MALEIC ANHYDRIDE GRAFTED POLYPROPYLENE COATINGS ON STEEL:

ADHESION AND WEAR

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Polymeric coatings are being used in a growing number of applications, contributing to protection against weather conditions and localized corrosion, reducing the friction and erosion wear on the substrate. In this study, various polypropylene (PP) coatings were applied onto steel substrates by compression molding. Chemical modification of PP has been performed to increase its adhesion to metallic surfaces by grafting of maleic anhydride (MAH) onto PP in the presence of dicumyl peroxide (DCP). Influence of different concentrations of MAH and DCP on the properties of resulting materials have been examined. The coated steel samples are characterized by scanning electron microscopy (SEM), shear adhesion testing, FTIR and tribometry. The coatings with 3 wt. % MAH have shown the maximum adhesion strength due to maximum amount of grafting. The wear rates increased with increasing the amount of MAH due to simultaneous increase in un-reacted MAH.
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1.1 Introduction

Polymers are considered as one among those important commercial materials without which surviving would be considered impossible. Polymer based materials in their capacity as bulk materials and thin films are highly valued and used in variety of applications including packaging, protective coatings [1], adhesion, friction [2] and wear [4, 5, 7], high performance membranes, biomaterials [1, 6] etc. The surface properties of polymers such as adhesion, friction, wear and permeation are largely influenced by the structures of the polymer surfaces and have a strong influence on the commercial applications of polymers. Polyolefins such as polypropylene (PP) and polyethylene (PE) exhibit dual benefit of ease of processing and also possess excellent physical/chemical properties [8]. However they have inert surfaces. Thus surface modification is an essential and convenient tool to combine both the original bulk property with the newly required surface properties [9, 10]. The ultimate purpose of modifying polymer surfaces is to bring about at least one of the following objectives: one is to increase the capability for surface interactions which may include promotion of adhesion and the other is to decrease the degree to which a surface reacts with a given material. Though there are boundless and complicated techniques for surface modification of polymeric materials, in general all surface modification techniques share the common aim of controlling the nature and number of chemical functional groups at the polymer surface. The research described here is focused on surface modification of PP polymer in order to enhance its adhesive properties - especially to metals. PP is a relatively stable material chemically
and has the lowest density in all of plastics; its specific gravity is 0.9 g/cm³. Moreover, it has a high tensile strength and elasticity. Therefore, it is most commercially and widely used engineering plastic. However, PP has poor adhesion or dyeing characteristics. The surface is chemically inert and shows hydrophobic behavior – the reason for poor adhesion. PP surface has been usually modified by methods such as plasma treatment [11, 12], ion treatment [13], use of compatibilizer, blending [14], flame treatment [15], grafting [16, 17], or photo chemical modification [18].

1.2 Polypropylene (PP)

1.2.1 Polypropylene Structure

Polypropylene (PP) was discovered in early 1950s. Since then PP has grown to a commodity polymer with numerous grades of specific end uses [19]. It is a thermoplastic polymer which falls under the category of polyolefinic or ethene-ic polymers and have ethylene i.e., H₂C = CH₂ as the basic monomer structure. Polypropylene homopolymer is semi crystalline in nature. Structurally PP is a vinyl polymer, and is similar to polyethylene. Polypropylene can be made from the monomer propylene by Ziegler-Natta polymerization and by metallocene catalysis polymerization [20].

Fig. 1.1 Polymerization of polypropylene from propylene monomer
The degree of crystallinity in PP is dependent on the tacticity of the chain. PP has three tactic forms – isotactic (i-PP), syndiotactic (s-PP) and atactic (a-PP) as shown in Fig. 1.2. Isotactic chains, in which the methyl groups have the same configuration with respect to the polymer backbone is the most often made commercial polypropylene [21]. Syndiotactic PP, on the other hand, has an alternating configuration of methyl groups. Atactic chains have methyl groups situated at random.

Fig. 1.2: Different tacticities of PP

PP is prepared industrially by polymerization of propylene (C\textsubscript{3}H\textsubscript{6}) in a low pressure process using a mixture of aluminum triethyl and titanium tetrachloride (Zeigler-Natta catalyst) catalysts as noted earlier. The reaction mechanism induces a chain with a helical structure that exhibits the same asymmetrical stereochemical configuration of carbon atoms. This leads to a macromolecule with a high degree of crystallinity. Hence PP has considerably better mechanical properties compared to polyethylene (PE); PP has a lower density than PE, it is stiffer, harder and has a higher
strength than most PE grades. Also, due to its higher melting point (160°C), it can be used for processes which involve high temperatures and it is only attacked by strong oxidizing agents. PP has high modulus and a lower isobaric thermal expansivity than PE. PP can be compounded with a very broad range and amount of fillers, reinforcing agents and other polymeric materials [22 – 24]. However, as already noted, poor adhesion of PP to the surface of other materials, especially metals is the primary concern. This situation provides one of the motivations for the present work.

1.3 Modification of Polymers

1.3.1 Introduction

Even before the concept of macromolecules was recognized and the polymeric nature of these materials was studied extensively, the chemical modification of naturally occurring materials such as cellulose or rubber was already in existence. The history of the rubber industry shows how the observed methods of chemical modification of the latex of *Hevea brasiliensis* led to the evolution of an important class of products. Similarly, modified chemical treatments of cellulose based on standard nitration/acetylation techniques led to the evolution of equally important families of products. Reduction on cellulose of the so called fiber reactive dyes was one of the important and initial examples of the heterogeneously conducted chemical modification of a polymeric material. This particular technique of dyeing cellulosics has been developed to serve wool and synthetic fiber industry. These and similar developments helped to obtain the blustering progress in polymer chemistry that exposed us to the present “Modern Plastic Age.” In order to compete successfully with other classes’ of materials such as metals and to accommodate to the diverse demands, the polymer
industry has to amplify the properties of its products and in order to satisfy specific demands such as conductivity, resistance to environmental attack, reactivity with specific groups of ions, wettability, good adhesion and biodegradability, etc. The enhancement of the desired bulk and surface properties of polymeric systems through modification of existing polymers is essential. In fact, instead of development and introduction of new polymers, the modification of existing polymers is preferred by the industry for economical and technical reasons. Techniques involving chemical modification of bio-polymers proved to be of great help in their study and for evaluation of their structures [25].

Reacting the polymers with others in solution and apparently, modifying them chemically has been studied extensively in the past [26]. Chemical treatments of fibers and films have provided the most obvious way for modification of their surface properties and such reactions have also been in use for several decades [27].
1.3.2 Need for Surface Modification

**TABLE I**

**Need for Surface Modification**

Why surface properties of polymers should be modified?

**Advantages of Common Polymers**
- Low cost (most often)
- Good processability (Films, bottles, fuel tanks, pipes, membranes, etc., can be fabricated.)

**Disadvantages of Common Polymers**
- Poor adhesion (most often)
- Bad barrier properties
- Low permeability/selectivity correlation for polymer membrane processability
- Often low antibacterial properties
- Large coefficient of friction

Two routes to enhance commercial properties which are defined by the surface layer properties

**High Cost**
- Synthesis of new polymer

**Low Cost**
- Surface modification
As already mentioned, PP has a hydrophobic surface due to the pendant methyl groups and a purely hydrocarbon backbone and this restricts its applications where surface polarity is required. Hence the dire need to modify PP arises. In general, the surface modification techniques basically share the common goal of controlling the nature and number of chemical functional groups at the polymer surface. Hence the term functional group is used generically to indicate any chemical moiety that would bring about a desired change on the surface. There is a rising need for material surface modification for basically two important reasons: first there has been a steady and fast growth in the fundamental understanding of the structure property relationship, especially between physicochemical structure and various aspects of surface performances. So the guidelines for the rational design of polymer surface modification are set. Second, there is also an increase in the availability of state-of-the-art analytical techniques, which make it possible to modify and then characterize the modified surface [29]. Not all possibilities for surface modification are feasible. Most of the chemical reactions are in solution i.e. they are homogenous, while most surfaces are heterogeneous. Also, the rates and yield of heterogeneous reactions are lower than the homogenous ones and the characterizations of the modifications are made on indirect evidences. All these possibilities and limitations have to be kept in mind when proceeding with the surface modification of any polymer.

1.4 Various Methods Used for Polymer Modification

The surface and bulk characteristics requisites of a particular polymer material may often vary. Sometimes the requirement might be, obtaining a biocompatible surface characterized by low friction as well as to have strong fibers within the material. Thus,
the modification techniques which would not affect the bulk properties, but those which will be restricted to the surface or to amorphous regions of a semi-crystalline polymer may offer a good solution. Thus depending upon requirements and desired properties of a polymer, there have been different innovative techniques which include:

- Surface modification of polymers
- Bulk modification of polymers with additives
- Compatibilization of polymers

1.4.1 Polymer Surface Modification

1.4.1.1 Physical Surface Modification

The physical surface modification techniques include:

- Flame treatment
- Corona discharge treatment
- Irradiation
- Plasma treatment

The activities aimed at physically modifying the surface can be categorized in two broad categories: the first by altering the surface layer and the second by depositing an extraneous layer on top of the existing layer, thereby generating a sharp interface. Thus physical modification techniques use the principles of surface segregation, radiation with electromagnetic waves, oxidation with gases and several more. Knowing the inert nature of PP surfaces, to use the first method would imply to generate high energy reactive species i.e. radicals, ions, etc. In nature, fire or thunder are the only two high energy media and for practical purposes fire, plasma and corona discharges simulate these real life sources. In flame treatments [30], oxygen containing functionalities are
introduced at PP surfaces, mainly to improve adhesion, printability or paintability. The active species formed at high temperature are radicals, ions and molecules in excited state. In corona treatments, the corona effect is used, that is the formation of high energy electromagnetic fields close to charged thin wires or points, with consequent ionization in their proximity [31]. In the ionized region, excited species such as ions, radicals, electrons and molecules are present, and these provide the active oxygen-containing functionality. With cold-plasma treatments, low temperature plasmas require low pressures but functional group contains high energy photons, electrons, ions, radicals. Using plasma chemistry has its own advantages and disadvantages: the former includes the formation of chemical bonds at the interface but there can also be the possibility of high degree of cross-linking on the plasma polymerized layer. With hot plasma treatments [32] plasmas generated at atmospheric pressures reach very high temperatures and these can then be used for metallurgical operations like physical vapor deposition (PVD) and chemical vapor deposition (CVD) etc., for depositing coatings. In ultraviolet treatments, photons with short wavelengths are the energetic species used to activate various chemical reactions. Most commodity polymers, especially PP [33, 34] have been extensively studied. Irradiation in the presence of oxygen or ozone is progressively used for improving wettability. Laser sources can be used to promote cross-linking or opposite scission effects. Lasers can have high enough intensities that can modify polymers even with high molecular weight (M). They are magnetic and spatially coherent.
1.4.1.2 Chemical Surface Modifications

In wet chemical surface modification, a material is treated with liquid reagents to generate reactive functional groups on the surface. This traditional approach can be easily conducted as it does not require specialized equipment and hence can be easily performed in a small-scale laboratory [35]. Also, in comparison to plasma and other energy source surface modification techniques, this makes easy penetration of the wet chemical through porous three-dimensional substrates as well as in-situ surface functionalization. On the other hand, these techniques are not very reproducible and may produce hazardous chemical wastes and irregular surface etching.

1.4.2 Bulk Modification of Polymers with Additives

Most of the macromolecular substances, especially solid polymers, that are received from manufacturing processes cannot be used as received. Almost every time, small amounts of additives have to be mixed as processing aids or to improve the properties of the polymer before molding or granulating these compounds [36]. The following additives are the most commonly used ones and are beneficial to processing:

- Lubricants are used to enhance the rheological properties during manufacture and to ease processing
- Stabilizers are added in melt to prevent thermooxidative degradation
- Plasticizers increase processability, flexibility and impact strength
- Antioxidants and light stabilizers are used as anti-ageing additives to protect against oxygen and light during service
- Fillers and reinforcing materials selectively modify certain predominant mechanical properties
Sometimes depending on the actual need and intended application of the polymer, the following agents are also added:

- Antistatic agents for protection against electrostatic charging
- Flame proofing agents to decrease flammability and combustibility
- Conducting additives, e.g., carbon black or graphite, to decrease electrical resistance
- Blowing agents for manufacture of foams
- Dyes and organic/inorganic pigments for coloring

1.4.3 Compatibilization

The goal of combining two or more polymers such as commercial ones or commercial and specialty polymers is to achieve a combination of favorable properties from each constituent of the blend. Compatibilization lowers the interfacial tension in a blend while also reducing the coalescence rate. However, when two immiscible polymers are blended without any compatibilization, what one would obtain is a mixture with physical properties that are worse than those of the individual polymers. Usually such blends have poor structural integrity combined with poor heat stability. On macroscopic levels, the blend appears to be heterogeneous and even structurally delaminated. When a compatibilizer is indeed used, one expects a synergistic combination of the favorable properties of the parent polymers in the blend. In short, the ultimate goal in making a compatible blend is to stabilize an appropriate morphology of the dispersed phase polymer in the matrix polymer. There are several methods of compatibilization of immiscible polymer blends but these can be broadly classified into two main strategies [37]: physical compatibilization and reactive compatibilization. The
first one (also called blending) consists of adding a pre-formed suitable substance such as a copolymer or a coupling agent to the immiscible blend. The second strategy (called grafting) involves the generation of the compatibilizer in-situ during the melt processing of the blend. These two processes will be explained in detail in the following Section.

1.4.3.1 Polymer Blending

In order to develop new organic materials from the existing ones a method called “polymer blending” serves as an effective method. This method is very important and can be used for many polymer systems [38]. However, Y.X. Pang et. al. in their paper quoted that most polymer pairs are essentially immiscible. Usually the blending of two or more polymers gives a way to a multiphase blend, instead of a homogeneous material [39]. The ultimate properties of these multiphase blends predominantly depend upon the morphology and interfaces between micro phases [40]. Thus in order to obtain effective blending as well as to acquire reproducibility in the properties of the blend, these factors must be under control. Many researchers have focused on the control of morphology and interfaces of immiscible polymer blends in order to improve their compatibility. It is now well known that copolymers, especially block and graft copolymers are effective for this purpose [41, 42]. These copolymers, which are called compatibilizers when used for this purpose, can be pre-formed and then added into the blend or, formed in situ during melt blending through interfacial chemical reaction of the polymeric components. Usually the compatibilizer concentrates at interfaces during blending, and plays the roles of strengthening interface adhesion, reducing interfacial tension and preventing coalescence [43], which results in the decrease of the domain size and improvement in mechanical properties as well.
Blending of PP with different engineering thermoplastics has been proved to be an effective way to improve the properties of PP. For example, PP + polyamide blends are intensively investigated [44]. Brostow et al. [45] reported that PP + PS (polystyrene) blends with styrene-ethylene/butylene-styrene (SEBS) compatibilizing agent improve the blend morphology and thermophysical properties of the blends. Bataille et al. [46] reported that PP + PET (polyethylene terephthalate) blends without compatibilizer exhibited weak interactions between the two phases. Hence, the resulting mechanical properties of the blend were poorer than for both neat PP and for PET individually. Although many papers in the literature have discussed effects of compatibilization on morphological and mechanical properties of immiscible blends, due to lack of ability to quantitatively measure the adhesion between the interfaces, important details of the interfaces such as adhesion strength, cohesion or cohesive forces etc., are still not clear. However, it is widely accepted that the improvement of mechanical properties of a compatibilized blend results from the improved interfacial adhesion [47 – 50].

1.4.3.2 Grafting

The various techniques available to graft polymers or monomers on polymeric backbones include chemical, radiation, photochemical, plasma-induced and enzymatic. When grafting is initiated by chemical means it can proceed along two major paths: free radical grafting or ionic grafting. Atom transfer radical polymerization is also pertinent. In free radical grafting, radicals are produced from initiators and transferred to the polymeric backbone to react with the monomer to form graft co-polymers. Radiation grafting through the ionic mode proceeds where ions are formed through high-energy irradiation. The polymer is irradiated, it forms polymeric ions; then on reacting with the
monomer, it forms a graft-copolymer. One big advantage of ionic grafting is the high reaction rate. In photochemical grafting, the grafting process is initiated when a chromophore on a macromolecule absorbs light and it becomes excited and dissociates into reactive free radicals. Plasma induced grafting has already been discussed. The Enzymatic grafting technique is new and the principle involves enzymes which initiate chemical/electrochemical grafting reactions.

Grafting can be done broadly by two different routes: ‘grafting from’ and ‘grafting to.’ The former utilizes active chemical species already present on the surface to initialize the polymerization process. The latter route utilizes preformed polymer chains carrying reactive groups at ends or sides which are covalently coupled to the surface. Also, grafting can take place on spherical substrates as well as plane surfaces. For reactive compatibilization, the functional groups are selected so that they are formed at the interface within the processing time at the extruder. Because of the limited yield of the interfacial reaction and the high viscosity of the reaction medium, highly reactive groups are required.

Norton et al. [51] and Sha et al. [52] in their work on the mechanism of reinforcement of the interface verified that the maximum surface density of graft molecules that can be effectively attached to the substrate surface is inversely proportional to the length of grafted chains measured by their degree of polymerization. Norton showed in his experiments that the maximum surface graft density ($\sigma$) was obtained when the length of the connector molecules ($N$) was small.

Grafting by UV radiation on semicrystalline polymers yields a bumped surface texture, likely due to the difference in the activation reaction between the crystalline and
the amorphous regions, and this creates adhesion sites by mechanical interlocking [53]. One of the good candidates for carrying out surface grafting with UV is hydroxyethylmethacrylate (HEMA). First it is inexpensive, can be easily grafted to polyolefins by UV grafting, and it contains polar hydroxyl groups that help in imparting the desired hydrophilicity. Exposing isotactic PP to ozone results in surface oxidation and formation of peroxides and hydroperoxides. With as little as 5 minutes of ozonation, the molecular weight of the PP is drastically reduced. Cellulose fibers exhibiting stimuli (pH) sensitive behavior have been prepared by ozone – induced graft polymerization.

The structure of grafted surface changes with the degree and amount of grafting. Grafting density changes in a wide range depending on the conformation of the graft chains and also whether it is in a good solvent or a poor solvent. A mushroom structure is formed at low grafting densities, whereas at high grafting densities stretched polymer brushes are obtained.

Maleic anhydride (MAH) has been extensively used to modify PP by the grafting process. Grafting PP with MAH increases its polarity, thus increasing its capacity for interfacial interaction [54]. PP-g-MAH has been used for several purposes: as a compatibilizer in polyolefin blends, as a coupling agent for chemically bonding reinforcing agents to the PP matrix, as an adhesive layer in multilayered coextruded laminates and also as surface coatings of metals. MAH in the copolymer improves the dyeability of PP fibers and PP-g-MAH is also used with reinforcing agents in laminated paper substitutes. For grafting functional PP, two methods, namely hydroperoxidation and halogenations, are used [55]. The hydroperoxidation of PP can be carried out by heating in an air/oxygen current at 70-80 °C. Five oxidation variables – temperature,
time, oxygen concentration, pressure and concentrations of initiator and surfactant – are considered to be important factors to attain peroxide content for a desired graft level. A number of monomers such as methyl methacrylate, vinyl chloride and vinyl acetate are used for the hydroperoxidation which is believed to be restricted to surface or intercrystalline amorphous regions. Halogenation is another method used to introduce functionality into the PP backbones. Thus a chlorine atom is introduced onto PP backbone turning nonpolar PP into a polar one.

The most common free-radical grafting reactions are grafting of unsaturated monomers, such as maleic anhydride or acrylic acid to polyolefins, to improve the adhesion of polyolefins to polar phases. References [67-69] are patents that relate to a method for appending carboxyl groups to polymers by reacting a mixture of MAH, a free-radical catalyst with a polymer above its melting point. Among the possible routes of obtaining polypropylene grafted with MAH (PP-g-MAH), reactive processing is worth mentioning, due to ease of performing the process and low cost. Grafting of MAH onto PP by reactive processing involves reacting the polymer melt with MAH in the presence of organic peroxides. Such reactions are usually carried out in the equipment like torque rheometers [70 – 73], single screw extruders [74 – 76], Brabenders [74] and in twin screw extruders [72, 77, 78].
CHAPTER 2
CHARACTERIZATION OF POLYMER COATINGS

A discussion of polymer coatings, the need for polymer modification and different methods involved in polymer modification was presented in Chapter 1. This chapter deals with the theoretical aspects of the characterization techniques which will be used to characterize and study the properties of coatings prepared in this project.

2.1 Adhesion

A coating with excellent properties in terms of resistance to scratch, chemicals, weather, wear and corrosion will be clearly worthless unless sufficient adhesion is obtained between the substrate and the coating. It is therefore necessary to provide for good adhesion features when coatings are formulated. Furthermore, the quantification of adhesion strength is also equally important in order to improve the properties of the coating.

Adhesion is the force of attraction between two materials in contact with each other. It refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred through the interface [56]. The forces that contribute to this interfacial force include Van der Walls forces, covalent bonding, mechanical interlocking and/or electrostatic attraction. “Chemical adhesion” refers to the adhesion at the interface due to chemical bonding. “Mechanical adhesion” refers to the adhesion developed due to the mechanical interlocking all over the interface. Thermodynamic adhesion [57] refers to interfacial forces that are in equilibrium, associated with the reversible processes such as work of adhesion or heat of wetting.
2.1.1 Components at the Interface

Usually a polymeric coating consists of more or less cross-linked macromolecules and a certain amount of pigments and fillers. Metals, wood, plastics, paper, leather, concrete, or masonry belong to the most important materials that can form the substrate for the coating.

The substrate materials may have rigidity higher than that of the coating. In those cases the fracture will occur within the coating when the system experiences external force of sufficient intensity. Cohesive failure will be the consequence, however, if the adhesion at the interface surpasses the cohesion of the coating layer. Otherwise, adhesive failure is obtained, indicating a definite separation between coating and substrate.

![Diagram of bonding situation at the interface of polymer layer and substrate](image)

Fig. 2.1. Bonding situation at the interface of polymer layer and substrate [58]

It is possible to base the predictions of where failure will occur by taking into consideration the energetic aspects at the interface and the effects of elasticity within the coating [59]. Though both types of adhesion damages occur in practice, existence of cohesive fracture would signal the attainment of good adhesion strength [58].
2.1.2 Causes of Failure

The bond between the coating and the substrate can be put under stress, and may thus finally fail due to several external factors, acting either alone or in combination. There are three basic types of stresses in adhesively bonded joints. These include mechanical stresses, thermal stresses, and chemical stresses, as shown in Fig. 2.2. Mechanical stresses can be further divided into tensile, shear, cleavage and peel stresses.

![Diagram](image)

**Fig. 2.2. Situation at the interface of polymer layer and substrate**

Due to temperature changes, sometimes rapid ones, the difference in the expansivity between substrate and the coating material can cause some interfacial stresses of such a high intensity that the paint film becomes detached from the substrate.

There may be, of course, an effect of a chemical that penetrates the coating and becomes absorbed at the interface, causing loss of adhesion.
2.1.3 Various Adhesion Tests for Adhesion Strength Evaluation

There are various possibilities for characterizing the results obtained in an adhesion test. The adhesion strength is defined as the maximum load at which the coating fails or it is the maximum mechanical stress that can be attained at the interface. The adhesion strength is expressed in terms of force per unit area and specified either as tensile or shear stress. There are various methods in practice for the evaluation of adhesion strengths between coating and a substrate. However the adhesion test methods are broadly divided into three classes based upon what exactly is being measured. As mentioned earlier, the three classes are mechanical adhesion, thermodynamic adhesion and chemical adhesion. Mittal [60] reported a large number of techniques for adhesion measurement ranging from most inexpensive methods to most sumptuous ones and from very primitive methods to very sophisticated. Zhao et al. [61] have introduced cross test method to test the adhesion ability of the coatings they prepared. Knife cutting methods, peel test methods, scratch methods and blister methods are also reported in the literature for the adhesion testing. The most popular test for the evaluation of the shear adhesion strength of the coatings to the substrate is the single lap shear test according to ASTM D1002 – 72 standard; this is the technique I have applied in my work. [62-66].

2.2 FTIR

Fourier transform infrared spectroscopy (FTIR) is an analytical technique useful in the detection of various functional groups by making use of vibration of atoms in those groups. This technique measures the absorption of infrared radiation by the sample material versus wavelength. FTIR is a powerful technique useful in identifying
the materials as well as characterize them quantitatively. In FTIR one uses the infrared absorption bands to identify the molecular components and their structures. The technique can also be used for characterization and identification of different phases in solids or liquids. It is quite sensitive to even small traces of materials present (ASM Handbook 1986).

When a material is irradiated with IR radiation, absorbed radiation usually excites the molecules into a higher vibrational state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and the excited vibrational states. The wavelength of light absorbed by the sample is characteristic of its molecular structure.

Fig. 2.3 shows the schematic of the FTIR apparatus. An FTIR spectrometer uses an interferometer to modulate the wavelength from a broadband infrared source. A detector measures the intensity of transmitted or reflected light as a function of its wavelength. The signal obtained from the detector is an interferogram, which can be analyzed with a computer using Joseph Fourier transforms to obtain a single-beam infrared spectrum. FTIR spectra are usually presented as plots of intensity versus wavenumber (in cm\(^{-1}\)). Wavenumber is the reciprocal of the wavelength. The intensity can be plotted as the percentage of light transmittance or absorbance at each wavenumber.
2.3 Tribology

The word tribology was coined only just over 20 years ago and appears only in the up-to-date of dictionaries; however, the topics with which tribologists are concerned have been of vital interest to scientists, engineers and those who design or operate machinery, for as long as the mechanical devices have existed. Formally, tribology is defined as “the science and technology of interacting surfaces in relative motion and of related subjects and practices.” [81] Tribology deals with every aspect of friction, lubrication and wear. The word tribology is derived from greek τριβος (TRIBOS)
meaning rubbing, although the subject embraces a great deal more than just the study of rubbing surfaces [79].

Tribology is crucial to modern machinery which uses sliding and rolling surfaces. Examples of productive wear are: writing with a pencil, machining, and polishing. Examples of productive friction are brakes, clutches, driving wheels on trains & automobiles, bolts and nuts. Examples of unproductive friction and wear are internal combustion and aircraft engines, gears, cams, bearings, and seals. Effective research in this area can save millions of dollars – currently wasted in unproductive friction and wear. Perhaps as much as one third of our global economy consumption is consumed wastefully in unproductive friction and wear. According to Peter Jost and his panel, in their report (1966, 1967), the U.K. could save approximately £ 500 million (British) per year. The U.S could save in excess of $ 16 billion (US) per year by better tribological practices [80 – 82].

Tribology in polymers is crucial to many applications, since polymeric materials vital in rolling and sliding are now standard in automobiles, machinery, airplanes, computers, etc. Solid lubricants, reinforcing fibers, and inorganic particulates have been used to enhance those properties [83, 84]. Fillers (whose hardness and modulus are higher than those of the polymer) in the form of particulates and fibers are often embedded into a polymeric matrix to improve its mechanical properties, adhesion properties and aid in creating transfer films by tribochemical reactions [85]. Zhang et al. reported the reduction in wear resistance and friction when nanosilica and nanoalumina were incorporated into the epoxy matrix [86 – 90]. However, Xu and Mellor studied the effects of fillers on the wear resistance of thermoplastic polymeric coatings and found
that silica and dolomite filled polymeric coatings had a higher wear rate than an unfilled polymer [91]. Larson et al. reported that addition of CuO increases wear relative to the neat epoxy [92]. Thus, dispersed fillers seem to be a two-edged sword in modification of tribological properties.

2.3.1 Wear

Wear is the progressive loss of substance from the operating surfaces of the mechanically interacting elements of tribo systems; it is an almost inevitable companion of friction. The economic consequences of wear are widespread and pervasive; they involve not only the costs of replacement parts, but also the expenses involved in machine downtime and lost production. A further significant factor can be the decreased efficiency of worn plant and equipment which can lead to both inferior performance and increased energy consumption. Wear rate of a rolling or sliding contact is conventionally defined as the volume lost from the wearing surface per unit sliding distance. The wear rate depends on various parameters: operating temperature, normal load, relative sliding speed, amount of lubrication, thermal, mechanical, and chemical properties of the materials in contact. If the interface is contaminated by solids (like dirt) the situation can be more complex.

Similar to friction, wear is not a material property but depends on the above mentioned parameters. Usually materials exhibiting high friction also exhibit high wear rate. However, this is not true always. Materials like polymers or interfaces with solid lubricants exhibit low friction but relatively high wear rates.
2.3.1.1 Types of Wear

Early research on wear was started by Belyi [93] and is continued by Mishkin, Petrokovets and coworkers in Homel, Belarus [94 – 96]. Wear can be of different types. Various wear mechanisms, however, do not necessarily act independently in many applications. “Industrial wear” is the term used to describe the incidence of multiple wear mechanisms occurring in unison.

- Adhesive wear: It occurs when two surfaces are slid over each other, or pressed into one another and fragments are pulled off one surface and adhere to another due to strong forces between atoms [82]. Surfaces which are held apart by lubricating films, oxide films etc. have a reduced tendency for adhesion to occur.
- Abrasive wear: It occurs when a hard rough surface slides across a softer one [82]. ASTM defines it as the loss of material due to hard particles or hard protuberances that are forced against and move along a solid surface [97].
- Surface fatigue: It is a process by which the surface of a material is weakened by cyclic loading, which is one type of general material fatigue. Microscopic wear caused by fatigue may be accompanied by “pitting” – macroscopic crumbling out caused by fatigue in individual surface sections of polymer based materials [93].
- Fretting wear: It is the repeated cyclical rubbing between two surfaces, over a period of time which will remove material from one or both surfaces in contact.
- Erosive wear: It is caused by the impact of particles of solid or liquid against the surface of an object [98]. The impacting particles gradually remove material from the surface through repeated deformations and cutting actions [99].
2.3.1.2 Wear Tests

Wear can be determined using various techniques. The technique used for my project is determining the volume loss by measuring the resulting wear track due to the pin-on-disc friction test as suggested by the G99 – 05 standard. Wear is calculated by measuring the cross-sectional area of the groove produced by the pin after the pin-on-disc testing. This can be done using a scanning electron microscope (SEM) or a profilometer. However, wear can also be calculated by mass loss measurement as described by the G99 – 05 standard. The results are reported as volume loss of the sample in cubic millimeters during sliding. Sliding wear can be determined by repetitive scratch testing as well. [100 – 103]

2.3.1.3 Pin-on-Disk Tribometry

The pin-on-disc tester measures dynamic friction and rolling wear properties of dry or lubricated surfaces of a variety of bulk materials and coatings. A pin-on-disc tribometer operates on the following principle: a flat, pin or sphere is loaded onto the test sample with a precisely known weight. The highly stiff elastic arm insures a nearly fixed contact point and thus a stable position in the friction track. Dynamic friction is determined during the test by measuring the deflection of the elastic arm by direct measurement of the change in torque. The normal load, rotational speed, and the wear track diameter are all usually controlled parameters. This technique can be used to determine friction not only for polymer - based materials but for diamond - like carbon coatings, thin films or electronic materials. Most pin-on-disc testers are computer controlled and store the measured dynamic friction versus time or distance plots for future reference. Fig. 2.4 shows a schematic of a pin on disc apparatus. The test is
relatively fast and the normal ranges of operational parameters are covered within 2 h. Further, influential parameters such as temperature, environmental gasses (air, nitrogen, oxygen, etc) can be controlled.

Fig. 2.4. Schematic of pin-on-disk test

2.4 Contact Angles and Surface Energies

Consider a liquid droplet resting on a flat, solid surface. The angle formed between the two interfaces at the three–phase line contact is known as the contact angle. The contact angle determines whether the liquid wets the solid or not. If the liquid is very strongly attracted to the solid surface (e.g., in the case of water when the solid is strongly hydrophilic) the droplet will completely spread out on the solid surface and the contact angle will be close to 0°. Less strongly hydrophilic solids will have a water contact angle up to 90°. If the surface is highly hydrophilic, water contact angles will be between 0° to 30°. If the solid surface is hydrophobic then, the water contact angle will be larger than 90°. On highly hydrophobic surfaces, the water contact angles are as high as 150° or even nearly 180°. On these surfaces, water droplets simply rest on the
surface, without actually wetting to any significant extent (examples of such kind are fluorinated surfaces like Teflon). A schematic of this explanation is shown in Fig. 2.5. Liu, Chen and Xin developed super hydrophobic surfaces using silica + fluoropolymer inspired by the behavior of lotus leaves which exhibit a self cleaning effect. [104]

![Schematic of contact angles](image)

**Fig. 2.5. Schematic of the contact angles formed by a liquid droplet**

In general, two different approaches are commonly used to measure contact angles of non-porous solids: goniometry and tensiometry. Goniometry involves the observation of a sessile drop of test liquid on a solid substrate. Tensiometry involves measuring the forces of interaction as a solid is contacted with a test liquid. The technique used for my project is the sessile drop goniometric technique. The practical
applications of determining the contact angle include: surface cleanliness determination, wettability, adhesion, and surface treatment and coatings evaluation.

Wetting ability of a liquid is a function of the surface energies of the solid – gas interface, the liquid – gas interface and the solid – liquid interface. The surface energy across an interface or the surface tension at the interface is a measure of the energy required to form a unit area of new surface at the interface. The intermolecular bonds or cohesive forces between the molecules of a liquid cause surface tension. When the liquid encounters another substance, there is usually an attraction between the two materials. The adhesive forces between the liquid and the second substance will compete against the cohesive forces of the liquid. Liquids with weak cohesive bonds and a strong attraction to another material (or the desire to create adhesive bonds) will tend to spread over the material. Liquids with strong cohesive bonds and weaker adhesive forces will tend to form a droplet when in contact with another material.

Surface energy measurements can be carried out using the dyne - pen method, contact meter method or tensiometer. However, the first two methods can be used on substrates or on dry coatings but the tensiometer method is restricted to solids where all exposed faces have the same composition.

Surface energy can be related to the contact angles by the Young’s equation:

\[ \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \]

where,

- \( \gamma_{sg} \) = solid – gas interfacial energy,
- \( \gamma_{sl} \) = solid – liquid interfacial energy,
- \( \gamma_{lg} \) = liquid – gas energy, and
- \( \theta \) = contact angle between the solid and the liquid
The Owens/Wendt theory divides the surface energy into two components: surface energy due to dispersive interactions and surface energy due to polar interactions. This theory is derived from the combination of Young’s relation, which relates the contact angle to the surface energies of the solid and liquid and to the interface tension, and Good’s equation, which relates the interface tension to the polar and dispersive components of the surface energy. The resulting principle equation is:

\[ \frac{\sigma_L (\cos \theta + 1)}{2\sqrt{\sigma_L^D}} = \sqrt{\sigma_S^P \sqrt{\sigma_L^P}} + \sqrt{\sigma_S^D} \]
CHAPTER 3
MATERIALS AND EXPERIMENTAL DETAILS

3.1 Materials

3.1.1 Polypropylene

Random copolymer polypropylene (Polypropylene P5L2Z.006) which is obtained in the form of pellets was used as the base polymer for coating bare steel coupons in this project. This PP as discussed earlier in Chapter 1 has been used for the modification purposes. It was received from Huntsman Corporation. The PP has a melt flow index of 2 g/10 min [105]. The chemical structure of PP has been shown in Fig. 1.1 & 1.2. The typical properties of PP are shown below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Flow g/10 min</td>
<td>2</td>
</tr>
<tr>
<td>Density g/cc</td>
<td>0.905</td>
</tr>
<tr>
<td>Tensile Strength, Yeild MPa</td>
<td>32</td>
</tr>
<tr>
<td>Melting Point deg C</td>
<td>140 - 155</td>
</tr>
</tbody>
</table>
3.1.2 Maleic Anhydride

Polyolefin functionalization with polar monomers leads to new routes of obtaining advanced materials [106 – 108] and in my research, I have used polar monomer maleic anhydride (MAH) for functionalization of PP. The Fluka™ maleic anhydride 63200 has been supplied by Sigma-Aldrich®. The MAH used was >= 99% pure.

Fig. 3.1. Chemical structure of maleic anhydride [109]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor Density (vs. air)</td>
<td>3.4</td>
</tr>
<tr>
<td>Vapor pressure mmHg @ 20°C</td>
<td>0.16</td>
</tr>
<tr>
<td>Assay (NT)</td>
<td>≥99.0%</td>
</tr>
<tr>
<td>Boiling point °C</td>
<td>200</td>
</tr>
<tr>
<td>Melting point °C</td>
<td>52-56</td>
</tr>
</tbody>
</table>
3.1.3 Dicumyl Peroxide

Dicumyl peroxide (DCP) with properties given in Table 3 is added as a reaction initiator for the MAH and PP. When the reactions are initiated by peroxides, the PP undergoes chain scission \([110,111]\). For my research the DCP was supplied by Sigma-Aldrich\textsuperscript{®} in the form of very small flakes. The linear formula for DCP is \([\text{C}_6\text{H}_5\text{C}((\text{CH}_3)_2]_2\text{O}_2\) and the chemical structure is shown below (Fig. 3.2).

![Chemical Structure of DCP](image)

Fig. 3.2: Chemical Structure of DCP\textsuperscript{(8)}

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapor density (vs. air)</td>
<td>9.3</td>
</tr>
<tr>
<td>Vapor pressure mmHg @ 20°C</td>
<td>15.4</td>
</tr>
<tr>
<td>Assay</td>
<td>98%</td>
</tr>
<tr>
<td>Melting point °C</td>
<td>39-41</td>
</tr>
</tbody>
</table>

TABLE IV:

Typical Properties of Dicumyl peroxide \([112]\)
3.1.4 Steel Substrate

The Steel substrates used for coating applications were 1/16th of an inch thick cut into 1" X 2" small coupons. The steel coupons obtained were to ASTM A366 steel standard specified cold rolled sheets. These ASTM A366 steel was supplied by Speedy Metals Company, Fraser, Michigan. The composition and properties of that steel are listed below:

**TABLE V**

Properties of ASTM A366 Steel [113]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (X1000 Kg/m³)</td>
<td>7.7 - 8.03</td>
<td>Carbon</td>
<td>0.15</td>
</tr>
<tr>
<td>Tensile strength (X1000PSI)</td>
<td>38 -50</td>
<td>Manganese</td>
<td>0.6</td>
</tr>
<tr>
<td>Elastic modulus(GPa)</td>
<td>190-210</td>
<td>Phosphorus</td>
<td>0.03</td>
</tr>
<tr>
<td>Yeild strength (X1000PSI)</td>
<td>25-35</td>
<td>Sulfur</td>
<td>0.0035</td>
</tr>
</tbody>
</table>
3.2 Sample Preparation

In this research, all the samples were prepared according to the following steps: after mixing the components the blends were pelletized and then compression molded into films and those films were again compression molded onto the steel coupons to obtain the final coatings. We shall now discuss each of the above steps.

3.2.1 Blend Mixture

The grafting reaction, i.e., the reaction of MAH with neat PP, was conducted by loading PP pellets into the mixing chamber of a Brabender type 6 mixer. Fig. 3.3 shows the mixer. It has a 120 mL total volume. The blades rotate in opposite directions and at slightly different speeds to ensure proper mixing. The volume with the blades inside is 60 mL and it is desirable to fill about 70 % of this volume to prepare the blends. Thus each run has approximately 50 g of material.

For all the blends, the conditions were:

- Speed of the blades: 30 rpm
- Temperature of processing: 160 °C
- Total time of mixing: 10 minutes.

Initially the PP pellets were loaded into the mixing chamber and made to mix for around 3 minutes at 160°C and 30 rpm. After 3 minutes, when the PP was molten, Dicumyl peroxide (DCP) was added and mixed for 4 minutes. Finally MAH was added for a further 3 minutes mixing.
There are three different sets of blends, varying the amount of DCP being prepared. The first set of blends contained 0.25 wt % DCP and second and third sets contained 0.5 wt% and 0.75 wt%, respectively. Each set in turn contained MAH varying from 1 wt% to 5 wt%.

3.2.2 Pelletizer

A milling machine (model LC-124) from Gilson Company, Inc, Lewis center, Ohio was used to pelletize the blends obtained from the Brabender. All the samples including neat polymers were pelletized for consistency in the processing history. Fig. 3.4 shows the pelletizer used.
3.2.3 Compression Molding

A Carver hydraulic compression molding machine (Model 3925 from Carver Inc, Wabash, IN) was used to prepare the films which were coated onto the ASTM A366 steel coupons. The temperature and pressure parameters for producing the film were optimized after many trials to the following conditions:

- Amount of polymer: 2 grams.
- Pressure: 1000 psi.
- Temperature: 193 °C.
- Compression time: 20 minutes.
The same Carver hydraulic press was used to melt the produced films onto ASTM A366 steel coupons (1” X 2”) to obtain smooth coatings. Before the coating application the steel substrates were degreased by cleaning them with acetone. The parameters used for coating the film were different compared to the parameters used for making a film. Following are the conditions for coating the films:

- Size of the film: 1”X 2”
- Pressure: 100 psi.
- Temperature: 160 °C.
- Compression time: 20 minutes.
3.3 Coatings Characterization

3.3.1 Adhesion Testing

The specimen geometries of the tensile single lap shear tests follow the ASTM D 1002-05 standard. The modified PP films obtained from the Carver press were sandwiched between two degreased steel substrates of 1” X 4” dimensions each by compression under the pressure of 200 psi and 160 °C for a period of 20 minutes. The laminate of steel substrate/ polymer/ steel substrate with 1” in width and 1” in overlap length as shown in Fig. 3.6 was prepared. After removing the samples from the compression molding press, they were air cooled to room temperature. The thickness of the polymer between two steel sheets was controlled to be constant by the applied pressure and inserts.

![Fig. 3.6. Adhesion sample dimensions.](image)

The tensile single lap shear tests were measured with an Instron Inc. model: 4482 testing machine (see Fig. 3.7). The load cell used has a capacity of 10 tons. The cross head speed was set at 0.1 in. / min. All the tests were performed at ambient temperatures (= 25 °C). The tests were continued until the specimens failed. The shear force-displacement data were collected and stored as data files. The adhesion strength or lap shear strength (LSS) is the maximum load divided by the area of bonded overlap.
Every reported value of LSS was the average of that for three specimens prepared under the same conditions.

Fig. 3.7. The Instron Universal testing machine

3.3.2 Compound Identification Through Fourier Transform Infrared Spectroscopy

An attempt to quantify the degree of grafting, i.e., the amount of MAH grafted on to PP chains has been made using a Thermo Nicolet Avatar 370 FTIR spectrometer. The FTIR spectra were collected in the range of 4000-400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. A total of 32 scans per analysis were employed.

The PP, and MAH – grafted PP samples were processed into thin films by the compression molding technique already discussed in Section 3.2.3. Further, for MAH and DCP films, the preparation technique was a little different. The MAH powder was
mixed homogeneously with potassium bromide (KBr) and was ground by means of mortar and pestle. Then this mixture was placed in a 13 mm steel die and pellets were prepared by using the hydraulic press. The spectrometer used for all the scans is shown in the Fig. 3.8.

![Fig. 3.8: The Nicolet Avatar spectrometer](image)

### 3.3.3 Scanning Electron Microscopy (SEM)

An FEI Quanta 200 SEM was used to investigate the tensile single lap shear fracture surfaces of the different specimens in the secondary electron mode with an acceleration voltage of 20 kV. All the investigated specimens were made electrically conductive by sputtering the surfaces with a thin layer (<20nm) of gold prior to being observed by SEM in order to avoid electrostatic charging during examination. Both the FEI Quanta SEM and the gold sputtering machine are shown in Fig. 3.9.
3.3.4 Pin on Disk Tribometer

In order to determine the wear and wear mechanisms of the applied coatings, a Nanovea series pin – on – disk tribometer, from Microphotonics Inc. was used. SS 302 grade stainless steel ball with diameter 3.20mm was used as the pin. The experimental conditions were:

Radius of the wear track: 2.0 mm

Rotation speed: 100 rpm

Load: 5.0 N
3.3.5 Profilometer

Cross-section areas of wear tracks remaining after the pin-on-disk test were determined using a Veeko Dektak 150 profilometer (See Fig. 3.11). A stylus with a tip radius of 12.5 µm was used. The force applied to the sample was 1.0 mg, and the scan rate was 26.7 µm/s. The scan length was 800 µm and the measurement range was 65.5 µm.

The profilometer amplifies and records the vertical motions of a stylus displaced at a constant speed by the surface to be measured [114]; as the stylus moves up, the stylus rides over the sample surface detecting surface deviations. All samples were cleaned by high pressure air to eliminate all debris before each test. At least 5 scans were run for each sample, and the average value of the area was used to calculate the wear rate.

Fig. 3.11. Veeko Dektak 150 Profilometer
The wear volume \( (V_m) \) of the tracks produced by the pin – on – disk test was determined using the cross-section area \( (A_m) \) obtained from the profilometer. The obtained cross-section area is multiplied by wear track length as shown below.

\[
V_m = 2\pi R_m A_m \tag{3.1}
\]

Where, \( R_m \) and \( A_m \) correspond to the radius of the wear track and to the average cross-sectional area of the wear track respectively.

Wear rate was then calculated using:

\[
Z = \frac{V_m}{Wx}
\]

or

\[
Z = \frac{V_m}{Wv_t}
\]

where, \( W \) is the normal load, \( V_m \) is the wear volume, \( v \) is sliding velocity, \( t \) is the test duration and \( x \) is the sliding distance. In all the tests performed on the coatings, the parameters used were as follows:

- Normal Load (\( W \)) : 2.0 N
- Sliding distance (\( x \)) : 37.68 m
- Radius of the wear track (\( R_m \)) : 2.0 mm

3.3.6 Differential Scanning Calorimetry (DSC)

The melting and crystallization behavior of the prepared blends and neat PP was studied using a Perkin Elmer DSC 7 instrument (Fig. 3.12) under nitrogen atmosphere. About 5-10 mg of sample was used for each run. A first heating scan is carried from 20°C to 200°C at a heating rate of 10°C/min. The sample was held at 200°C for one
minute and then cooled from 200°C to 20°C at a cooling rate of 20°C/min. The second
heating scan is a repetition of the first heating scan except that the rate of heating was
changed to 20°C/min.

The percentage crystallinity of the blends and neat PP was determined by using
the following relationship:

\[
\% \text{ Crystallinity} = X_{DSC} = \frac{\Delta H_m}{\Delta H_m^0 \times m} \times 100
\]

where, \(\Delta H_m\) and \(\Delta H_m^0\) are the heat of melting of the sample and heat of melting of 100
% crystalline polypropylene respectively and \(m\) is the mass fraction of the polymer.

Fig. 3.12. Differential scanning calorimetry (DSC)
3.3.7 Goniometry

The contact angles and surface energies on the surfaces of the coatings are determined using a sessile drop technique. A Ramé – Hart Instrument Co, Netcong, NJ., goniometer (Fig. 3.13) was used for this purpose. A polar liquid (water) and an apolar liquid (diiodomethane) were used as testing liquids [115]. Surface tensions @ 20 °C of water and diiodomethane are 72.80 mN/m and 50.80 mN/m, respectively [116]. Equal amounts of test liquids were maintained throughout the test by rotating 4 divisions on the syringe for testing with water and 1 division for testing with diiodomethane. At least five contact angles for each sample were measured and averaged.

![Ramé – Hart Goniometer](image)

**Fig. 3.13: Ramé – Hart Goniometer.**

The surface energy values were calculated directly by the software using the contact angles obtained by the goniometer. The software is programmed to use Wu’s equations.
(harmonic-method) to calculate the surface energies\((115)\). These relations are as follows:

\[
(1 + \cos \theta_1) \gamma_1 = 4 \left( \frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} \right) \tag{3.3}
\]

\[
(1 + \cos \theta_2) \gamma_2 = 4 \left( \frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right) \tag{3.4}
\]

where, \(\theta_1\) = Contact angle made by liquid 1 on the solid

\(\theta_2\) = Contact angle made by liquid 2 on the solid

\(\gamma_1\) = Surface tension of liquid 1

\(\gamma_2\) = Surface tension of liquid 2

\(\gamma_1^d\) = Dispersion component of surface tension of liquid 1

\(\gamma_2^d\) = Dispersion component of surface tension of liquid 2

\(\gamma_s^d\) = Dispersion component of surface energy of solid

\(\gamma_1^p\) = Polar component of surface tension of liquid 1

\(\gamma_2^p\) = Polar component of surface tension of liquid 2

\(\gamma_s^p\) = Polar component of surface energy of solid

All the variables in the above equations are known except for the dispersion and polar components of the surface energy of the solid. The software solves the above mentioned two equations and gives the values for surface energy of the solid.
3.3.8 Thickness Measurement

The thickness of the coatings was measured by cutting each sample into two halves (perpendicular to its length) using a TechCut 4 low speed saw from Allied High Tech. Productions Inc. The speed used for cutting was 250 rpm. The cross section of each sample was analyzed using a Nikon Eclipse ME 60 optical microscope. The thickness of the coatings was calculated by taking the mean of 10 thickness values on each sample.

Fig. 3.14: TechCut 4 low speed saw and Nikon Eclipse ME 60 optical microscope
4.1 Reaction Mechanism

The reaction mechanism of grafting of MAH onto PP chains is illustrated in Fig. 4.1 [117, 118]. It follows from the Fig. that the grafting of neat PP with MAH does not proceed according to a simple chain transfer mechanism; rather the grafting reaction takes place only after PP chain scission.

The first step of the grafting mechanism can be summarized as follows: Homolytic scission of each organic peroxide produces two radicals. Polypropylene pending hydrogen is abstracted by a radical attack which results in a new radical onto PP. The radical onto a PP chain leads to a $\beta$- scission. $\beta$- scission is a fast intramolecular reaction which is predominant in the melt state in the presence of organic peroxide [119 – 121]. The Grafting reaction takes place after PP chain scission, when PP free end radical adds onto a double bond of MAH and an end double bond from another PP fragment enters an “ene-reaction” with MAH.
Fig. 4.1. Reaction mechanism for the grafting of MAH onto PP
4.2 Adhesion Strength

In order to understand the effect of varying MAH and DCP contents in the blends on the adhesive properties, it is pertinent to study the adhesion strength between the polypropylene coatings and the steel substrate. The adhesion strength/lap shear strength is measured following the ASTM D 1002-05 standard.

4.2.1 Adhesion Strength and Load - Displacement Curves

The effect MAH content on adhesion strength/lap shear strength of the adhesively bonded laminates (steel/polymer/steel) is shown in Fig. 4.2, 4.3 and 4.4. The amount of DCP content is varied in each case.

From the figures it can be seen that the introduction of MAH into the PP matrix (surface modification of PP) results in significant improvement of the fracture strength of the adhesive bonded steel/polymer/steel laminates. The adhesion strength of steel sheets and pure PP is 0.73 MPa as seen in all the cases. Addition of a small proportion, about 1 wt % of MAH grafted onto PP chains, leads to substantial increase in the adhesion strength as seen. With the PP content increasing up to 3 wt %, the adhesion strength reaches the maximum value, 11.75 (±0.36) in Fig. 4.2 for the case with 0.25 wt % DCP, 12.36 (±0.75) for the case with 0.5 wt % DCP (Fig. 4.3) and 12.33 (±0.46) for the case with 0.75 wt % DCP (Fig. 4.4). However, the adhesion strength declines with further increase of MAH content.
Fig. 4.2. Effect of MAH content on adhesion strength with 0.25 wt% DCP

Fig. 4.3. Effect of MAH content on adhesion strength with 0.5 wt% DCP
Fig. 4.4. Effect of MAH content on adhesion strength with 0.75 wt% DCP

The adhesion strength of 0.73 MPa in the steel sheets bonded with neat PP represents the mechanical interlocking between the PP and the roughness surface of the steel sheets. With the grafting of MAH onto PP chains, the increased adhesion strength can be ascribed to the contribution of chemical interactions at the interface as well as to the introduction of polar MAH molecules onto the PP surface.

However, the simultaneous increase in MAH content leads to increasing of curing density, which decreases the flexibility of polymeric matrix [104] and thus adhesion decreases.

Fig. 4.5 – 4.7 presents load-displacement curves of the tensile single lap shear tests/adhesion tests up to maximum loads of all the specimens.
Fig. 4.5. Load vs displacement curves for specimens with 1 wt % to 5 wt % MAH and 0.25 wt % DCP

Fig. 4.6. Load vs displacement curves for specimens with 1 wt % to 5 wt % MAH and 0.5 wt % DCP
Fig. 4.7. Load vs displacement curves for specimen with 1 wt % to 5 wt % MAH and 0.5 wt % DCP

From Fig. 4.6 and 4.7, it can be clearly seen that the load is nonlinear vs the displacement, especially for the samples which are bonded with MAH grafted PP (MAH-g-PP). In the samples bonded with neat PP, the displacement at the maximum load is less than 0.01 in., whereas in all the samples bonded with MAH-g-PP, the displacements at the maximum load increase. However, both the maximum load and displacement at the maximum load are maximum in the samples containing 3 wt % MAH in PP.

The increased displacement at the maximum load for the samples bonded with modified PP (i.e., MAH-g-PP) is because of the non elastic deformation in the polymer film used in the steel/polymer/steel laminates. This is not the case for samples bonded with neat PP, where interfacial fracture is observed at the surface. This observation is explained in detail in Section 4.2.2. Finally, from Fig. 4.5–4.7, it can be concluded that
good shear and adhesive properties could be achieved by grafting MAH on to the PP chains and 3 wt % of MAH is the optimum concentration to be added.

Fig. 4.8 shows the effect of peroxide content on the adhesion/ lap shear strength.

![Fig. 4.8. Effect of peroxide content on adhesion strength/ lap shear strength](image)

The effect of peroxide content observed on adhesion strength/ lap shear strength is quite small, as seen in the Fig.. We can also see that samples bonded with 3 wt % MAH-g-PP show the maximum adhesion strength. Further, among all the samples, one with 0.5 wt % DCP content has a slightly higher adhesion strength compared to other concentrations of DCP. However, the effect of peroxide content on adhesion strength is not as significant as the effect of MAH content.

### 4.2.2 Fractured Surfaces after Adhesion/ Lap Shear Tests

The fractured surfaces of the bonded samples after the adhesion test have been studied macroscopically and microscopically as well. Fig. 4.9(a - d) shows the macroscopic images of the separated surfaces of steel sheets. In Fig. 4.9(a), which is for separated surface of neat PP, very little residual polymer is observed on the surface
- indicating the interfacial failure. Whereas, in Fig. 4.9(b), 4.9(c) and 4.9(d), which are the separated surfaces of samples bonded with 3 wt%, 4 wt% and 5 wt% MAH-g-PP respectively, the residual polymer can be seen sticking onto the steel surface. This suggests that a considerable improvement of adhesive bonding at the interface is achieved with respect to pure PP.

![Macroscopic images of fractured surfaces after adhesion tests of samples bonded with (a) neat PP (b) 3 wt % MAH-g-PP (c) 4 wt % MAH-g-PP (d) 5 wt % MAH-g-PP.](image)

Fig. 4.9. Macroscopic images of fractured surfaces after adhesion tests of samples bonded with (a) neat PP (b) 3 wt % MAH-g-PP (c) 4 wt % MAH-g-PP (d) 5 wt % MAH-g-PP.

Fig. 4.10 shows the SEM micrographs of the lap shear fracture surfaces when there is no MAH grafted onto PP. In Fig. 4.10(a) large areas of PP can be seen and also large areas of uncovered steel surfaces can be viewed. Fig. 4.10(b) is the micrograph showing an area on the separated surface, in which we can see a little area covered with neat PP and a little area uncovered. Fig. 4.10(c) is the micrograph showing the same neat PP as in Fig. 4.10(b) but zoomed to a higher magnification.
Fig. 4.10(a), 4.10(b), 4.10(c). SEMicrographs of lap shear fractured surfaces of the samples bonded with neat PP

From Fig. 4.10(c) above, it can be seen that PP underwent some extent of plastic deformation. Though a little amount of neat PP is found on the fractured surfaces, most of the parts were uncovered as seen in Fig. 4.9(a). The reason for very little adhesion of neat PP onto the steel surface is as we all know lack of polar groups on the PP surface.
Further there is no chemical interaction at the interface and the mechanical interlocking (physical interaction) of neat PP with steel surface is very weak.

The SEM micrographs of the fractured surfaces of the samples bonded with 3 wt % MAH-g-PP are shown in Fig. 4.11. In Fig. 4.11(a), what can be seen is that the steel surface is well covered with the polymer, indicating that the failure is cohesive through the adhesively bonded polymer film layer. Fig. 4.11(b) and 4.11(c) are the higher magnification micrographs of Fig. 4.11(a). In the Fig., fibrillar structure with many elliptic holes along the tensile shear direction and pores into the polymer are clearly visible, indicating the occurrence of significant plastic deformation in the polymer film layer during the lap shear test. A similar behavior is observed in the samples bonded with 4 wt % MAH-g-PP as shown in Fig. 4.12.
Fig. 4.11 SEMicrographs of fractured surface bonded with 3wt % PP-g-MAH
Fig. 4.12. SEMicrographs of fractured surface bonded with 4 wt% PP-g-MAH

4.3 FTIR Spectroscopy

The Fourier transformed infra-red spectra of neat PP and modified PP grafted with 1-5 wt% of MAH are shown in Fig. 4.13. This Fig. shows the appearance of new peaks at 1710-1795 cm\(^{-1}\) indicating the occurrence of grafting reaction.

Fig. 4.13. FTIR Spectra of neat PP and modified PP grafted with 1-5 wt% MAH in increasing order.
The transmission curves of neat PP and that of MAH-g-PP with 3 wt % of MAH are compared in Fig. 4.14. The peaks appearing at 2950-2700 cm\(^{-1}\) are assignable to –CH stretching vibration of –CH, –CH\(_2\), –CH\(_3\) groups. Absorption around 1460 cm\(^{-1}\) is indicative of –CH\(_2\) and –CH\(_3\) groups; that at 1375 cm\(^{-1}\) and the bands at 972 cm\(^{-1}\) are indicative of –CH\(_3\) groups; the band at 1162-1167cm\(^{-1}\) is assigned to –CHCH\(_3\). The appearance of strong peak at 1710-1795 cm\(^{-1}\) indicates the presence of carboxylic group in MAH-g-PP. The IR spectra of grafted copolymers showed bands at 1710 cm\(^{-1}\), 1784 cm\(^{-1}\) and 1792 cm\(^{-1}\), characteristics for cyclic anhydride groups. By contrast, in the IR spectra of neat PP there are no peaks appearing in the range between 1600 and 2000 cm\(^{-1}\). This result clearly shows that the maleic anhydride monomer has been successfully grafted onto the polypropylene chain. Further, in the spectra of the grafted polymer, the intensity of the few characteristic bands of PP reduce and broadening of some other peaks takes place, showing that MAH has been introduced as a graft into the PP backbone.
Fig. 4.14. FTIR spectra of PP and 3 wt % MAH-g-PP

Fig. 4.15 shows the absorbance spectra of neat polypropylene and that of 3 wt% MAH-g-PP. As can be seen from the Fig., the 3 wt % MAH-g-PP shows two intense overlapping absorption bands at 1784 cm$^{-1}$ and 1792 cm$^{-1}$. These absorption bands at 1784 cm$^{-1}$ and 1792 cm$^{-1}$ can be assigned to grafted anhydride because five – member cyclic anhydrides exhibit an intense absorption band near 1780 cm$^{-1}$ due to symmetric C=O stretching. These peaks in the range of 1600 cm$^{-1}$- 2000 cm$^{-1}$ are missing in the FTIR spectra of neat PP.
Fig. 4.15 FTIR absorbance spectra of neat PP and 3 wt% MAH-g-PP

An attempt can be made to calculate the amount of MAH incorporated onto the PP chains (degree of grafting) using FTIR absorbance curves. As discussed earlier, a strong absorption band is observed for the MAH-g-PP at 1792 cm$^{-1}$ (Abs$_{1792}$), corresponding to carbonyl stretching. This absorption is being compared with the absorption at 1166 cm$^{-1}$ (ABS$_{1166}$), characteristic of the PP methyl group. Ratios Abs$_{1792}$/Abs$_{1166}$ can be related to the MAH incorporated on to the PP chains. The variation of this absorbance ratio with the percentage MAH is shown in Fig. 4.16.
Fig. 4.16. Variation of absorbance ratio $\text{Abs}_{1792}/\text{Abs}_{1166}$ with the MAH content

The aspect of adhesion strength can also be explained by correlating the amount of MAH incorporated on the PP chains (degree of grafting) and the adhesion strength values. (See Fig. 4.4 and 4.16)

Fig. 4.16 and 4.4. Fig. comparing the grafting ratio and adhesion strengths
Since the ratio $\text{Abs}_{1792}/\text{Abs}_{1166}$ (grafting ratio) can be related to MAH incorporated on the PP chains, we can say that there is a direct relation between the absorbance ration and degree of grafting. Further, this absorbance ratio follows the same trend as the adhesion strength. If we can compare Fig. 4.4 and Fig. 4.16, we can see that maximum adhesion strength is obtained for the polymer which has maximum amount of MAH grafted to its chain and the adhesion strength varies with amount of MAH grafted.

4.4 Pin – on - Disk Wear Determination

4.4.1 Profilometer Cross Section of Wear Tracks

The tribological data present in this section were obtained using a pin-on-disk type of tribometer at an average contact pressure ($p$) of 70 MPa and sliding velocity ($v$) of 4.19 mm/s. Note that the $pv$ condition used here (2.92 MPa $\times$ m/s) is high relative to the similar studies, which are about 1.725 MPa $\times$ m/s [122], 1.5MPa $\times$ m/s [123] or below [124 – 127]. The different wear and friction behaviors were expected for observation.

Fig. 4.17- 4.19 show the profilometer cross section of wear tracks for all the samples.
Fig. 4.17. Profilometer cross section of wear traces for samples with 0.25 wt % DCP and (a) neat PP (b) 1 wt % MAH (c) 2 wt % MAH (d) 3 wt % MAH (e) 4 wt % MAH (e) 5 wt % MAH.
Fig. 4.18. Profilometer cross section of wear traces for samples with 0.5 wt % DCP and (a) neat PP (b) 1 wt % MAH (c) 2 wt % MAH (d) 3 wt % MAH (e) 4 wt % MAH (e) 5 wt % MAH.
Fig. 4.19. Profilometer cross section of wear traces for samples with 0.75 wt % DCP and (a) neat PP (b) 1 wt % MAH (c) 2 wt % MAH (d) 3 wt % MAH (e) 4 wt % MAH (e) 5 wt % MAH.

From Fig. 4.17-4.19 we can see that as the amount of MAH is increasing, the cross sectional area of the wear tracks is increasing. This cross sectional area obtained from the profilometer is used to calculate the wear rate as discussed earlier in Section 3.3.5.
4.4.2 Effect of MAH on Wear Rate

Fig. 4.20 shows the effect of addition of MAH on the wear rate of the coatings.

![Graph showing the effect of MAH content on wear rate.](image)

Fig. 4.20. Effect of MAH content on wear rate.

Sclavons, et. al in their work have shown that the grafted polymer generally contains residual amounts of free (ungrafted) MAH [128]. As we can see from the above Fig., the wear rate increases as the amount of MAH is increased for all three DCP concentrations. A possible reason for this behavior might be: the wear rate is increasing due to the increase in unreacted MAH present in the polymer after grafting and this amount of unreacted MAH obviously is increasing with the increase in MAH content.

4.4.3 Effect of DCP content on wear rate
Fig. 4.21 shows the effect of DCP content on the wear rate. Here we can see that there is no significant change in the wear rate with the change in the amount of DCP added to initialize the reaction. Although there is no significant change, the samples coated with the blends containing 0.5 wt % DCP show the highest wear rates whereas the samples coated with blends having 0.75 wt % DCP show the least wear rates.

Fig. 4.21. Effect of DCP content on wear rate.
4.5 Contact Angles and Surface Energies

The measure of hydrophilicity can be expressed by the water contact angle. The dependence of water contact angle vs. MAH content in the grafted PP is presented in Fig. 4.22. The water contact angle on the hydrophobic PP surface has a value 102°. As the surface of modified PP is more hydrophilic than the surface of neat PP, consequently the value of contact angle decreases. From the Fig. it can be seen that the samples coated with 3 wt % MAH-g-PP have the least contact angle compared to the other compositions. That means the sample coated with 3 wt % MAH-g-PP is the most hydrophilic among all the samples. These results indicate that the increase of the grafted MAH content causes significant hydrophilicity [64, 130] growth of MAH-g-PP.

Further, the water contact angles of the samples follow the same trend as we have seen for adhesion and the degree of grafting curves (Fig. 4.2 and 4.4). In those Fig. we saw that samples coated with 3 wt% MAH-g-PP had the maximum adhesion strength – corresponding to the maximum degree of grafting. Consequently, the sample coated with 3 wt % MAH-g-PP has the lowest contact angle - indicating that maximum number of non polar MAH molecules have been attached to this particular sample.
Fig. 4.22. Water contact angles Vs. MAH content

The surface energies for the modified PP as a function of the MAH content is shown in Fig. 4.23. From the Fig. we can see that neat PP has the least surface energy; as the MAH content is increased, the polar MAH molecules are being attached to the PP chains and as a result the surface energy increases. Further, we can also see that the surface energies, just like contact angle and adhesion strength, depend on the amount of MAH grafted (degree of grafting) onto the PP chains. The maximum surface energies can be seen for the samples coated with 3 wt % MAH-g-PP due to the maximum amount of grafting obtained for this particular composition as seen in earlier sections. The increase in surface energy can also be attributed to the introduction of carbonyl moiety which introduces polarity into the PP backbone.
4.6 Differential Scanning Calorimetry

Fig. 4.24(a) shows the DSC cooling curves for PP and MAH-g-PP (1 wt % MAH - 5 wt % MAH). The exotherms obtained for neat PP and MAH-g-PP are at different temperatures, for neat PP at 81°C and for the grafted ones higher than that, indicating higher crystallization temperatures for grafted samples. The observed increase in crystallization temperature can be attributed to the MAH acting as a nucleating agent.
Rybrinker et al. (130) also observed nucleation due to incorporation of carbonyl group in neat PP. Fig. 4.24(b) shows the DSC heating curves for neat PP and MAH-g-PP. The heat of fusion ($\Delta H_m$) for pure PP is 34.4 J/g and for grafted PP it has decreased to approx. 24.0 J/g; melting temperature ($T_m$) for neat PP is 142 °C and it decreases to 122 °C after modification of PP.

The percentage of crystallinity was calculated on the assumption that the heat of fusion of 100% crystalline PP is 138 J/g. An apparent decrease in heat of fusion is due to the decrease in weight fraction of crystalline PP in the copolymer due to the incorporation of MAH. The decrease in crystallinity is probably due to the grafted branches, which disrupted the regularity of the chain structures in PP and increased the spacing between the chains. A similar trend was observed by Mukherjee et al. [131] for MAH-g-PP.
Fig. 4.24(b). DSC thermogram of PP and MAH-g-PP during heating
CHAPTER 5

CONCLUSIONS

Based on the results of the investigations on the modified Polypropylene (PP) coatings, it may be concluded that:

For neat PP, low adhesion strengths of the adhesive bonded steel/PP/steel, 0.73 MPa in all three concentrations of DCP are obtained because of mechanical interlocking of the PP surface and the steel surface. Fracture occurs at the interface and no or very little residual polymer is left over after the fracture.

Modification of PP with addition of 1 - 5 wt % of MAH is an effective way for improvement of the adhesion strength. Grafting of just 1 wt% of MAH onto PP leads to more than five fold increase in the adhesive shear strength. The maximum values of the adhesion strengths, 11.75 MPa, 12.36 MPa and 12.33 MPa for three concentrations of DCP, are obtained for the samples bonded with 3 wt% MAH-g-PP.

With further increase in MAH content, the adhesion strength decreases due to increase in curing density, which in turn decreases the flexibility of the polymer matrix.

Improvement of interfacial adhesive strength is due to the chemical interactions between –OH or Fe$^{2+}$ at the surface of the steel sheets and the polar functional anhydride groups and carboxylic groups –COOH on PP-g-MAH.

The FTIR results confirmed the occurrence of grafting reaction of MAH with neat PP. The appearance of new transmission and absorption peaks at 1710 – 1795 cm$^{-1}$ are the characteristics for cyclic anhydride groups.
The grafting ratio \( (\text{ABS}_{1792}/\text{ABS}_{1166}) \) represents the grafting degree. The samples with maximum adhesion have the highest degree of grafting. Thus the adhesion strengths depends upon degree of grafting.

DSC results show that, the MAH incorporated in neat PP acts as a nucleating agent, thus increasing the crystallization temperature. Further, the MAH grafted onto PP disrupts the regularity of the PP chain, decreasing the crystallinity of grafted polymer.

The wear rate increases with increase in unreacted MAH content in the copolymer.

The contact angles decreased with the grafting of MAH onto neat PP, indicating that the hydrophilicity of the coated samples has increased.

The surface energy increases with the incorporation of MAH. The Higher the grafting of MAH onto neat PP, the higher the surface energy.
REFERENCE LIST


[116] http://www.surface-tension.de/


