerization of a monomer in the presence of other polymer and the introduction of interface graft copolymer onto the polymer chains.

3.6 Reinforecd Polymer Blends

Thermoplastic composites with various fillers and reinforcements are well established for a variety of applications. It is, however, less well known that the matrix of a number of these composites is a polymer blend itself. Composites are defined as materials consisting of two or more distinct phases with an interface between them. This definition is generally used for materials containing reinforcements characterized by a high aspect ratio (i.e., the ratio of length to thickness), as is the case for fibers, platelets, and flakes. The incorporation of these materials into thermoplastic matrices results in improved, but possibly anisotropic, mechanical and thermal properties. On the other hand, fillers with a low aspect ratio are mostly used to reduce cost and may even sacrifice some mechanical properties (e.g., strength and toughness). Nevertheless, the distinction between reinforced and filled polymers is often arbitrary.

The roles of the matrix, reinforcement, and interface in composites are well defined. The matrix is responsible for transferring the load from the matrix to the reinforcement, for distributing the stress among the reinforcement elements, for protecting the reinforcement from environmental attack, and for positioning the reinforcing material. Meanwhile, the task of the reinforcement is to carry the load, due to its higher stiffness and strength compared with that of the matrix. The interface, (for two dimensions) or the interphase (for three dimensions) is a negligible or finite thin layer with its own properties, and its role is stress transfer from the matrix to the reinforcement.

The blended polymer, usually present as a fine dispersion in the matrix, can take on many different roles: flame retardant, processing aid, surface finish, impact modifier, adhesion promoter between the matrix and reinforcement, and so on. Nevertheless, in the majority of cases, blending is aimed at improving the toughness of the composites, or more exactly, to achieving the desired balance between stiffness and toughness. It is widely assumed that stiffness and strength characteristics are related to the reinforcement and that toughness is related to the matrix; however, this presumption generally does not hold. The toughness-enhancing mechanisms are quite complex, and both matrix deformation and fiber-related failure events are involved. It is appropriate to call attention to the large gap between the trade and patent literature and the scientific literature in terms of their attention to the field of reinforced polymer blends.

Blending of the matrix polymer for thermoplastic composite applications is done when the matrix tends to undergo brittle fracture and/or exhibits notch sensitivity. Brittle fracture is favored, for example, by temperatures far below the glass transition temperature *Tg,* by low average molecular weight (MW), by deficient tie-molecule density, and by high crystallinity. Blending may also be the right tool for cost-reduction purposes. Last but not least, adding a second polymer may substantially increase the interfacial adhesion between fiber and matrix.

The mechanical performance of reinforced thermoplastic blends is affected by the following factors

(a) blend composition and morphology

(b) type and amount of the reinforcement

(c) interface or interphase between matrix and reinforcement

(d) processing methods and conditions, and

(e) testing conditions.

3.7 Isocyanates [27]

Diisocyanate products are required for making elastomers, whilst high functionality MDI (diisocyanato-diphenylmethane)-rich in polyisocyantes is desirable for the manufacture of rigid foams and binding materials. Within the latter group, wide variation in the molecular weight distribution and functionality is possible, giving considerable control over reactivity, viscosity, and application properties.

Aliphatic diisocyanates, which are much less reactive than the aromatic diisocyanate, are therefore used for applications requiring high resistance to yellowing. Those most widely available are 1-isocyanato-3-isocyanatomethyl-3,5,5,-trimethylcyclohexane (isophorone diisocyanate or IPDI),1,6-diisocyanato-haxane (hexamethyl diisocyanate or HDI) and 4,4-diisocyanato-dicyclohexylmethane (hydrogenate MDI or HMDI).The isomeric diisocyanates,2,4-and 1,3-di(isocyanato-dimethyl-methyl)-benzene(m- and p- tetramethyl xylene diisocyanate or m- and p-TMXDI),which behave like aliphatic diisocyanates, are also available.

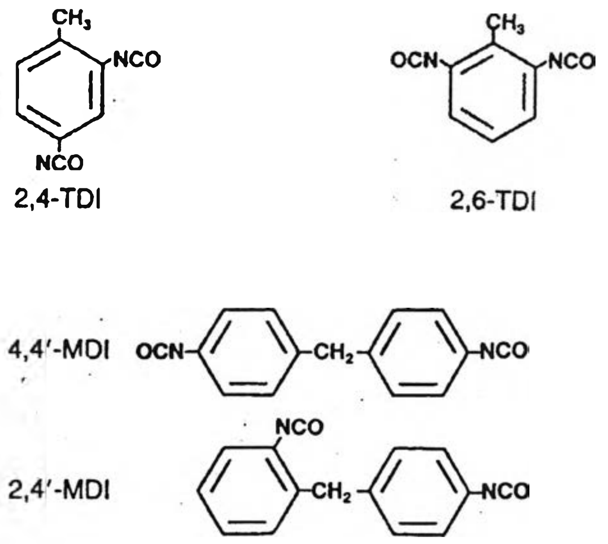


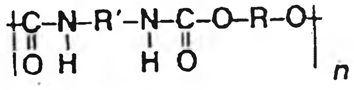
Figure 3.7.1 Structure of Diisocyanates

3.7.1 Reactions of isocyanates

With polyols : the reaction of di- or poly-isocyanates with polyols form polyurethanes :

Polyol + Diisocyanate ——————→ Polyurethane

OH–R–OH + OCN–R'–NCO



$$\left[\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{H}}{N}-R'-\underset{\overset{|}{H}}{N}-\underset{\overset{\|}{O}}{C}-O-R-O\right]_n$$

Figure 3.7.2 Polyurethane addition reaction

The reaction is exothermic. The rate of the polymerization reaction depends upon the structure of both the isocyanate and the polyol. Aliphatic polyols with primary hydroxyl end groups are the most reactive. They react with isocyanates 10 times faster than similar polyols with secondary hydroxyl groups. Phenol reacts with isocyanates more slowly and the resulting urethane groups are easily broken on heating to yield the original isocyanate and the phenol. This reversible reaction is used in manufacture of "blocked" isocyanates which are activated by heating.The isocyanate group (-NCO) can react with any compound containing “active” hydrogen atom and diisocynates may therefore be used to modify many other product.

3.8 Mechanical Properties

The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength[28]. These values are normally derived from the technical literature provided by material suppliers. The basic understanding of stress-strain behavior of polymer is of almost importance to design engineers. One such typical stress-strain diagram is illustrated in Figure 3.8.1.

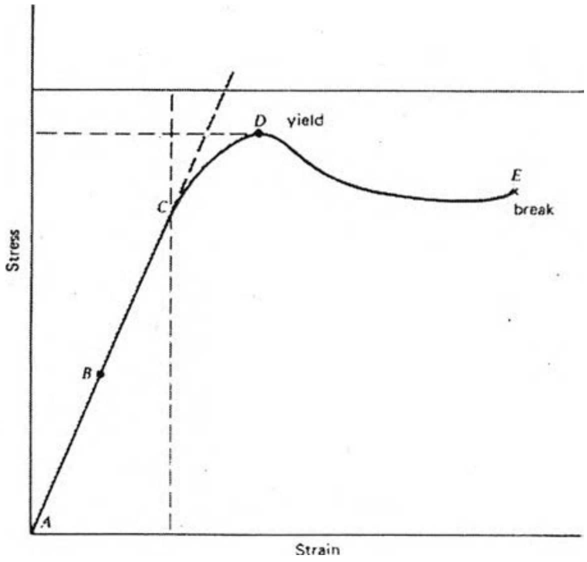


Figure 3.8.1 A typical stress-strain curve

For a better understanding of the stress-strain curve, it is necessary to define a few basic terms that are associated with the stress-strain diagram.

3.8.1 Stress-Strain Diagram

3.8.1.1 Stress

Stress is the internal resistance, or counterfource, of a material to the distorting effects of an external force or load. These counterforces tend to return the atoms to their normal positions. The total resistance developed is equal to the external load. This resistance is known as stress. Although it is impossible to measure the intensity of this stress, the external load and the area to which it is applied can be measured. Stress (σ) can be equated to the load per unit area or the force (F) applied per cross-sectional area (A) perpendicular to the force as shown in Equation (3.2)

$$\text{Stress}(\sigma) = F/A \tag{3.2}$$

where: σ = stress (psi or lbs of force per in.^{2})

F = applied force (lbs of force per in.^{2})

A = cross-sectional area (in.^{2})

In mechanical properties, we are mainly interested in the effect of applying surfaces forces such as stress or pressure **[29]**.

3.8.1.2 Strain

For mechanical engineering purposes, a given state of stress usually exists in a considerable volume of the material. Reaction of the atomic structure will manifest itself on a macroscopic scale. Therefore, whenever a stress (no matter how small) is applied to a specimen, a proportional dimensional change or distortion must take place. When forces are applied to a material, the atoms change position in response to the force and this change in known as strain. It is defined as ratio of the elongation to the gauge length of the test specimen, or simply stated, change in length per unit of the original length ($\Delta l/l$).

3.8.1.3 Elongation

The increase in the length of a test specimen produced by a tensile load (Δl) is called Elongation. Elongation is a type of deformation. Deformation is simply a change in shape that anything undergoes under stress.

Usually we talk about percent elongation, which is just the length the polymer sample is after it is stretched (L), divided by the original length of the sample (l), and then multiplied by 100.

3.8.1.4 Yield Point

The first point on the stress-strain curve at which an increase in strain occurs without the increase in stress (Point D) is called Yield point.

3.8.1.5 Yield Strength

The stress at which a material exhibits a specified limiting deviation from proportionality of stress to strain is called Yield Strength. This stress will be at yield point.

3.8.1.6 Proportional Limit

The greatest stress at which a material is capable of sustaining the applied load without any deviation from proportionality of stress to strain is called proportional limit. Below this limiting value of stress, the ratio of stress to strain is constant, and the material is said to obey Hooke's Law (stress is proportional to strain).

3.8.1.7 Modulus of Elasticity

The ratio of stress to corresponding strain below the proportional limit of the material is called Modulus of Elasticity.

3.8.1.8 Break Point

The point which at a material breaks or ruptures in tension due to plastic deformation is called Break point.

The stress-strain diagram illustrated in Figure 3.8.1 is typical of that obtained in tension for a constant rate of loading. However, the curves can be obtained from other loading conditions such as compression or shear.

The behavior of polymer below the proportional limit (Point C in Figure 3.8.1) is elastic in nature and therefore the deformations are recoverable. At Point B, the deformation are relatively small and have been associated with the bending and stretching of the interatomic bonds between atoms of polymer molecules as shown in Figure 3.8.2(a). At Point C in Figure 3.8.1, the deformation is similar to a straightening out of a coiled portion of the molecular chain [Figure 3.8.2(b)]. There is no intermolecular slippage and the deformations can be recovered ultimately. The extensions that occur beyond the yield point of the polymer are not recoverable [Figure 3.8.2(c)].

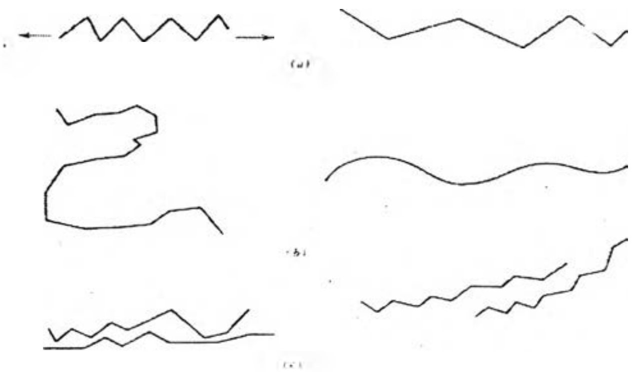


Figure 3.8.2 Extension types (a) bond bending (b) uncoiling (c) slippage

3.8.2 Type of Stress-Strain Curve

The polymeric material can be broadly classified in term of their softness, brittleness, hardness, and toughness. The tensile stress-strain diagram serves as a basic for such a classification. Figure 3.8.3 illustrates typical tensile stress-strain curve for several type of polymer. The area under curve is considered as the toughness. Table 3.8.1 lists characteristic features of stress-strain curve as they relate to the polymer properties.

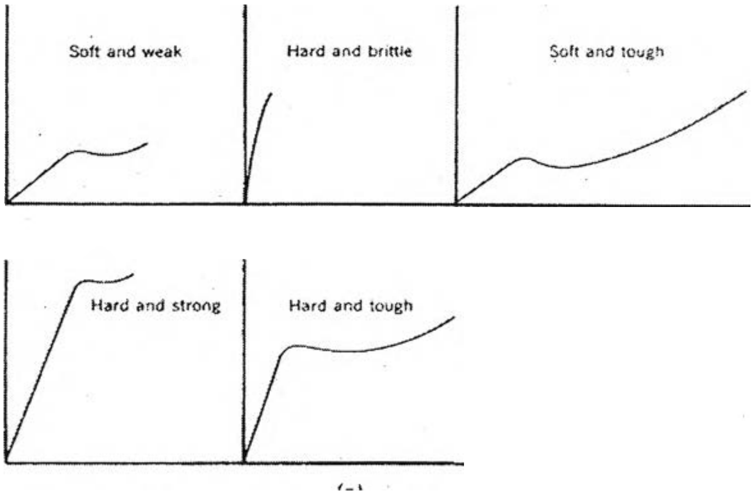


Figure 3.8.3 Types of stress-strain curve

Table 3.8.1 Characteristic features of stress-strain curve as they relate to the polymer properties.

Description of polymer	Modulus	Yield stress	Ultimate strength	Elongation at break
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Yield stress	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

3.8.3 Tensile Tests

The tensile test supplies three descriptive facts about a material. These are the stress at which observable plastic deformation or "yielding" begins; the ultimate tensile strength or maximum intensity of load that can be carried in tension; and the percent elongation or strain (the amount the material will stretch) and the accompanying percent reduction of the cross-sectional area caused by stretching. The rupture or fracture point can also be determined.

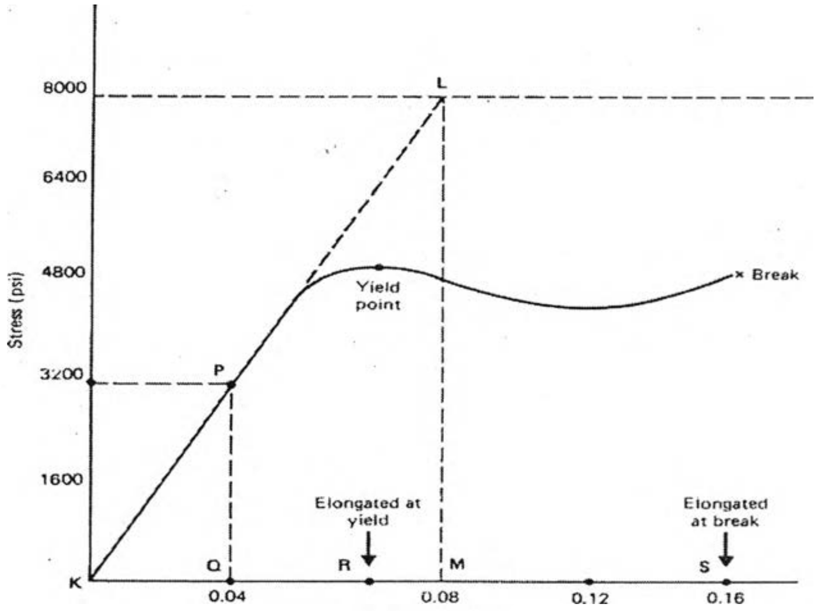


Figure 3.8.4 Diagram illustrating stress-strain curve form which modulus and elongation values are derived

3.8.3.1 Tensile strength

Tensile strength = Force (load)/Cross section area

Tensile strength at yield = Maximum load recorded/Cross section area

= Tensile stress at yield point

Tensile strength at break = Load recorded at break/Cross section area

= Tensile stress at break point

3.8.3.2 Tensile modulus and elongation

Tensile modulus	= Difference in stress/Difference in strain
	= Slope of stress-strain curve in elastic range
Elongation at yield	= Strain at yield x Original length
Percent elongation at yield	= Elongation at yield x 100
Elongation at break	= Strain at break x Original length
Percent elongation at break	= Elongation at break x 100

3.9 Dynamic Mechanical Analysis [30]

3.9.1 Introduction to dynamic mechanical analysis

Rheology, the study of the deformation and flow of materials, has a reputation of desire a fair degree of mathematical sophistication. These information are about major transition as well as secondary and tertiary transitions not readily identifiable by other methods. It also allows characterization of bulk properties directly affecting material performance.

3.9.2 Basic principles

DMA can be simply described as applying an oscillating force to a sample and analyzing the material's response to that force (Figure 3.9.1). From this, one calculates properties like the tendency to flow (called viscosity) from the phase lag and the stiffness (modulus) from the sample recovery. These properties are often described as the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity). One way to describe what we are studying is the relaxation of the polymer chains. Another way would be to discuss the changes in the free volume of the polymer that occur. Both descriptions allow one to visualize and describe the changes in the sample.

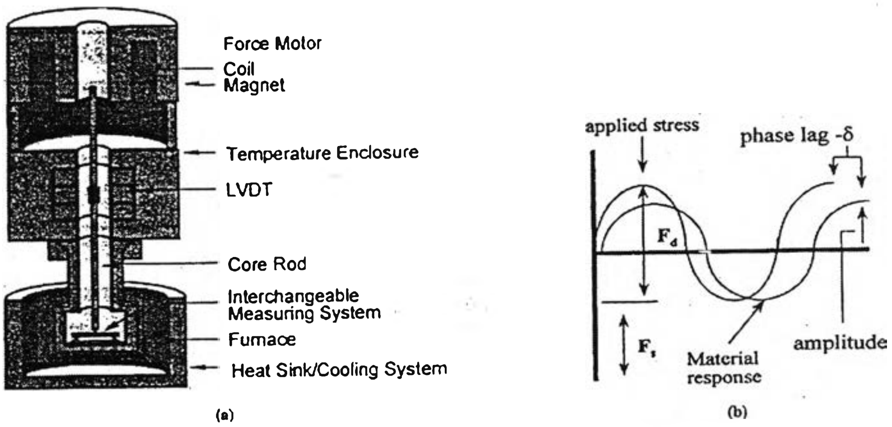


Figure 3.9.1 How a DMA works

The applied force is called stress and is denoted by the Greek letter,σ. When subjected to a stress, a material will exhibit a deformation or strain,γ. Most of us working with materials are used to seeing stress-strain curves as shown Figure 3.9.2. These data have traditionally been obtained from mechanical tensile testing at a fixed temperature. The slope of the line gives the relationship of the stress to strain and is a measure of the material's stiffness, the modulus. The modulus is dependent on the temperature and the applied stress. The modulus indicates how well a material will work in specific application in the real world

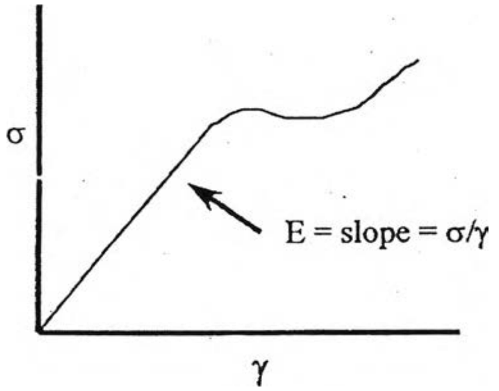


Figure 3.9.2 Stress-strain curves relate force to deformation

The modulus measured in DMA is, however, not exactly the same as the Young's modulus of the classic stress-strain curve (Figure 3.9.3). Young's modulus is the slope of a stress-strain curve in the initial linear region. In DMA, a complex modulus (E∗), an elastic modulus (E′), and an imaginary (loss) modulus (E″) are calculated from the material response to the sine wave. These different moduli allow better characterization of the material, because we can now examine the ability of the material to return or store energy (E′), to its ability to lose energy (E″), and the ratio of these effects (tan δ), which is called damping.

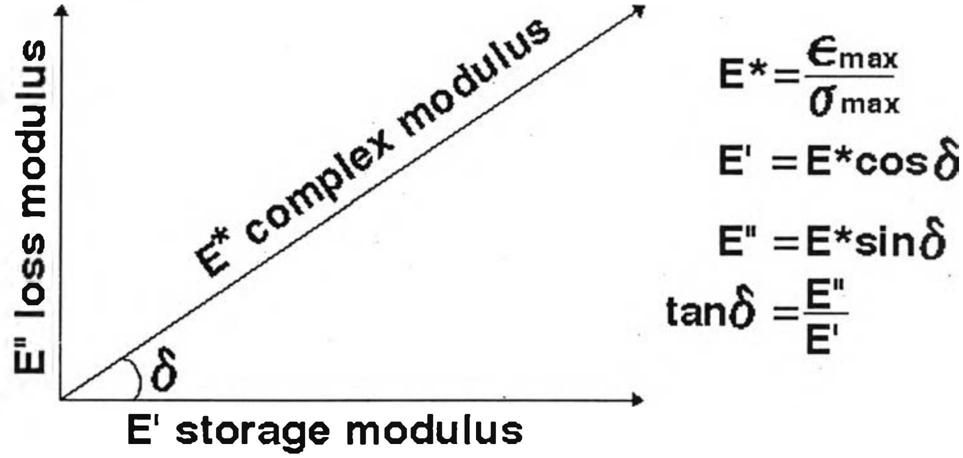


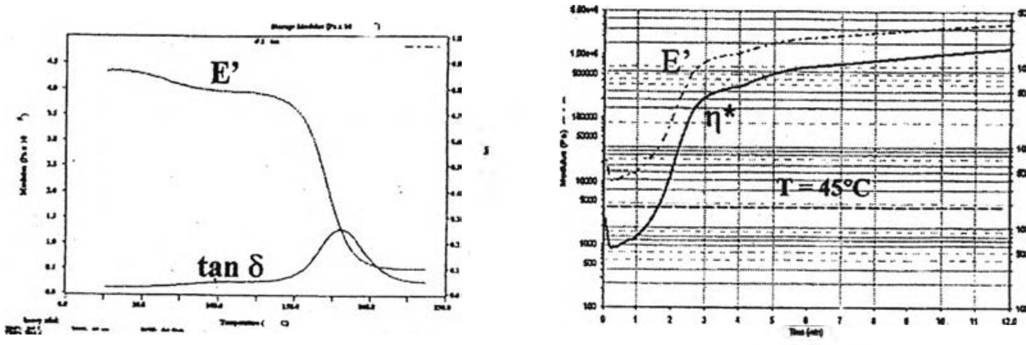
Figure 3.9.3 DMA relationships

Figure 3.9.4 Storage and loss

3.9.3 Time-Temperature Scans

One of most common uses of the DMA for users from a thermal analysis background is the measurement of the various transitions in a polymer. A lot of users exploit the greater sensitivity of the DMA to measure T_g's undetectable by the differential scanning calorimeter (DSC) or the differential thermal analyzer (DTA). For more sophisticated users, DMA temperature scanning techniques can investigate the relaxation processes of a polymer. In this topic, we will look at how time and temperature can be used to study the properties of polymers.

If we start with a polymer at very low temperature and oscillate it at a set frequency while increasing the temperature, we are performing a temperature scan (Figure 3.9.5a). This is what most thermal analysis think of as a DMA run. Similarly, we could also hold the material at a set temperature and see how its properties change over time (Figure 3.9.5b).



(a) Temperature Scan

(b) Time Scan

Figure 3.9.5 Time-temperature studies in the DMA (a) Vary temperature (b) Hold temperature constant

3.9.3.1 Transition in polymer

The thermal transitions on polymers can be described in terms of either free volume change or relaxation times. While the latter tends to be preferred by engineers and rheologists in contrast to chemist and polymer physicists who lean toward the former, both descriptions are equivalent. Changes in free volume,v^f, can be monitored as a volumetric change in the polymer ; by the absorption or release of heat associated with that change ; the loss of stiffness ; increase flow ; or by a change in relaxation time.

3.9.3.2 Sub-T_g Transitions

As we move from very low, where the molecule is tightly compressed, we pass first through the solid state transitions. This process is shown in Figure 3.9.6(6). As the material warms and expands, the free volume increases so that localized bond movements (bending and stretching) and side chain movements can occur. This is the gamma transition, T_γ, which may also involve associations with water. As the temperature and the free volume continue to increase, the whole side chains and localized groups of four to eight backbone atoms begin to have enough space to move and the material starts to develop some toughness. This transition, called the beta transition, T_β, is not as clearly defined as we are describing here (Figure 3.9.6(5)). Often it is the T_g of a secondary component in a blend or of a specific block in a block copolymer. However, a correlation with toughness is seen empirically. The area of sub-T_g or higher order transitions has been heavily studied, as these transitions have been associated with mechanical properties.

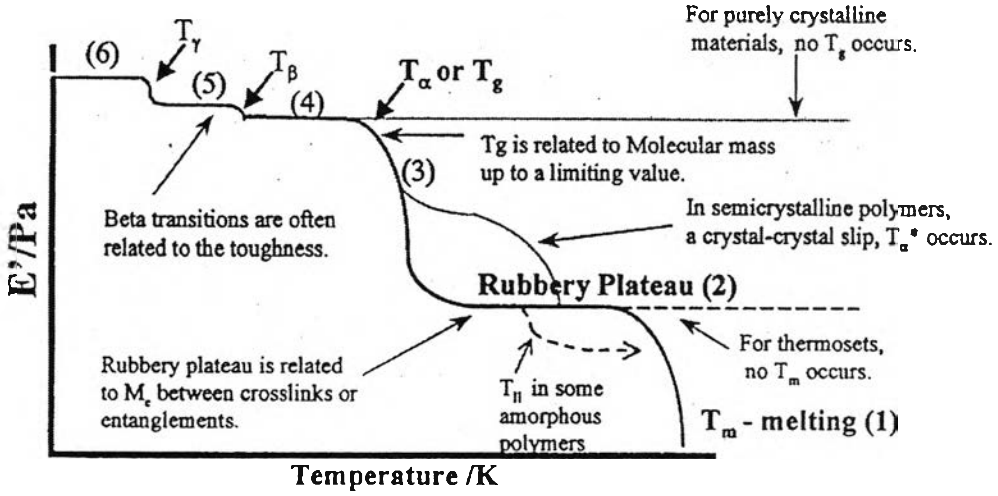
3.9.3.3 The glass transition (T_g or T_α)

As heating continues, the free volume continues to increase with increasing temperature, we reach the T_g or glass transition. The large segments of the chain start moving. This transition is also called the alpha transition, T_α(Figure 3.9.6(4)). One classical description of this region is that the amorphous regions have begun to melt.

Since the T_g only occurs in amorphous material, in a 100% crystalline material we would see not a T_g. The T_g represents a major transition for many polymer, as physical properties changes drastically as the material goes from a hard glassy to a rubbery state. It defines one end of the temperature range over which the polymer can be used, often called the operating range of the polymer, and examples of this range are shown in Figure 3.9.7.

3.9.3.4 The rubbery plateau, T_α^* and T_{II}

Continued heating bring us to the T_α^* and T_{II} (Figure 3.9.6(3)). For alpha star transition, T_α^*, the former occurs in crystalline or semicrystalline polymer and is a slippage of the crystallites past each other. In amorphous polymers, we stead see the T_{II}, a liquid-liquid transition associated with increased chain mobility and segment-segment association. The latter is a movement of coordinated segments in the amorphous phase that relates to reduced viscosity. These two transitions are not accepted by everyone, and their existence is still a matter of some disagreement.



(6)	(5)	(4)	(3)	(2)	(1)
local motions	bend and stretch	side groups	gradual main chain	large scale chain	chain slippage

Figure 3.9.6 Ideallized temperature scan of a polymer

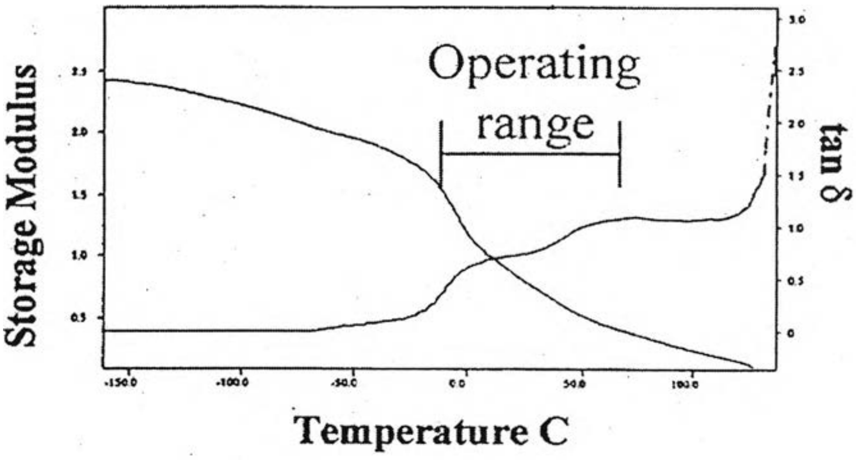


Figure 3.9.7 Operating range by DMA of Polypropylene

3.9.3.5 The terminal region

Finally, we reach the melt (Figure 3.9.6(2)) where large-scale chain slippage occurs and the free volume has increased so that the chains slide can past each other and the material flows. This is the melting temperature, T_m. For a cured thermosetting polymer, nothing happens after the T_g until the sample begins to burn and degrade because the cross-links prevent the chains from slipping past each other.