CHAPTER I
INTRODUCTION

1.1 General Aspects

Tribology is the study of lubrication, friction and wear of materials. The word "Tribology" is derived from the Greek words "tribos" meaning rubbing and "logos" meaning reason (Conton, 1996). The three main kinds of materials that tribologists study are metals, ceramics, and polymers by employing several techniques to reduce friction and wear. Tribology of metals and ceramics has been studied extensively but polymer tribology is very new and so far few researchers have studied it. Presently, the consumption of polymer usage is increasing day by day; for example, automobile parts are made up of polymers instead of metals and they are used even in high performance vehicles. Because the polymers have many advantages comparing to the metals, such as a stronger chemical resistance, lightness and a higher strength for the same weight, etc. Therefore, investigation in polymer tribology is now desired and most challenging for the tribologists.

Tribology knowledge cannot be easily utilized in polymer applications. For metals, the most efficient way to decrease wear and friction is by using external lubricants, but they will not necessarily work with polymers because they can also cause the polymers to swell. The reduction of friction and wear on polymers with external lubricants is much worse than virgin polymers. We can also use internal lubricants which can migrate slowly to the polymer surface; but they are available for very few commercial grade polymers (Garbassi, 1994).

At present, the most widely used method of the polymers for improving tribological properties are surface coating application or in bulk; for example, polymer composites. For surface coating and adhesive application, the main requirement for this application is that the polymer must adhere well onto the substrates; at the same time, it must have also good wear or scratch resistance properties. These two properties are preferred but hardly met simultaneously. Scratch and mar resistances of automotive coating (Schuls, 2001) and friction and wear resistance of organic coating on steel (Carlson, 2001) are typical examples. Frying

pan, which is coated by Teflon, is a good example why we need to intensively study polymer tribology. It is known that there are many kinds of polymer that have good adhesion properties but they can be easily scratched. One of the relatively high scratch resistance thermoplastic polymers is polymethyl methacrylate (PMMA) in comparing to other polymers and which has relatively high adhesion properties. It also has good mechanical properties, good chemical and weather resistance, and it is transparent and colorless and easy to be colored. Even though PMMA has a high scratch resistance but it is still lower than glass.

Many practical studies of the tribological properties of PMMA have been done. Briscoe (1996), Briscoe, (1998), Chateauminois, (1998), Briscoe, (1999), Briscoe, (2000), Chateauminois, (2000), Adam, (2001), Flichy (2001) studied the properties of pure PMMA. The study of tribological properties of fluoropolymer addition epoxy (Brostown, 2001) by Brostow (2002) is also interesting. This idea can be applied to PMMA too; there are 2 routes; blending and synthesis. Variety of conditions and properties of blending of PMMA and fluoropolymer have been investigated (Petrenko, 1990). Copolymer between PMMA and PVDF via emulsion polymerization was the early study and is now commercially available under the production of Paints and Coating Industry Co., Ltd. (2). The fluorine contained monomer, which is more interesting than PVDF, is perfluoroalkylethyl methacrylate monomer (FMA). Its structure is very similar to MMA monomer and exhibits extremely a low surface energy (Park, 1996). We can expect advantages including compatibility, ease in copolymerization, and a higher in energy dissipation capability resulting in lower friction and wear. Fluorine as a long side chain will give a better "polymer brush" structure which will play an important role in tribological properties relative to PVDF (Yoshinobu, 1999). Synthesized of fluorine containing graft copolymer of poly(perfluoroalkyethyl methacrylate)-g-poly(methyl methalcrylate) by macromonomer technique and emulsion polymerization method as Park(1997), and now we find it as commercial grade graft copolymer of PFMA-g-PMMA with MMA branched produced by Soken Chemical & Engineering Co., Ltd.(3). Since atom transfer radical polymerization (ATRP) was studied as far back as 1995; this method has many advantages compared to the typical living free radical polymerization method (Wang, 1995). Via ATRP method, fluorinated methacrylic

polymer was synthesized by statistical copolymerization in solution (Haddleton, 1999). ATRP technique was also used to synthesize a PFOMA-b-PMMA by polymerization in supercritical carbon dioxide (Xia, 1999). However, there is no systematical study in tribological properties for these three copolymers.

1.2 Theoretical background

1.2.1 Polymer Tribology

Polymers have some friction and wear properties that can not be obtained by any other groups of material. For examples, the materials which can produce the minimum friction coefficient are polymers. In addition, the high chemical stability of many polymer molecules leads to a surface which is not considerably changed by reactions with the environment, such as oxidation. There are also secondary properties of polymers which favor their application in our field of interest, for example, their high capacity for damping vibrations (internal friction) and their corrosion resistance. From these properties most of the applications can be derived in which friction and wear play a role (Rigney, 1981).

In Figure 1.1 the abrasive wear resistance of ceramics, metal, and polymer is compared. It is quite evident that differences exist between these three groups. The most pronounced difference between polymers and other materials is simply due to the difference in hardness. Friction and wear are not directly correlated with the properties of the bulk material because of the system's dependence on the tribological behavior. However, the material-related aspects may influence the tribological behavior considerably, see Table 1.1. Polymeric materials are superior over metals with respect to their low interfacial adhesion energy, for examples PTFE and PE, leading to lower friction coefficient values. However, lower Herzian contact pressures may not be beneficial for these materials as they are a consequence of viscoelastic and plastic deformations which may occur at low loads (Czichos, 1995).

Over the past 30 years or so, the tribological of polymer have been extensively studied. The main purpose is to optimize the friction and wear properties of the polymeric materials. There have been numerous investigations exploring the influence of test conditions, contact geometry and environment on the friction and

wear behavior. There is now an extensive literature on the tribology of polymers. The frictional behavior has been well explained by Briscoe and others in terms of adhesion, shearing and ploughing but the deformation processes are viscoelastic: further, the resistance to shear increases with contact pressure. Because polymers are relatively poor thermal conductors, frictional heating is liable to produce softening and surface melthing. In some cases, especially with thin polymeric films, electrostatic charges may produce strong interfacial adhesion and so may dominate the frictional behavior. In the study of wear, the level of friction is important but it is the life time of the operating parts which often determines whether a mechanical system is economically or functionally viable. Many types of wear processes have been investigated in details and are reasonably well understood. A substantial advance has been made in delineating the regimes in which they operate by the construction of "wear map" pioneered by Ashby and his colleges. The wear rate is plotted as a function of nominal contact pressure (expressed as a dimensionless ratio of pressure to hardness) and as a function of velocity (expressed as a dimensionless ratio of sliding speed the velocity of thermal diffusion). Nevertheless, the problem still remains that in many practical situations the wear is not dominated by a single wear mechanism. There is an overlapping of wear regimes, and this in turn involves the interaction, often in an unpredictable way, of several wear processes. For this reason some workers find it useful to apply systems analysis to the assessment of wear (Tabor, 1995).

Terminology

Friction: The resisting force tangential to the common boundary between two bodies when, under the action of external force, one body moves, or tends to moves relative to the surface of the other (Peterson, 1980).

Wear: The progressive lost of substance from the operating surface of a body occurring as a result of relative motion at the surface (Peterson, 1980).

Lubrication: The reduction of frictional resistance and wear of other forms of surface deterioration between two load-bearing surfaces by application of lubricant (Peterson, 1980).
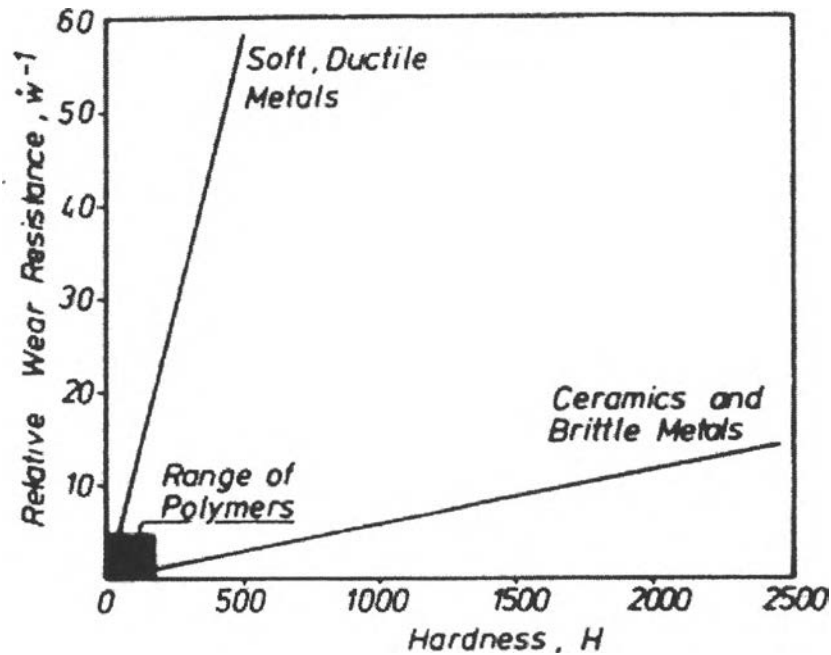
Figure 1.1 Comparison of ranges of wear resistance of metallic ceramics and polymeric materials(Khrushchove,1967).

Table 1.1 Tribological characteristic in relation to material types (Czichos, 1995)

Mass forces	$F_{polymer} < F_{ceramics} < F_{metal}$
Herzian pressures	$P_{polymer} < P_{metal} < P_{ceramics}$
Friction-induce temperature increase	$T_{metal} < T_{polymer} < T_{ceramics}$
Adhesion energy (surface tension)	$Ad_{polymer} < Ad_{metal} < Ad_{ceramics}$
Abrasion	$Ab_{ceramics} < Ab_{metal} < Ab_{polymer}$
Tribochemical reactivity	$R_{polymer}, R_{ceramics} < R_{metal}$

1.2.2 The Relationship Between Structure and Tribological Properties of Polymeric Materials

1.2.2.1 Molecules

Many aspects of the frictional behavior of polymers are directly related to the molecular structure, therefore, some characteristics of polymer molecules will be discussed here, and first we must distinguish straight, stiff

molecules from those which have a tendency to coil (Table 1.1, Fig.1.2). Straight molecules are able to form crystals while coiled; branched molecules can only form glassy structure. Some chains form helices, as, for example, PTFE. Its large F-atoms cause great stiffness, which in turn leads to a high crystallinity, in spite of the weakness of the intermolecular bonds (Chanda, 2000).

Table 1.2 Structure of the polymer molecules used for most of the experiment

Polymer	Structure of chains
PE	
Isotactic PP	
PTFE	
PA6	

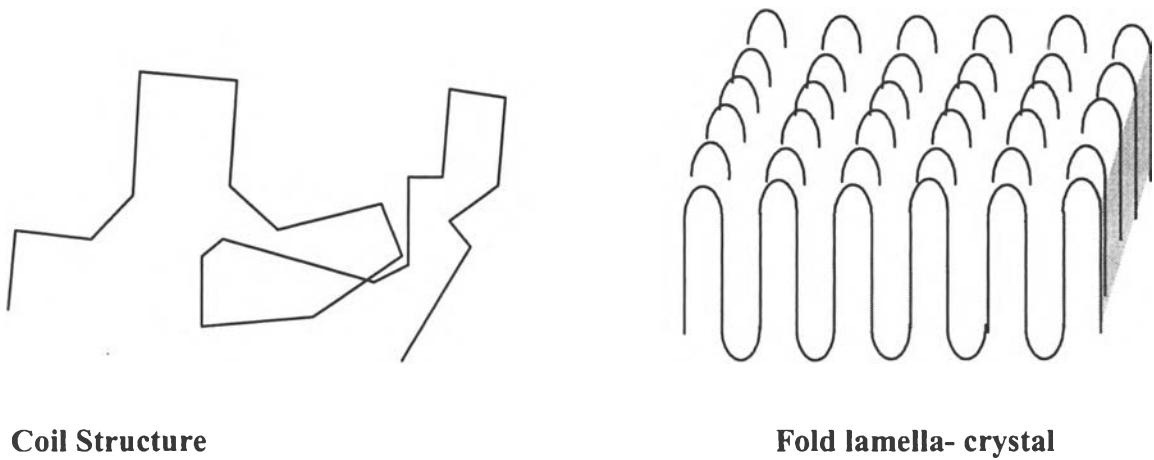**Coil Structure**   **Fold lamella- crystal**

Figure 1.2 Example of molecular arrangement.

The molecule itself can be symmetric or asymmetric, depending on the position of side groups (radicals)(Fig.1.3). A consequence of asymmetric shape of the molecule is the formation of net electric dipole moments, which in turn form the basis for a strong intermolecular bonding. All high strength thermoplastic polymers are characterized by the existence of strong dipoles (polyvinyl chloride, PVC; polypropylene, PP) or of the still stronger hydrogen bonds (polyamides, PA). Side groups can be arranged in a disordered or ordered way (tacticity) (Fig. 1.4). High tacticity favor crystallization. For symmetric molecules, the dipole moment of each individual bond compensates each other so that the bond between individual molecules becomes relatively weak. This weakness of the intermolecular bond coincides with a low surface energy of the material (Charles, 1996).

The strongest intermolecular bond is caused by cross-linking, which is effective in thermosetting polymers, elastomers, and cement. The existence of this type of bond excludes the possibility of plastic deformation. The strength of unsaturated bonds in the surface will determine the surface energy. High cohesion between molecules is favored by a high density of strong bond, i.e. or by high tacticity and high crystallinity (Odian, 1991).
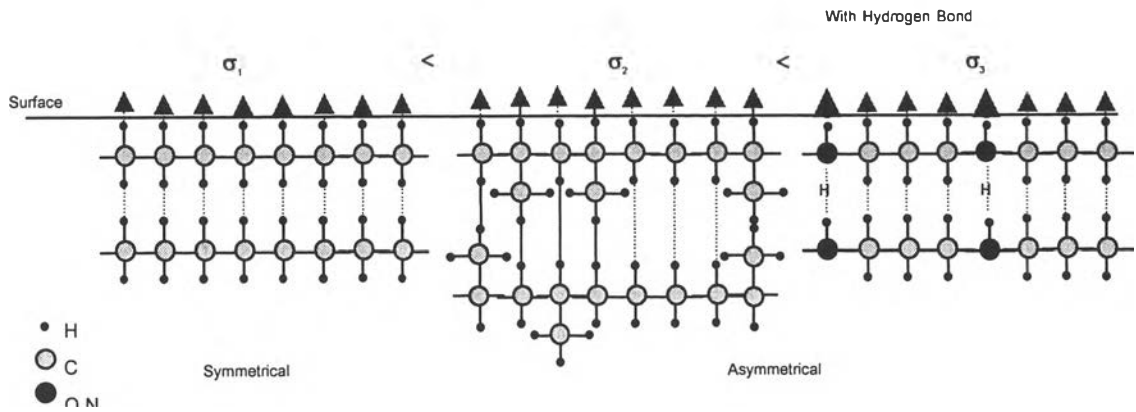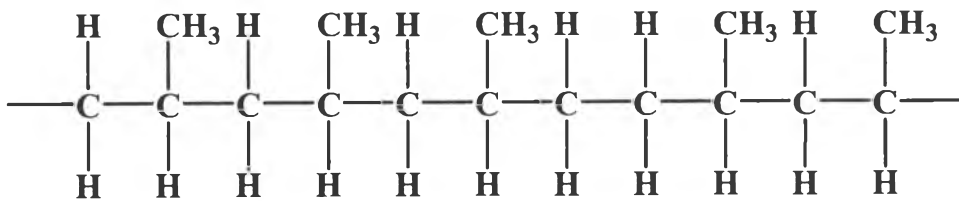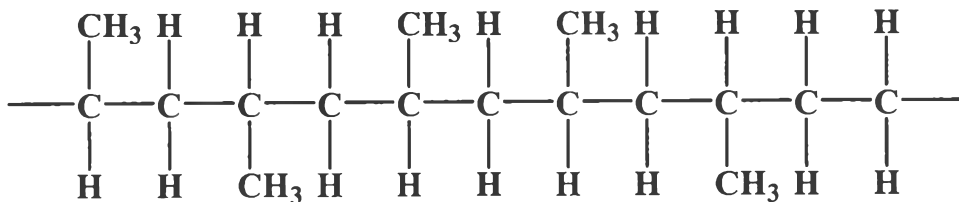
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Figure 1.3 Influence of different types of intermolecular bonding on surface energy and cohesion.

Isotacatic PP

Atactic PP

Figure 1.4 Isotactic and atactic configuration of propylene molecules.

1.2.2.2 Morphology

There is wide range of possibilities of the arrangement of molecules inside the bulk material, i.e., of morphologies of the polymer. The most

important cases will be mentioned here. All thermosetting materials and elastomers and some thermoplastic materials are glasses. In the undeformed state, they show a random arrangement of the molecular chains. The conformation of the molecules themselves varies between coiled and straight. Most thermoplastic materials are mixtures of crystalline and glassy regions (Sperling, 1993).

The elementary crystalline element is the folded lamella. These lamellae in turn are stacked into packages, surrounded and tied together by non-crystalline portion of the micro structures. Some of special arrangements are the microcrystalline structure and spherulitic structure. Cohesion between molecules increases with degree of crystallization. Cohesion of polyethylene (PE) and PTFE is predominantly due to their high crystallinity, while their specific intermolecular bonds are relatively weak. Intermolecular bond in PP are stronger; however. A high tacticity is required to permit crystallization (Chanda, 2000).

In an intermediate range of temperature and strain rate all thermoplastic materials can deform plastically, and, as a consequence, the molecules become aligned. During sliding, the maximum amount of deformation in the surface can surpass that obtained in tensile tests. The structure is then characterized by a high degree of molecular alignment in the direction of sliding (Rigney, 1981).

There exists a large number of heterogeneous structures in undeformed polymers. An important case is the coarse spherulitic structure in which small-molecular-weight portions have been rejected during crystallization, so that the boundery regions between the spherulites are amorphous. The amount of crystallinity and therefore cohesion is high inside the spherulites (Sperling, 1993).

Often organic or inorganic admixtures are contained within polymeric materials. In these cases additional interfaces are produced which may be important, especially in connection with separation processes during wear. One function of such additives can be the reduction of adhesion between foils. For example, SiO_2 particles in PP reduce the tendency of foils to stick to each other. Such additives may induce decohesion by local cracking, and they may also form debris which can cause abrasion (Rigney, 1981).

1.2.2.3 Bulk Physical Properties

The bulk properties of polymers are much different from those of metals in tow respects. Mechanical properties vary over an extremely wide range, from high elastic modulus and brittle behavior at low temperatures through work hardening and relatively tough or rubber-elastic behavior at intermediate temperature, to viscous behavior at still higher temperatures. The transition to the liquid state is continuous above the glass transition temperature for amorphous polymers. The existence of crystalline portions leads to a partially discontinuous transition to the liquid state at the melting temperature. Analogous transitions are found in the deformation behavior of rubbed surfaces. The surface temperature, however, can be raised considerably by the frictional heat because of the low heat conductivity (Fig.1.5). This is a property which polymers have in common with ceramics. Table 1.3 shows that their heat conductivities at ambient temperature are typically only one thousandth of those of metals and alloys. This property together with the low melting temperature of most of the polymer leads to the particular sensitivity of all experimental results with respect to temperature, velocity of sliding, and load. This is one reason for a low degree of reprodcucibility of experimental results and the wide range of data found in the literature (Rigney, 1981).
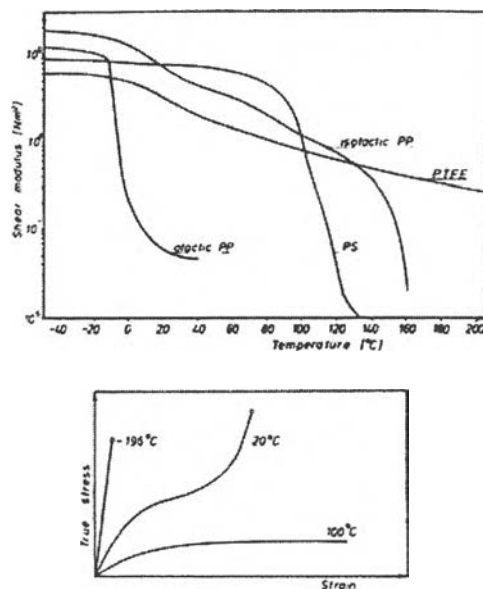

Figure 1.5 Temperature dependence of mechanical properties: (top) shear modulus of several thermoplastics; (bottom) typical stress strain curves of PP . (Rigney,1981).

Table 1.3 Melting point, glass transition temperature, heat conductivity, surface energy of several materials (Rigney, 1981)

Materials	Melting Point $(T_m, {}^{\circ}C)$	Glass transition temperature $(T_g, {}^{\circ}C)$	Heat conductivity (λ), $J/ms^{\circ}C$	Surface energy (σ), $10^{-3}J/m^{-2}$
PTFE	327	126	0.244	22
HDPE	137	-120	0.337	24
PP	165	-18	0.221	26
PS	240	100	0.174	28.9
Atactic PP	-	-	0.163	36
PVC	212	87	0.163	36.5
PA66	250	-	0.244	36.9
PMMA	160	105	0.186	38.3
SiO_2	2427	-	2.3	320
Ag	961	-	400	920
Cu	1083	-	380	1100
γ-Fe-18Cr-8Ni	1400	-	16	1400

1.2.3 Mechanism of Friction

1.2.3.1 General Considerations

(i) When relative motion between the contacting bodies occurs, the friction force, F_F, always acts in a direction opposite to that of the relative velocity of the surfaces:

$$F_F = f \times F_N \tag{1}$$

Through this relationship, it is possible to define a coefficient of friction, f

$$f = F_F/F_N \tag{2}$$

(ii) The friction force, F_F, is proportional to the normal force, F_N

(iii) The Friction force is independent of the apparent geometric area of contact

These relations, known as, "Amontons-Coulomb Laws" (Blue,1992) of dry sliding friction are used as simple guiding rules in tribological applications.

Table 1.4 Energy –based overview of friction phenomena (Freidrich,1986)

I.	**Introduction of mechanical energy into the contact zone**
	Formation of real area of contact
II.	**Transformation of mechanical energy**
	Elastic deformation and elastic hysteresis
	Plastic deformation
	Ploughing
	Adhesion
III.	**Dissipation of mechanical energy**
	(a) Thermal transformation
	Generation of heat and entropy
	(b) Storage
	Generation of point defects and dislocations
	Strain energy storage
	Phase transformations
	(c) Emission
	Thermal radiation and conduction
	Phonons (acoustic waves, noise)
	Photons (triboluminescence)
	Electrons (exo-electrons)

Tabor pointed out that we recognize that three basic phenomena are involved in the friction of unlubricated solids.

(a) the area of real area of contact between the sliding surfaces;

(b) the type of strength of bond and that is formed at the interface where contact occurs; and

(c) the way in which the material in and around the contacting regions is sheared and ruptured during sliding.

Because friction is essentially an energy dissipation process, the energy consideration of friction may also be useful. Accordingly, the whole course of the "loss" process of mechanical energy due to the friction may be formally divided into different phases as compiled in Table 1.2. Firstly, mechanical energy is introduced in to the contact zone by the formation of the real area of contact. Secondly, the transformation of mechanical energy takes place mainly by the effect of plastic deformation, ploughing and adhesion. Thirdly, the dissipation phenomena include the effects of thermal dissipation, storage or emission.

1.2.3.2 Real Area of Contact

Consider the contact of two nominally flat solid bodies. There has been considerable interest in recent years in surface topography and its role in tribologicalcontact formation and performance. The surfaces of tribological contact are covered with asperities of a certain height distribution which deform elastically or plastically under the given load. The summation of individual contact spots gives the real area of contact with generally is much smaller than the apparent geometrical contact area. There are two classes of properties, namely deformation properties and surface topology characteristics. Without going into details, it can be said that, for example, the behavior of metals in contact is determined by a deformation criterion. Namely, the so-called plasticity index. If a tangential force is introduced, a junction growth of asperity contacts may occurred leading to a considerably larger area of contact. For polymeric materials in contact, viscoelastic and viscoplastic effects and relaxation phenomena must be taken into consideration. These influences lead to a time-dependence of the contact area and to hysteresis loss in loading/ unloading cycles (Freidrich, 1986).

1.2.3.3 Adhesion Component of Friction

The adhesion component of friction is due to the formation and rupture of interfacial adhesion bonds. There have been theoretical papers to explain this interaction, especially for the contact of clean metals, in terms of the electronic structure of the contacting partners. Theoretically, the attractive interaction forces between two contacting solids include, at least in principle, all those type of interaction that contribute to the cohesion of solids, such as metallic, covalent and ionic, i.e. primary chemical bonds (short-range forces) as well as secondary van der Waals bonds (long-range forces. For example, two pieces of clean gold placed in contact will form metallic bonds over the regions of atomic contact and the interface will have the strength of bulk gold. With a clean diamond, the surface forces will resemble the valency forces. With rock salt, the surface forces will be partly ionic. All these forces are essentially short rubber-like materials and between polymeric solids. It is evident from these examples of metals, ceramics and polymers that interfacial adhesioni s as natural as cohesion which determines the bulk strength of materials with in a solid (Freidrich, 1986).

In considering the adhesion component of friction, it must be emphasized the relevant influencing properties, such as the interfacial shear strength or the surface energy, are characteristics related to the given pair of materials rather than to the single component involved (Freidrich, 1986).

1.2.3.4 Deformation Component of Friction

Because of the deformation during sliding contact, mechanical energy may be dissipated through plastic deformation effects. Green (1955) analyzed the deformation of the surface asperity contact using the slip-line field for a rigid-perfectly plastic material. In a similar way, in applying a two-dimensional stress analysis of Prandtl, Drescher has worked out a slip-line deformation model of friction as summarized in Figure 1.7 in this model, it is assumed that, under an asperity contact (A in Figure 1.7) tree regions of plastically deformed material may develop which are described in Figure 4 by the regions ABE, BED, and BDC. The maximum shear stress in these areas is equal to the flow shear stress of the pertinent material. An important parameter in this model is factor, λ, the
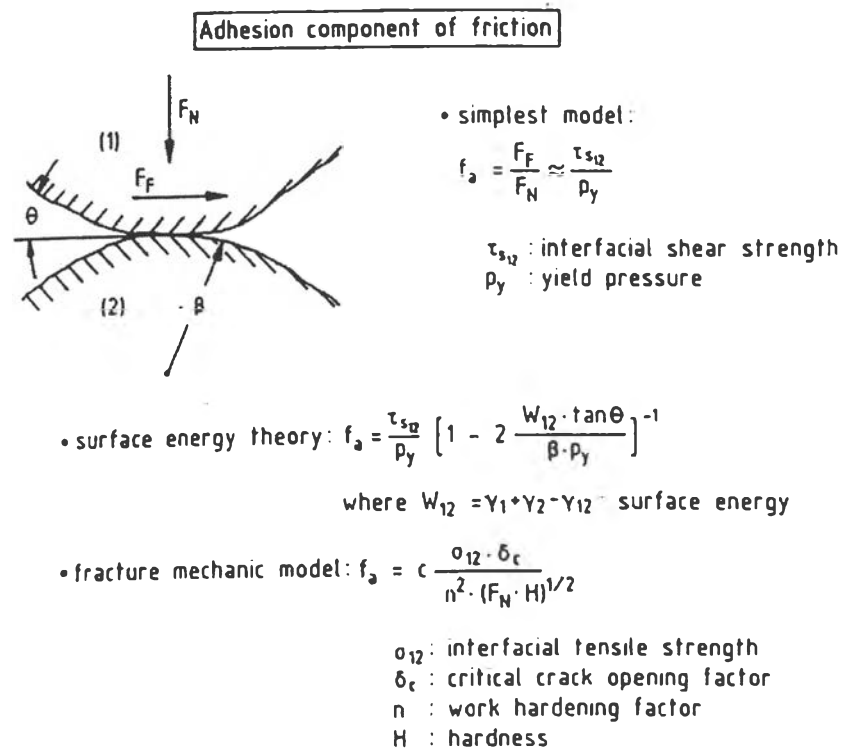
Figure 1.6 Characteristic of adhesion model of friction (Freidrich, 1986).

proportion of the plastically supported load which is related in complicated manner to the ratio of the hardness to the elastic modulus. If the asperity is completely plastic and the asperity slope is $45°$, a friction coefficient of $f = 1.0$ results. This values goes down to $f = 0.55$ if the asperity slope approached zero. In discussing the deformation component for friction, Drescher pointed out that this model is a very simple one and that some other material properties such as the microstructure of the materials, work hardening effects, thermal softening, and the influence of interfacial layers should be considered (Drescher, 1959).

A recent model of the slip-line theory of the deformation component of friction was advance by Challen and Oxley (Chellen, 1979).

Another model of the deformation component of friction, which relates friction mainly to plastic deformation, was suggested recently by Heilmann and Rigney (Heilmann, 1981). The main assumption is that the frictional

work performed is equal to the work of plastic deformation during steady-state sliding. As summarized in Figure 4, there are three main parameters characterizing this model.

(a) The real area of contact.

(b) The ultimate shear strength of the material which can be achieved during shear.

(c) The average shear strength actually achieved at in the interface during sliding.

This quantity may depend on many experimental parameters such as operating conditions (load, sliding velocity, temperature) and other material characteristics such as crystals structure, microstructure, work hardening rate and recovery rate.
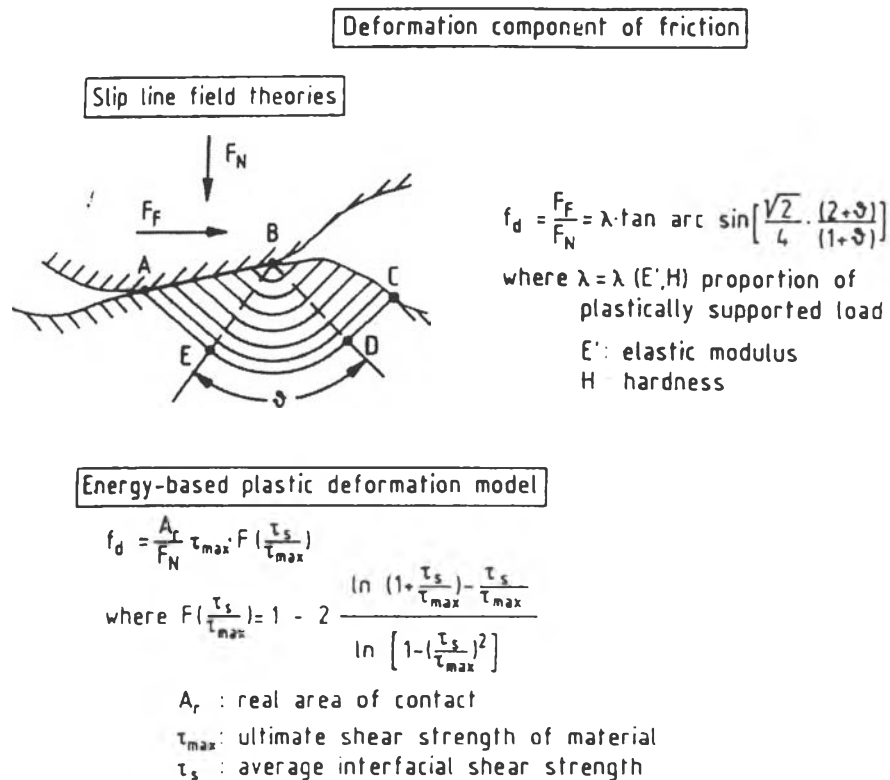

Figure 1.7 Characteristic of deformation model of friction. (Freidrich, 1986)

1.2.4 Mechanism of Wear

1.2.4.1 Generation Consideration

Similar to friction, the wear behavior of materials is also a very complicated phenomenon in which various mechanisms and influencing factors are involved. A great step forward in our understanding of wear was the classification of wear mechanisms given by Burwell in the 1950s (Burwell, 1958), according to which wear mechanisms may be divided into four broad general classes under the headings of abrasion. Adhesion, surface fatigue and tribochemical processes.

In recent year, an increasing number of studies have been devoted to wear which indicate that wear, i.e. "the removal of material from interacting surfaces in relative motion", results from various interaction processes. In quoting a summarizing description of Suh (1982), it may be said that "wear of materials occurs by many different mechanisms depending on the materials, the environmental and operating conditions and geometry of the wearing bodies. These wear mechanisms may be classified into two groups: those primarily dominated by the mechanical behavior of solids and those primarily dominated by the chemical behavior of materials. What determine the dominant wear behavior are mechanical properties, chemical stability of materials, temperature and operating conditions" (Freidrich, 1986).

Tabor divided wear into three groups: "the first is that in which wear arises primarily from adhesion between the sliding surfaces, the second is that deriving primarily from non-adhesive process and the third is that very broad class in which there is interaction between the adhesive and non-adhesive process to produce a type of wear that seems to have characteristics of its own. The way which these mechanisms interact with one another depends extremely sensitively on the specific operating conditions. In addition, the frictional process itself can produce profound structural changes and modifications of the physical and chemical properties of the sliding surfaces. Considerably, unless a single wear process dominates, these surface changes and complex interactions must necessarily make wear predictions extremely difficult and elusive" (Freidrich, 1986).

1.2.4.2 Surface Fatigue and Delamination Wear Mechanisms

As is known from the mechanical behavior of bulk materials under repeated mechanical stressing, microstructural changes in the material may occur which result in gross mechanical failure. Similarly under repeated tribological loading, surface fatigue phenomena may occur leading finally to the generation of wear particles. These effects are mainly based on the action of stresses in or below the surfaces without needing a direct physical solid contact of the surfaces under consideration. This follows from the observation that surface fatigue effects are observed to occur in journal bearing where the interacting surfaces are fully separated by a thick lubrication film. The effect of fatigue is especially associated with repeated stress cycling in rolling contact. However, the asperities also undergo cyclic stress in sliding, leading to stress concentration effects and the generation and propagation of cracks. On the basis of the dislocation theory, there are several possible mechanisms for crack initiation and propagation. A contribution of to the theory of surface fatigue wear mechanisms was put forward by Halling. This model incorporates the concept of fatigue failure and also of simple plastic deformation failure (Halling, 1975).

In studying the plastic- elastic stress fields in the sub-surface regions of sliding asperity contacts and the possible dislocation interaction, a "delamination theory of wear" has been put forward by Suh. (Suh, 1973) in which the generation of sheet like wear particles is explained on the basis of the chain events as follow,

    (i)   transmittance of stresses at contact points

    (ii) incremental plastic deformation per cycle

    (iii) subsurface void and crack nucleation

    (iv) crack formation and propagation

    (v) delamination of sheet-wear particles