

# **Chapter one**

## **Introduction**

### **1.1 Polymers background**

Polymeric materials are large molecules made by joining together thousands of small molecular units known as monomers. The process of monomer joining the molecules is called polymerization and the number of these units in the polymer is known as the degree of polymerization. The names of many polymers consist of the name of the monomer with the suffix poly-. For example, polypropylene and polystyrene monomers are propylene and styrene respectively.

The words polymers and plastics are often taken as synonymous but in fact there is a distinction. The polymer is the pure material which results from the process of polymerization and is usually taken as the family name for materials which have long chain-like molecules (and this includes rubbers). Pure polymers are seldom used on their own and it is when additives are present that the term plastic is applied. Polymers contain additives for a number of reasons. There are two important classes of plastics thermo and thermoset.

#### **1.1.1 Thermoplastic**

In a thermoplastic material the very long chain-like molecules are held together by relatively weak Vander Waals forces. A useful image of the structure is a mass of randomly distributed long strands of sticky wool. When the material is heated the intermolecular forces are weakened so that it becomes soft and

flexible and eventually, at high temperatures, it is a viscous melt. When the material is allowed to cool it solidifies again. This cycle of softening by heat and solidifying on cooling can be repeated more or less indefinitely and is a major advantage in that it is the basis of most processing methods for these materials. It does have its drawbacks, however, because it means that the properties of thermoplastics are heat sensitive. A useful analogy which is often used to describe these materials is that, like candle wax, they can be repeatedly softened by heat and will solidify when cooled. Examples of thermoplastics are polyethylene, polyvinyl chloride, polystyrene, nylon, acetal, polycarbonate, polymethyl methacrylate and polypropylene (R.J. Crawford 2005).

An important subdivision within the thermoplastic group of materials is related to whether they have a crystalline (ordered) or an amorphous (random) structure. In practice, of course, it is not possible for a moulded plastic to have a completely crystalline structure due to the complex physical nature of the molecular chains. Some plastics, such as polyethylene and nylon, can achieve a high degree of crystallinity but they are probably more accurately described as partially crystalline or semi-crystalline. Other plastics such as acrylic and polystyrene are always amorphous. The presence of crystallinity in those plastics capable of crystallizing is very dependent on their thermal history and hence on the processing conditions used to produce the moulded article (R.J. Crawford 2005).

### **1.1.2 Thermosetting plastics**

A thermosetting plastic is produced by a chemical reaction which has two stages. The first stage results in the formation of long chain-like molecules similar to those present in thermoplastics, but still capable of further reaction. The second stage of the reaction (cross-linking of chains) takes place during moulding, usually under the application of heat and pressure. The resultant moulding will be rigid when cooled but a close network structure has been set up within the material. During the second stage the long molecular chains have been interlinked by strong bonds so that the material cannot be softened again by the application of heat. If excess heat is applied to these materials they will char and degrade. This type of behavior is analogous to boiling an egg. Once the egg has cooled and is hard, it cannot be softened again by the application of heat. Since the cross-linking of molecules is by strong chemical bonds, thermosetting materials are characteristically quite rigid materials and their mechanical properties are not heat sensitive. Examples of thermosets are phenol formaldehyde, melamine formaldehyde, urea formaldehyde, epoxies and some polyester (R.J. Crawford 2005).

### **1.2 Khartoum Petrochemical Company (KPC)**

Khartoum Petrochemical Company (KPC) Sudan produces two grades of polypropylene homo polymer under ASTM standard those are:

1. Extrusion grade (KPC 113).
2. Injection grade (KPC 114).

KPC Sudan products have been distributed into wide area including Sudan, Egypt, Ethiopia, Kenya and Syria etc. Hence polypropylene is inexpensive and available raw material for local market in Sudan. Sudanese polypropylene (PP) market demand in 2012 about 9329.2 ton/month (3327 ton/month for extrusion grade and 6002.2 ton/month for Injection grade). The domestic polypropylene plant (KPC) caters to local demand about 1500 ton/month (about 16.1%) and 7829.2 ton/month are imported from outside Sudan (83.9%).

### **1.3 Problem statement**

Sudanese polypropylene (KPC polypropylene) distributed into wide area including Sudan, Egypt, Ethiopia, Kenya and Syria etc. Hence polypropylene is inexpensive and available raw material for local market in Sudan. The major problems of KPC product are raised by the local consumers are the following:

#### **1. Density**

Standard Isotactic polypropylene has standard density range (905 -940) kg/m<sup>3</sup>. But based on local consumer experience the density of KPC polypropylene is well below the standard compared to same imported grade of polypropylene.

#### **2. Brittleness**

Standard Isotactic polypropylene is brittle in comparison with high density polyethylene (HDPE).But KPC polypropylene is very brittle even if compared with standard polypropylene (based on local consumer experience).

#### **3. Melt strength**

Standard Isotactic polypropylene has low melt strength and also KPC polypropylene compared to high density polyethylene

(HDPE) (Based on local consumer experience there is no difference between extrusion and injection grades of KPC polypropylene).

#### **1.4 Objectives:**

- Comparison of the inherent mechanical, thermal and rheological properties of KPC polypropylene with standard isotactic polypropylene grades and to previous studies.
- Investigation of the problems associated with KPC polypropylene in local industry in conjunction with respect standard isotactic polypropylene grades and to previous studies.
- Develop processing techniques to improve melt strength and brittleness of KPC polypropylene.
- Improvement and evaluation of KPC polypropylene through blending with thermoplastics to form composites with fillers and additives.

## Chapter two

### Literature Review

#### **2.1 Polypropylene (PP)**

Polypropylene (PP) is a thermoplastic material that is produced by polymerizing propylene molecules, which are the monomer units, into very long polymer molecule or chains. There are a number of different ways to link the monomers together, but PP as a commercially used material in its most widely used form is made with catalysts that produce crystallizable polymer chains. This give rise to a product that is a semi crystalline solid with good physical, mechanical, and thermal properties. Another form of PP, produced in much lower volumes as a byproduct of semi crystalline PP production and having very poor mechanical and thermal properties, is a soft, tacky material used in adhesives, sealants, and caulk products. The above two products are often referred to as isotactic (crystallizable) PP (i-PP) and atactic (non-crystallizable) PP (a-PP), respectively (Kock et al., 2013).

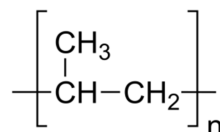


Figure (2.1) Polypropylene chemical structure

As is typical with most thermoplastic materials, the main properties of PP in the melt state are derived from the average length of the polymer chains and the breadth of the distribution of the polymer chain lengths in a given product. In the solid state, the main properties of the PP material reflect the type and amount of crystalline and amorphous regions formed from the polymer chains. Semi crystalline PP is a thermoplastic material containing both

crystalline and amorphous phases. The relative amount of each phase depends on structural and stereo chemical characteristics of the polymer chains and the conditions under which the resin is converted to final products such as fibers, films, and various other geometric shapes during fabrication by extrusion, thermoforming, or molding.

These properties can be varied in a relatively simple manner by altering the chain regularity (tacticity) content and distribution, the average chain lengths, the incorporation of a comonomer such as ethylene into the polymer chains, and the incorporation of an impact modifier into the resin formulation. Polypropylene containing only propylene monomer in the semi crystalline solid form is referred to as homopolymer PP (HPP), and we use this to mean isotactic PP form. Polypropylene containing ethylene as a comonomer in the PP chains at levels in about the 1–8% range is referred to as random copolymer (RCP). HPP containing a commixed RCP phase that has an ethylene content of 45–65 % is referred to as an impact copolymer (ICP). Each of these product types is described below in more detail.

### **2.1.1 Polypropylene tacticity**

The solid-state characteristics of PP occur because the propylene monomer is asymmetrical in shape. It differs from the ethylene monomer in that it has a methyl group attached to one of the olefinic carbons. This asymmetrical nature of the propylene monomer thus creates several possibilities for linking them together into polymer chains that are not possible with the symmetrical ethylene monomer, and gives rise to what are known as structural isomers and stereo chemical isomers in the PP chain. In structural isomerism, polymer scientists refer to the olefinic carbon with the

methyl group on it as the ‘head’ (h) and the other olefinic carbon as the ‘tail’ (t) of the monomer. The most common method of polymerization uses catalysts that link the monomers together in the ‘‘head-to-tail’’ fashion. Occasionally there is a ‘‘mistake’’ made and the monomers form a ‘head-to-head’ or a ‘tail-to-tail’ linkage, but these tend to be rare. Stereo chemical isomerism is possible in PP because propylene monomers can link together such that the methyl groups can be situated in one spatial arrangement or another in the polymer. If the methyl groups are all on one side of the chain, they are referred to as being in the ‘isotactic’ arrangement, and if they are on alternate sides of the chain, they are referred to as being in the ‘syndiotactic’ arrangement.

Each chain has a regular and repeating symmetrical arrangement of methyl groups that form different unit cell crystal types in the solid state. A random arrangement of methyl groups along the chain provides little or no symmetry, and a polymer with this type of arrangement is known as Atactic polypropylene. When polymer scientists discuss the stereo chemical features of PP, they usually discuss it in terms of tacticity or percent tacticity of polypropylene, and in the marketplace the term polypropylene is generally used to refer to a material that has high tacticity, meaning high isotactic content. The high-tacticity PP materials have desirable physical, mechanical and thermal properties in the solid state. Atactic material is a soft, sticky, gummy material that is mainly used in sealants, caulks, and other applications where stickiness is desirable. Syndiotactic PP, not a large-volume commercial material, is far less crystalline than isotactic PP (Kock et al., 2013).



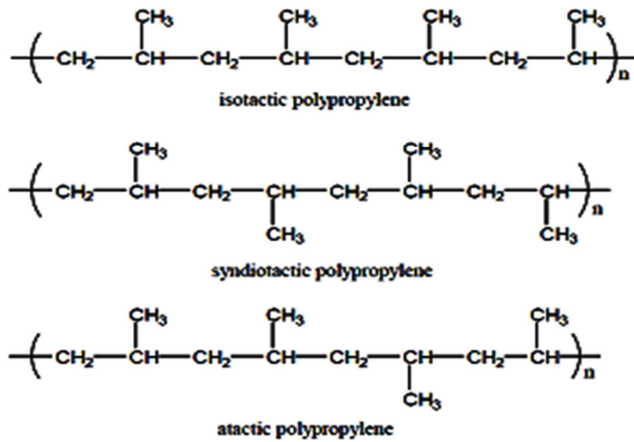


Figure (2.2) Polypropylene polymer molecules

### 2.1.2 Major advantages of polypropylene properties

PP is very popular as a high-volume commodity plastic. However, it is referred to as a low-cost engineering plastic. Higher stiffness at lower density and resistance to higher temperatures when not subjected to mechanical stress (particularly in comparison to high and low density PE (HDPE and LDPE)) are the key properties. In addition to this, PP offers good fatigue resistance, good chemical resistance, good environmental stress cracking resistance, good detergent resistance, good hardness and contact transparency and ease of machining, together with good processibility by injection molding and extrusion (Tripathi, 2002). The properties of PP are compared with other competitive thermoplastics as shown in Table (2.1). It can be seen from the table that PP offers advantages over most of its competitive materials on the basis of specific modulus (modulus to density ratio), heat deflection temperature (HDT), maximum continuous use temperature or modulus to cost ratio. Environmental and food legislation may further tip the balance in favor of PP.

Polypropylene is available in a wide variety of melt flow rates, ranging from 0.3 to over 1000 g/10min, and it is easily recycled. It can be processed by virtually all methods, including injection molding, blow molding, extrusion, blown and cast film, and thermoforming (Clive Maier, Teresa Calafut, 1998).

Table (2.1) Comparison of unmodified PP with other materials-1

<b>Property</b>	<b>PP</b>	<b>LDPE</b>	<b>HDPE</b>	<b>HIPS</b>	<b>PVC</b>	<b>ABS</b>
Flexural Modulus (GPa)	1.3	0.3	1.3	2.1	3.0	2.7
Tensile strength (MPa)	33	10	32	42	51	47
Specific density (cm <sup>3</sup> /g)	0.905	0.92	0.96	1.08	1.4	1.05
Specific modulus (GPa)	1.66	0.33	1.35	1.94	2.14	2.57
HDT at 0.45 MPA(°C)	105	50	75	85	70	98
Max continuous use temp (°C)	100	50	55	50	50	70
Cost (£/ton)	660	730	660	875	905	1550
Modulus per unit cost (MPa/£)	2.27	0.41	1.97	2.4	3.31	1.47

Many available grades with different properties make polypropylene useful in applications such as fibers, films, filaments, and injection molded parts for automobiles, rigid packaging, appliances, medical equipment, food packaging, and consumer products. It is being substituted for glass, metal, and engineering plastics such as ABS, polycarbonate, polystyrene, and nylon in kitchen appliances and large appliances such as ovens, dishwashers, refrigerators, and washing machines, and high flow grades are used in molding large house wares. Super - soft grades are replacing polyvinyl chloride in medical bags and tubing and in hospital gowns (Clive Maier, Teresa Calafut, 1998).

### 2.1.3 Major disadvantages of polypropylene properties

The major disadvantages of PP compared with other competitive thermoplastics are evident from Table (2.1). It can be seen that PP has significantly higher mould shrinkage, higher thermal expansion and lower impact strength, particularly at sub-ambient temperatures, than HIPS, PVC and ABS. However, PP has lower mould shrinkage and thermal expansion coefficient than HDPE and LDPE. Poor UV resistance and poor oxidative resistance in the presence of certain metals such as copper are other disadvantages of PP. As any semi-crystalline material, PP also suffers from high creep under sustained load in comparison to an amorphous plastic such as ABS or PVC (Clive Maier, Teresa Calafut, 1998).

Other disadvantages of PP are difficult solvent and adhesive bonding, poor flammability, warpage, limited transparency; poor wear properties, unsuitability for frictional applications and poor resistance to gamma radiation. However, most of these disadvantages could be overcome, either completely or to a certain degree, by proper selection of material, sensible design and good processing. The processing of PP by thermoforming and blow molding is difficult. Vacuum forming of PP is also difficult.

Table (2.2) Comparison of unmodified PP with other materials-2

Property	PP	LDPE	HDPE	HIPS	PVC	ABS
Mould shrinkage (%)	1.9	3.0	3.0	0.5	0.4	0.6
Thermal expansion ( $\times 10^{-5}$ )	10	20	12	7	6	8
Notched Izod impact strength (kJ/m) at 23°C	0.07	>1.06	0.15	0.1	0.08	0.2

PP is not hazardous to health; however, it can release volatile organic compounds (VOCs) into the surrounding air during high-temperature processing. Workers at the processing plant can be subjected to these VOCs through inhalation or skin contact. Good ventilation using exhaust fans can minimize the exposure. Residual monomer and catalysts present in the resin can increase the toxicity.

#### **2.1.4 Applications of Polypropylene**

PP should really be considered a group of polymers, not just a single polymer. Because the properties of PPs cover a substantial range, the applications of PP are quite diverse (Kock et al., 2013). This, of course, belies the usual classification of PP as a commodity resin. Organizing a discussion on applications is challenging because the question arises as to whether similarity of uses or similarity of the fabricated products or similarity of the fabrication techniques should be used as the criterion for arranging information. None of the methods is perfect. Here the material is organized in a fashion that intertwines these, but it seems logical to the authors based on our experience. The most important applications of PP are:

##### **2.1.4.1 Fibers and Fabrics**

A great volume of PP finds its way into an area that may be classified as fibers and fabrics. Fibers, which broadly speaking include slit film or slit tape, are produced in various kinds of extrusion processes. The advantages offered by PP include low specific gravity, which means greater bulk per given weight, strength, chemical resistance, and stain resistance (Kock et al., 2013).



Figure (2.3) Polypropylene non-woven fabric

#### **2.1.4.2 Strapping**

Strapping is similar to slit film but thicker, being on the order of 20 mils. As the name implies, strapping is used to secure large packages or boxes or to hold stacks together. It takes the place of steel strapping, and its most important property is strength, although the moisture resistance of PP is also an important attribute. It is produced from either direct extrusion or from sheet that is slit. Uniaxial orientation is applied by drawing. Homopolymer resins of low MFR (between 1.0 and 1.5 g/10 min) are used for this application (Kock et al., 2013).



Figure (2.4) Polypropylene strapping

### 2.1.4.3 Film

By definition, film is less than 10 mils thick. There are two broad classes of film are cast film and oriented film. In cast film processes, polypropylene is extruded through a die into a chill roll and the resulting film is eventually taken up on winding equipment. Cast film is essentially unoriented but is still fairly clear because of the quench cooling that occurs. Film thickness usually ranges between 1 and 4 mils. An important feature of cast film is its softness and lack of cellophane-like crispness. Both homopolymer and random copolymers are used in cast film, the MFR most commonly being around 8 g/10 min. Random copolymers give slightly clearer, softer, and more impact-resistant film. In case of biaxially oriented polypropylene film. There are two methods are widely used for producing biaxially oriented PP (BOPP) film. One is the enter process, and the other is the tubular or bubble process. In both, homo polymer of about 3g/10 min MFR is most widely used (Kock et al., 2013).



Figure (2.5) Polypropylene film

#### **2.1.4.4 Sheet**

Sheet is an extruded product that is greater than 10mm in thickness (below this the product is identified as film), 40mm being typical. Resin is extruded through a die and passes through a cooling roll stack and conveyed to nip rolls, after which sheet is wound on rolls or cut and stacked or conveyed directly to a thermoforming machine.



Figure (2.6) Polypropylene sheet

#### **2.1.4.5 Automotive**

Polypropylene has a large presence in cars and other vehicles. For the most part, impact copolymers predominate. One of the original uses was in battery cases; in this application, which goes back more than 25 years, injection-molded impact copolymer, colored black, replaced black hard rubber. Now, cases of other colors and of natural translucent material are the norm. Another long-standing use of PP in a car has been for heat and air conditioning ducts, which are mostly unseen. Fan blades of various types are produced from filled (usually with talc) PP.



Figure (2.7) Polypropylene Fan blades

## 2.2 Linear low density polyethylene (LLDPE)

### 2.2.1 Polyethylene (PE)

Polyethylene is virtually defined by its very name as a polymer of ethylene produced by addition polymerization, linear polymers with the formula  $(\text{CH}_2)_n$  have also been prepared by condensation reactions. Commercially, polyethylene is produced from ethylene, the polymer being produced by this route in March 1933 and reported verbally by Fawcett in 1935. The basic patent relating to the polymerization of ethylene was applied for by ICI on 4th February 1936 and accepted on 6th September 1937. Until the mid-1950s all commercial polyethylene was produced by high pressure processes developed from those described in the basic patent. These materials were somewhat branched materials and of moderate number average molecular weight, generally less than 50,000. However, about 1954 two other routes were developed, one using metal oxide catalysts (e.g. the Phillips process) and the other aluminum alkyl or similar materials (the Ziegler process). By these processes polymers could be prepared at lower temperature and pressures and with a modified structure. Because of these modifications these polymers had a higher density, were harder and had high softening points. These materials are known as high-density polyethylene (HDPE), while the earlier materials are known as low-density polyethylene (LDPE).

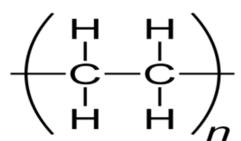


Figure (2.8) Polyethylene polymer molecules



At the end of the 1970s considerable interest developed in what became known as linear low density polyethylene (LLDPE) which is intermediate in properties and structure to the high pressure and low pressure materials. While strictly speaking these are copolymers it is most convenient to consider them alongside the homopolymers. The LLDPE materials were rapidly accepted by industry particularly in the manufacture of film. The very low density polyethylene (VLDPE) introduced by Union Carbide in 1985 were closely related. During the 1990s there was enormous activity in the development of a further type of polyethylene based on metallocene catalysis methods. One patent search revealed that over 950 patent applications had been filed on the subject by the summer of 1996 and has since shown no signs of abating. Commercial production commenced in the late 1990s and it is estimated that in 2000 metallocene-catalyzed polyethylene will comprise about 2 % of the total polyethylene market. This is somewhat less spectacular than achieved by LLDPE and reflects the fact that although these materials may have many superior properties in the finished product they are more expensive than the traditional materials and in some respects more difficult to process. Whereas the metallocene polymers can be of LDPE, LLDPE and HDPE types it is anticipated that LLDPE types (referred to as mLLDPE) will take over 50 % of the market; mainly for film application. By the mid- 1990 s capacity for polyethylene production was about 50,000000 t.p.a, much greater than for any other type of plastics material. Of this capacity about 40 % was for HDPE, 36 % for LDPE and about 24 % for LLDPE. Since then

considerable extra capacity has been or is in the course of being built but at the time of writing financial and economic problems around the world make an accurate assessment of effective capacity both difficult and academic. It is, however, apparent that the capacity data above is not reflected in consumption of the three main types of material where usage of LLDPE is now of the same order as the other two materials. Some 75 % of the HDPE and LLDPE produced to use for film applications and about 60 % of HDPE for injection and blow moulding. Polymers of low molecular weight and of very high molecular weight are also available but since they are somewhat atypical in their behaviour they will be considered separately (J. A. Brydson, 1999).

### **2.2.2 Making LLDPE and Metallocene Polyethylene**

Over the years many methods have been developed in order to produce polyethylene with short chain branches but no long chain branches. Amongst the earliest of these were a process operated by Du Pont Canada and another developed by Phillips, both in the late 1950s. More recently Union Carbide has developed a gas phase process. Gaseous monomers and a catalyst are fed to a fluid bed reactor at pressures of 100-300  $\text{lb}_f/\text{in}^2$  (0.7-2.1 MPa) at temperatures of 100 °C and below. The short branches are produced by including small amounts of propene, but-1-ene, hex-1-ene or oct-1-ene into the monomer feed. Somewhat similar products are produced by Dow using a liquid phase process, thought to be based on a Ziegler-type catalyst system and again using higher alkenes to introduce branching. There has been recent interest in the use of the Dow constrained geometry catalyst system to produce linear low-

density polyethylene with enhanced properties based, particularly, on ethylene and oct-1-ene. LLDPE materials are now available in a range of densities from around 0.900 g/cm<sup>3</sup> for VLDPE materials to 0.935 g/cm<sup>3</sup> for ethylene-octene copolymers. The bulk of materials are of density approx. 0.920 g/cm<sup>3</sup> using butene in particular as the co-monomer (J. A. Brydson, 1999).

In recent years the market for LLDPE has increased substantially and is now more than half the total for LDPE and for HDPE. Mention has already been made of metallocene - catalyzed polyethylene. Such metallocene catalysts are transition metal compounds, usually zirconium or titanium, incorporated into a cyclopentadiene based structure. During the late 1990s several systems were developed where the new catalysts could be employed in existing polymerization processes for producing LLDPE-type polymers. These include high pressure autoclave and solution processes as well as gas phase processes. At the present time it remains to be seen what methods will become predominant. Mention may also be made of catalyst systems based on iron and cobalt announced in 1998 by BP Chemicals working in collaboration with Imperial College London and, separately, by DuPont working in collaboration with the University of North Carolina. The DuPont NNC catalysts are said to be based on tridentate pyridine bis-imine ligands coordinated to iron and cobalt. These are capable of polymerizing ethylene at low pressures (200-600 psi) yielding polymers with very low branching (0.4 branches per 1000 carbon atoms) and melting points as high as 139

°C. The BP/ICL team claims that their system provides many of the advantages of metallocene but at lower cost.

### **2.2.3 Properties of LLDPE**

The present position of polyethylene as a general purpose thermoplastic material is due in no small measure to the low cost and easy processability of the polymer. The characteristics of polyethylene which lead to its widespread use may be summarized as follows:

- 1) Low cost.
- 2) Easy processability.
- 3) Excellent electrical insulation properties.
- 4) Excellent chemical resistance.
- 5) Toughness and flexibility even at low temperatures.
- 6) Reasonable clarity of thin films.
- 7) Freedom from odor and toxicity.
- 8) Sufficiently low water vapor permeability for many packaging, and agricultural applications building.

To these could also be added the fact that a great quantity of information is available concerning the processing and properties of this material and that its properties are reasonably well known and understood by the public at large. The limitations of the polymer are:

- 1) The low softening point.
- 2) The susceptibility of low molecular weight grades to environmental stress cracking.
- 3) The susceptibility to oxidation (however, polyethylene is better in this respect than many other polymers).
- 4) The opacity of the material in bulk.
- 5) The wax-like appearance.
- 6) The poor scratch resistance.

- 7) The lack of rigidity (a limitation in some applications but a virtue in others).
- 8) The low tensile strength.
- 9) The high gas permeability.

As with LDPE and HDPE materials, there is a wide range of linear low-density polyethylene (LLDPEs). Primarily competitive with LDPE, the 'linear low' materials have found rapid acceptance because of their high toughness (at low, normal and high temperatures), tensile strength, elongation at break and puncture resistance compared to LDPE materials of similar melt flow index and density (J. A. Brydson, 1999). More specifically the improved resistance to environmental stress cracking has been emphasized by suppliers as also has the ability to use dishwashers to clean LLDPE kitchen utensils, a consequence of the higher heat deformation resistance.

The very low density materials (VLDPEs) introduced in the mid-1980s is generally considered as alternatives to plasticized PVC and ethylene-vinyl acetate (EVA) plastics. They have no volatile or extractable plasticizers as in plasticized PVC or do they have the odor or moulding problems associated with EVA. Whilst VLDPE materials can match the flexibility of EVA they also have better environmental stress cracking resistance, improved toughness and a higher softening point. Some comparative data for a VLDPE copolymer based on ethylene and oct-1-ene and an EVA material (91 % ethylene, 9 % vinyl acetate) are given in Table (2.3).

Table (2.3) Comparison of VLDPE and EVA (9% VA)

Property	VLDPE	EVA
Density (g/cm <sup>3</sup> )	0.911	0.926
MFI (g/10 min)	7	9
Tear strength (N/mm <sup>2</sup> )	11.4	6.1
Elongation at break (%)	710	475
Vicat temperature (°C)	78	51
Low-temperature brittle point (°C)	-135	-130
Hardness (Shore D)	42	32
Stress crack time (h)	600	240

#### 2.2.4 LLDPE Processing

LDPE and LLDPE have unique rheological or melt flow properties. LLDPE is less shear sensitive because of its narrower molecular weight distribution and shorter chain branching. During shearing process, such as extrusion, LLDPE remains more viscous and, therefore, harder to process than LDPE of equivalent melt index. The lower shear sensitivity of LLDPE allows for a faster stress relaxation of the polymer chains during extrusion, and, therefore, the physical properties are susceptible to changes in blow-up ratios. In melt extension, LLDPE has lower viscosity at all strain rates. This means it will not strain harden the way LDPE does when elongated. As the deformation rate of the polyethylene increases, LDPE demonstrates a dramatic rise in viscosity because of chain entanglement. This phenomenon is not observed with LLDPE because of the lack of long-chain branching in LLDPE allows the chains to slide by one another upon elongation without becoming entangled. This characteristic is important for film applications because LLDPE films can be down gauged easily while maintaining high strength and toughness. The rheological properties of LLDPE are summarized as "stiff in shear" and "soft in

extension". It is not taken in most curbside pickups in communities. LLDPE can be recycled though into other things like trash can liners, lumber, landscaping ties, floor tiles, compost bins, and shipping envelopes (J. A. Brydson, 1999).

### **2.2.5 LLDPE applications**

Polyethylene was introduced initially as a special purpose dielectric material of particular value for high-frequency insulation. With increasing availability the polymer subsequently began to be used for chemical plant and, to a small extent, for water piping. Since World War II there has been a considerable and continuing expansion in polyethylene production and this, together with increasing competition between manufacturers, has resulted in the material becoming available in a wide range of grades, most of which are sold in the lowest price bracket for plastics materials. For many purposes these limitations are not serious whilst in other cases the correct choice of polymer, additives, processing conditions and after-treatment can help considerably. The world capacity to produce polyethylene was of the order of so c.  $50 \times 10^6$  t.p.a. in the late 1990s although production to that level is not expected until about 2002. By type, this market is shared between LDPE, HDPE and LLDPE approximately in the blend ratio 40: 36: 24. In the early 1990 s it was estimated that the geographical breakdown for production capacity was Western Europe 26 %, North America 33 %, Japan 8 %, Eastern Europe 8% and Rest of the World 25 % (J. A. Brydson, 1999).

Major applications for LDPE film include heavy duty sacks, refuse sacks, carrier bags and for general packaging. Many of these uses may now be considered to be mature and future growth will become more closely tied to national economic situations. Similar comments may also be made about the extensive use of polyethylene film in the building industry. Areas expected to be

capable of further development are shrink film for food wrapping and film for agricultural purposes. One technical development in this area is the increased use of up to 20% of ethylene propylene rubber in LDPE film formulations. This arises from the improved low-temperature properties and higher impact strength of the blends compared with corresponding unblended LDPE. The LDPE film market has now been partly eroded by LLDPE (J.A.Brydson, 1999). Polymerization plants for LLDPE are cheaper to build, easier to operate and maintain, have lower energy requirements and are more versatile than the high-pressure plants. For these reasons manufacturing costs are reduced. There are also some technical advantages to the user since films from LLDPE have a higher impact strength, tensile strength and extensibility. Such properties allow the possibility of making film of lower gauge but with the same mechanical performance. LLDPE materials show lower gloss, greater haze, are less suitable for shrink film and have a narrower heat sealing range (J.A.Brydson, 1999). LLDPE has penetrated almost all traditional markets for polyethylene; it is used for plastic bags and sheets (where it allows using lower thickness than comparable LDPE), plastic wrap, stretch wrap, pouches, toys, covers, lids, pipes, buckets and containers, covering of cables, geomembranes (Geosynthetic Lining Systems, 2015) and mainly flexible tubing. In 2013, the world market for LLDPE reached a volume of \$40 billion. LLDPE is manufactured by using metallocene catalysts labeled mLLDPE (Market Study, 2015).

### **2.3 Talc**

Talc continues to be favored as a reinforcing filler in PP for automotive parts (under-the hood/bonnet, instrument panel retainers and carriers, bumper, interior and exterior trim), as well as in household appliances (Geoffrey Pritchard, 2005). It is valued for its ability to impart high flexural modulus, heat distortion temperature,



surface hardness and impact strength, measured at both ambient and low temperatures. Luzenac has introduced a new range of Jet fine ultrafine talc fillers with a very high aspect ratio for exterior automotive parts. Half of all the particles have diameters of less than one micron, and there is claimed to be excellent orientation of the lamellae during injection moulding. Borealis is marketing a new range of Borcom micro composites with less than 10% filler, including mostly talc but also kaolin and calcium carbonate, with an average particle size in the range 0.1 to 10 microns, for use in automotive products, including body panels. Talc is also recognized as filler in plastics for sound and vibration absorption in the construction industry. Nano talc is being developed for use in automotive applications (Geoffrey Pritchard, 2005).

#### **2.4 Calcium Carbonate (CaCO<sub>3</sub>)**

In tonnage terms, calcium carbonate is completely dominant. The great majority of calcium carbonate is used in PVC and to a lesser extent unsaturated polyester thermosetting polymer (Geoffrey Pritchard, 2005). Much of it is destined for the construction market or the automotive, domestic appliance and household or consumer products industries. New applications include packaging, especially medical and pharmaceutical packaging, biaxially oriented PP film, flexible film, and injection and blow moulded articles. Research and development is being targeted at calcium carbonates that produce tougher film and makes mouldings without reducing their tensile strength or resistance to tearing. There is also a desire to improve the barrier properties of calcium carbonate-filled LLDPE films. Omya markets a fine activated white marble powder called Omya film 728B for making white film, including microporous breathable film. (Microporous breathable film consists of polyolefin film, highly filled to 50 to 70% w/w with calcium carbonate, usually

marble for whiteness, such that when the film is stretched, the filler particles introduce small voids to allow breathability.) The main applications are in hygiene products such as nappies (diapers), adult incontinence pads and disposable clothing. Other Omya grades aim at high water vapor transmission combined with resistance to water pressure. Breathable film can also be used in construction for films that are inserted under roof tiles, and in wall coverings. Omya film is claimed to give high film extrusion speeds, with less frequent changes of screen packs. Horticultural film can have its optical characteristics modified by mineral fillers (Geoffrey Pritchard, 2005).

### **2.5 Previous works of Polypropylene general properties**

Polymer composition have continued to attract interest from researchers due to inherent benefits from working with polymers, which are ease of processability and productivity, combined with the addition of filler and other additives, can significantly alter the base polymer properties resulting in a low-cost material with potentially very useful properties (Rumer Franz, 2011, Luciana Castillo et al., 2012). Nevertheless, incorporation of filler and other additives in a polymer will affect the melt rheological behavior of the compound which will be critically important in defining the process ability of the polymer compound. The importance of identifying the melt rheological behavior is noted by several workers such as composition of Polypropylene (PP), ethylene propylene diene monomer (EPDM) and zinc dimethacrylate (Chen et al., 2013). Furthermore, this behavior important to study the mechanism by which addition of filler influences the original polymer and to determine those combinations in which such affect occurred (Shri Kant et al., 2013)

Polypropylene (PP) is a versatile thermoplastics offering a useful balance of heat (160°C) and chemical resistance, good

mechanical and electrical properties and easy processing. Besides PE and PVC, PP is the third commodity polymer produced and applied in large quantities. Crystalline polymers of propylene were first described in the literature in 1954 by G.Natta and his associates at the Chemical Industrial Politechnico in Milano (Arun Kumar et al., 2012). Earlier efforts to initiate propylene polymerization had only resulted in non crystalline polymers of little or no importance. With the introduction of heterogeneous, stereospecific catalyst discovered by K. Ziegler for the low-pressure polymerization of ethylene, the scene suddenly changed. These reactions are products of transition metal compounds with selected organometallic compounds contained active sites for polymerization, such that each new propylene molecule was incorporated in the polymer chain in a regular, geometric manner identical to all preceding methyl groups. Three geometric forms of the PP chain can be obtained. Natta classified them as:

1. Isotactic: All methyl groups aligned on one side of the chain.
2. Syndiotactic: Methyl groups alternating.
3. Atactic: Methyl groups randomly positioned.

Both isotactic and syndiotactic forms will crystallize when there are cooled from molten states. Commercial injection molding and extrusion grade PP are generally 94 to 97% isotactic. Fabricated parts are typically 60% crystalline, with a range of polyhedral spherulite forms and sizes, depending on the particular mode of crystallization from the melt. Atactic polypropylene is not suited to structural plastic uses, have been developed as modifiers in hot melt adhesives, roofing compounds, and communications cable-filler gels. PP can be made into a multidimensional range of products with properties and characteristics interdependent on:

- Type of polymer (homopolymer, random, or block copolymer).
- Molecular weight and molecular weight distribution.
- Morphology and crystalline structure.

- Additives.
- Fillers and reinforcing materials.
- Processing techniques.

Homopolymer have resistance to deformation at elevated temperatures, while high stiffness, tensile strength, surface hardness and good toughness can be observed at ambient temperatures. Random ethylene-propylene copolymers are characterized by higher melt strengths. They have good clarity and resistance to impact at low temperature, gained at some sacrifice in stiffness, tensile strength and hardness. Block copolymers, preferably with ethylene, are classified as having medium, high, or extra-high impact strength with particular respect to sub-zero temperatures.

## **2.6 Thermal properties of polypropylene**

Almost all plastic have a high heat capacity (specific heat). At their normal moulding temperatures the total heat content of plastics compare with the heat content let say 20°C, can be greater than zinc or brass at their melting points. This heat content always referred as enthalpy. This heat content can be put into the plastic as well as being taken out and the former process takes places at cylinder and later in mould. Figure (2.8) plots the enthalpy of some plastics, including polypropylene, against temperature. In this figure, it is shown that crystalline materials such as polypropylene and polyethylene have heat content exceed 50cal/g (Arun Kumar et al., 2012).

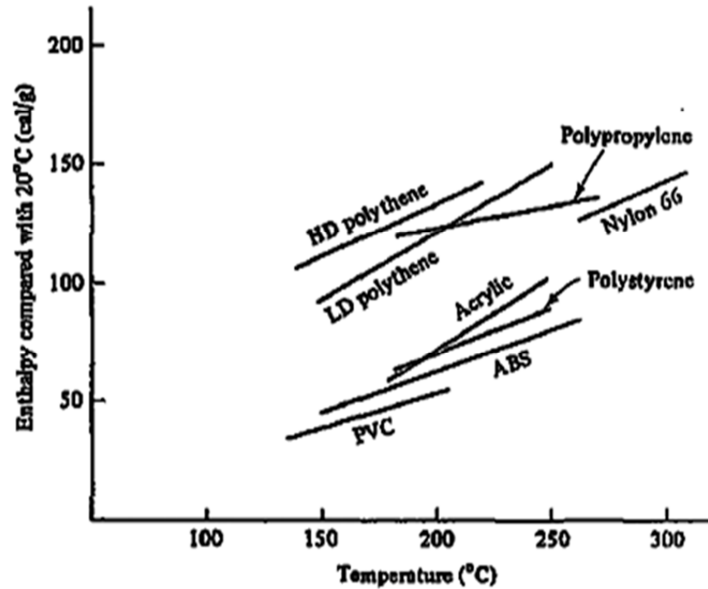


Figure (2.9) Enthalpy of some plastics against temperature

Therefore the understanding of material's thermal properties is necessary for the selection appropriate process of manufacturing. The thermal properties of polypropylene are stated as Table (2.4)

Table (2.4) Thermal properties of polypropylene

Thermal properties of Polypropylene	Values
Thermal conductivity (Wm-K)	0.1382
Processing temperatures (°C)	200-250
Onset decomposition temperatures (°C)	280
Thermal diffusion constants ( $m^2 \text{ sec}^{-1}$ )	$0.9 \times 10^{-7}$
Specific heat	0.46
Mould temperature (°C)	30-80
Thermal diffusivity ( $m^2 \text{ } ^\circ\text{c}^{-1} \text{ sec}^{-1}$ )	$6.5 \times 10^{-9}$

Quote an example, a research about thermo mechanical environment and the microstructure of polypropylene has been carried out. Such as Arun Kumar et al (2012) studied the effect of surface treated sisal fiber on the mechanical, thermal, flammability, and morphological properties of sisal fiber (SF) reinforced recycled

polypropylene (RPP) composites was investigated (Moho Hilmi Othman, 2008). The surface of sisal fiber was modified with different chemical reagent to improve the compatibility with the matrix polymer. The experimental results revealed an improvement in the tensile strength and impact strength sisal fiber reinforced recycled Polypropylene (RPP/SF) composites, respectively, as compared to RPP. The thermo gravimetric analysis (TGA), differential scanning calorimeter (DSC), and heat deflection temperature (HDT) results revealed improved thermal stability as compared with RPP. The flammability behaviour of treated SF/RPP composites also was studied. The morphological analysis through scanning electron micrograph (SEM) supports improves surface interaction between fiber surface and polymer matrix.

Another research work Akira et al (2013) about the thermal properties of polypropylene concluded a process for producing a polypropylene-based material is provided with which it is possible to improve the heat resistance of a polypropylene based material .The process for producing a polypropylene-based material comprises the melting step in which a polypropylene-based material is melted at a temperature that is higher than [(melting peak temperature  $T_m$  of the polypropylene-based material measured by DSC +5 °C] but not higher than [(melting peak temperature  $T_m$ )+80 °C]; and a heat treatment step in which the polypropylene-based material melted in the melting step is heat-treated at a temperature that is [(melting peak temperature  $T_m$ )-20 °C] or higher but lower than [(melting peak temperature  $T_m$ )-10 °C] Akira et al (2013). Also one of the researches is a polypropylene

composition Kristin et al (2013) studied comprising comonomer units derived from ethylene in an amount of from 0.5 wt% to 25 wt%, and from at least one C5-12 alpha-olefin in an amount of from 1.0 mol% to 3.0 mol%, wherein the polypropylene composition has an amount of xylene soluble XS of at least 20 wt%, and the xylene soluble have an amount of ethylene-derived comonomer units of from 4 wt% to 50 wt%. The search obtained improving on sealing and thermal properties of polypropylene.

## **2.7 Mechanical properties of polypropylene**

### **2.7.1 Impact strength of polypropylene**

Plastic products are exposed to many impact encounters during their service life. Recently a comprehensive review of the many factors that influence impact resistance and determine toughness of a fabricated or molded part subjected to an end-use application were carried. Toughness is defined as a measure of the ability of material structure or molded part to endure the application of a sudden applied load without experiencing “failure”. The toughness of composites, based on semi crystalline resins for engineering applications, is of major concern in meeting finished product requirements necessary for good performance. High strain rates, low temperatures, and the presence of stress risers often lead to brittle failure of materials even though they behave in a ductile manner at low strain rates or higher temperatures. During early plastic product development, the commercial success of high-impact polystyrene (HIPS) and acrylonitrile-butadiene-styrene (ABS) led to the development of a whole new group of rubber toughened plastics. Since then, about 80% of blended or filled

thermoplastics are compounded with some type of modifier to give products having improved impact resistance during their service lifetime. Indeed, toughness enhancement of the polymer matrix has become a major new field of polymer science and is very often the decisive characteristic used in material selection for a large variety of applications (e.g., automotive, home appliances, construction, utilities, and sporting goods). Because impact modification of PP blends and composites represents an important area of commercial interest, materials scientists seek a fundamental understanding of the mechanisms underlying fracture failure processes (Kock et al., 2013). Most of these mechanisms also operate in the neat polymers; however, the incorporation of a secondary phase or component alters their modus operandi or introduces impact behavior that does not occur in the neat polymer. Combinations of PP with fillers or thermoplastic blends affect the balance of stiffness and impact resistance. The challenge to product design is how to attain a favorable balance of properties that suit the particular end-use application. Rather than depending on guesswork, the development of cost-effective formulations requires guidelines based on proven hypotheses of impact fracture mechanisms.

There are many researches work about impact of polypropylene has been conducted. One of them is done by G.Karian et al (2003) studied polypropylene/polyethylene blends as models for high-impact propylene-ethylene copolymers, Relation between composition and mechanical performance. The relation between composition and mechanical performance of a series of



binary polyolefin blends was studied in this article (G.Karian, 2003).

There are still many works that involve impact properties of polypropylene material, which are still ongoing. Such as Shri Kant et al (2013) titled improve the mechanical properties of PP/talc composites by grafting acetoxy groups onto the talc surface. The study disclosed reduction in particle size and increase in hydrophobic character, improves particle dispersion and interfacial adhesion in these composites. Incorporating modified talc leads to significant improvements in yield strength, elongation at break and toughness, although the effect on the modulus is less pronounced (Shri Kant et al., 2013).

### **2.7.2 Scratch resistance of polypropylene**

The use of polypropylene is expanding at an increasing rate in the fields of exterior and interior automotive trims, in electrical equipment device housing and covers as well as household and personal articles. However polypropylene is poor or inadequate in heat resistance, stiffness, scratch resistance and impact resistance. These deficiencies are obstacles in opening up new applications for polypropylene, particularly applications which have traditionally been injection molded. In order to overcome these shortcomings, especially inadequate impact and scratch resistance, polypropylene has been blended with a rubbery elastic material such as ethylene propylene copolymer rubber, ethylene propylene-diene copolymer rubber or ethylene butene copolymer rubber and other additives (G.Karian, 2003). For example, Cornelia et al (2013) obtained improve scratch resistance polypropylene at high flow of Injection molded article comprising at least 60wt % of a hetero phasic propylene copolymer at least three polypropylene fractions, the

three polypropylene fractions differ from each other by the melt flow rate and at least one of the three polypropylene fractions has a melt flow rate in the range of 1.0 to 20.0 g/10min, and an elastomeric propylene copolymer dispersed in matrix, wherein said hetero phasic propylene copolymer has a melt flow rate of equal or more than 20.0 g/10min and the amorphous phase of the xylene cold soluble fraction of the hetero phasic propylene copolymer has an intrinsic viscosity of equal or higher than 2.0 dl/g. Another example for improve scratch resistant polypropylene is Pham et al (2013) disclosed the polypropylene substrate is for instance polypropylene homopolymer or TPO. Component is for instance maleated polypropylene or the reaction product of an alpha-olefin and maleic anhydride. The fatty acid amide is for instance stearyl erucamide or oleyl palmitamide. The molded parts are suitable for automotive parts. The molded parts also advantageously contain filler, for example talc.

## **2.8 Polypropylene rheology**

Polypropylene is formed into articles almost exclusively by melt processes that rely on the flow of the melted material at elevated temperatures. Injection molding, blow molding, extrusion, and thermoforming are all examples of melt processing. An understanding of melt flow is essential for success with these processes. The study of the flow of materials including that of polymers is known as rheology. The rheology of a thermoplastics melt is complex, being very dependent on temperature and shear rate. This means that the melt viscosity the characteristic that makes flow easy or difficult can vary widely in the melt condition. The two key points about the flow of thermoplastics are that the behavior is non-Newtonian and that viscosities are very high (Kock et al., 2013).

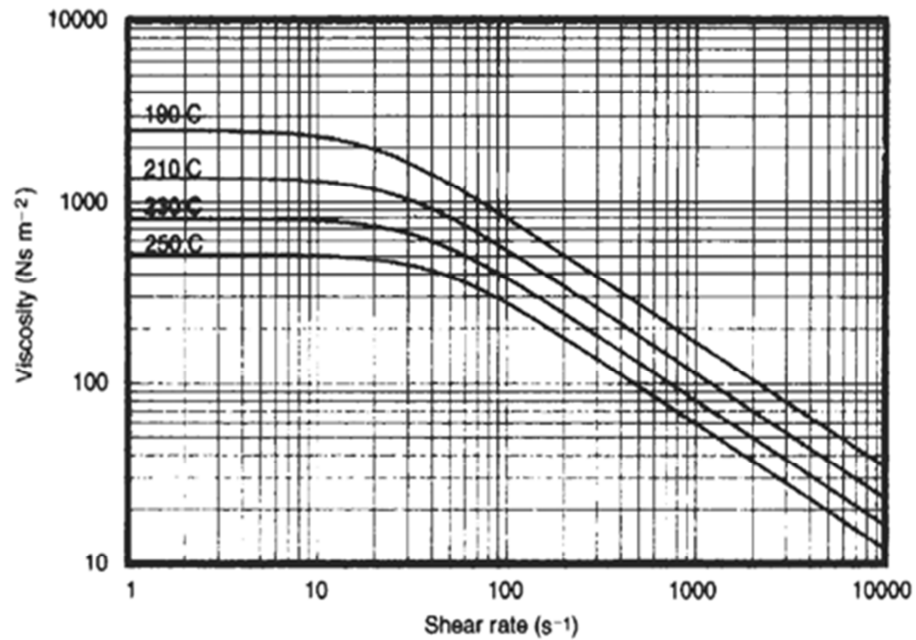


Figure (2.10) Viscosity curves for polypropylene

These characteristics are dictated by the long polymer chain molecular structure of the materials. One practical consequence is that considerable force is required to make a plastics melt flow into a mold or through a die. This explains why plastics processing machinery and molds must be so robust and are costly. To understand and control melt processes, it is necessary to define the way in which melt viscosity changes with temperature and shear rate. The shear rate is a measure of how fast the melt passes through a channel or orifice. One of the researches about flow properties of polypropylene are done by Katja et al (2014) concluded use additives mixture containing linear polypropylene and at least one additive in a polypropylene composition comprising additive mixture and a branched polypropylene to lead to reduce the gel index of polypropylene composition. Another work related to flow properties of polypropylene is Markus et al (2013) concluded that polymer composition of a propylene copolymer and a high density polyethylene, wherein composition

has a MFR of at least 25.0 g/10min and propylene copolymer has a xylene cold soluble content in the range of 7.0 to below 20.0 wt%; a comonomer content in the range of 3.0 to 12.0 wt%; a shear thinning index (SHI 0/50) of at least 7.5; wherein further the xylene cold soluble fraction of the propylene copolymer has a comonomer content in the range of 25.0 to 45.0 wt%.

## **2.9 Polypropylene morphology**

By using Ziegler-Natta catalysts, polypropylene (PP) has been produced from monomer of propylene. When cooled to temperatures below the melting point (the crystallization temperature), polypropylene molecules associate to form supra molecular structures. Polypropylene is a semi crystalline polymer; varying degrees of crystallinity and different types of crystal structures are possible, depending on the stereo chemical structure, the processing or crystallization conditions, and the presence of additives. Crystallinity arises from the stereo regularity in the molecular structure; occasional irregularities such as branching or tail-to-tail addition during polymerization or the presence of copolymers limit the extent of crystallization. Atactic polypropylene, with its random, irregular molecular structure, is predominantly amorphous. Semi crystalline polymers have high strength, stiffness, and density and sharp melting points. Amorphous polymers are tough and ductile, with higher impact strength, lower density, and lower haze. Properties of a polypropylene resin can be adjusted, depending on processing conditions and catalysts, by varying the level of crystallinity in the polymer (Kock et al., 2013).

The usefulness properties of polypropylene and its copolymers make this polymer become an excellent choice for many applications such as house ware, automobile parts, packaging products, laboratory ware, hospital ware, toys, sports and others

(Arun Kumar et al., 2012). As the previous example which the mechanical, thermal, flammability, and morphological properties of treated sisal fiber (SF) reinforced recycled polypropylene (RPP) composites was investigated (Moho Hilmi Othman, 2008). The morphological analysis through scanning electron micrograph (SEM) supports improves surface interaction between fiber surface and polymer matrix. Another research about the morphology of polypropylene is done by Simon et al (2013) obtained blends of polypropylene homopolymer and propylene- $\alpha$ -olefin inter polymer. Process of producing polymeric compositions comprising control-cooling heated blends of polypropylene and propylene- $\alpha$ -olefin inter polymer. Such polymeric compositions can be employed in forming coated wires and cables.

## **2.10 Literature related to present work**

### **2.10.1 Polypropylene compounds**

Polypropylene (PP) compounds have been used in large quantities in numerous fields of applications for many years. The success of PP compounds lies in its extremely advantageous price/volume/performance relations, with the result that polypropylene composition successfully penetrates fields traditionally occupied by other engineering plastic material such as ABS and nylon. Considerable efforts have been made to extend the application of polypropylene composition to fields where engineering thermoplastic have been used. Particularly in the automotive industry for the production of bumpers, heater housings, door pockets and trimmings, timing belt covers cladding. Other common fillers include Calcium carbonate, kaolin, mica and carbon black, while glass fiber is still one of the most commonly used fibrous reinforcements in polypropylene (Nor Azura Abdul Rahim et al., 2010).

### **2.10.2 Talc filled polypropylene**

Throughout the years, research has been intensively going on which various publications on the use of polypropylene as base of compounds, coupled with other polymers, various types of modified as well as unmodified fillers and reinforcements could be found in abundance in almost every polymer journal. Comprehensive studies, which concentrate on a particular property of filled polypropylene, have been done consist mineral fillers and commonly used are talc, calcium carbonate, kaolin, magnesium carbonate, silica, alumina, titanium dioxide and mica. Example of these studies Chi-Ming chan et al (2001) disclosed talc filled with polypropylene improve the mechanical and thermal properties of polypropylene. Also study the effect of polymeric additives on the rheological properties of peroxide and metal salt treated of polypropylene/EPDM blend concluded that addition of metal salt improve crystallinity and mechanical properties of polypropylene. The impact properties of filled polypropylene composites were also tackled by several workers such as Nor Azura Abdul Rahim et al (2010) concluded that the addition of calcium carbonates improve the physical characteristics of polypropylene.

### **2.10.3 Polypropylene blend**

Generally, crystalline poly olefins such as high density polyethylene (HDPE) and polypropylene have been blended with low modulus/elastomeric polyolefin's such as low density polyethylene (LDPE), Poly isobutylene, in order to improve the toughness. Hence toughened polyolefin has traditionally constituted the major volume of polyolefin blends used commercially (L.A.Utracki, 2002). Most of the toughened polyolefin blends are simple mechanical mixtures of polyolefin's and olefinic elastomers melt blended in an extruder without a compatibilizer. However, recent advances in polymerization technology has allowed the

production of toughened polypropylenes, through sequential polymerization of ethylene-propylene copolymer in PP matrix leading to blends with some block or graft copolymer exhibiting somewhat improved modulus/toughness balance. Another recent development in polyolefin blends is the technology of dynamic vulcanization by which an elastomer is dispersed and cured in the matrix of the thermoplastic polypropylene (L.A.Utracki, 2002).

#### **2.10.4 Polypropylene/LLDPE blend**

Polypropylene/polyethylene (PP/PE) blends are amongst polymer blends that were studied by various researchers (Zhang X. M, Aji A, 2005). The different types of polyethylene, especially LDPE, HDPE and linear low density polyethylene (LLDPE) were used to modify the physical and mechanical behaviour of polypropylene by forming physical blends (Ogah, Afiukwa, 2012). The interest in polypropylene and polyethylene is specifically due to the fact that both these polymers are widely used as important engineering materials in the automotive, electrical appliances and packaging industries due to their excellent properties such as rigidity and stiffness, oil resistance and their thermal stability. Apart from these good properties that polypropylene has, its applications are often limited due to its low impact strength and Young's modulus, particularly at low and high temperature loading conditions. These polypropylene drawbacks can be considerably improved by blending polypropylene with other polymers (Wang Y et al., 2002). Blending of polypropylene and different polyethylene's largely depends on the miscibility or immiscibility of the two components. Polypropylene, LDPE or HDPE are generally considered immiscible in the whole composition range

and shows a remarkable phase separation during cooling/crystallization (González J et al., 2012). On the other hand, blend of PP and LLDPE are considered to be compatible in the liquid state (Long Y et al., 1996). However, PP/LLDPE miscibility is restricted by the processing conditions, composition and high temperatures. If a blend of PP and LLDPE is cooled from a miscible melt it may separate into two phases resulting in an immiscible blend (Yi Liua et al., 2013). The melt rheological properties of PP/LLDPE were also investigated by several workers such as Abu Yi Liua et al (2013) obtained blending of LLDPE/PP in improved compatibility between LLDPE and PP phases, made the pseudo plastic behavior of the melt decrease and the melt viscosity and the balance torque increase slightly. Moreover, in the range of high shear rate, the die-swell ratio of the blends decreased with increasing LLDPE/PP content.

Also D. G. Dikobe et al (2010) investigated the mechanical and thermal properties of polypropylene and linear low density polyethylene were studied such as the effect of maleic anhydride grafted polypropylene (MAPP)/LLDPE blend and the morphologies, as well as mechanical and thermal properties, of the blends and the blend composites. The MAPP/LLDPE blend and composites showed better properties than the PP/LLDPE blend and composites as a result of the stronger interfacial interaction between MAPP, LLDPE and wood powder. There are still many works that involve the characterization of PP/LLDPE blend. For example Ghalia et al (2011) investigated PP/LLDPE (60/40) at different fraction of calcium carbonate (0-40%).The results indicated that the



increase in LLDPE contents lead to decrease the tensile and flexural properties while the impact resistance of PP/LLDPE blends increase. However the increase in  $\text{CaCO}_3$  amounts lead to increase both flexural strength and modulus. In the second part of that study, apparent viscosity of PP/LLDPE blends is affected by LLDPE contents due to lack of matrix reinforcement. On the other hand, incorporated of  $\text{CaCO}_3$  into PP/LLDPE blends (60:40) has successfully increased the viscosity while  $\text{CaCO}_3$  treated by aminopropyltriethoxy (AMPTES) coupling agent enhances the rheological properties. In the third part of that research, thermal properties were studied. Thermogravimetric analysis indicated that the total weight loss of PP/LLDPE/ $\text{CaCO}_3$  composites decreases with increasing  $\text{CaCO}_3$  loading. Heat deflection temperature of PP/LLDPE blends increases at all  $\text{CaCO}_3$  loading.

## Chapter three

### Materials and Methods

#### **3.1 Polypropylene (PP)**

Table (3.1) shows the specifications of Polypropylene product supplied by Khartoum Petrochemical Company (KPC, Sudan), in powder with the following particulars:

Table (3.1) Specifications of Polypropylene KPC 114

<b>Trade name</b>	<b>KPC Polypropylene (PP 114)</b>
Density	0.910 g·cm <sup>-3</sup>
Melting point	230 °C
Melt flow index (MFI)	30 g/10 min (230°C, 2.16 kg).
Tensile stress at Yield	27.5 MPa
Flexural Modulus	950 MPa
Izod impact resistance	20 J/m
Heat deflection temperature (HDT)	71 °C

#### **3.2 Linear Low Density Polyethylene (LLDPE)**

Specification of LLDPE in present work supplied by SABIC (Saudi Arabia) blow moulding grade in pellets with the following particulars in table (3.2):

Table (3.2) Specification of SABIC LLDPE

Trade name	LLDPE-218N
Density	0.918 g·cm <sup>-3</sup>
Melting point	190 °C
Melt flow index (MFI)	2 g/10 min (190°C, 2.16 kg).
Melt temperature	185 – 205 °C
Tensile stress at Yield	12 MPa
Flexural Modulus	260 MPa
Dart Impact Strength	5 g
Vicat Softening Point	98 °C

### 3.3 Talc and Calcium Carbonate

Talc and calcium carbonate used on experimental of present work as additives (fillers) in powder form (white powder).

### 3.4 The Methods

#### 3.4.1 PP/LLDPE blends

In the experimental study, blends of PP/LLDP were prepared according to the required compounds as 90/10, 80/20, 70/30, 60/40 and 50/50 to make up a total of 300 g. The samples were prepared in injection moulding machine at 180 °C – 220 °C. The processed samples were allowed to cool at room temperature for 48 hours and 50 ± 5 % humidity. Then different tests were carried out such as flexural modulus and impact resistance as mechanical test. In addition heat deflection temperature (HDT) as thermal test. Finally, the melt flow index (MFI) of the blend has been determined as rheological test. The formulations of blends to produce PP/LLDPE blends are shown in table (3.3).

Table (3.3) Formulations of PP/LLDPE blends

Sample No	Materials	
	PP (wt %)	LLDPE (wt %)
1	90	10
2	80	20
3	70	30
4	60	40
5	50	50

#### 3.4.2 PP/LLDPE/Talc/CaCO<sub>3</sub> compounds

Also in experimental study, four different talc and calcium carbonate concentrations were added to PP/LLDPE (70/30) by weight to produce composites make up a total of 1kg as in table (3.4). The samples were prepared in injection moulding machine at 180°C - 220°C. Then the impact resistance, hardness tests were

carried out as mechanical tests. The melt flow index (MFI) and melt density has been determined as rheological tests. In addition density test has been determined.

Table (3.4) Formulations of PP/LLDPE compounds

Sample No	Materials			
	PP (wt %)	LLDPE (wt %)	Talc (wt %)	CaCO <sub>3</sub> (wt %)
1	70	30	-	-
2	56	24	20	-
3	56	24	-	20
4	56	24	10	10
5	42	18	20	20

### 3.4.3 Testing methods

#### 3.4.3.1 Flexural test

The flexural test of the blends was carried out on a Hounsfield universal testing machine according to the ASTM D790. A computer was connected to the Hounsfield load cell and data acquisition program recorded the force measured by the load cell. Test specimens were molded in a size of 12.7 mm (width) and 3.2 mm (thickness). Prior to the test all specimens were kept at room temperature at least 48 h and 50 ± 5 % humidity. To calculate the flexural stress  $\sigma_f$  expressed in megapascals, using the following equation:

$$\sigma_f = \frac{3FL}{2bh^2} \quad \text{--- (3.1)}$$

Where

F ≡ is the applied force, in newton;

L ≡ is the span, in millimetres;

b ≡ is the width, in millimetres, of the specimen;

h ≡ is the thickness, in millimetres, of the specimen.

For the measurement of the flexural modulus, calculate the deflections  $s_1$  and  $s_2$ , which correspond to the values of flexural strain  $\varepsilon_{f1} = 0.0005$  and  $\varepsilon_{f2} = 0.0025$ , by the following equation:

$$s_i = \frac{\varepsilon_{fi} L^2}{6h} \quad (i = 1; 2) \quad \text{————— (3.2)}$$

Where

$s_i \equiv$  is an individual deflection, in millimetres;

$\varepsilon_{fi} \equiv$  is the corresponding flexural strain.

$L \equiv$  is the span, in millimetres;

$h \equiv$  is the thickness, in millimetres, of the specimen.

Calculate the flexural modulus  $E_f$ , expressed in megapascals, using the following equation:

$$E_f = \frac{\sigma_{f2} - \sigma_{f1}}{\varepsilon_{f2} - \varepsilon_{f1}} \quad \text{————— (3.3)}$$

Where

$\sigma_{f1} \equiv$  is the flexural stress, expressed in mega Pascal's, measured at the deflection  $s_1$ ;

$\sigma_{f2} \equiv$  is the flexural stress, expressed in mega Pascal's, measured at the deflection  $s_2$ ;

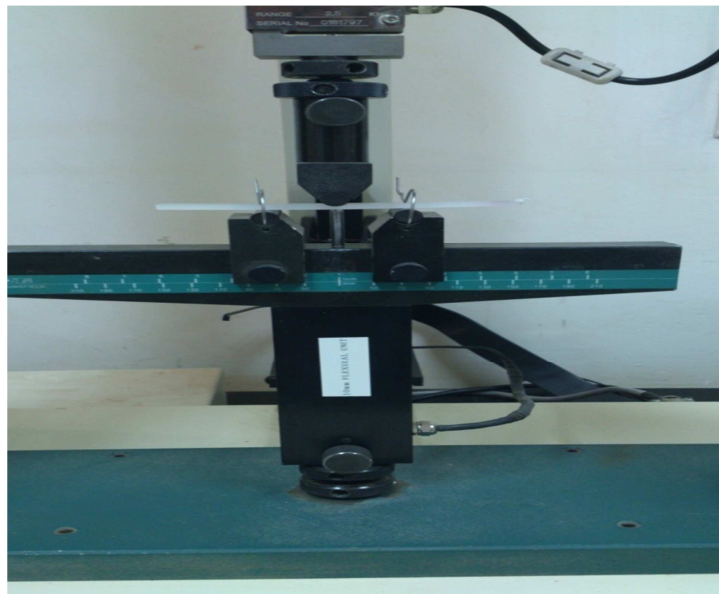


Figure (3.1) Instrumented flexural test device

### 3.4.3.2 Impact test

Izod impact strength values of the blends were evaluated with a Resil impact test instrument according to the ASTM D256 test procedure at room temperature. Izod impact tests specimens were molded in a size of 12.7 mm (width), 3.2 mm (thickness) and notched width 10.20mm. Prior to the test all specimens were kept at room temperature at least 48 h and  $50 \pm 5$  % humidity. To calculate the Izod impact strength of notched specimens,  $a_{iN}$ , expressed in kilo joules per square meter, with notches  $N = A$  or  $B$ , using the formula:

$$a_{iN} = \frac{W}{h b_N} \times 10^3 \text{ (3.4)}$$

Where

$W \equiv$  is the corrected energy, in joules, absorbed by breaking the test specimen;

$h \equiv$  is the thickness, in millimetres, of the test specimen;

$b_N \equiv$  is the remaining width, in millimetres, at the notch base of the test specimen.



Figure (3.2) Resil Impactor machine

### 3.4.3.3 Heat deflection temperature (HDT) test

The thermal properties of the blends were evaluating through HDT test. The test was carried out on a Ceast tester machine according to the ASTM D648. The tests specimens were molded in a size of 12.7 mm (width), 3.2 mm (thickness). Prior to the test all specimens were kept at room temperature at least 48 h and  $50 \pm 5$  % humidity. In the three-point loading method employed in this International Standard, the force applied to the test specimen is given, in newtons, as a function of the flexural stress by one of the following equations: For the preferred (flatwise) position:

$$F = \frac{2\sigma_f b h^2}{3h} \quad \text{—————} \quad (3.5)$$

Where

$F \equiv$  is the load, in newtons;

$\sigma_f \equiv$  is the flexural stress, in megapascals, at the test-specimen surface;

$b \equiv$  is the width, in millimetres, of the test specimen;

$h \equiv$  is the thickness, in millimetres, of the test specimen;

$L \equiv$  is the span, in millimetres, between the supports.

The span used and the flexural-strain increase given in the relevant part of this International Standard. It is calculated for the preferred (flatwise) position as follows:

$$\Delta s = \frac{L^2 \Delta \varepsilon_f}{600h} \quad \text{—————} \quad (3.6)$$

Where

$\Delta s \equiv$  is the standard deflection, in millimetres;

$L \equiv$  is the span, in millimetres, between the lines of contact of the test specimen and the specimen supports;

$\Delta \varepsilon_f \equiv$  is the flexural-strain increase, in percent;

$h \equiv$  is the thickness, in millimetres, of the test specimen;

$b \equiv$  is the width, in millimetres, of the test specimen.

A standard test specimen is subjected to three-point bending under a constant load in the flatwise (preferred) or the edgewise position to produce one of the flexural stresses given in the relevant part of this International Standard. The temperature is raised at a uniform rate, and the temperature at which the standard deflection, corresponding to the specified increase in flexural strain, occurs is measured.



Figure (3.3) HDT VICAT instrument



### 3.4.3.4 Melt flow index and Melt density tests

The MFI PP/LLDPE blends were determined by a Shijiazhu Ang Zhong Shi testing machine according to the procedure ISO 1133:2005 method and facilities of automatic cutting. The die diameter of 2.095mm, temperature control range of 100-400°C, charge canister diameter 9.55mm, length 160mm and applied dead mass of 325g. The melt-flow index rate was quoted as a measure of the mass in grams of melted polymer extruded in 10 minutes through the capillary die. The melt mass-flow rate (MFR), expressed in grams per 10 min and is given by the equation:

$$MFR(\theta, m_{nom}) = \frac{t_{ref} m}{t} \quad \text{—————} \quad (3.7)$$

Where

$\theta$  ≡ is the test temperature, in degrees Celsius;

$m_{nom}$  ≡ is the nominal load, in kilograms;

$m$  ≡ is the average mass, in grams, of the cut-offs;

$t_{ref}$  ≡ is the reference time (10 min), m seconds (600 s);

$t$  ≡ is the cut-off time-interval, in seconds.

The melt volume-flow rate (MVR), expressed in cubic centimeters per 10 min, and is given by the equation:

$$MVR(\theta, m_{nom}) = \frac{A t_{ref} m}{t} = \frac{427 l}{t} \quad \text{—————} \quad (3.8)$$

Where

$\theta$  ≡ is the test temperature, in degrees Celsius;

$m_{nom}$  ≡ is the nominal load, in kilograms;

$A \equiv$  is the mean cross-sectional area, in square centimeters of the piston and the cylinder ( $= 0.711\text{cm}^2$ );

$t_{\text{ref}} \equiv$  is the reference time (10min), in seconds (600 s);

$t \equiv$  is the predetermined time of measurement or the mean value of the individual time measurements in seconds;

$l \equiv$  is the predetermined distance moved by the piston or the mean value of the individual distance measurements in centimeters.



Figure (3.4) Shijiazhu Ang Zhong Shi MFI Instrument

#### 3.4.3.5 Hardness test (Shore D)

The hardness test of the compound was carried out on a Innova testing machine according to the ASTM D 2240 and ISO 868. The hardness testing of plastics is most commonly measured by the Shore (Durometer) test or Rockwell hardness test. Both methods measure the resistance of the plastic toward indentation. Both

scales provide an empirical hardness value that doesn't correlate to other properties or fundamental characteristics. Shore Hardness, using either the Shore A or Shore D scale, is the preferred method for rubbers/elastomers and is also commonly used for 'softer' plastics such as polyolefins, fluoropolymers, and vinyls. The Shore A scale is used for 'softer' rubbers while the Shore D scale is used for 'harder' ones. For shore A the indenter consists of a truncated cone of included angle  $35^\circ$  and diameter at the flat of 0.79 mm, operating under a spring pressure given by:

$$F = 550 + 75H_a \text{ ————— (3.9)}$$

Where

$F \equiv$  the applied force in mN

$H_a \equiv$  the hardness (Shore A).

The Shore D scale is suitable for typical harder plastics materials. This has a sharper indenter of included angle  $30^\circ$  with only a slightly rounded (0.1 mm radius) tip and operates under a spring given by:

$$F = 445H_d \text{ ————— (3.10)}$$

Where

$H_d \equiv$  the hardness (shore D).



Figure (3.5) Innova Hardness testing machine

#### 3.4.3.6 Density test

The density test of the compound was carried out on BOROSIL Pycnometer (25ml) according to the ASTM D 1505. The density at 23°C,  $\rho$  calculated using the equation:

$$\rho = \frac{m_1 - m_0}{V} + \rho_a \quad \text{————— (3.11)}$$

Where

$m_1$   $\equiv$  is the apparent mass, in grams, of the filled pycnometer at 23°C.

$m_0$   $\equiv$  is the apparent mass, in grams, of the empty pycnometer at 23°C.

$\rho_a$   $\equiv$  is the density of air.

To determine the volume of the pycnometer at 23°C using distilled water, use the equation:

$$V = \frac{m_2 - m_0}{\rho_e - \rho_a} = \frac{m_2 - m_0}{0.9964} \quad \text{————— (3.12)}$$

Where

$m_2$   $\equiv$  is the apparent mass, in grams, of the pycnometer filled with distilled water at 23°C.

$\rho_e$   $\equiv$  is the density of distilled water at 23°C = 0, 9976 g/ml.



Figure (3.5.3.6) BOROSIL Pycnometer

## **Chapter four**

### **Results and discussion**

The mechanical, thermal and rheological test of PP/LLDPE blend and PP/LLDPE/Talc/CaCO<sub>3</sub> are as follows:

#### **4.1 PP/LLDPE blends**

##### **4.1.1 Mechanical properties**

The flexural test and impact resistance test were used to investigate the mechanical properties polypropylene and PP/LLDPE blend.

##### **4.1.1.1 Flexural test**

Flexural properties of PP/LLDPE are summarized in Table (4.1). Figure (4.1) shows the effect of LLDPE contents on modulus of rigidity of the PP. The flexural modulus of PP was 950MPa. The addition of LLDPE (10, 20 and 30wt %) to PP increased the flexural modulus to 5.8 to 39.8%. However, addition of LLDPE (40 and 50wt %) decreased the flexural modulus to 21 to 34 %, compared with PP. These observations were also in agreement with z Kock (2014) and Clive et al (1998). That disentanglement or rupture of tie-molecules was the dominant molecular mechanism in environmental stress cracking of polypropylene and in slow crack growth. The tie-molecules have also been identified as exhibiting similar mechanisms in impact and yield strengths. Thus, tie-molecules are important to all strength properties of polypropylene. Hence the increasing concentrations of LLDPE introduced tie-molecules into the polymer blend.

Table (4.1) Flexural modulus of PP/LLDPE blend

LLDPE Load (wt %)	Flexural Modulus (MPa)
PP <sub>575P</sub> (Reference)	1600
PP <sub>114</sub> (zero loading)	950
10	1328
20	1005
30	1257
40	755
50	629

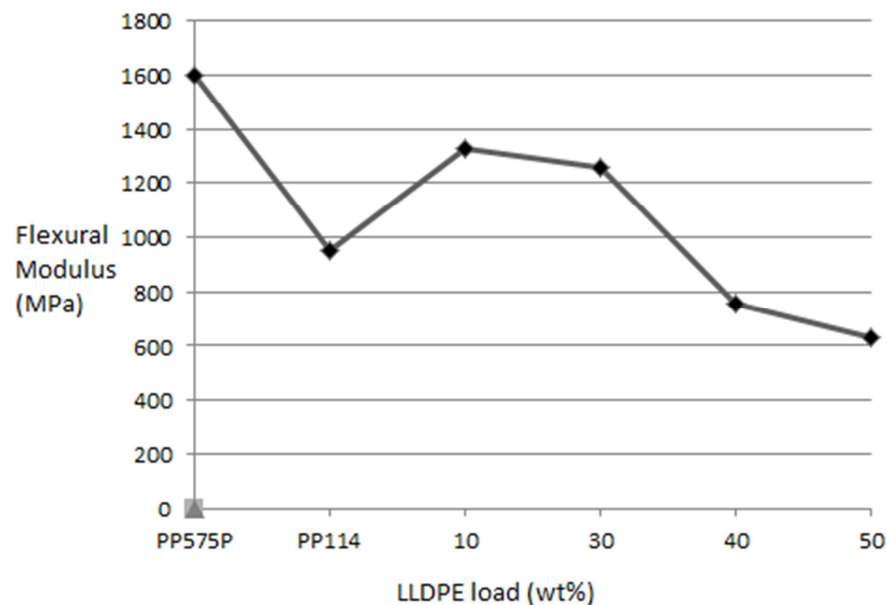


Figure (4.1) Flexural modulus of PP/LLDPE blend

#### 4.1.1.2 Impact test

The impact resistances of PP/LLDPE manufactured by the one-step methods are summarized in Table (4.2). The impact resistance of PP was 20J/m. Figure (4.2) shows the effect of LLDPE contents on the impact resistance of PP. The addition of LLDPE (10, 20, 30, 40 and 50 wt %) to PP clearly seen that significant increasing on the

impact resistance to 23.5 to 50%. The optimum weight percentage of LLDPE on PP provides the best impact resistance is 30 wt %. These observations were also in agreement with Kock et al (2013), Shri Kant et al (2013). As known the brittleness of polypropylene is related to the spherulite morphology and the intrinsic tendency of PP for crazing followed by unstable craze growth and crack propagation under conditions of stress concentration and/or low temperatures. So the impact test results indicate that the LLDPE dispersions in PP provide multiple sites for crazing and localized shear yielding as mechanisms for the impact energy dissipation. From the results of flexural and impact tests, in general, the obtained results are in good agreement with the literature such as Abu Ghalia et al (2011) when the effects of LLDPE on the PP are considered, respectively.

Table (4.2) Impact resistance of PP/LLDPE blends

<b>LLDPE load (wt %)</b>	<b>Impact resistance (J/m)</b>
PP <sub>575P</sub> (Reference)	22
PP <sub>114</sub> (zero loading)	20
10	26.01
20	24.69
30	30.01
40	28.44
50	27.5



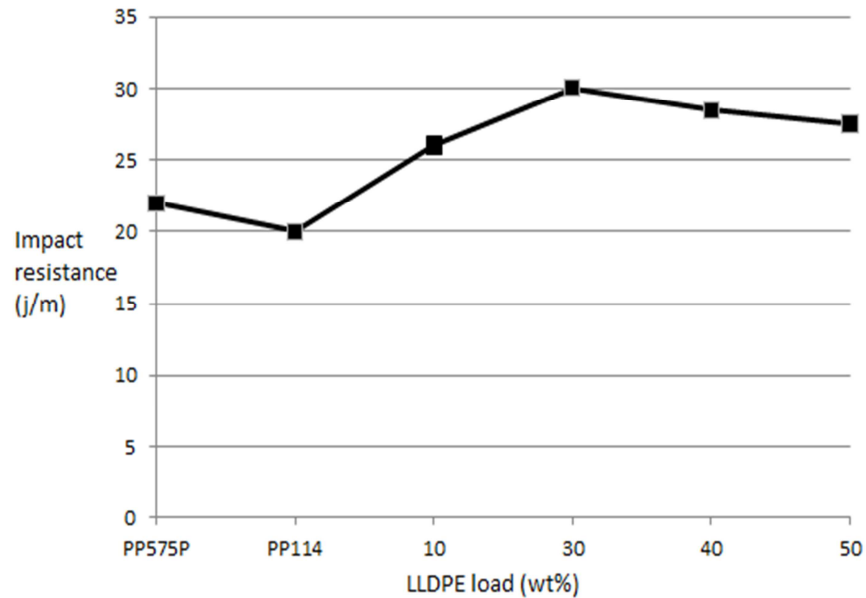


Figure (4.2) Impact resistance of PP/LLDPE blend

#### 4.1.2 Thermal properties

The HDT test is used to investigate the thermal properties of polypropylene and PP/LLDPE blend. HDT of PP and PP/LLDPE blends are shown in Table (4.3). HDT of PP was 71°C. Figure (4.3) shows the effect of LLDPE contents on the HDT of PP. The addition of LLDPE (10, 20, 30, 40 and 50 wt %) to PP increased the HDT to 11 to 68.2%. The figure (4.3) showed the optimum compound percentage of LLDPE on PP provides the best HDT is 30 wt %. From the results of the heat deflection temperature test, in general, the obtained results are in good agreement with the literature such as Kristin et al (2013) and Abu Ghalia et al (2011) when the effects of LLDPE on the PP are considered, respectively.

Table (4.3) HDT of PP/LLDPE blend

LLDPE load (wt %)	HDT (°C)
PP <sub>575P</sub> (Reference)	98.0
PP <sub>114</sub> (zero loading)	71.0
10	81.2
20	86.6
30	119.4
40	80.9
50	78.9

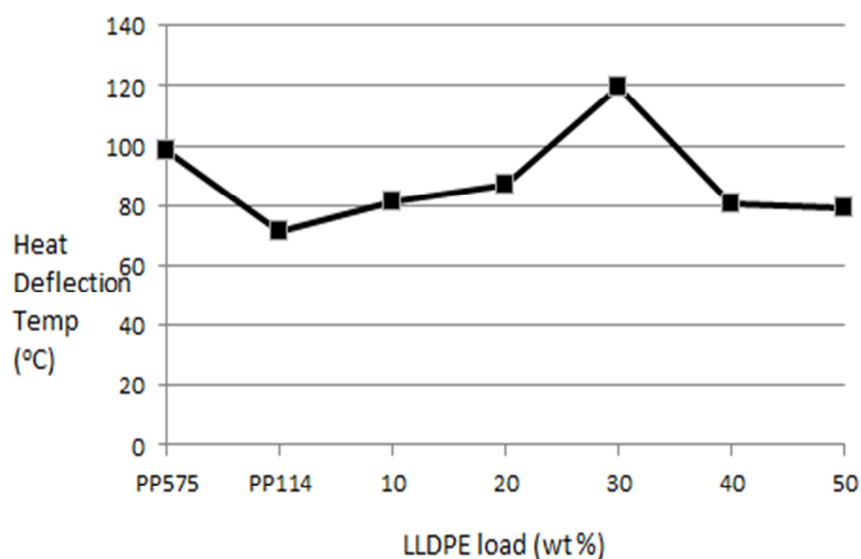


Figure (4.3) HDT of PP/LLDPE blend

#### 4.1.3 Rheological properties

The melt flow index (MFI) test is used to investigate the flow properties of polypropylene and PP/LLDPE blend. The HDT of PP and PP/LLDPE blends are shown in Table (4.4). Figure (4.4) shows the effect of LLDPE contents on the melt flow index of PP. The Melt flow index (MFI) of PP was 30(g/10min). The addition of LLDPE (10, 20, 30, 40 and 50 wt %) to PP decreased the MFI to

4.3 to 46.3 %. The result showed that with increasing LLDPE concentrations, the melt flow index of the composite decreased. This may be attributed to the absence of branching in PP. It is reasonable perhaps, to assign the difference in melt flow properties between the PP and that of LLDPE blend to the presence of short chain branching (SCB) in LLDPE. This is because the SCB tends to increase the entanglement at low shear rate (high elasticity), but at high shear rates the chain would disentangle, thus reducing the viscosity. From the results of the melt flow index test, in general, the obtained results are in good agreement with the literature such as Abu Ghalia et al (2011) when the effects of LLDPE on the PP are considered, respectively.

Table (4.4) MFI of PP/LLDPE blend

<b>LLDPE load (wt %)</b>	<b>MFI (g/10min)</b>
PP <sub>575P</sub> (Reference)	11.00
PP <sub>114</sub> (zero loading)	30.87
10	29.53
20	26.13
30	23.53
40	18.93
50	16.50

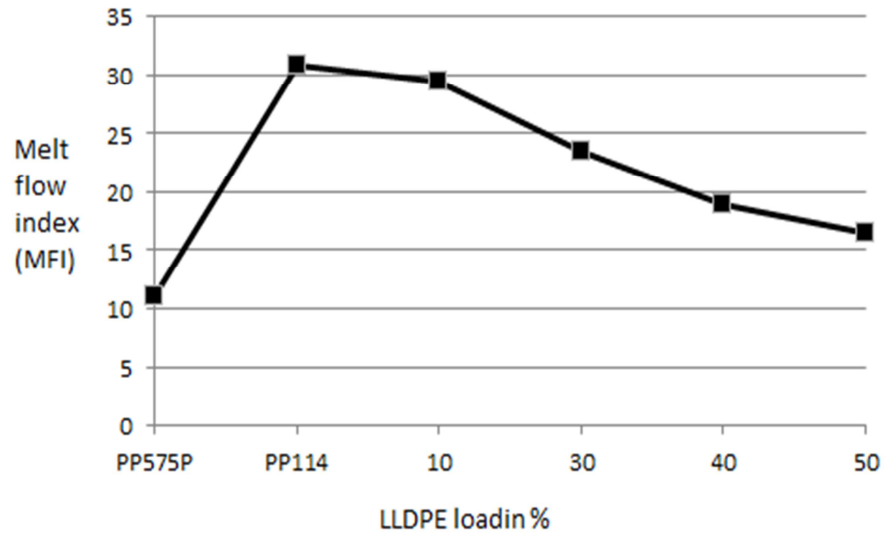


Figure (4.4) Melt flow index (MFI) of PP/LLDPE blend

#### 4.1.4 PP/LLDPE blend tests summary

The table (4.5) and figure (4.5) shows the summary of mechanical, thermal and rheological test of PP/LLDPE blend.

Table (4.5) PP/LLDPE tests summary

LLDPE Load (wt %)	Flexural Modulus (MPa)	Impact resistance (J/m)	HDT (°C)	MFI (g/10min)
PP <sub>575P</sub> (Reference)	1600	22	98	11
PP <sub>114</sub> (Base of blend)	950	20	71	30.87
10	1328	26.01	81.2	29.53
20	1005	24.69	86.6	26.13
30	1257	30.01	119.4	23.53
40	755	28.44	80.9	18.93
50	629	27.5	78.9	16.50

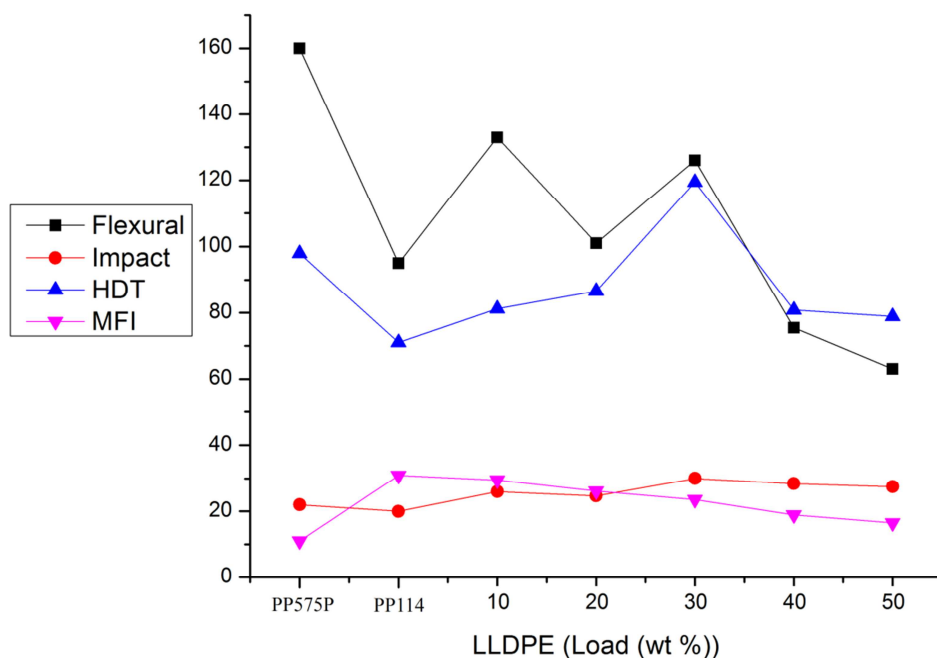


Figure (4.5) PP/LLDPE blend tests summary

From the summary of tests the optimum formulation of PP/LLDPE blends provided the best mechanical, thermal properties and a moderate rheological property is (70/30).

## 4.2 PP/LLDPE/Talc/CaCO<sub>3</sub> compounds

### 4.2.1 Mechanical properties

#### 4.2.1.1 Impact test

The impact properties of PP/LLDPE blend and compound are summarized in Table (4.6) and Figure (4.6). The impact resistance of PP/LLDPE blend was 30.01 J/m. It is clearly seen that the addition 20 wt % of talc to PP/LLDPE has decreased the impact resistance to 20.53 %. The addition of 20 wt % calcium carbonate has decreased the impact resistance to 30.59%. It can also be seen that the addition of 10 wt % of talc and calcium carbonate has decreased on the impact resistance to 29.89%. Also 20 wt % of talc and of calcium carbonate has decreased the impact

resistance to 24.03%. This result may be related to the effects of LLDPE, talc and calcium carbonate on PP. It is well documented that LLDPE increases the impact strength, while talc and calcium carbonate decreases, especially for higher contents (G.Karian, 2003 and Abu Ghalia et al (2011)

Table (4.6) Impact resistance of PP/LLDPE and compounds

Sample no	Impact resistance (J/m)
1	30.01
2	23.85
3	20.83
4	21.04
5	22.80

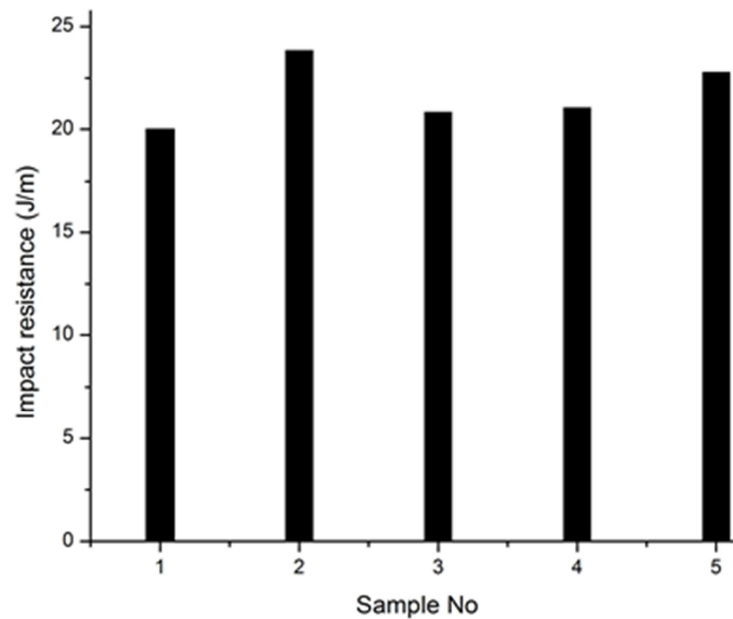


Figure (4.6) Impact resistance of PP/LLDPE and compound

#### 4.2.1.2 Hardness test

The hardness of PP/LLDPE and compound are shown in table (4.7) and Figure (4.7). Hardness of PP/LLDPE blend was

66.2. Addition of 20 wt% of talc to PP/LLDPE has increased the hardness to 18.6%. It can also be seen that the addition of 20 wt % calcium carbonate has increased the hardness to 15.3%. It can also be seen that the addition of 10 wt % of talc and calcium carbonate has increased the hardness to 9.9%. While the addition of 20 wt % of talc and of calcium carbonate has increased hardness to 8.9%. The hardness result may relate to the interaction between PP/LLDPE and talc/calcium carbonate and this restricts the mobility and deformability of the PP/LLDPE (G.Karian, 2003).

Table (4.7) Hardness of PP/LLDPE and compound

Sample No	Hardness
1	57.4
2	68.1
3	66.2
4	63.1
5	62.5

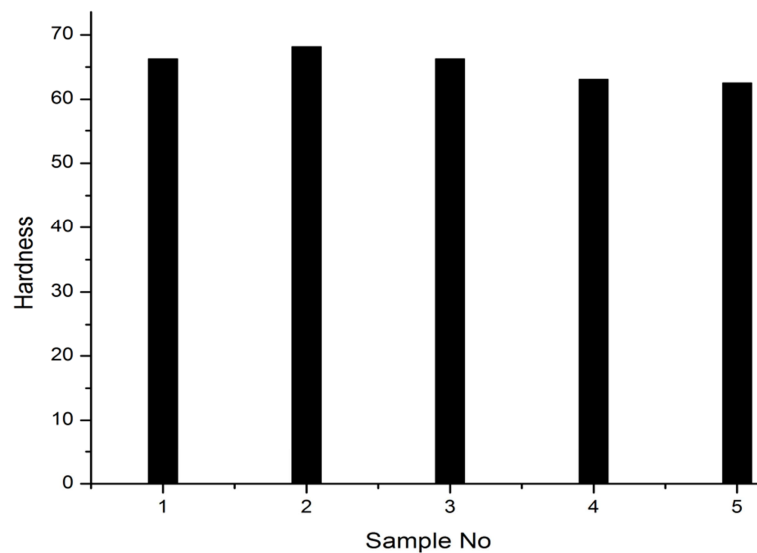


Figure (4.7) Hardness of PP/LLDPE and compound

## 4.2.2 Rheological properties

### 4.2.2.1 Melt flow index (MFI) test

The melt flow index (MFI) test is used to investigate the flow properties of PP/LLDPE and compound are shown in Table (4.8) and Figure (4.8). MFI of PP/LLDPE blend was 23.53g/10min. The result showed addition of 20 wt% of talc to PP/LLDPE increased MFI to 82.75%. It can also be seen that the addition of 20 wt % calcium carbonate increased MFI to 50.02%.

Table (4.8) MFI of PP/LLDPE and compounds

Sample No	MFI (g/10min)
1	23.53
2	43.00
3	35.30
4	31.80
5	26.27

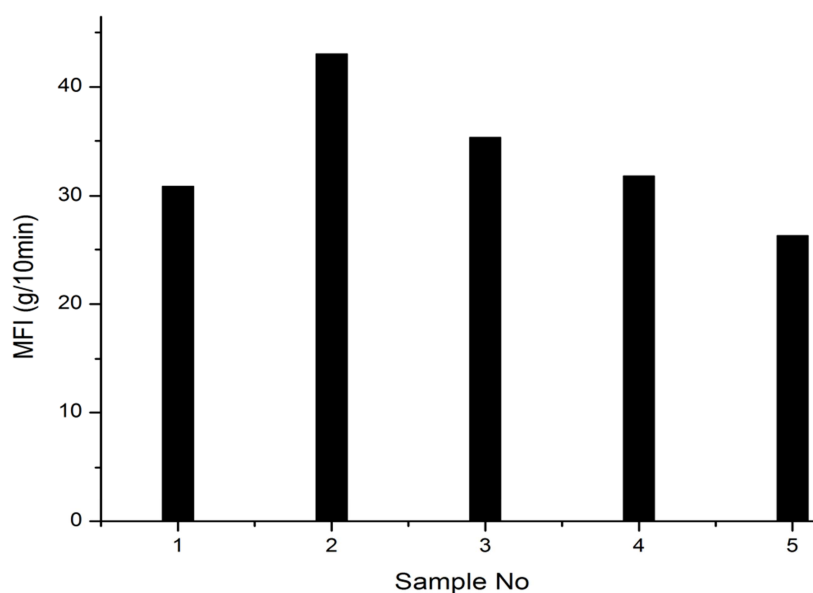


Figure (4.8) MFI of PP/LLDPE and compound



#### 4.2.2.2 Melt density test

The melt density test of PP/LLDPE and compound are shown in Table (4.9) and Figure (4.9). The melt density of PP/LLDPE blend was 0.705g/cm<sup>3</sup>. The result showed addition of 20 wt% of talc to PP/LLDPE has increased melt density to 15.77%. It can also be seen that the addition of 20 wt % calcium carbonate to PP/LLDPE increased melt density to 18.04%. It can also be seen that the addition of 10 wt % of talc and calcium carbonate to PP/LLDPE increased the melt density to 24.86%. While the addition of 20 wt % of talc and of calcium carbonate to PP/LLDPE has increased melt density to 23.01%. This result may be directly related to the undeform ability of the filler and its lack of contribution to the flow (G.Karian, 2003).

Table (4.9) Melt density of PP/LLDPE and compounds

<b>Sample No</b>	<b>The Melt Density (g/cm<sup>3</sup>)</b>
1	0.704
2	0.815
3	0.831
4	0.879
5	0.866

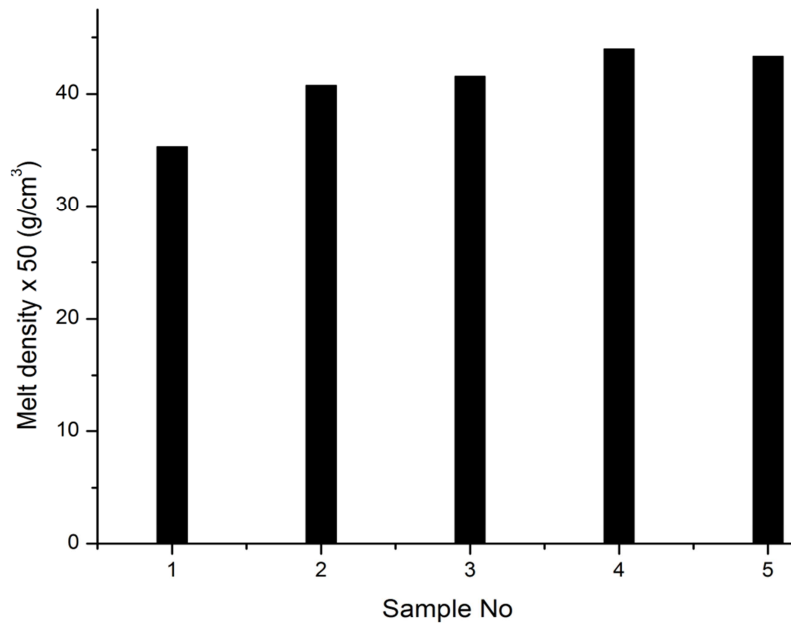


Figure (4.9) Melt density of PP/LLDPE and compound

#### 4.2.3 Density test

It used to investigate the flow properties of PP/LLDPE compound are shown in Table (4.10) and Figure (4.10). Density of PP/LLDPE blend was  $0.782\text{g/cm}^3$ . The result showed addition of 20 wt% of talc to PP/LLDPE (56/24) increased density to 17.63%. It can also be seen that the addition of 20 wt % calcium carbonate has increased density to 14.74%. It can also be seen that the addition of 10 wt % of talc and calcium carbonate has increased the density to 19.77%. While the addition of 20 wt % of talc and of calcium carbonate has increased density s to 30.98%. This result may be related to the effects of LLDPE, talc and calcium carbonate on PP matrix. LLDPE decreases the density, while talc and calcium carbonate increases, especially for higher contents.

Table (4.10) Density of PP/LLDPE and compounds

Sample No	Density (g/cm <sup>3</sup> )
1	0.782
2	0.934
3	0.911
4	0.951
5	1.040

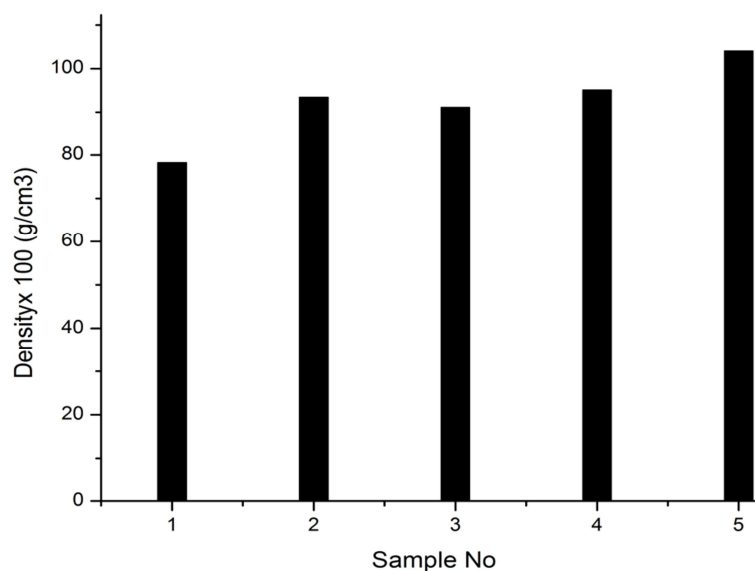


Figure (4.10) Density of PP/LLDPE and compound

#### 4.2.4 PP/LLDPE compound tests summary

The table (4.11) and figure (4.11) shows the mechanical, thermal and rheological test of PP/LLDPE compound.

Table (4.11) PP/LLDPE compounds tests summary

Sample No	Impact resistance (J/m)	Hardness	MFI (g/10min)	The Melt Density (g.cm <sup>-3</sup> )	Density (g.cm <sup>-3</sup> )
1	30.01	57.4	23.53	0.704	0.782
2	23.85	68.1	43.00	0.815	0.934
3	20.83	66.2	35.30	0.831	0.911
4	21.04	63.1	31.80	0.879	0.951
5	22.80	62.5	26.27	0.866	1.040

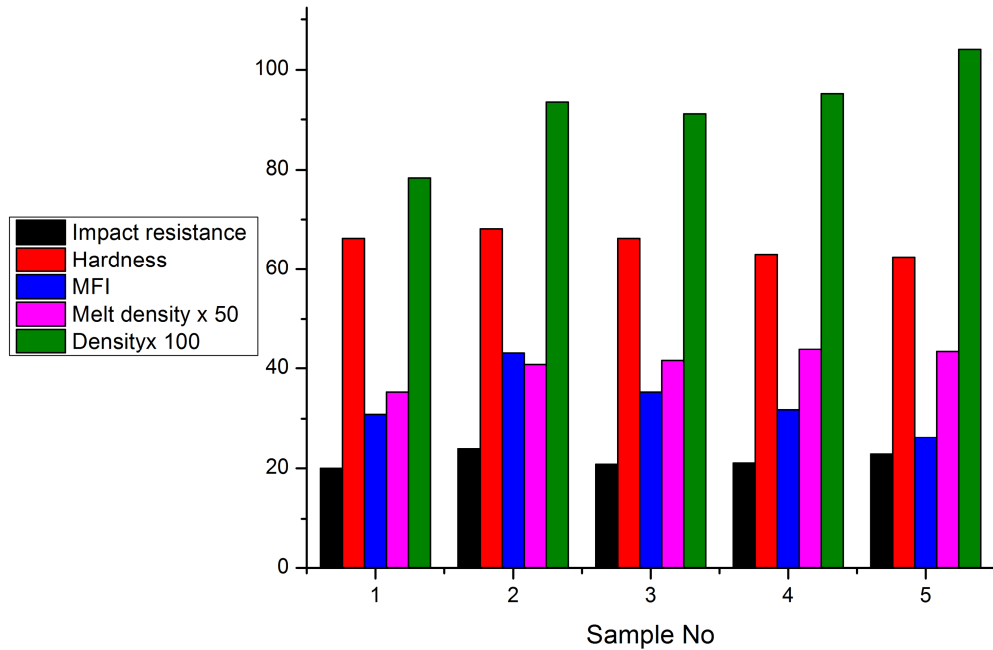


Figure (4.11) PP/LLDPE compounds tests

From the summary of the tests the optimum compounds provided the good balance of cost and performance (mechanical, rheological properties and density) of PP/LLDPE/Talc/CaCO<sub>3</sub> is (42/18/20/20) wt% respectively.

### 4.3 Economic assessment and performance

Cost estimation is the effective application of professional and technical expertise to plan and control resources, costs; it is a systematic approach to managing cost throughout the life cycle of any enterprise, program, facility, project, product, or service. Individual response map for each important property are useful for determining general trends as a function of compound. However, they may be used to determine operating windows for desired balance between mechanical properties and cost of the blended

resin (John K.Hollmann, 2006). In present work the following information's are used in the current materials cost for calculation in present work (Tariq Mahdi, 2014):

1. PP<sub>KPC</sub> cost is 2.6 \$/kg (Sudanese plastics market).
2. PP<sub>SABIC</sub> cost is 3.0 \$/kg (Used as reference).
3. LLDPE<sub>SABIC</sub> cost is 3.0 \$/kg.
4. Talc cost is 0.29 \$/kg.
5. Calcium carbonates cost is 1.6 \$/kg.
6. The cost of compounding (processing) is 0.17 \$/kg.

The cost of polypropylene and PP/LLDPE blend and polypropylene compounds (include processing cost) and the performance are shown in Table (4.13). In the economic impact column PP<sub>KPC-114</sub> cost value is considered as base value (Base material of this work). Then subtract cost value of the materials from PP<sub>KPC-114</sub> cost value if the result is less cost value than PP<sub>KPC-114</sub> it considered as negative percentage value (-) and high cost value is positive percentage value (+). The percentage of materials is calculated by dividing the cost value of each material per PP<sub>KPC-114</sub> cost value. The column of performance is classified base on summary of work tests (Mechanical, Thermal, Rheological and density) in compare to PP<sub>SABIC</sub> as in table (4.12).

Table (4.12) Specifications of SABIC Polypropylene (PP 575P)

<b>Trade name</b>	<b>Polypropylene (PP 575P)</b>
Density	0.905 g/cm <sup>3</sup>
Melting point	230 °C
Melt flow index (MFI)	11 g/10 min (230 °C, 2.16 kg)
Tensile stress at Yield	35 MPa
Flexural Modulus	1600 MPa
Izod impact resistance	22 J/m
Heat deflection temperature (HDT)	98 °C

Table (4.13) Economical and performance of PP/LLDPE & compounds

<b>Material/s</b>	<b>Cost(\$)/ kg</b>	<b>Economical assessment (%)</b>	<b>Performance</b>
PP <sub>KPC-114</sub>	2.6	0	Inferior
PP <sub>SABIC-575</sub>	3.0	-13	Excellent
PP <sub>KPC-114</sub> / LLDPE <sub>-218 N</sub> (70/30)	2.8	-7	Excellent
PP <sub>KPC-114</sub> / LLDPE <sub>-218 N</sub> /Talc (56/24/20)	2.3	+13	Good
PP <sub>KPC-114</sub> / LLDPE <sub>-218 N</sub> /CaCO <sub>3</sub> (56/24/20)	2.7	-4	Good
PP <sub>KPC-114</sub> / LLDPE <sub>-218 N</sub> /Talc/CaCO <sub>3</sub> (56/24/10/10)	2.6	0	V-good
PP <sub>KPC-114</sub> / LLDPE <sub>-218 N</sub> /Talc/CaCO <sub>3</sub> (42/18/20/20)	2.1	+23	V-good

## Chapter five

### Conclusion and Recommendations

#### **5.1 Conclusion**

The present work aimed to study the effect of linear low density polyethylene (LLDPE), talc and calcium carbonate on mechanical, thermal and rheological properties of local homopolymer polypropylene (PP<sub>KPC-114</sub>) for injection moulding application. In the experimental study, five formulations of PP and LLDPE viz. 90/10, 80/20, 70/30, 60/40 and 50/50 wt % were prepared for injection moulding machine.

Results showed improvement of the mechanical, thermal and rheological properties as addition of linear low density polyethylene (LLDPE) to polypropylene (PP) in most cases such as increase the flexural modulus to 5.8 to 39.8%, impact resistance to 23.5 to 50%, HDT to 11 to 68.2% and decrease the MFI to 4.3 to 46.3%. It is then concluded that the optimum formulation of PP/LLDPE blends provided the good mechanical, thermal properties and a moderate rheological property is (70/30).

Therefore PP/LLDPE (70/30) by weight was selected and investigated at different four fractions of talc and calcium carbonate. Incorporate talc and calcium carbonate as fillers on PP/LLDPE blend led to increase the hardness, MFI, melt density and density, while decreased the impact resistance of PP/LLDPE blend. The work determined the optimum compound provided the good balance of cost and performance is PP/LLDPE/Talc/Calcium carbonate (42/18/20/20) weight ratio % respectively.

## 5.2 Recommendations

- Development processing techniques (Extrusion and injection moulding processes) to improve the properties of polypropylene PP<sub>KPC-114</sub>.
- Investigation of blending of polypropylene PP<sub>KPC-114</sub> injection grade with PP<sub>KPC-113</sub> extrusion grade.
- Investigation of blending polypropylene PP<sub>KPC-113</sub> extrusion grade and linear low density polyethylene (LLDPE<sub>SABIC-218</sub>) and others LLDPE extrusion grades.
- Blending of polypropylene PP<sub>KPC-114</sub> with rubber and thermoplastic rubber such as polyethylene vinyl acetate (EVA).
- Investigation of blending polypropylene PP<sub>KPC-113</sub> extrusion grade and linear low density polyethylene (LLDPE<sub>SABIC-218</sub>) blend filled with fillers (such as talc and calcium carbonates).
- Investigation of effect of shelf life (storage) on properties of PP<sub>KPC-114</sub> injection grade and PP<sub>KPC-113</sub> extrusion grade.



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