

**PREPARATION AND CHARACTERIZATION OF
POLYPROPYLENE - WOOD POWDER COMPOSITES**

by

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DEDICATION

I dedicate this work to my family, Mokhele John Salemane (father), Nthabiseng Elizabeth Salemane (mother), my younger sisters and brother Puleng Joyce, Pulane Jeanette, Potsoko Aubrey, Dieketseng Constance and my uncle George Mei Salemane.

“But as for you, be strong and do not give up, for your work will be rewarded”

2 Chronicles 15 ÷ 7

ABSTRACT

The preparation and characterization of modified and unmodified polypropylene - wood powder composites were done under fixed processing conditions (mixing temperature, rate of rotation and mixing time). The mixing of samples was done using a Brabender plastograph mixer and sheets were formed by melt pressing the samples. Different techniques were used to study the effect of both wood powder size and content, as well as compatibilizer content on the properties of the composites. The results point to the fact that wood powder, WP, is settled in the amorphous part of the matrix and create new crystalline phases/zones. Scanning electron microscopy, SEM, micrographs and polarized optical microscopy, POM, photos show an even distribution of WP in the polypropylene, PP, matrix, which contributed to improvements observed in the properties of the material. Hg-porosimetry results indicate that the PP matrix, which has a low pore volume, was incorporated into the WP structure and filled the pores in the WP particles. This reduced the total volume of pores in the PP/WP composites. This observation was also supported by a general decrease in gas permeability of the material. Thermal analysis results indicate that the presence of both WP and maleic anhydride grafted polypropylene, MAPP, lead to an increase in enthalpy values of the composites, but also to a decrease in lamellar thickness in the composites containing MAPP. The thermal stability of the composite materials was also improved to a certain extent. There were distinctive differences between the results for composites containing different WP particle sizes, as well as for composites prepared in the presence and absence of MAPP. It is clear from the results that the presence of MAPP generally improves the tensile properties of the composites, probably because of an interaction between the reactive groups in MAPP and WP. Generally the larger WP particles gave rise to better tensile properties, in the presence and absence of MAPP, probably because of better stress transfer between the WP particles and the PP and PP/MAPP matrices.

INDEX

	Page
DECLARATION	ii
DEDICATION	iii
ABSTRACT	iv
CHAPTER ONE: INTRODUCTION	1
1.1. Natural fibers	1
1.1.1. The use of natural fibers	2
1.1.2. Limitations	3
1.1.3. Typical fibers	4
1.1.4. Reinforcement	6
1.1.4.1. Fiber-reinforced composites	6
1.1.4.2. Influence of fiber size/length	7
1.2. Polymer composites	7
1.2.1. Aspects of polymer composites	7
1.2.2. Composites modification	9
1.3. Previous studies on PP/WP composites	12
1.4. Composition analysis of polymer composites	13
1.5. Objectives of this study	14
CHAPTER TWO: MATERIALS AND METHODS	15
2.1. Materials	15
2.2. Structures of materials	15
2.3. Properties of the materials	16
2.4. Sample preparation	16
2.4.1. Wood powder	16
2.4.2. Mixing of sample components	16
2.4.3. Modification	17
2.5. Analysis	17
2.5.1. The DSC	17

2.5.2. The TGA	17
2.5.3. Tensile testing	17
2.5.4. Surface free energy evaluation	18
2.5.5. Permeability testing	18
2.5.6. Pore size determination	18
2.5.7. The SEM	19
2.5.8. Polarized Optical Microscopy	19
CHAPTER THREE: RESULTS AND DISCUSSION	20
3.1. SEM	20
3.2. Polarized Optical Microscopy	21
3.3. Porosity	22
3.4. Permeability testing	24
3.5. DSC	25
3.6. TGA	31
3.7. Tensile testing	39
3.8. Surface free energy system	45
CHAPTER FOUR: CONCLUSIONS	53
REFERENCES	55
ACKNOWLEDGEMENTS	58

Chapter One

Introduction

1.1 Natural fillers

Natural fillers can be harvested from renewable resources, possess long aspect ratio for efficient stress transfer, and certain aspects of their mechanical properties are comparable to existing inorganic glass fibres [1, 2]. Production of natural fillers results in less severe environmental impact compared to production of for example glass fibres. Cultivation of these particles depends on solar energy, and their production and extraction use small quantities of fossil fuel energy [1]. These fillers are advantageous in processing because of their low abrasivity and the physiological harmlessness. They also offer numerous advantages compared to “man-made” fillers, such as low cost, low density, good specific mechanical properties, physiological harmlessness during processing and use, recyclability, etc. [3]. Natural fillers may be used in the form of particles or bundles, and may act as reinforcement for plastics [4].

The various finely divided powders called fillers were discovered to dramatically increase the mechanical properties of synthetic polymers. Initially these particles were introduced merely to lower the cost of the final material but, after it was noticed that some of these greatly affected the physical properties, fillers became a standard additive in the field of chemistry e.g. rubber chemistry. Additive fillers can be grouped into two main groups: (1) reinforcing fillers (enhance physical properties e.g. carbon black and silica), and (2) non-reinforcing fillers (volume extenders which help to lower cost e.g. clays and inorganic oxides other than those of silicon) [5].

Cellulosic fillers/fibres can be classified under three categories depending on their performance when incorporated in a plastic matrix. Wood flour and other low cost agricultural based flour can be considered as particulate fillers that enhance the tensile and flexural moduli of the composite with little effect on the composite strength. Wood fibres and recycled newspaper fibers have higher aspect ratio and contribute to an increase in the moduli of the composites, and can also improve strength of the composite when suitable additives are used to improve stress transfer between the matrix and the fibres. However, the improvement in modulus is not significantly different from that of the cellulosic particulate fillers [1].

Unlike synthetic fibres, e.g. glass fibres, natural fillers can be incinerated after the composite component has served its useful life. The incineration of natural fillers theoretically results in no net addition to CO₂ emissions, because plants, from which these fibres are obtained, sequester

atmospheric CO₂ during their growth, which is released during the combustion of natural fillers. Hence incineration of natural filler reinforced composites leads to positive carbon credits and a lower global warming effect [6]. It was discovered that most of the natural fillers lose their strength at about 160 °C [7].

1.1.1 The use of natural fillers

Natural fillers have recently attracted the attention of scientists and technologists because of the advantages that these provide over conventional reinforcement materials such as glass fibres, talc, mica, etc. [8, 9, 10]. The use of fillers to reinforce or fill plastics leads to an increase in strength as well as stiffness [4]. Addition of fillers to polymers matrices (e.g. polypropylene) enhances many of its mechanical and thermal characteristics, including stiffness, creep resistance, heat deflection temperature and shrinkage. On the other hand, the presence of fillers usually deteriorates strength and toughness and counteracts the increasing mobility of the macromolecules, which leads to an increase of the modulus [2, 11]. Among factors that affect the properties of the final material, the most common are filler content and particle size. Filler particle size plays an important role in determining the mechanical properties like strength, modulus, and fracture toughness of filler reinforced thermoplastic composites. This influence on mechanical properties on introduction of filler is also observed for composites reinforced with short fibers. These reinforced polymeric composites have gained importance due to considerable processing advantages and improvements in certain mechanical properties. Short fibres such as short glass fibres or shop carbon filers added to thermoplastics result in composite materials having greatly improved mechanical properties [12, 13]. At low fiber loading the matrix is not restrained by enough fibres and highly localized strain occurs in the matrix at low stresses, causing the bond between the matrix and fibre to break leaving the matrix diluted by non-reinforcing de-bonded fibres [14].

Some of mechanical properties of composites material like yield stress deteriorates with increasing filler loading. This behaviour can be ascribed to poor adhesion between the polymer matrix and the filler, which allows de-bonding at the onset of plastic deformation. A decrease in strain at break caused by incorporation of the lowest amount of a filler (10 wt %) indicates debonding at the interface during the tensile deformation [15].

Aggregation of particles, especially finer particles, is another factor that can influence the final properties of the composite. In most instances aggregation occurs at higher filler contents (20 and 30 wt %) and it overshadows the differences between individual fillers. Very fine filler particles are difficult to disperse and the agglomerates then behave as large single particles. Low interfacial adhesion and particle agglomeration initiate crack formation. The corresponding

decrease in strain at break is more pronounced with uncoated filler and increases with increasing filler content [15].

Incorporation of fillers can also affect the phase separation due to the interaction of the individual components of the blend with the solid surface. This is the case in the binary polymer immiscible blend. Many researchers reported the use of fillers of inorganic nature for the purpose of compatibilization. Hofmann [4] found that the use of mineral filler like silica could serve as a compatibilizer for an immiscible mixture of polyolefin with polyacrylates and polymethacrylates. For a filler to act as a compatibilizer, it needs to exist on a nanometer scale. In amorphous polymers (for an example SBR), after loading with fillers, the T_g of the matrix shifted to higher temperatures which reflects new molecular interactions at the boundaries, resulting from the presence of the filler at the interface between two blends components. Filler incorporation into blends causes a decrease in the equilibrium swelling in a solvent. This proves that the filler increased the polarity of the overall system due to the presence of hydroxyl groups on its surface, and this lowers the interactions with that specific solvent [16].

For composites based on semicrystalline matrix polymers, the crystallinity is an important factor that determines the stiffness and fracture behaviour of the crystallized matrix polymer. The crystallinity depends upon processing parameters, e.g. T_c , cooling rate, nucleation, density, and annealing time. The morphological features such as degree of crystallinity, spherulite size, lamellar thickness and crystallite orientation have a profound effect on the ultimate properties of the polymer matrix, and thus the composite. In sisal fibre composites, thermal stability of materials was found to be higher than that of the fibre and matrix respectively. This increase in stability of composites is due to improved fibre-matrix interaction [17].

1.1.2 Limitations

The primary drawback of the use of natural fillers is the lower processing temperature permissible due to the possibility of lignocellulosic degradation and/or the possibility of volatile emissions that could affect composite properties. The processing temperatures are thus limited to about 200 °C, although it is possible to use higher temperatures for short periods. This limits the type of thermoplastics that can be used with natural fibres to commodity thermoplastics such as polyethylene, polypropylene, poly(vinyl chloride) and polystyrene. The second drawback is the high moisture absorption of the natural fillers. Moisture absorption can result in swelling of the fillers and concerns on the dimension stability of the natural filler composites cannot be ignored. The absorption of moisture by the fillers is minimized in the composite due to encapsulation by the polymer. But it is difficult to entirely eliminate the absorption of moisture without using expensive

surface barriers on the composites surface. Good fibre-matrix bonding can also decrease the rate and amount of water absorption by the composite [1].

1.1.3 Typical fibres

Apart from fillers there are fibres which are used to reinforce rather than fill the plastic composites.

1.1.3.1 Glass fibres

The glass fibres are divided into three classes; E-glass, S-glass and C-glass. The E-glass is designated for electrical use and the S-glass for high strength. The C-glass is for high corrosion resistance, and it is uncommon for civil engineering applications. The fibres are drawn into very fine filaments with diameters ranging from 2 to 13×10^{-6} m. The glass fibre strength and modulus can degrade with increasing temperature. They give rise in composites that are strong, corrosion resistant and light-weight, but not very stiff and cannot be used at high temperatures. Their applications include auto and boat bodies, and aircraft components [18].

1.1.3.2 Aramid fibres

These are synthetic organic fibres consisting of aromatic polyamides. Aramid has excellent fatigue and creep resistance. Although there are several commercial grades of aramid fibres available, the two commonly used in industrial applications are Kevlar 29 and Kevlar 49. They can be used as textile fibres and their applications include bullet-proof vests, tyres, and brakes and clutches [18].

1.1.3.3 Carbon fibres

The graphite or carbon fibre is made from three types of polymer precursors, polyacrylonitrile (PAN) fibre, rayon fibre, and pitch. The carbon fibre is an anisotropic material, and its transverse modulus is an order of magnitude less than its longitudinal modulus (highest specific modulus). They give rise to composites that are strong, inert, and allow high temperature use. Their applications include fishing rods and aircraft components. The material has a very high fatigue and creep resistance [18].

1.1.3.4 Sisal fibres

The fibre obtained from the leaves of the sisal plant (*Agave sisalana*) is used for hard fibre cordage. Native to Central America, it is grown extensively in the West Indies and Africa. It is used in various papers requiring high strength characteristics. The fibre has also been called Sisal Hemp. Sisal fibre is manufactured from the vascular tissue from the sisal plant. It consists of tough, tan-colored fibres that are available in several grades, with average fibre lengths from 1/16 inch to 1/2 inch. It is used in automotive friction parts (brakes, clutches), where it imports green strength to preforms, and in enhancing texture in coatings applications. Sisal is a strong, stable and versatile material that can be woven into boucles and rib weaves, flat weaves, and jacquard patterns and many dyed colors. It can be a little rough underfoot, but less so when combined with other fibers such as wool. Sisal carpets are naturally sound-absorbing, anti-static, and extremely durable because of the inherent qualities of this tough, hard-wearing fiber. It is also naturally insulating and difficult to ignite. Like most plant fibers, however, sisal absorbs moisture readily, therefore it is recommended that its materials be used only indoors [19].

1.1.3.5 Wood filler

Wood is one of the oldest and most widely used structural materials. Its composites are of strong and flexible cellulose fibers (linear polymer) surrounded and held together by a matrix of lignin and other polymers [20]. Wood fillers are biodegradable and non-abrasive during processing, unlike other reinforcing fillers/fibres. Wood flour is one of the most common natural fillers used in the thermoplastics industry. It is produced commercially from post-industrial sources such as plane shavings and sawdust. One variable used to characterize wood flour is particle size. This can be obtained by the use of an analytical sieve or a screen used to differentiate between particle sizes. However, extra screening of wood flour, for example screening out fines to narrow the particle size distribution, raises the cost of the flour. For this reason typical commercial grades include a mixture of particle sizes. It was found somewhat difficult to characterize the properties of commercial wood flour/plastic composites on the basis of specific particle sizes [20].

In general, wood flour is used as filler for plastics, which tends to increase the stiffness of the composite, but does not improve its strength. Wood and other natural fillers typically have higher aspect ratios than that of wood flour [4].

1.1.4 Reinforcement

Reinforcement of an elastomer may be defined as an increase in physical properties that results from the inclusion of suitable filler into the polymer matrix during the mixing process [23]. The filler is an important constituent in composites [18]. This reinforcement is thought to be the result of a reduction in the mobility of the polymer chains brought about by physical and chemical interactions between the filler and the polymer. For a filler to be used as reinforcement, there are certain properties that it requires to display. The individual filler particle must exhibit a strong interaction with the polymer and a weak interaction with other filler particles. These properties are affected by three major parameters, i.e. particle size, filler structure and surface activity [24, 25]. Particle size determines the interfacial area between the matrix and filler particle. The larger the interfacial area per unit mass of filler, the greater the possibility of interaction between filler and matrix. The second parameter influencing the reinforcing character of the filler is the structure of the filler particles, that is, the surface morphology (the physical shape of a single particle of filler). The third parameter is the surface activity of the filler. This is considered the most important parameter as it dominates the polymer-filler, filler-filler and filler-additive interactions. These interactions in turn dominate the reinforcing character and behaviour of a specific filler. The surface activity of the filler is a result of its chemistry (functional groups) and surface energy [24-30].

1.1.4.1 Filler-reinforced composites

The primary advantages of using lignocellulosic fillers and fibres as fillers/reinforcements in plastics are low density, non-abrasive, high filling levels possible resulting in high stiffness properties, high specific properties, easily recyclable, wide variety of fillers and fibres available throughout the world, low energy consumption and most importantly low cost [1]. In many applications, like in aircrafts parts, there is a need for high strength per unit weight (specific strength). This can be achieved by composites consisting of a low-density (and soft) matrix reinforced with stiff fillers. The strength depends on the filler size or length and its orientation with respect to the stress applied. The efficiency of load transfer between matrix and filler depends on the interfacial bond [20].

1.1.4.2 Influence of filler size / fibre length

Fine/small filler particles, as compared to large ones, are found to improve the mechanical properties of the composites to a high extent. The only drawback to the use of finer particles is their tendency to agglomerate and as a result behave as larger particles [15, 30, 31].

Normally the matrix has a much lower modulus than the filler so it strains more. This occurs at a distance from the filler. Right next to the filler, the strain is limited by the filler. Thus, for a composite under tension, specifically composites reinforced with fibres, a shear stress appears in the matrix that pulls it from the fibre. The pull is uniform over the area of the fibre. This makes the force on the fibre to be a minimum at the ends and a maximum in the middle, like in a tug-of-war game [31].

The major factors that govern the properties of small/short fibre composites are fibre dispersion, fibre length distribution, fibre orientation and fibre-matrix adhesion. Mixing the polar and hydrophilic fibres with non-polar and hydrophobic matrix can result in difficulties in dispersing the fibres in the matrix. Using long filaments during the compounding stage can result in higher distribution. However, long fibres sometimes increase the amount of clumping resulting in areas concentrated with fibres and areas with excessive matrix. This ultimately reduces the composite efficiency [1].

Chen *et al.* [32] found that a composite filled with 25 μm SiO_2 at 60 wt % filler had the highest modulus, lowest coefficient of thermal expansion (CTE_z) and acceptable dielectric properties. Composites with different sizes of filler showed a similar trend of decreasing tensile strength and CTE_z , and increasing tensile modulus, water absorption and dielectric properties as the filler content increased. Furthermore, the composites filled with small-size filler showed higher water absorption and dielectric loss properties due to the presence of higher SiO_2 surface area. Poor adhesion between filler and matrix is a primary cause of low tensile properties and lack of increase in thermal stability.

1.2 Polymer composites

1.2.1 Aspects of polymer composites

A composite is any material made of more than one component, e.g. concrete and balloon. Usual composites have just two phases:

- Matrix (continuous)
- Dispersed phase (particulates, fillers/fibres)

The properties of the composites depend on the properties of the phases, the geometry of the dispersed phase (particle size, distribution, orientation) and amount of phase. There are three main categories of composites classification, that is particle-reinforced (large-particle and dispersion-strengthened), fibre-reinforced (continuous (aligned) and short fibers (aligned or random)) and structural (laminates and sandwich panels). The filler is embedded in the matrix in order to make the matrix stronger, and the matrix adds toughness to the composite. Filler reinforced composites are strong and light [31].

To achieve effective strengthening and stiffening, the fillers must be larger than a critical length, l_c , defined as the minimum length at which the center of the filler reaches the ultimate (tensile) strength σ_f , when the matrix achieves the maximum shear strength τ_m :

$$l_c = \sigma_f d / 2 \tau_m, \quad [1.1]$$

where d is the diameter [31].

Composites are anisotropic materials with their strength being different in different directions. Their stress-strain curves are linearly elastic to the point of failure by rupture. They have many excellent structural qualities and some examples are high strength, material toughness, fatigue endurance, and light weight. Other highly desirable qualities are high resistance to elevated temperature, abrasion, corrosion, and chemical attack. Some advantages in the use of composite materials include ease of manufacturing, fabrication, and handling. Composites can be formulated and designed for high performance, durability and extended service life. They have excellent strength-to-weight ratios. If durability can be proven to last 75 years, composites can be economically justified using the life-cycle cost method [18].

The development of a hard interlayer is assumed in particulate filled polymers and filler or fibre reinforced composites. The interphase forms as a result of the adsorption of polymer chains onto the filler or fiber surface. These chains have limited mobility and therefore the deformability of the composite decreases as well [29]. The interaction energy determines the interface thickness which controls the extent of the reactions possible in the interfacial zone. The interface exists within an area around the filler surface. At the interface the local properties, including the morphological features, chemical composition and thermo-mechanical properties, begin to change from the bulk matrix properties. The formation of such an interface around the filler results from local chemical or physical changes imposed by the filler surface, namely cross-linking, immobilization, interdiffusion, crystallization and others [30, 31].

Polarity also affects the properties of the composites to some extent. In a wood/Nylon composite, due to the polar nature of both, it is expected that nylon and wood may combine with

strong adhesion, resulting in a composite material with higher stiffness and strength. There were, however, voids present which were created by the non-adhering fibres, leading to stress concentrations and therefore decreasing strength with increasing fibre content [31]. A high level of moisture absorption, poor wettability by non-polar plastics, and insufficient adhesion between untreated fillers/fibres and the polymer matrix, can lead to debonding with age. When the interface bonding is relatively weak, debonding and frictional sliding occur readily upon crack extension, allowing fillers to remain intact and bridge the crack. A strong interface would inhibit interface sliding and lead to filler fracture instead of crack bridging by intact fillers [14, 33, 34, 35].

High temperatures were also found to play a role in the reduction in modulus by softening the matrix. On increasing the temperature, the drop of matrix modulus is compensated for by the filler stiffness. The decrease in stiffness in the filler-filled system at temperatures much above ambient is associated with filler de-bonding due to the increased viscoelastic deformation of the matrix at higher temperatures. As the temperature is increased, some kind of molecular matrix is unfrozen, and a relaxation process is initiated. Thermal expansion also occurs resulting in reduced intermolecular forces [36]. Continuous fibre-reinforced thermoset plastic materials are widely used in high volume industrial applications such as pipes, tanks, boats, etc. The higher performance categories of these materials have been accepted for use in critical applications in aircraft, spacecraft and sports equipment with very high demand on performance. Two major drawbacks connected with these materials are the common extensive use of solvents, and the lack of methods for recycling the materials after use [34].

As organic materials, the polymer and the wood fillers are very sensitive to flame. Flame retardancy can be achieved by the disruption of the burning process at any of the stages that can lead to the termination of the process before actual ignition occurs. The most widely used additive type flame-retardants are inorganic compounds, halogenated compounds and phosphorous compounds [37, 38].

1.2.2 Composites modification

The nature of the interface determines the ultimate mechanical properties of the composite. Bonding the hydrophobic plastic material to wood to create new wood-plastic materials with improved mechanical and physical properties that incorporate the desirable features of each constituent, is difficult to achieve. Therefore, due to the difference in polarity of both components, their interface needs to be modified to induce interfacial adhesion [38, 39].

Compatibilization is a method that is very often used to control the phase morphology, phase stabilization and interfacial adhesion in polymer composites and immiscible polymer blends

[38]. Most of wood powder/plastic composites result in materials with a weak interfacial region, which is found to reduce the efficiency of stress transfer from the matrix to the reinforcement component and low strength. In some instances the addition of wood filler to a polymer exhibits a concentration of holes left after the fillers were de-bonded from the matrix. The hole proximity indicates that the sawdust fillers exist in the form of bubbles that could not provide an efficient stress transfer from the matrix [2, 39, 40]. In natural filler composites, weak adhesion may result from poor dispersion and incompatibility between the hydrophilic natural fillers and the hydrophobic polymer [40].

The use a compatibilizer (possessing both polar and non-polar moieties) can improve adhesion and thus enhance the tensile properties of the composite. Polypropylene/sawdust composites show a change in the properties as the maleated polypropylene (MAPP) concentration is increased. These changes are observed at high MAPP dosage. The composites with MAPP content lower than 20 wt % have lower tensile properties. The improved filler matrix adhesion observed on addition of MAPP can be attributed to the esterification reaction between the hydroxyl groups of the cellulose filler and the anhydride functionalities of MAPP [7, 11, 39]. Interactions between the anhydride groups of the maleated coupling agents and the hydroxyl groups of the natural fillers can overcome the incompatibility problem to increase tensile and flexural strengths of natural filler-thermoplastic composites [4]. Only a maleated coupling agent with the correct balance of maleic anhydride and molecular weight can achieve peak performance in natural filler composites [40].

From previous research [41], it was noted that the effect of a compatibilizer is not only to increase Young's modulus but also the tensile strength. This is due to interaction causing lesser slippage at the interface at low elongation.

Maleated polyolefins (MaPO) is one of the coupling agents that is used to strengthen composites containing filler and fibre reinforcements. The success of MaPO couplers pertains to their excellent balance of properties to bridge the interface between polar and non-polar species. This coupler holds dissimilar materials together. The coupler may co-crystallize with the continuous polyolefin while the maleic anhydride portion of the molecule can interact with the more polar wood surface. It was suggested from earlier work that the interaction between the coupler and wood may be of a covalent nature. Mechanical interlocking may occur between the wood and coupler and the polymer and coupler. All these bonding forms may concurrently exist across the interface at varying degrees. There are other factors influencing the performance of the compatibilizer, i.e. molecular weight and acid number. Low molecular weight will not allow the coupler to interact and entangle sufficiently with the polyolefin phase. Too high molecular weight may not allow the coupler to reside at the interface. A low acid number may not give the coupler enough sites for attachment to the polar filler. Too high an acid number may hold the coupler close

to the polar surface and not allow sufficient interaction with the continuous non-polar phase. Maleated couplers need enough acid functionality to attract the filler and enough molecular weight to entangle or crystallize into the base polymer [41].

Narayan *et al.* [42] discovered that to create new materials with improved properties, it is imperative to employ an interfacial agent like well-defined cellulose-polystyrene graft polymers. In this investigation, the cellulose backbone of the graft polymer is available for bonding the wood with existing commercial resins, while the heat employed to cure the resin causes the polystyrene side chains to melt and flow into the polystyrene component of the mixture. But there are problems encountered in this work. Most of the work done in preparation of cellulosic graft polymers involved free-radical polymerization methods. With these procedures, very few high molecular weight molecules were actually grafted.

The other method of improving adhesion in wood powder/plastic composites is by using treated fillers. Different surface treatments have been applied for cellulose fillers to alter their nucleating ability [43, 44]. An example is the use of chromated copper arsenate (CCA)-treated wood. Though the incineration of CCA-treated wood has the advantages of allowing the recovery of copper, chromium, and arsenic from the ash, and the energy during burning, there are problems associated with the recycling of these materials. These are the toxic fumes and air borne particles produced during the cutting and machining of wood containing heavy metals and the air quality during the hot pressing of the composites. Occupational exposure to copper, chromium and arsenic from wood sawdust may constitute a health hazard. Apart from disadvantages, the chromium in CCA-treated wood contributes to the stabilization of the wood surface against UV light degradation. Other researchers found that CCA-treatment retarded the progressive photo-oxidation of lignin compared to photo-oxidation in untreated samples [6].

Surface treatment can lead to the development of a weak interface between the components of the composite material. There are two possible reasons for this behaviour. Firstly, the prolonged treatment time can be found to cause a significant decrease in the fibre strength and this certainly affects the cumulative distribution of fragment lengths. Secondly, it is possible that the larger amount of stearic acid (produced by the surface modifier), deposited on the fibre surface, may act more as a lubricant than as a compatibilizer and hence it severely weakens the interface. Not only are the mechanical properties of the composites improved by modification of interface, but wettability as well [33].

1.3 Previous studies on PP/WP composites

In general, the results from previous research indicated that the presence of filler in the polymer matrix increases the stiffness of the material and lowers the elongation. Furthermore, the addition of MAPP as a compatibilizer improved adhesion between the wood filler and polypropylene matrix.

Very good adhesion between the filler and matrix makes it difficult to de-bond the filler from the matrix and the fracture path passes from the matrix through the interface and wood fillers. Fillers with higher stiffness than the matrix can increase the modulus of the composites, but generally fillers cause a dramatic decrease in the elongation at break. Almost all the elongation occurs in the matrix if the filler is rigid. Apart from the structure and properties of wood powder, temperature and moisture were found to be other factors influencing the properties of the PP/WP composites. These parameters affect, among others, creep and impact properties. It was also reported that the filler size and geometry plays a role in the improvement of properties. Large wood filler - PP composites showed better creep modulus than hard wood - PP composites. Wood filler size probably affected the adhesion between wood filler and polypropylene. Large wood filler reinforced composites were found to be much more hygroscopic than the hard wood filler. It was also found likely that wood fillers can be completely isolated and covered by PP owing to their high wettability to the wood cell wall and high permeability into narrow macro-cavities. However, high wettability does not directly result in chemical bonding. In the case of polymer blends, the presence of wood in PP blends has a definitive effect on the crystallization and morphology of the resulting material. From these types of composites, crystal growth kinetics revealed that neither the wood nor the additive had an influence on the growth rate of the PP crystals [33, 34].

From earlier work it was found that the cellulose fillers tend to form aggregates during the mixing due to the high degree of intermolecular hydrogen bonding [36].

Different types of compatibilizers and filler/fiber surface treatments, for example CCA, MaPO, MAPP, silane based components (fluorocarbon silane, CF-silane), and EMAA copolymer were applied to modify the composites. With CCA, the quality of the adhesion of CCA-treated wood surfaces depends on the surface properties of treated wood and the type of adhesives used. In cases where MaPO and MAPP are used (individually), the compatibilizer bonds with the filler on the one end and with the matrix on the other. Silane based components at high amounts were discovered to lower the work of adhesion between treated glass and polypropylene, while the EMAA was found to increase the mobility of the chain segments in low density polyethylene (LDPE)/wood flour composites. MAPP is the most common compatibilizer used in the studies of PP/WP composites. This compound was found to noticeably improve the adhesion between the

matrix and the filler. MAPP compatibilizer has a positive effect on the tensile strength in all the composites. An increase in tensile strength means that the stress has been transferred from the PP matrix to the WP particles. The tensile strength of many filled polymers can be improved using adhesion promoters (compatibilizers), which will also improve the nature of the fibre [34, 36, 37].

In blends of acrylonitrile-butadiene rubber (NBR) and styrene-butadiene rubber (SBR) it is known that the physico-mechanical properties of the pure components are very weak in the absence of a reinforcing filler, and consequently the physico-mechanical properties of the blends are also inferior. This originates principally from the incompatibility of both components with each other in view of the fact the NBR has more polarity than SBR. After loading with filler, montmorillonite clay in this case, the T_g of the blend shifted to higher temperatures, which reflected new molecular interactions at the boundaries resulting from the presence of the filler at the interface between the NBR and SBR [31].

1.4 Composition analysis of polymer composites

The analysis of polymer composites often includes the measurements of mechanical and thermal properties. Among these methods of measurement, there are methods available that allow not only the property to be measured, but with suitable calibration of the equipment and technique, the individual contributions of each component of the composite or blend are determined. Some of the methods [31] available that allow determination of composite composition are:

- ❖ Thermal methods of analysis, e.g. differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), which require sufficient thermal separation of events.
- ❖ Surface energy evaluation (SEE), which analyses the influence of different degrees of polarity of the components on that of the composite.
- ❖ Fourier transform infrared (FTIR), which gives information on the interaction between different components of the composites (functional groups and their positions).

1.5 Objectives of this study

For thermoplastic wood composites, the selection of processing aids and parameters influences the morphology of the material, which impacts on mechanical properties. The goal of this study is to investigate the influence of wood powder as well as compatibilizer on the thermal and mechanical properties of PP/WP composites.

Specific objectives of this research are to investigate the influence of:

1. Wood powder particle size
2. Wood powder content
3. Compatibilizer (MAPP) on the properties of PP/WP composites.

Chapter Two

Materials and Methods

2.1 Materials

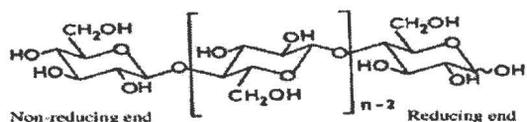
Materials in this work were used as received from the suppliers.

Material	Supplier
Pine wood powder (WP)	FBW Taurus, Phuthaditjhaba, South Africa
Polypropylene (PP)	Sasol Polymers, Johannesburg, South Africa
Maleic anhydride grafted polypropylene (MAPP)	Pluss Polymers Pvt. Ltd., India

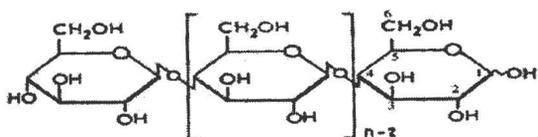
2.2 Structure of materials

2.2.1 Wood powder

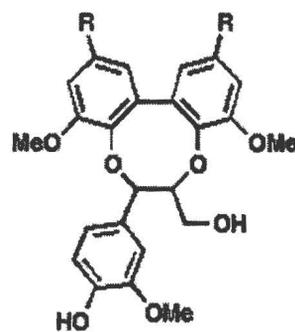
Wood powder consists mainly of cellulose and lignin, the structures of which are shown below.



Sometimes shown as



Cellulose

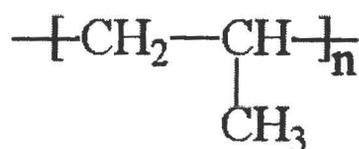


1

Lignin

2.2.2 Polypropylene

Polypropylene has the following general structure:



2.2.3 Maleic anhydride grafted polypropylene (MAPP)

This material is produced from the reaction between polypropylene, maleic anhydride (MAH) and a crosslinking agent (in most cases dicumyl peroxide (DCP) is used).

2.3 Properties of the materials

Properties	WP	PP	MAPP
Density / g.cm ⁻³	1.5	0.9	0.91
Melt flow index (MFI) at 230 °C and 2.16 kg [g/10 min]	-	12	55
Melting temperature (T _m) / °C	-	160	163
Tensile strength at yield / MPa	-	30	-
Elongation at yield / %	-	7.5	-
Flexural modulus / MPa	-	1360	-
Minimum maleic anhydride (MAH) content / %	-	-	1.0

2.4 Sample preparation

2.4.1 Wood powder

The wood powder was separated into different particle sizes using laboratory test sieves with pore sizes 600, 300, 150 and 38 µm. PP and PP/MAPP composites, containing respectively 10, 20 and 30 wt.% wood powder, were prepared with each of these separated wood samples, as well as with the wood powder as received.

2.4.2 Mixing of sample components

Samples were weighed according to the desired ratios to make up a total mass of 40 g (which is the mass that is required to thoroughly mix the different components), and mixed in a Brabender Plastograph at 180 °C at a speed of 60 rpm for 10 minutes. Before the mixing, wood powder and MAPP were dried in an oven at 100 °C for 24 hrs and 1 hr respectively. Composites with and without MAPP were prepared for further analysis. After preparation, the samples were melt pressed at 190 °C for 3 minutes at a pressure of 50 bar, and were allowed to cool for 5 minutes at room temperature.

2.4.3 Modification

Maleated polypropylene, MAPP, was used as a compatibilizer for PP/WP composites. The samples were prepared with different MAPP contents to investigate the effect of MAPP content on the composites. The compatibilizer was fed into the Brabender mixer at the same time as PP and WP.

2.5 Analyses

2.5.1 Differential scanning calorimetry (DSC)

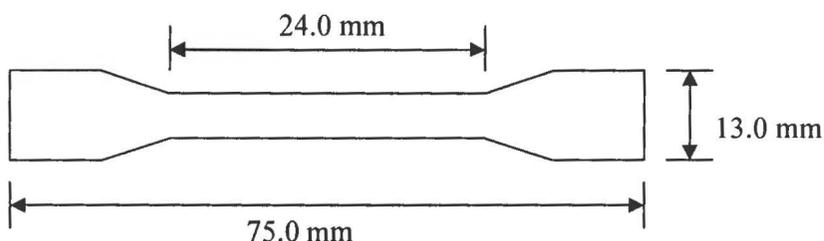
DSC analyses were carried out on a Perkin-Elmer DSC7 thermal analyser under flowing nitrogen atmosphere. The calibration of the instrument was done using the onset temperatures of melting of indium and zinc standards, as well as the melting enthalpy of indium. The samples were cut using a standard hollow steel punch to produce uniform samples. 5-10 mg samples were heated from 50 to 250 °C at a rate of 10 °C min⁻¹, held at 50 °C for one minute to eliminate any thermal history effects, cooled to 50 °C at the same rate, and reheated. The enthalpies, $\Delta H / \text{J.g}^{-1}$, and melting temperatures, $T_m / ^\circ\text{C}$, were determined from the second scan.

2.5.2 Thermogravimetric analysis (TGA)

TGA analysis was carried out on a Perkin-Elmer TGA7 thermogravimetric analyser. Samples ranging between 10 and 15 mg were heated from 50 to 600 °C at a heating rate of 20 °C min⁻¹ under flowing nitrogen.

2.5.3 Tensile testing

Tensile properties were determined using a Hounsfield H5KS tensile tester. At least seven test pieces were cut using a dumbbell cutter. The dimensions of the dumbbell shaped sample were as follows:

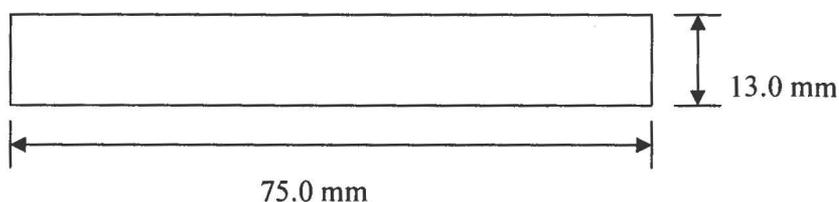


The instrument settings for the analyses were as follows:

Load range: 200.0 N
Extension range: 300.0 mm
Gauge length: 24 mm
Speed: 10 mm.min⁻¹
Approach speed: 0.02 mm.min⁻¹

2.5.4 Surface free energy evaluation

A surface energy evaluation system (SEES) from the Czech Republic was used and the contact angles were measured. For surface energy measurements, samples were cut to a rectangular shape with the following dimensions:



Five different solvents (water, ethylene glycol, benzene alcohol, aniline and formamide) were used, and the tip of the micro-pipette was replaced after the use of each solvent. At least 15 drops from each solvent were placed on the sample for the measurements.

2.5.5 Permeability testing

Permeability measurements were done using a Sierra Smart-Trak mass flow meter connected to a setup illustrated in Figure 2.1. To determine the gas permeability of the composites, oxygen was used. Different oxygen flow rates were used to construct the permeability graphs.

2.5.6 Pore size determination

A mercury porosimetry method was used for the determination of the total volume between the PP monofilaments and the pore volumes in the PP composites with WP in the presence and absence of MAPP compatibiliser, the evaluation of pore size distributions, as well as the determination of the specific surface. The measurements were carried out in a Porozimetro 1500

Carlo Erba instrument connected to a calculation unit CVT 960. The maximum used pressure of mercury was 150 MPa, which allowed determination of pore sizes down to 5 nm.

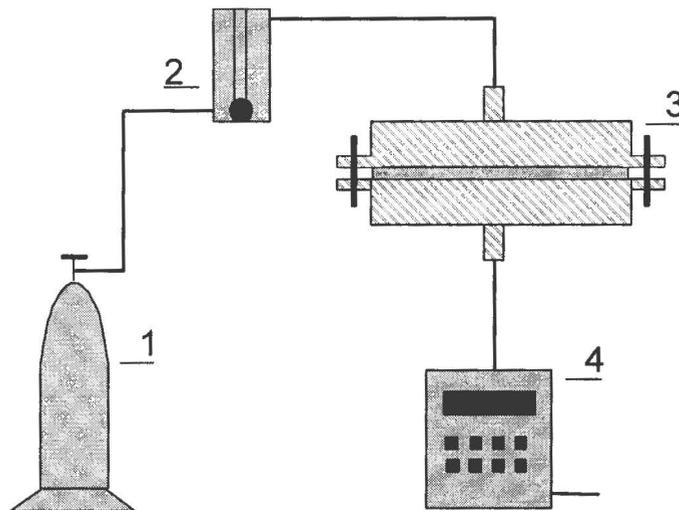


Figure 2.1 The setup for permeability measurements (1 - gas bottle, 2 - rotameter, 3 - chamber, 4 - digital mass flow meter)

2.5.7 Scanning electron microscopy (SEM)

The morphological aspects of the PP/WP interfaces at fracture surfaces were observed by using a Jeol 6400 WINSEM scanning electron microscopy model at 5 keV.

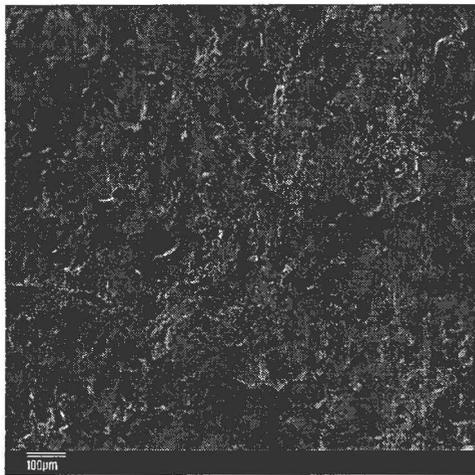
2.5.8 Polarized Optical Microscopy (POM)

Polarized optical micrograms were taken at 100 x and 400 x magnifications, using a CETI polarized optical microscope made in Belgium. The photographs were taken with a Ceist DCM digital camera. The samples were placed on the glass plate for analysis.

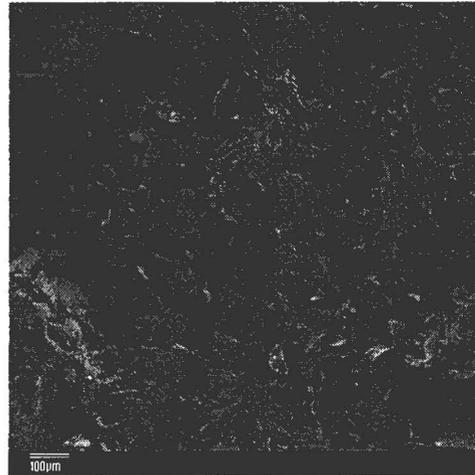
Chapter Three

Results and Discussion

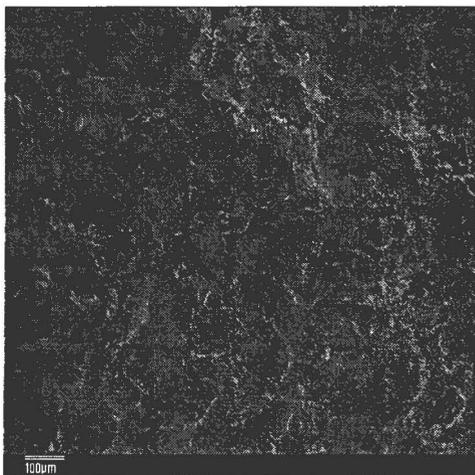
3.1 Scanning electron (SEM) and polarised optical microscopy



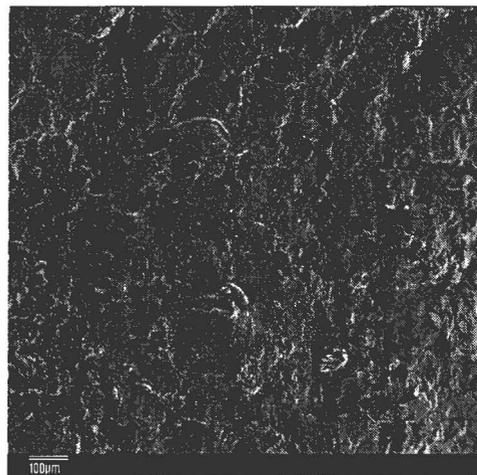
A 60/40 w/w PP/WP ($< 38 \mu\text{m}$)



B 60/40 w/w PP/WP (300 – 600 μm)



C 60/10/30 w/w PP/MAPP/
WP ($< 38 \mu\text{m}$)



D 60/10/30 w/w PP/MAPP/WP
(300-600 μm)

Figure 3.1 SEM micrographs for modified and unmodified PP/WP composites at 100x magnification

3.2 Polarized Optical Microscopy (POM)

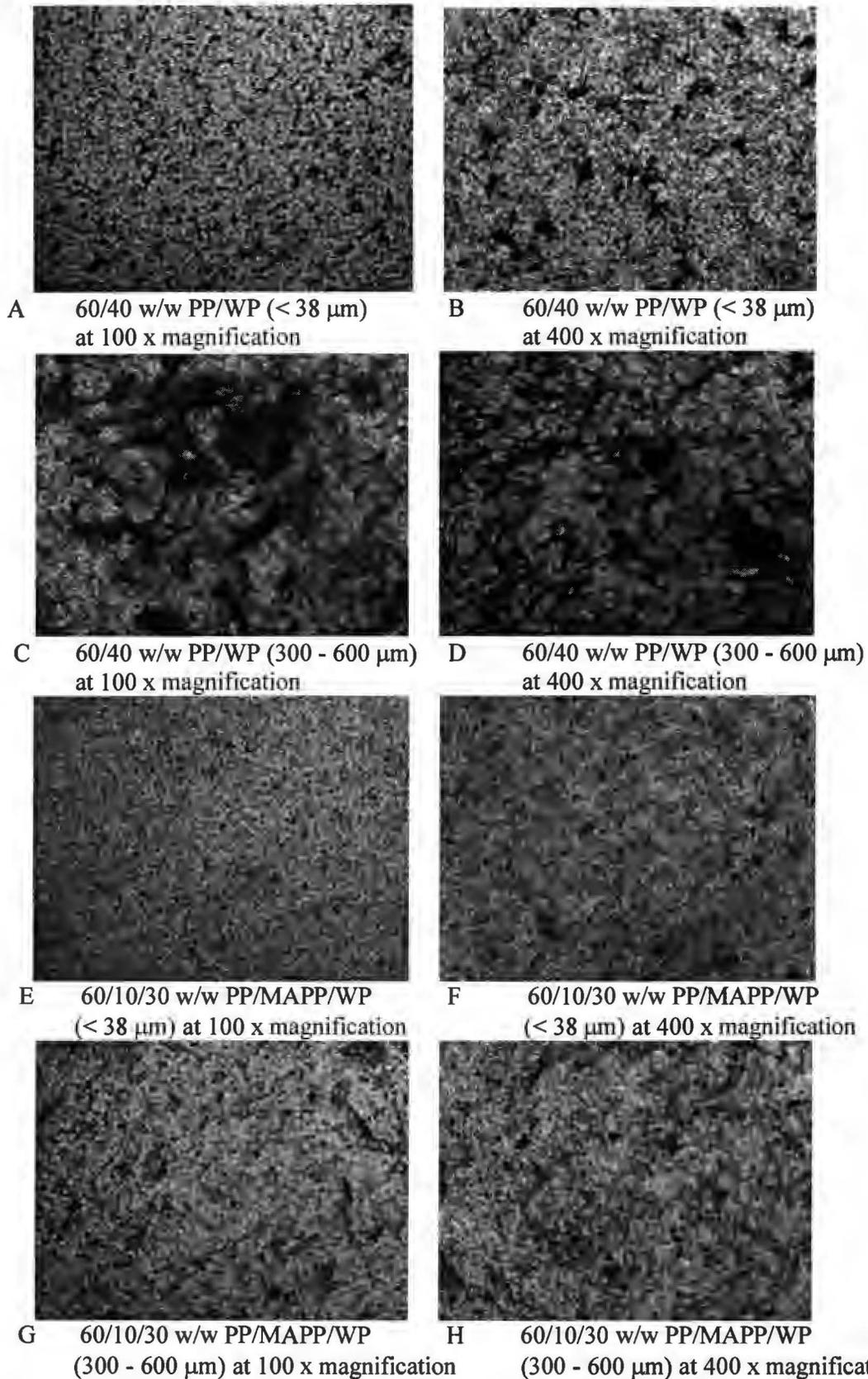


Figure 3.2 Polarised optical microscope photos of modified and unmodified PP/WP composites

Figures 3.1 and 3.2 respectively show the SEM micrographs and polarised optical microscope (POM) photos of PP/WP composites. The difference in wood powder particle size is clear from Figure 3.1. For composites with small WP particles ($< 38 \mu\text{m}$), the surface is smoother than for the samples containing larger particles ($300 - 600 \mu\text{m}$). When MAPP is introduced into the composite material (samples **C** and **D**), the surfaces are even smoother than in the cases where there is no MAPP. In this case the smaller WP particles also give rise to a smoother surface. These observations are supported by the polarized optical microscope photos (Figure 3.2). In both sets of photos there is no clear distinction between WP filler and PP matrix. It therefore seems as if the composite mixtures are homogeneous and that the WP particles are evenly distributed in the polymer matrix.

3.2 Porosity

The Hg-porosimetry results for pure WP and PP/WP composites are shown in Figures 3.3 and 3.4. WP appears to have a large pores volume. Pores with radii from 10 to 2511 nm take up a relatively large volume, confirming that WP is a very porous material (Figure 3.3). PP has a relatively large volume of small pores (Figure 3.4), but the volume decreases rapidly with increasing pore size, which is the result of its crystallinity. When WP is added into the polymer matrix, the pore size distribution does not change much from that of pure PP. This behaviour is in line with the SEM and POM results that indicated that WP is well dispersed into the polymer matrix. A possible explanation is that PP completely fills the pores in WP during mixing. The same is observed for composites with 10 % MAPP. The smooth surfaces, observed on the SEM micrographs for composites with 10 % MAPP, may indicate better adhesion. This is confirmed by surface free energy results, where the polar component shows an increase. These results point to good interfacial adhesion as a result of mechanical interlocking. This is further emphasised by looking at the mean pore radius at $V_p = 50 \% / \text{nm}$. For pure WP the value is 3041.5 nm and for pure PP it is 48.9 nm (obtained from computer printout of porosity results). These values further decrease to 15.0 nm with the introduction of WP into the matrix, and to 13.6 nm with the addition of MAPP into the composite material.

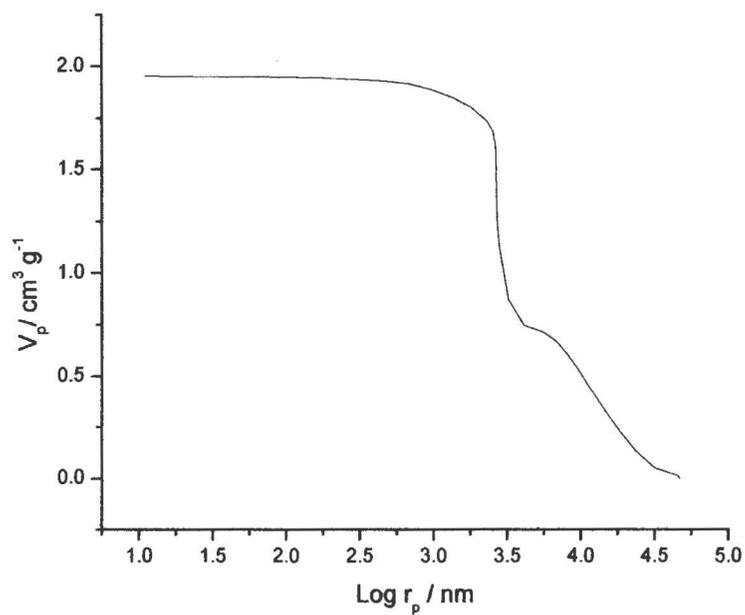


Figure 3.3 Pore volume as function of pore size for pure WP

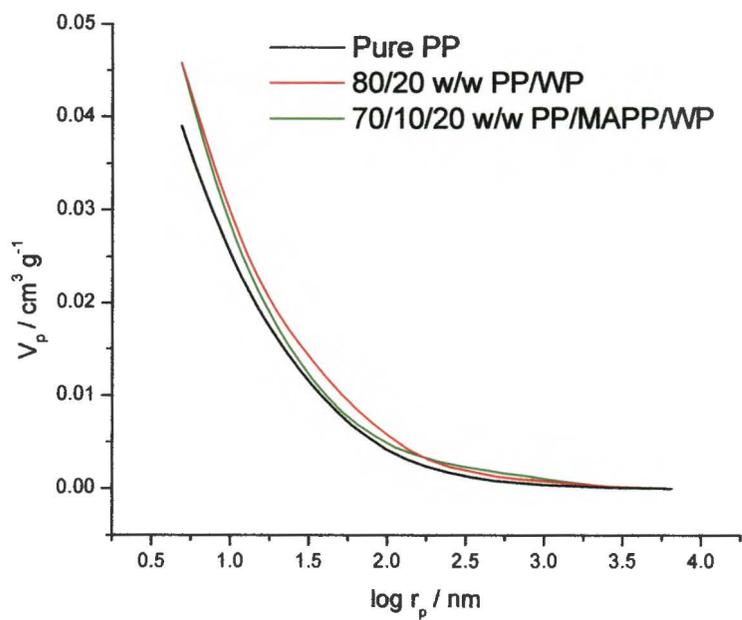


Figure 3.4 Pore volume as function of pore size for PP and composites containing $< 38 \mu\text{m}$ WP

3.3 Permeability

It is commonly known that PP has a high oxygen permeability [49, 50]. Composites containing WP with particle size $< 38 \mu\text{m}$ have a lower gas permeability than pure PP (Figure 3.5). Addition of MAPP somewhat increases the permeability, although the effect is very small. This is not only the result of PP and/or MAPP filling the pores in WP, but also of increased crystallinity of the matrix in the presence of WP (see discussion below). It is well known that higher crystallinity gives rise to lower permeability. For composites with large WP particles ($300 - 600 \mu\text{m}$), the permeability of oxygen gas is much higher than in the case of composites containing small WP particles, and even higher than that of the pure polymer. Also in this case the addition of MAPP led to a slight decrease in the permeability. This is probably due to the size of the WP particles. The increase in crystallinity is similar to that for composites containing the small WP particles, and therefore the higher permeability is probably the result of polymer molecules not completely filling the pores in the WP particles. There may also be some cracks at the interface between WP and the matrix, allowing gas molecules to pass through. Another explanation may be that surface failure occurred in the matrix, and not at the interface between WP and PP [51].

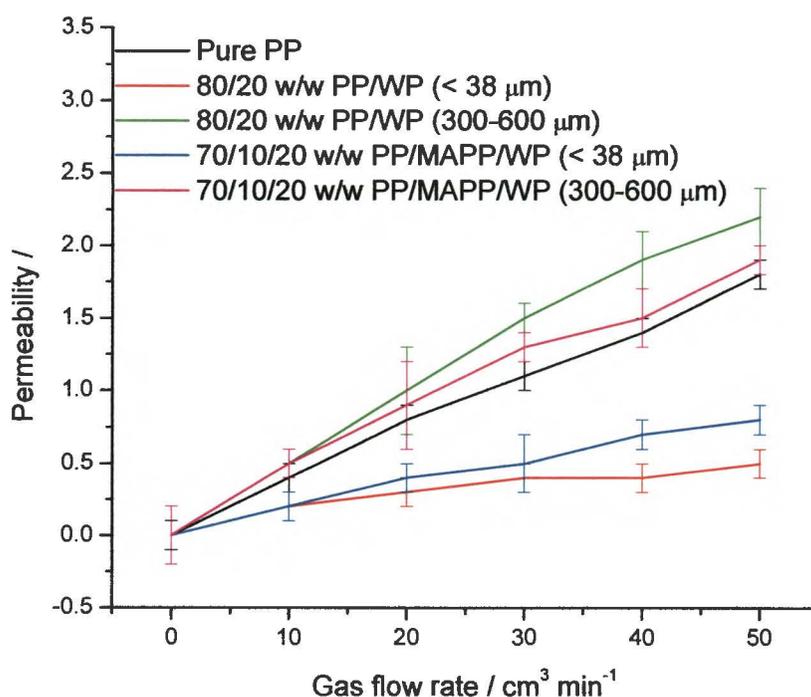


Figure 3.5 Permeability as a function of oxygen gas flow rate for composites with and without compatibiliser

3.4 Thermal properties

3.3.1 Differential scanning calorimetry (DSC)

The DSC curves are shown in Figures 3.5 – 3.13, and the values of the onset and peak temperatures, as well as the experimentally observed and theoretically expected enthalpies (calculated based on the amount of PP), are summarized in Table 3.1. It can be seen from the data that for both the composites containing $< 38 \mu\text{m}$ and $300 - 600 \mu\text{m}$ WP sizes, an increase in WP content leads to higher enthalpy values compared to the theoretically expected values, and since enthalpy is proportional to crystallinity, this also indicates an increase in crystallinity of the material. A possible explanation for this observation is that, when WP is introduced into the PP matrix, it settles in the amorphous region, and as a result new crystalline zones are formed around the WP particles through epitaxial crystallization on their surfaces. For all WP sizes, the peak temperature of melting of the composites are somewhat lower than that of pure PP, indicating a decrease in lamellar thickness (Figure 3.7), which is probably also a result of epitaxial crystallization on the WP surfaces.

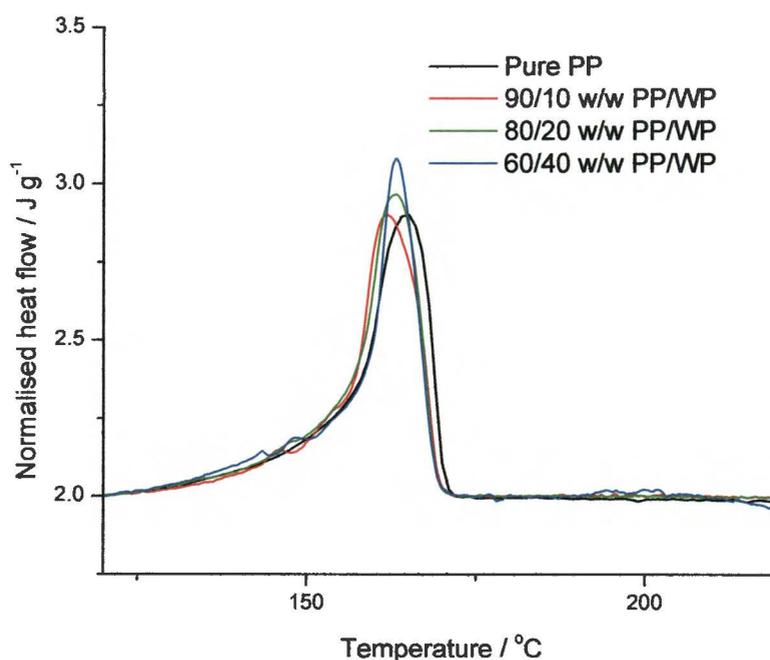


Figure 3.5 DSC heating curves for composites containing $< 38 \mu\text{m}$ WP particles

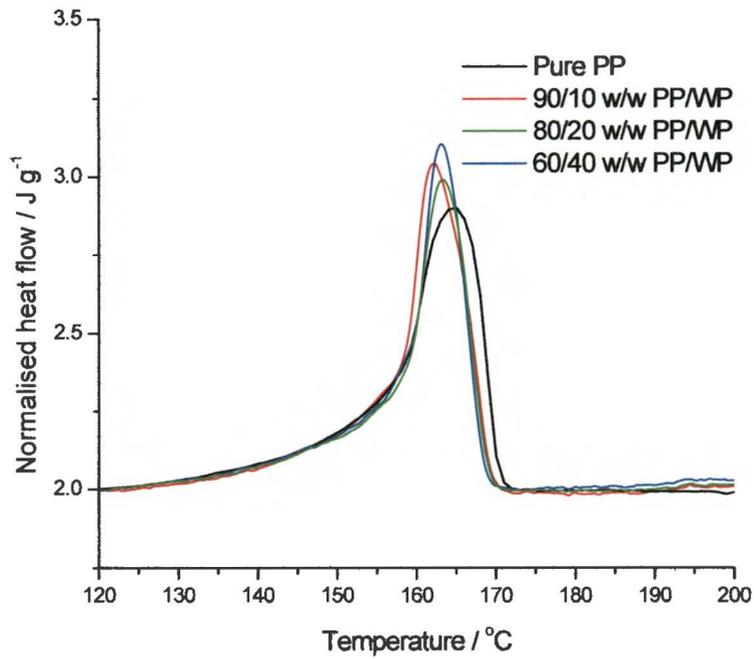


Figure 3.6 DSC heating curves for composites containing 300 – 600 μm WP particles

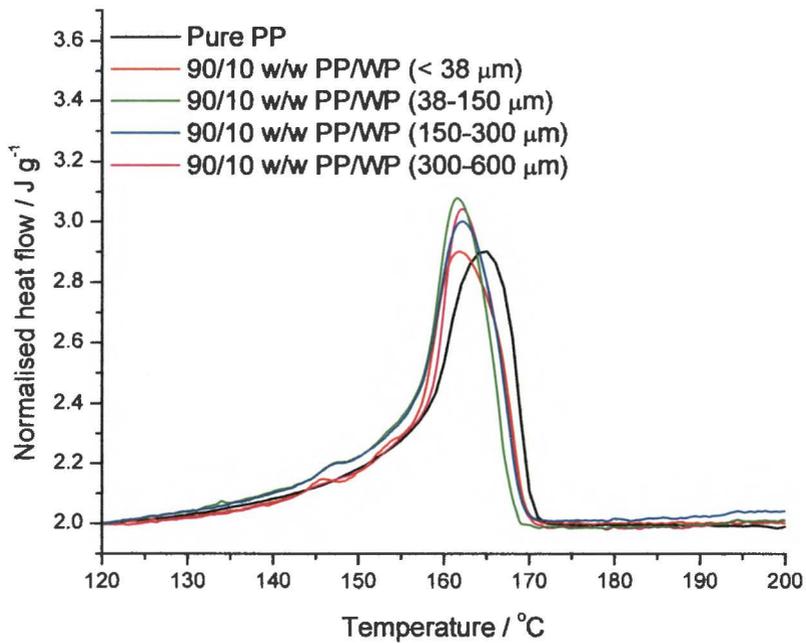


Figure 3.7 DSC heating curves for composites containing different WP particle sizes

The crystallinity can be calculated using Equation 3.1 with $\Delta H_m^* = 209 \text{ J g}^{-1}$ the specific melting enthalpy for 100 % crystalline polypropylene [52]. The value increases from 32.3 % for pure PP to 35.9 % and 40.4 % for 90/10 and 80/20 w/w PP/WP respectively.

$$X_c = \Delta H / \Delta H_m^* \quad (3.1)$$

where ΔH_m is specific melting enthalpy of polypropylene.

The presence of MAPP in the composites does not seem to have a major influence on the enthalpy values or peak temperatures of the composites (Figures 3.8 – 3.12 and Table 3.1). These values are similar to those for composites prepared in the absence of MAPP. It is, however, interesting that the 90/10 w/w PP/MAPP blend shows a double melting peak with peak temperatures at about 157 and 162 °C (Figures 3.8 – 3.10), while the PP/MAPP/WP composites containing 10 wt.% MAPP show only one well defined melting peak at about 164 °C. It seems as if in the absence of WP, the MAPP and PP crystallizes into two distinguishable fractions, both of which melt in the temperature range at which MAPP melts, indicating the formation of thinner lamellae than those of pure PP (Figure 3.13). The presence of WP seems to initiate co-crystallization of PP and MAPP into thicker lamellae that melt in the same temperature range than pure PP. This may be the result of a possible interaction between the hydroxyl groups in WP and the anhydride groups in MAPP.

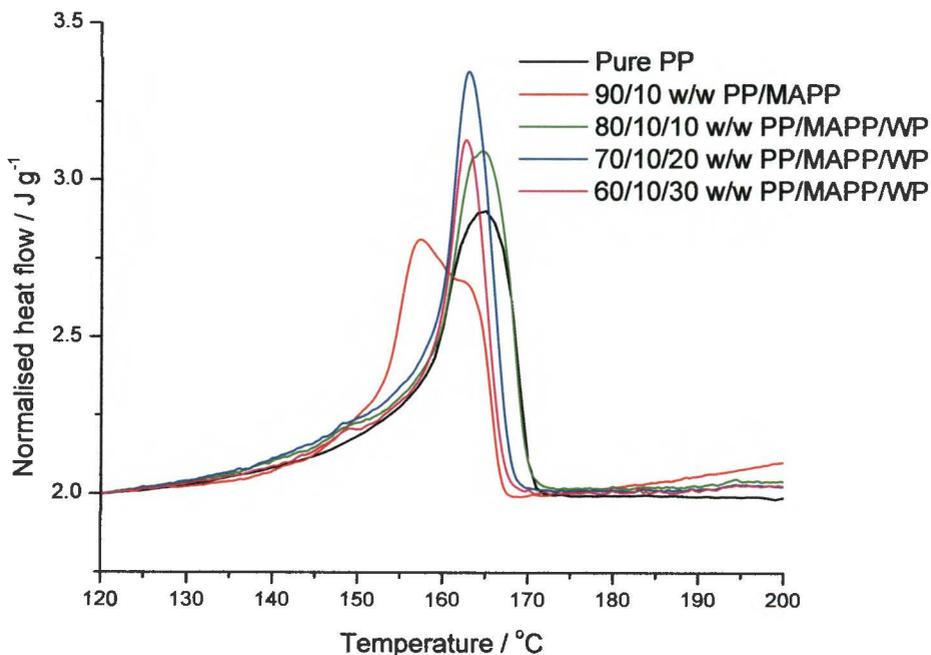


Figure 3.8 DSC heating curves for composites containing $< 38 \mu\text{m}$ WP particles and 10 % MAPP

Table 3.1 Summarized DSC results

PP/MAPP/WP (w/w)	$\Delta H_m^{obs} / J g^{-1}$	$\Delta H_m^{exp} / J g^{-1}$	$T_{o,m} / ^\circ C$	$T_{p,m} / ^\circ C$
100/0/0	67.5	-	156.8	164.9
0/100/0	72.1	-	153.2	159.0
95/5 /0	68.5	-	152.5	158.2
90/10/0	72.8	-	151.3	157.5
90/0/10 (< 38 μm)	60.6	60.8	156.1	162.0
80/0/20 (< 38 μm)	63.2	54.0	156.4	163.2
60/0/40 (< 38 μm)	63.5	40.5	158.5	163.4
90/0/10 (300 - 600 μm)	67.4	60.8	157.4	162.4
80/0/20 (300 - 600 μm)	52.9	54.0	157.8	163.4
60/0/40 (300 - 600 μm)	53.5	40.5	158.7	163.2
90/0/10 (38 - 150 μm)	62.9	60.8	156.2	161.7
90/0/10 (150 - 300 μm)	61.0	60.8	155.8	162.4
85/5/10 (< 38 μm)	66.9	60.8	158.7	164.2
80/10/10 (< 38 μm)	60.1	45.8	158.1	164.9
70/10/20 (< 38 μm)	68.1	42.9	158.6	163.0
60/10/30 (< 38 μm)	53.6	43.4	158.2	162.7
85/5/10 (300 - 600 μm)	63.2	60.8	158.8	163.2
80/10/10 (300 - 600 μm)	68.3	45.8	158.6	163.4
70/10/20 (300 - 600 μm)	63.2	42.9	158.8	163.7
60/10/30 (300 - 600 μm)	64.4	43.4	158.8	163.7
80/10/10 (38 - 150 μm)	66.0	45.8	156.7	162.0
80/10/10 (150 - 300 μm)	61.3	45.8	156.1	163.7

ΔH_m^{obs} – experimentally observed melting enthalpy; ΔH_m^{exp} – theoretically expected melting enthalpy; $T_{o,m}$ – onset temperature of melting; $T_{o,p}$ – peak temperature of melting

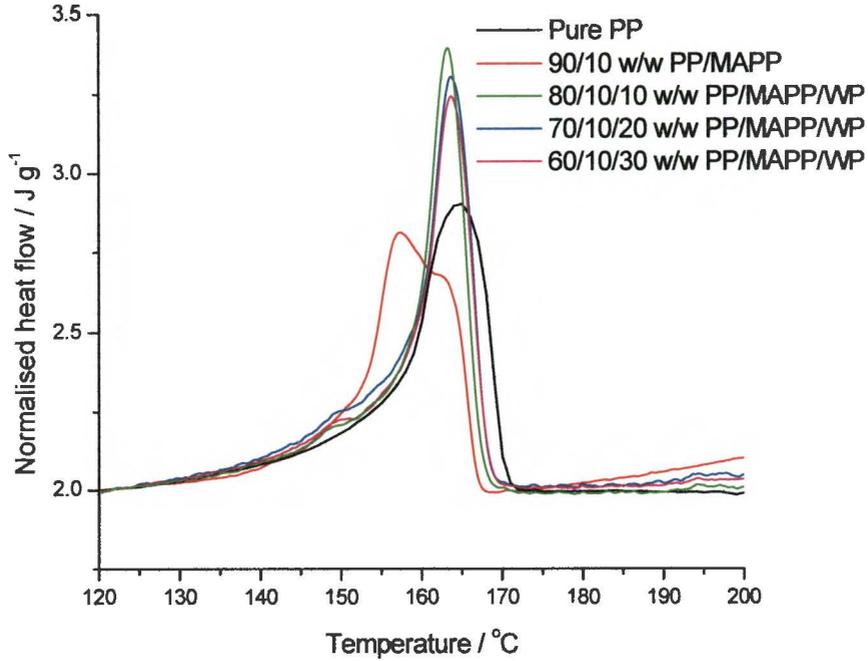


Figure 3.9 DSC heating curves for composites containing (300 – 600) μm WP particles and 10 % MAPP

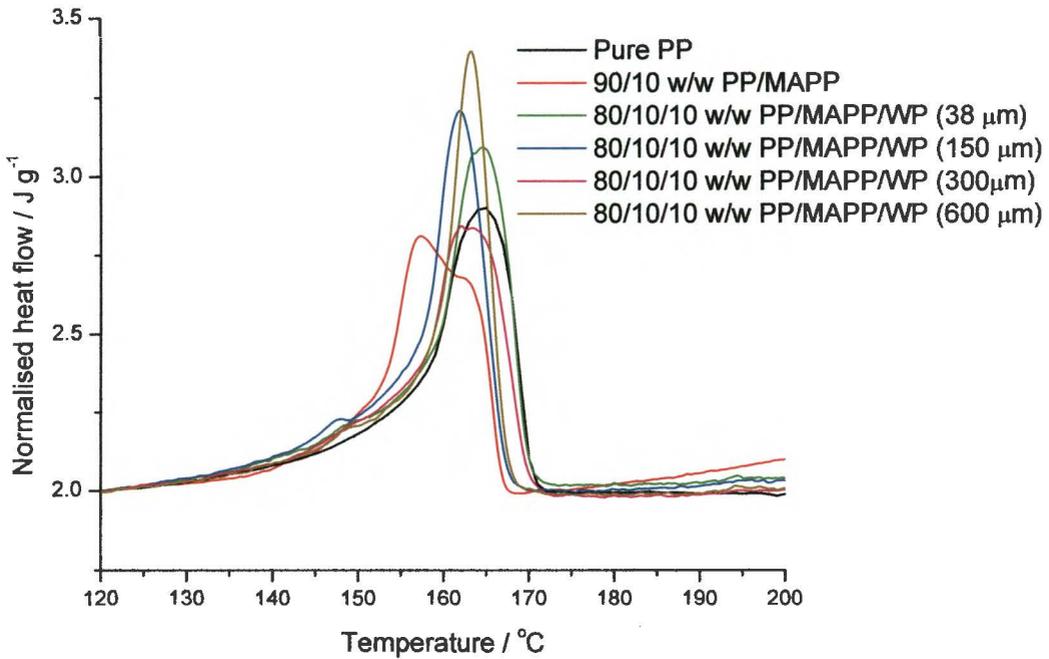


Figure 3.10 DSC heating curves for composites containing different WP particle sizes 10 % MAPP

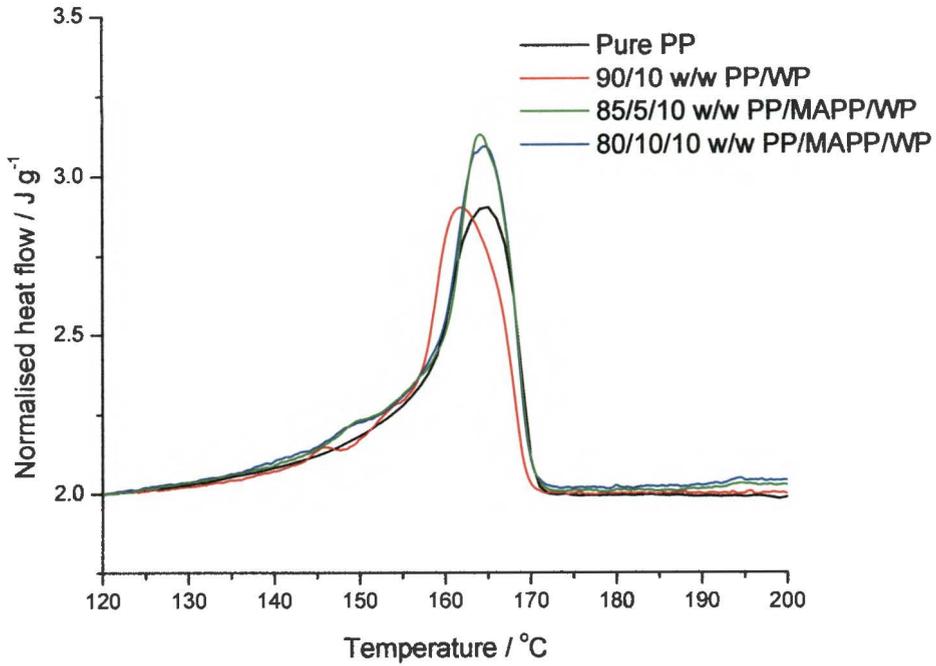


Figure 3.11 DSC heating curves for composites containing < 38 μm WP particles and different MAPP contents

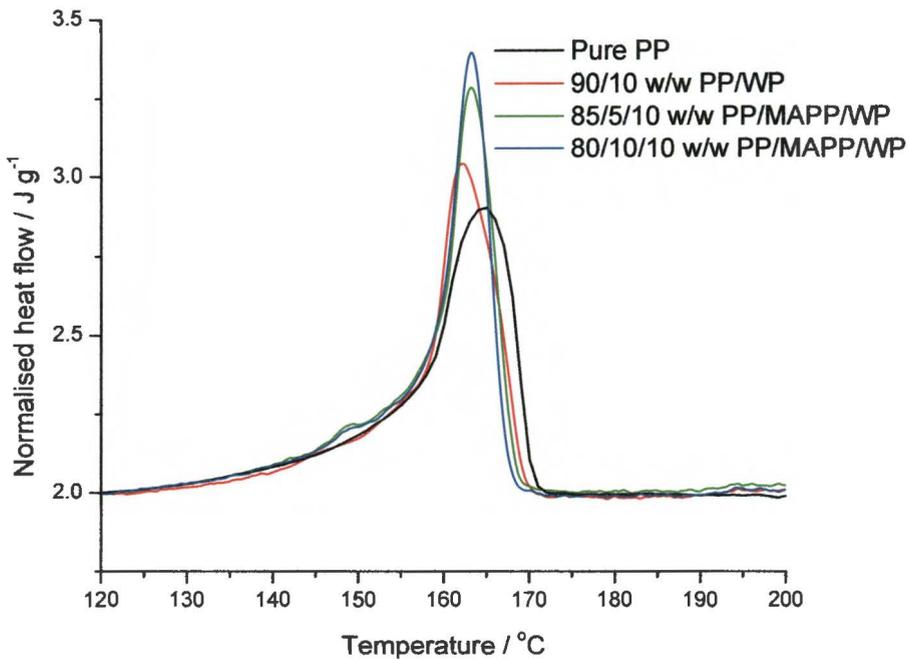


Figure 3.12 DSC heating curves for composites containing (300 – 600) μm WP particles and different MAPP contents

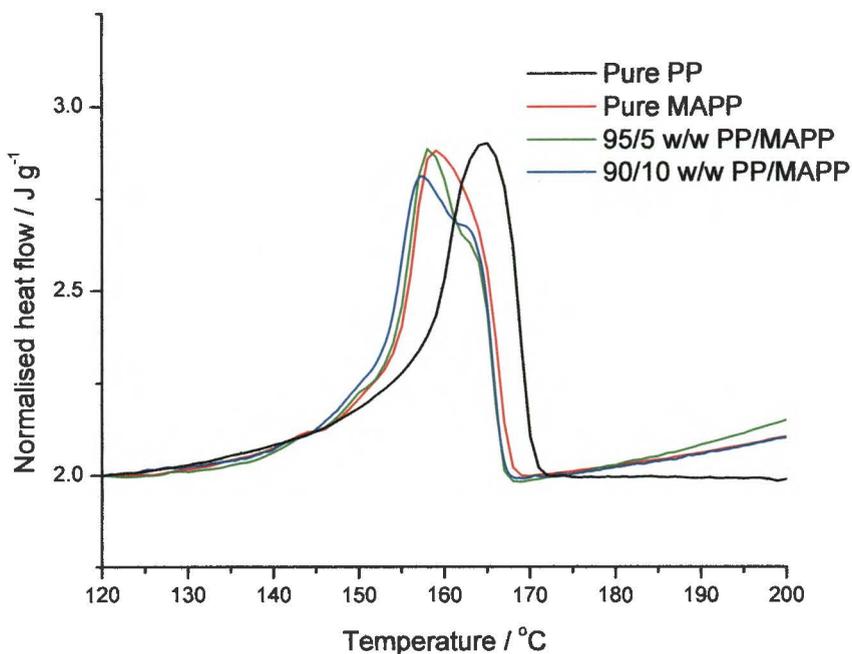


Figure 3.13 DSC heating curves for PP, MAPP and their blends

3.3.2 Thermogravimetric analysis (TGA)

Figure 3.14 shows the TGA curves of pure PP, pure MAPP and their blends. MAPP is clearly less thermally stable than PP, with almost a 200 °C difference between their respective onset temperatures of decomposition. The blends start decomposing at about the same temperature than MAPP, despite the fact that the MAPP contents in the blends are relatively small. This is probably the result of maleic anhydride groups decomposing at lower temperatures, forming free radicals that initiate further decomposition of MAPP and/or PP/MAPP. The TGA and DTGA curves for the MAPP modified and unmodified PP/WP composites are shown in Figures 3.15 – 3.25.

The WP powder curve (Figure 3.15) shows more than one decomposition step. At about 60 °C there is dehydration of moisture that was probably trapped inside the WP particles, and at 308 °C the depolymerization of lignocellulosic fibres in WP occurs, followed by further breakage of the chains. Increased WP (< 38 µm particle size) seems to increase the thermal stability of the composites, and only one decomposition step can be observed for low WP contents. This observation is probably the result of higher PP crystallinity in the presence of WP, as already explained in section 3.3.1. As the WP content increases to 40 %, two decomposition steps are observed. This may result from the high content of WP, which may leave WP particles that are not in intimate contact with PP, and which will start decomposing before the rest of the composite.

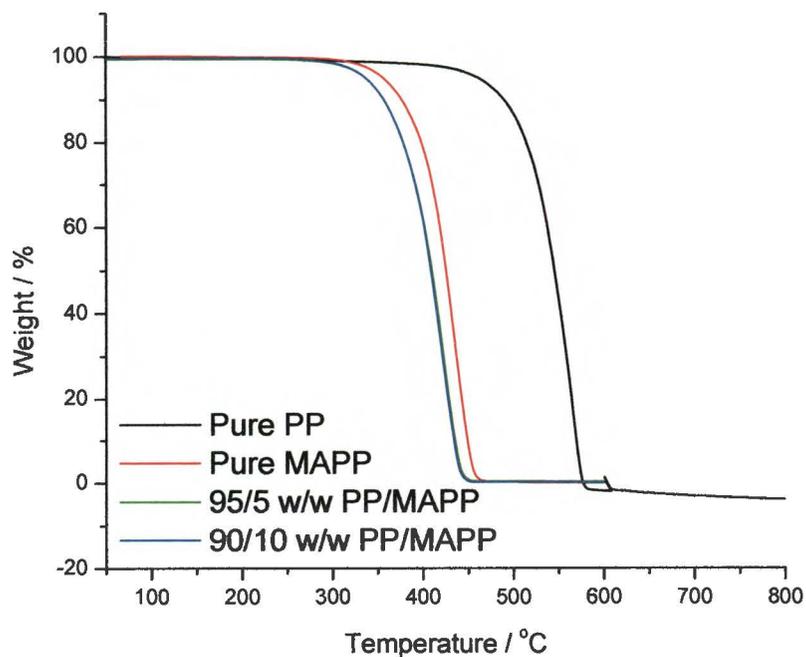


Figure 3.14 TGA curves for PP, MAPP and their blends

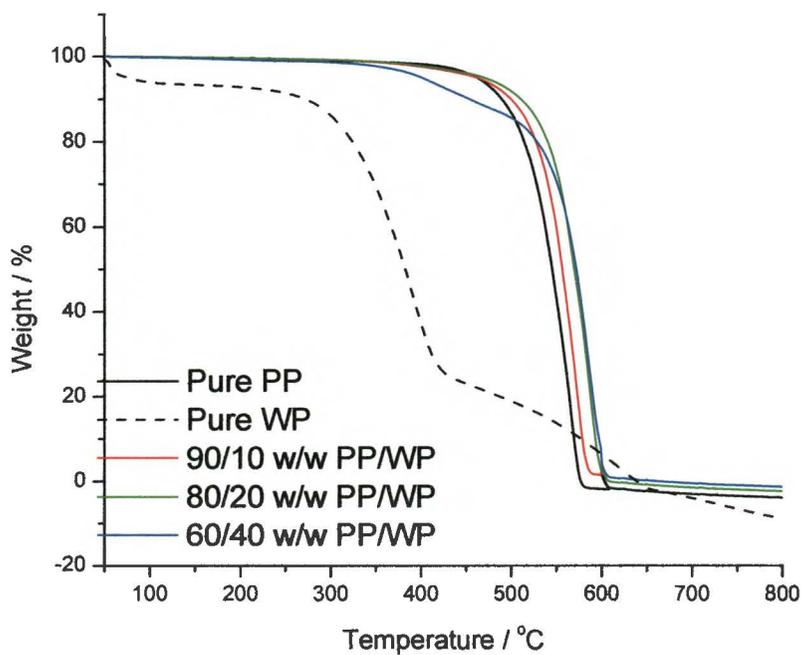


Figure 3.15 TGA curves for composites containing $< 38 \mu\text{m}$ WP particles

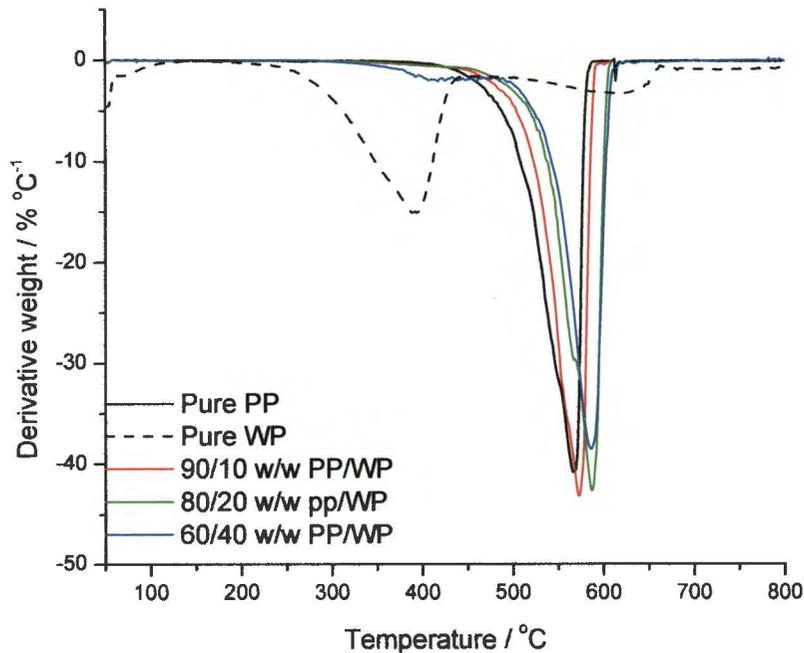


Figure 3.16 DTGA curves for composites containing < 38 μm WP particles

For composites with larger WP particles (300 - 600 μm), Figure 3.17, the WP seems to improve the thermal stability of PP. For the composites the decomposition is, however, a two-step process. The first step between 300 and 400 $^{\circ}\text{C}$ can be associated with the decomposition of lignocellulosic fibers in WP. The second step is the decomposition of PP, and this occurs at a higher temperature than that of pure PP. This may result from the larger particle size of WP, which may leave WP particles that are not in intimate contact with PP, and which will start decomposing before the rest of the composite

When comparing the influence of WP size on the thermal stability of PP-WP composites (Figure 3.19), it is clear that increase in WP particle size improves the thermal stability of the composites. However, there is not much difference between the thermal stabilities of the composites containing WP particle sizes of respectively 38 – 150, 150 – 300 and 300 – 600 μm . These samples also show a two-step decomposition, indicating that part of the WP starts decomposing before the rest of the composite.

In the presence of MAPP, the composite containing 10 % of < 38 μm WP particles seems to be more thermally stable than either PP or the composites containing higher WP contents (Figure 3.20). The latter composites have almost the same thermal stability as PP. It is not clear what the reason for this behaviour is. Composites containing larger WP particles (300 – 600 μm) in the

presence of MAPP show a decrease in thermal stability compared to that of pure PP (Figure 3.21). It is, however, still much higher than that of WP alone or the PP/MAPP blend.

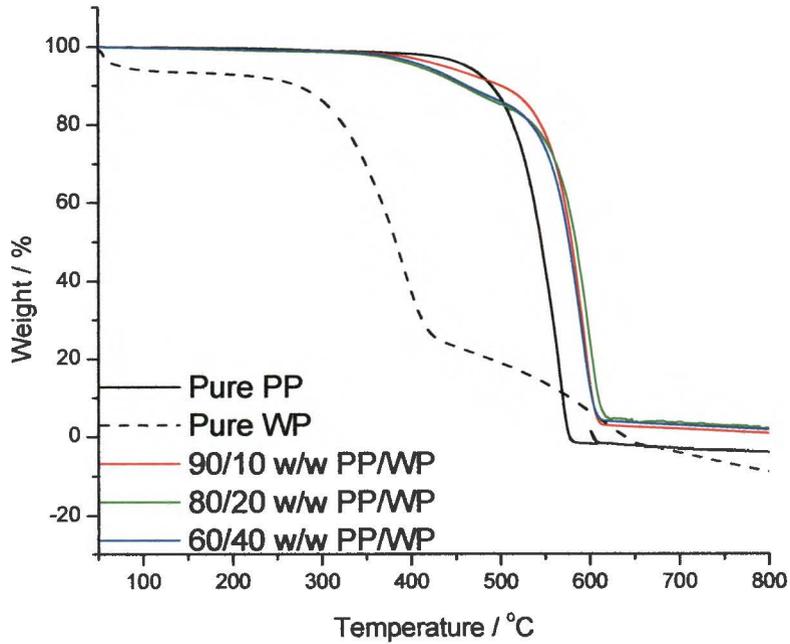


Figure 3.17 TGA curves for composites containing 300 – 600 μm WP particles

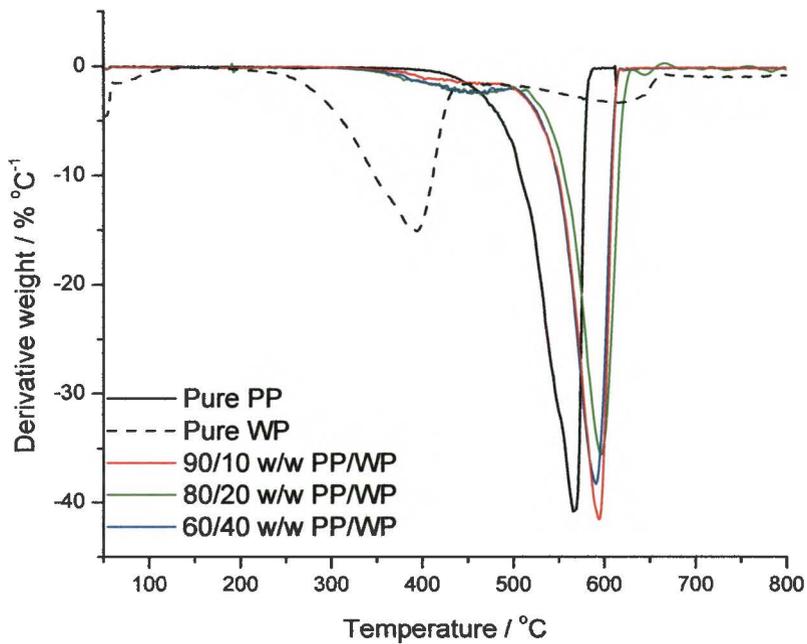


Figure 3.18 DTGA curves for composites containing 300 – 600 μm WP particles

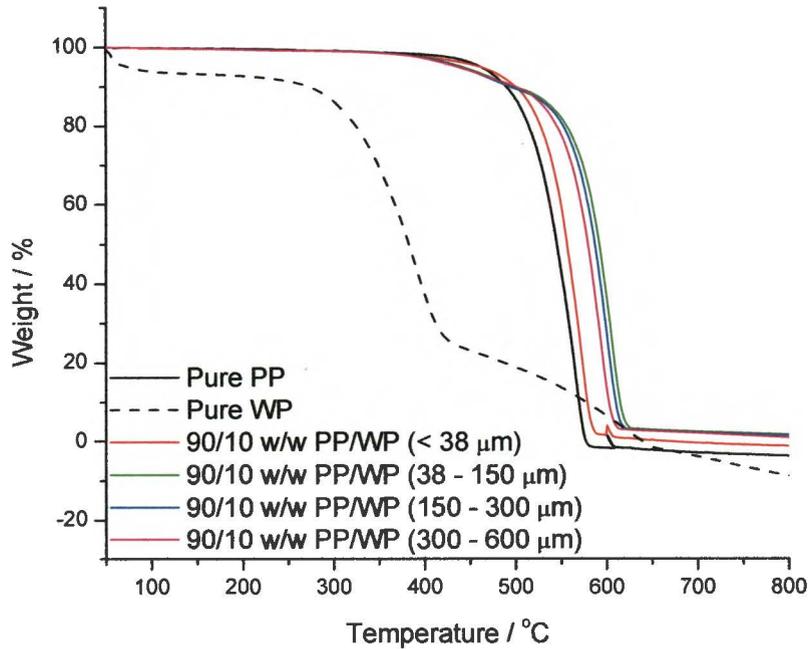


Figure 3.19 TGA curves for composites containing different WP particle sizes

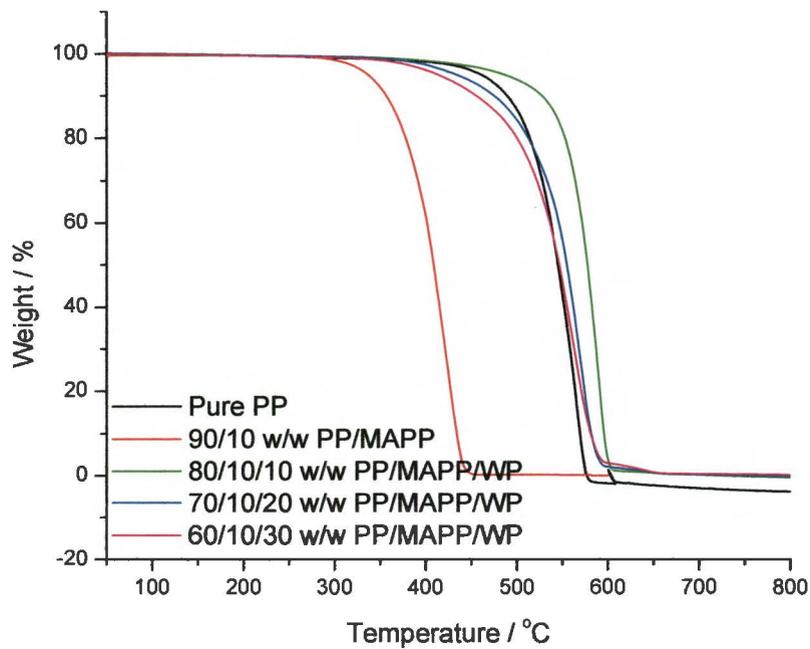


Figure 3.20 TGA curves for composites containing < 38 μm WP particles and 10 % MAPP

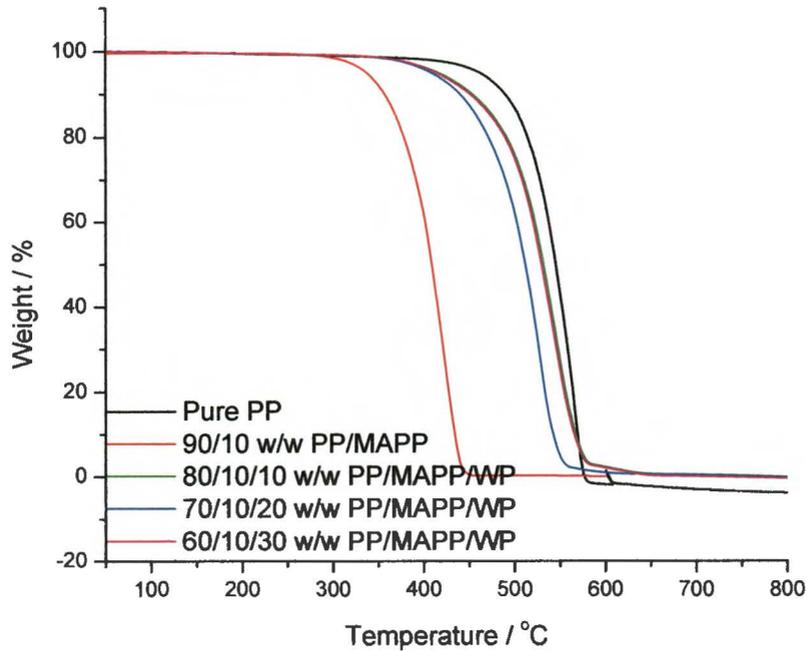


Figure 3.21 TGA curves for composites containing 300 – 600 μm WP particles and 10 % MAPP

When comparing composites with the same WP content but different MAPP contents (Figures 3.22 and 3.23), it is clear that for small ($< 38 \mu\text{m}$) WP particle sizes an increase in MAPP content increases the thermal stability of the composites above that of pure PP. This is probably the result of stronger interfacial interaction in the presence of MAPP. A similar trend was observed for composites containing 300 – 600 μm WP particles, although the sample containing 10 % MAPP seems to be out of line. The reason for this observation is not clear.

For composites containing different WP particle sizes and 10 % MAPP an increase in thermal stability is observed with increasing WP particle size (Figure 3.24). The composite containing 300 – 600 μm WP particles is again the exception, with the thermal stability in this case lower than that of pure PP.

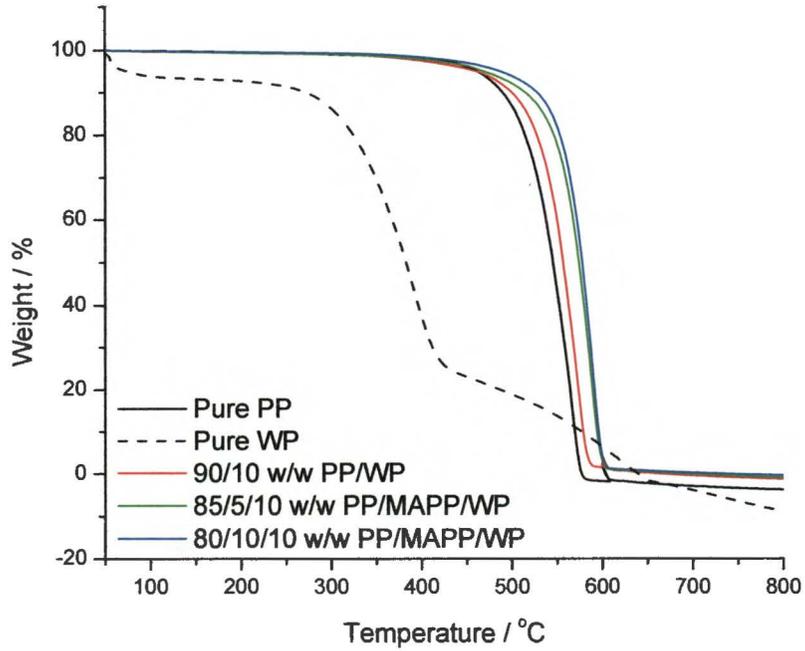


Figure 3.22 TGA curves for composites containing $< 38 \mu\text{m}$ WP particles and different MAPP contents

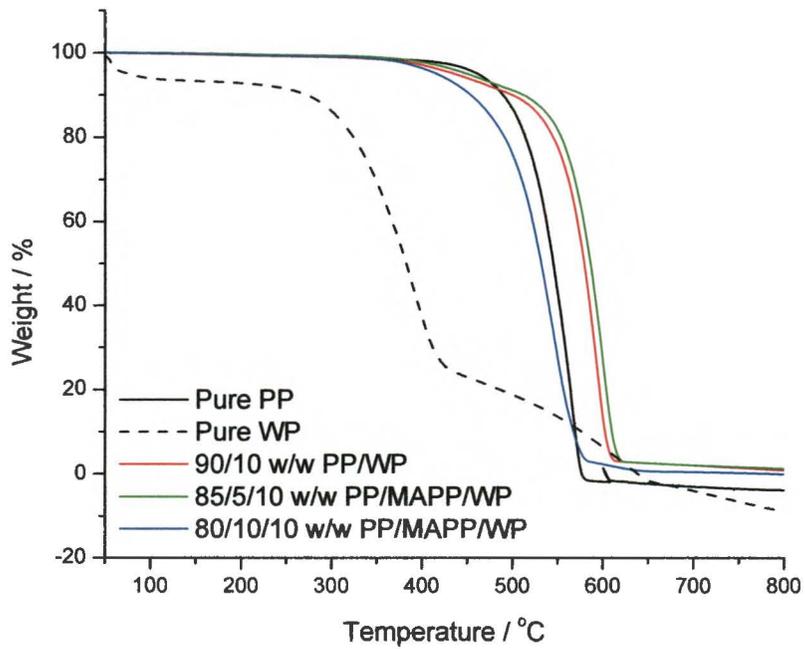


Figure 3.23 TGA curves for composites containing $300 - 600 \mu\text{m}$ WP particles and different MAPP contents

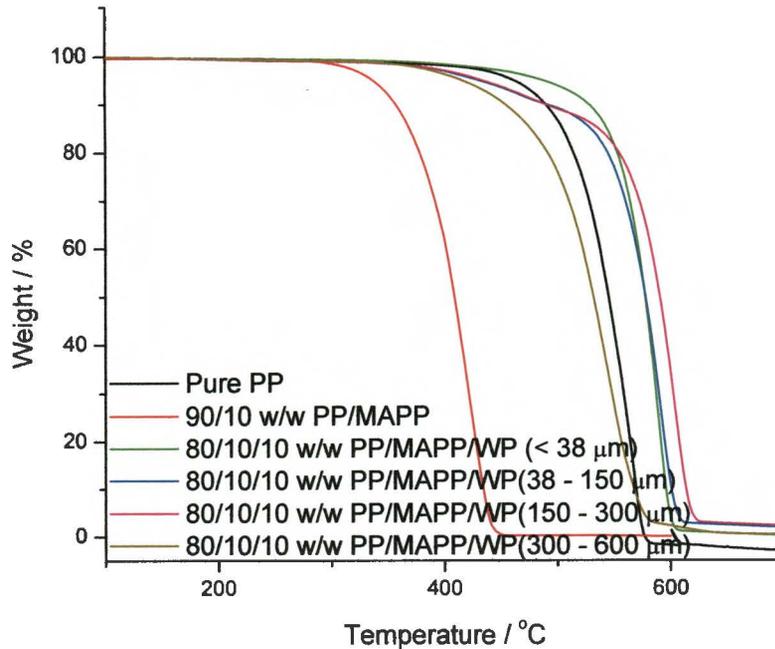


Figure 3.24 TGA curves for composites containing different WP particle sizes and 10 % MAPP

3.4 Tensile testing

The tensile properties were determined for a variety of samples containing different amounts of wood powder in different size ranges, as well as for samples prepared in the absence and presence of different amounts of maleic anhydride grafted polypropylene (MAPP). Figure 3.25 shows a decrease in elongation at break for composites containing 38 – 150 and 300 – 600 μm WP particle sizes. This indicates that the presence of WP in the matrix reduces the ability of the sample to deform by restricting the mobility of the polymer chains. As a consequence, it is difficult for the segments of the material to easily slip past each other. Because the sample cannot deform very much before it breaks, it shows that the energy was not able to dissipate, giving rise to a brittle sample that breaks easily. For the composite containing $< 38 \mu\text{m}$ WP, there is a slight increase in elongation at break for the sample containing 10 % WP. However, this value slightly decreases for higher WP contents. A probable reason may be that, in the case of 10 % WP, the particles are almost evenly distributed in the matrix. Since the WP particles are small and of low content, it has little influence on PP chain mobility. As discussed in section 3.3.1, the crystallinity of the matrix increases on introduction of $< 38 \mu\text{m}$ WP. As the WP settles in the amorphous region of the matrix, it enhances the formation of new crystalline zones around or on the surface of its particles, resulting

in an increase in the crystallinity of the matrix. Therefore, due to a possible increase in crystallinity, the flexibility of the chain segments will be restricted, leading to a decrease in elongation at break.

In Figure 3.26 a general decrease in the stress at break can be observed for all composites. This behaviour is not in line with the increase in crystallinity of the material, but probably results from the fact that, due to poor interaction between the polymer and filler, interfacial adhesion is low and the material loses its toughness. It is known that the matrix adds toughness to a composite, and therefore an increase in filler content will result in a decrease in matrix content, resulting in less matrix to withstand the applied stress [53]. Another explanation for the decrease in the ultimate properties is the possibility of cracks that might have been initiated at points of high stress concentration such as the filler ends or at the interface region. It is also possible that failure might have occurred in the matrix and not at the interface. As a consequence, there is less stress required to break [51].

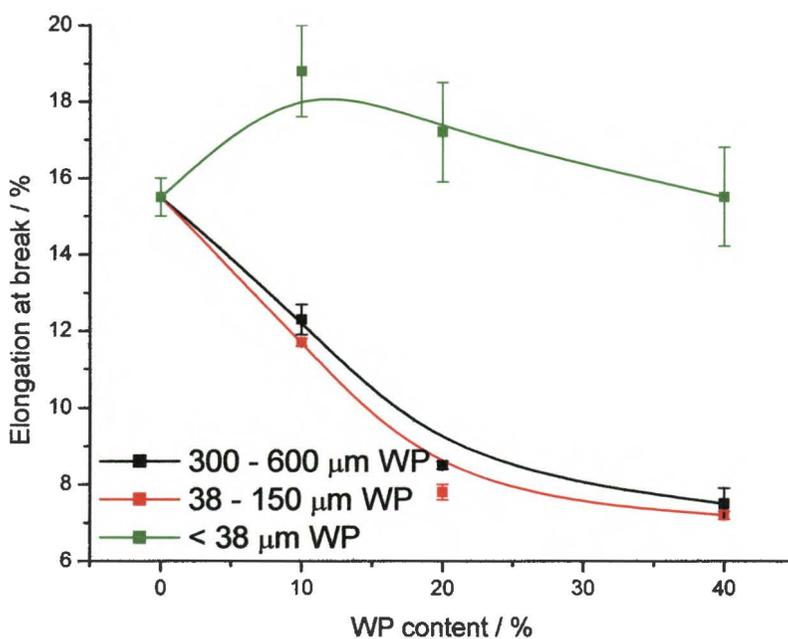


Figure 3.25 Elongation at break as function of WP content for composites with different WP sizes and no compatibilizer

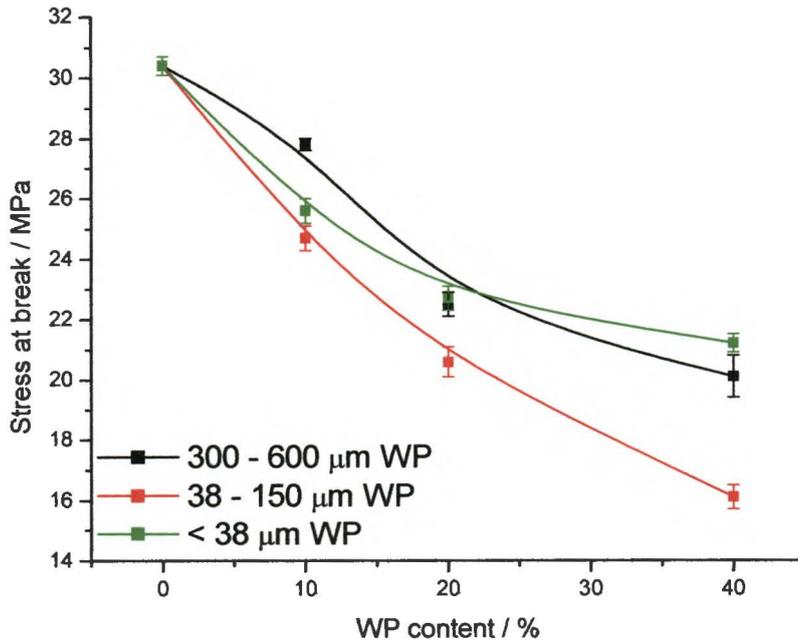


Figure 3.26 Stress at break as function of WP content for composites with different WP sizes and no compatibilizer

Figure 3.27 shows an appreciable increase in Young's modulus with increasing WP content for composites with 38 – 150 and 300 – 600 μm WP particles. This is common behaviour for polymer-filler composites, especially for composites filled with natural fillers. Fillers are said to be much stiffer than polymer matrices and as a result they add stiffness to the final product [51]. For the composites with 38 μm WP particles, there is only a slight increase in Young's modulus. In this case the small size allows more PP chain mobility.

Figures 3.28 and 3.29 shows elongation and stress at break curves as function of WP particle size for composites with different MAPP contents. The presence of MAPP seems to slightly increase the elongation at break compared to samples containing no MAPP. This effect is more pronounced for the samples containing larger WP particles. Other investigations, however, showed that MAPP has a negative impact on elongation at break [51]. Improvement of the interaction between the matrix and filler particles, due to the presence of MAPP, causes less slippage of chain segments at the interface [54, 60, 61].

Figure 3.29 shows an initial decrease followed by an increase in stress at break of the composites. This effect is more pronounced in the presence of MAPP and for larger WP particle sizes. The reason is probably that MAPP improves the interfacial adhesion in the composite, especially for larger WP particles where the interlocking mechanism will be more pronounced.

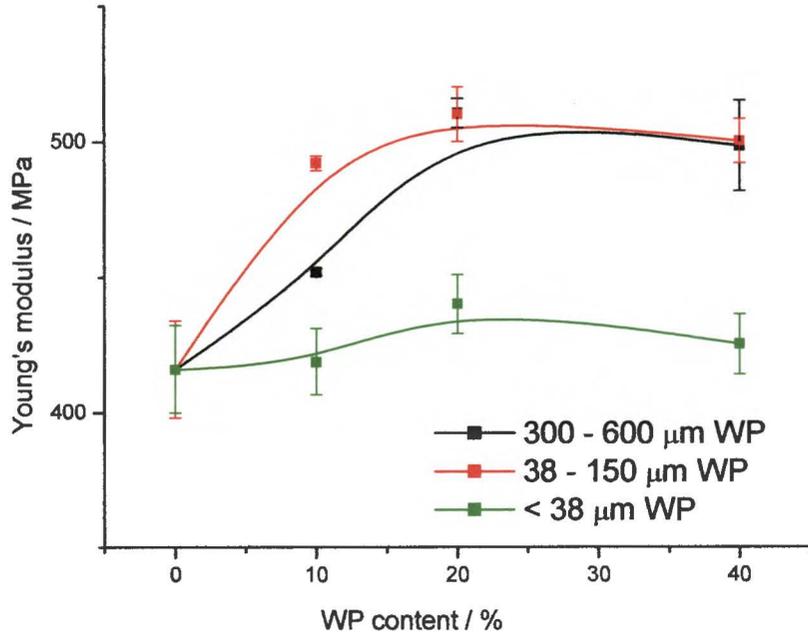


Figure 3.27 Young's modulus as function of WP content for composites with different WP sizes and no compatibilizer

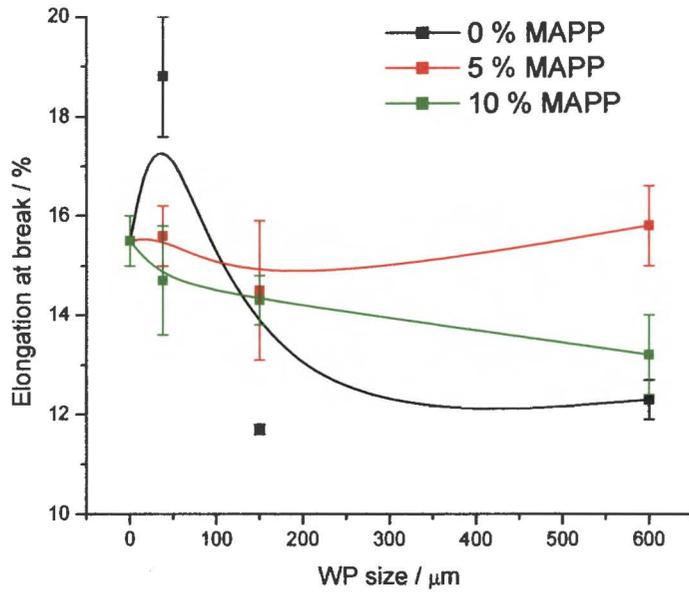


Figure 3.28 Elongation at break as function of WP size for composites containing 10 % WP and different amounts of compatibiliser

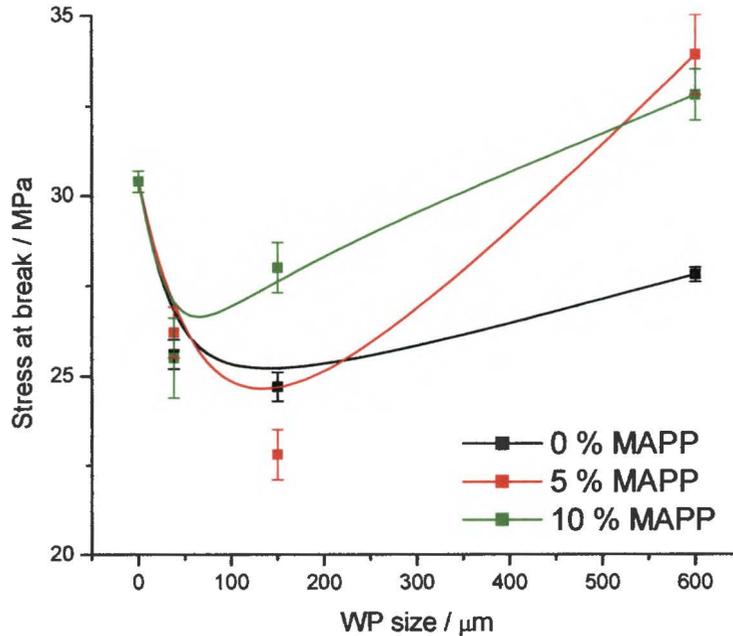


Figure 3.29 Stress at break as function of WP size for composites containing 10 % WP and different amounts of compatibilizer

In Figure 3.30 there is a general increase in Young's modulus in all cases except for composites containing no MAPP, where Young's modulus decrease for larger WP particles. This can also be explained as being the result of better interaction between WP and the matrix in the presence of MAPP, which reduces chain mobility and increases stiffness.

Elongation at break for composites with different WP size but constant MAPP content decreases with an increase in WP content (Figure 3.31). As discussed in section 3.3.1, there probably is strong interaction between MAPP and WP particles, even for small particle sizes. This will reduce chain mobility, and decrease elongation at break with increasing WP content.

In Figures 3.32 and 3.33 large WP particles seems to increase the stress at break as well as Young's modulus with increasing WP content. This improvement can be attributed to two effects: (i) the compatibilizer (MAPP) locates at the interfaces between the phases and enhances the stress transfer, resulting in the enhancement of mechanical properties, particularly the modulus, and (ii) upon addition of the compatibilizer, the drop size of the matrix decreases, leading to improved properties [58, 59].

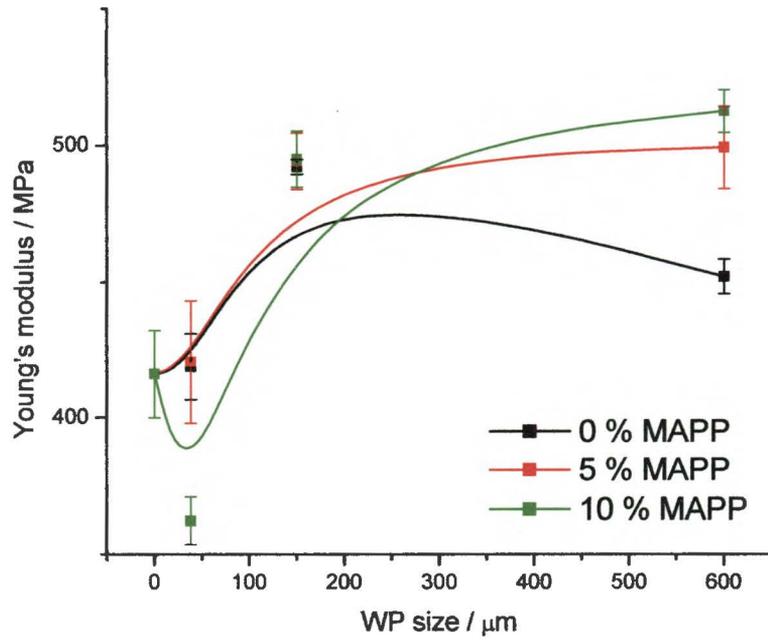


Figure 3.30 Young's modulus as function of WP size for composites containing 10 % WP and different amounts of compatibilizer

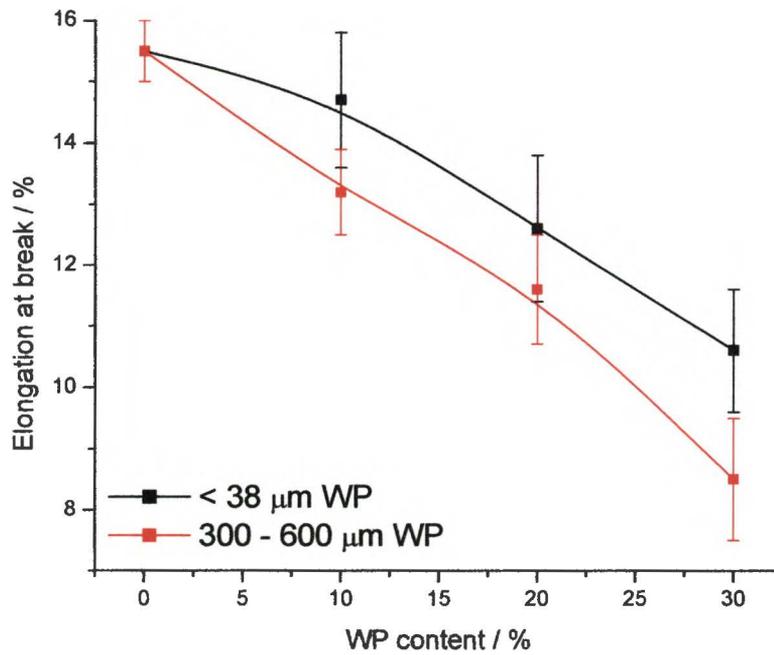


Figure 3.31 Elongation at break as function of WP content for composites with 10 % MAPP

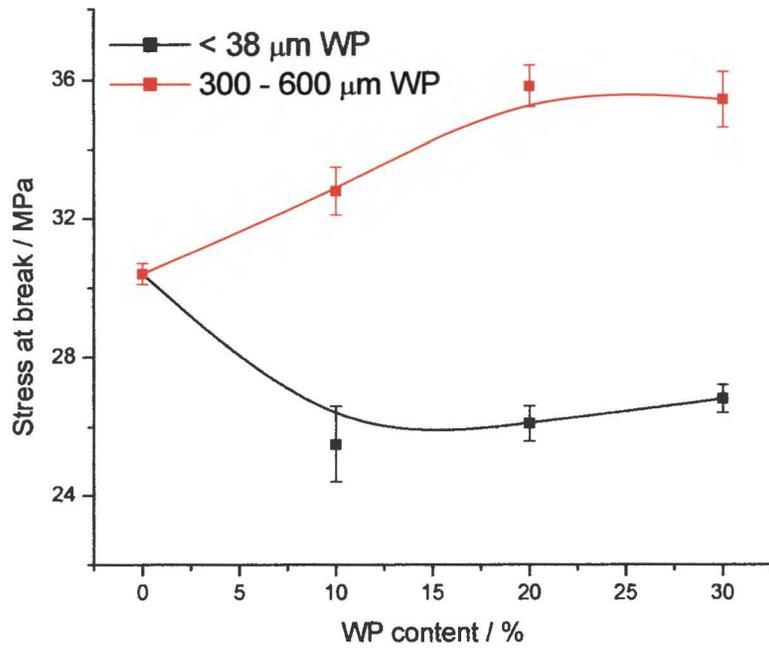


Figure 3.32 Stress at break as function of WP content for composites with 10 % MAPP

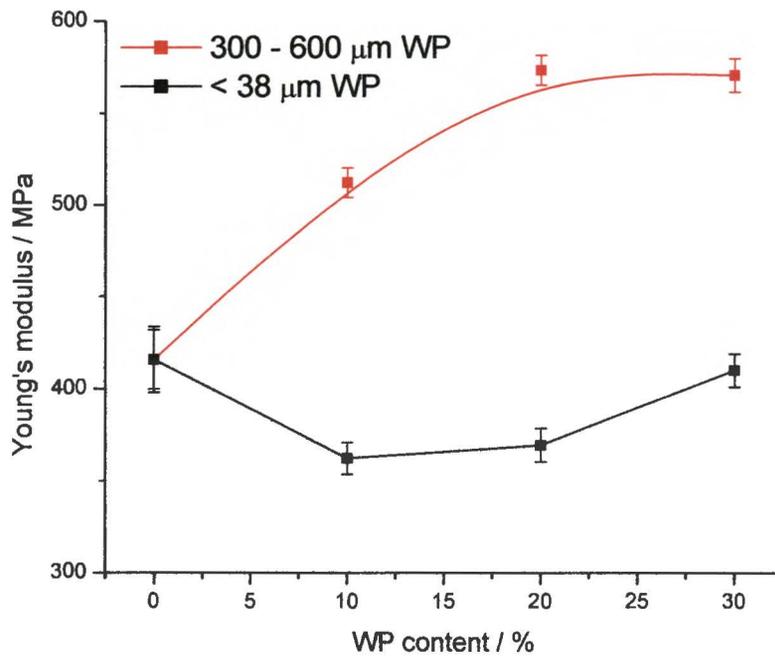


Figure 3.33 Young's modulus as function of WP content for composites with 10 % MAPP

Table 3.2 Summarized results for tensile properties

PP/MAPP/WP (w/w)	$\epsilon_b / \% \pm s\epsilon_b$	$\sigma_b / \text{MPa} \pm s\sigma_b$	$E / \text{MPa} \pm sE$
100/0/0	15.5 ± 0.5	30.4 ± 0.3	416.0 ± 16.7
90/0/10 (< 38 μm WP)	18.8 ± 1.2	25.6 ± 0.4	418.8 ± 12.1
80/0/20 (< 38 μm WP)	17.2 ± 1.3	22.7 ± 0.4	440.0 ± 10.9
60/0/40 (< 38 μm WP)	15.5 ± 1.3	21.2 ± 0.3	445.1 ± 11.0
90/0/10 (38 – 150 μm WP)	11.7 ± 0.1	24.7 ± 0.4	492.0 ± 2.7
80/0/20 (38 - 150 μm WP)	7.8 ± 0.2	20.6 ± 0.5	510.0 ± 10.0
60/0/40 (38 - 150 μm WP)	7.2 ± 0.1	16.1 ± 0.4	500.0 ± 8.2
90/0/10 (300 - 600 μm WP)	12.3 ± 0.4	27.8 ± 0.2	451.9 ± 1.3
80/0/20 (300 - 600 μm WP)	8.5 ± 0.1	22.5 ± 0.4	510.4 ± 5.3
60/0/40 (300 - 600 μm WP)	7.5 ± 0.4	20.1 ± 0.7	498.2 ± 16.7
85/5/10 (< 38 μm WP)	15.6 ± 2.6	26.2 ± 0.3	420.5 ± 22.6
80/10/10 (< 38 μm WP)	14.7 ± 1.1	25.5 ± 1.1	362.3 ± 8.7
70/10/20 (< 38 μm WP)	12.6 ± 0.0	26.1 ± 0.5	369.4 ± 9.0
60/10/30 (< 38 μm WP)	10.6 ± 1.0	26.8 ± 0.4	410.0 ± 9.1
85/5/10 (38 - 150 μm WP)	14.5 ± 1.4	22.8 ± 0.7	494.1 ± 10.3
80/10/10 (38 - 150 μm WP)	14.3 ± 0.5	28.0 ± 0.7	494.9 ± 10.3
85/5/10 (300 - 600 μm WP)	15.8 ± 0.8	33.9 ± 1.1	499.0 ± 15.0
80/10/10 (300 - 600 μm WP)	13.2 ± 0.7	32.8 ± 0.7	512.0 ± 7.9
70/10/20 (300 - 600 μm WP)	11.6 ± 0.9	35.8 ± 0.6	573.1 ± 8.0
60/10/30 (300 - 600 μm WP)	8.5 ± 1.0	35.4 ± 0.8	570.2 ± 9.0

ϵ_b – Elongation at break; σ_b – stress at break; E – Young’s modulus; s indicates standard deviation

3.5 Surface free energy

Surface free energy results for composites with < 38 and $300 - 600 \mu\text{m}$ as function of WP content are shown in Figures 3.34 and 3.35. In Figure 3.34, there is a slight increase in total surface free energy, and a stronger increase in the polar part for the composite containing 10 % WP. For 20 % WP there is an increase in total surface free energy, but a decrease in the polar part. For 40 % WP the total surface free energy slightly decreases and the polar part slightly increases. This behaviour is not in line with what is expected. The introduction of WP should result in an increase in polar part due to the presence of polar groups inside WP. The explanation for this observation is not clear. For composites with larger WP size, Figure 3.35, the observations are similar to those described for $< 38 \mu\text{m}$ WP particles. The surface free energy values in Figure 3.36 do not show a trend, but it is obvious that for all WP particle sizes, the polar part of the surface free energy is higher than that for pure PP. Since cellulose is more polar than PP, this observation can be expected.

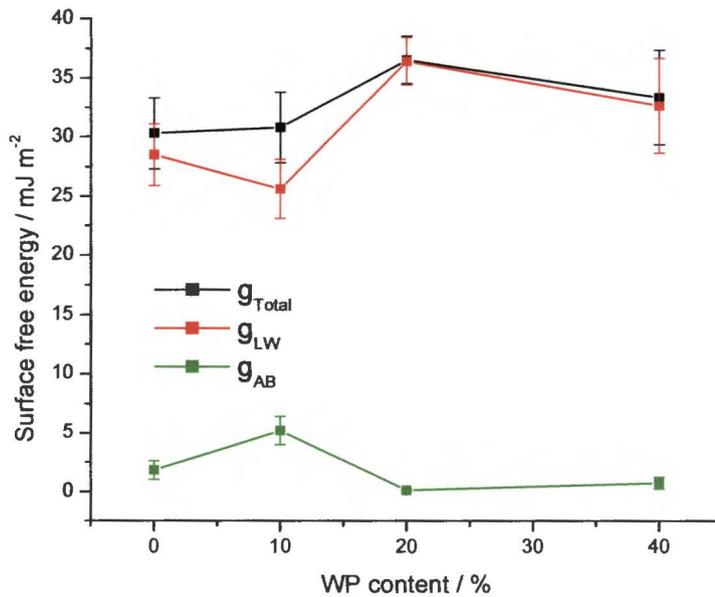


Figure 3.34 Surface free energy as function of WP content of composites with $< 38 \mu\text{m}$ WP particles

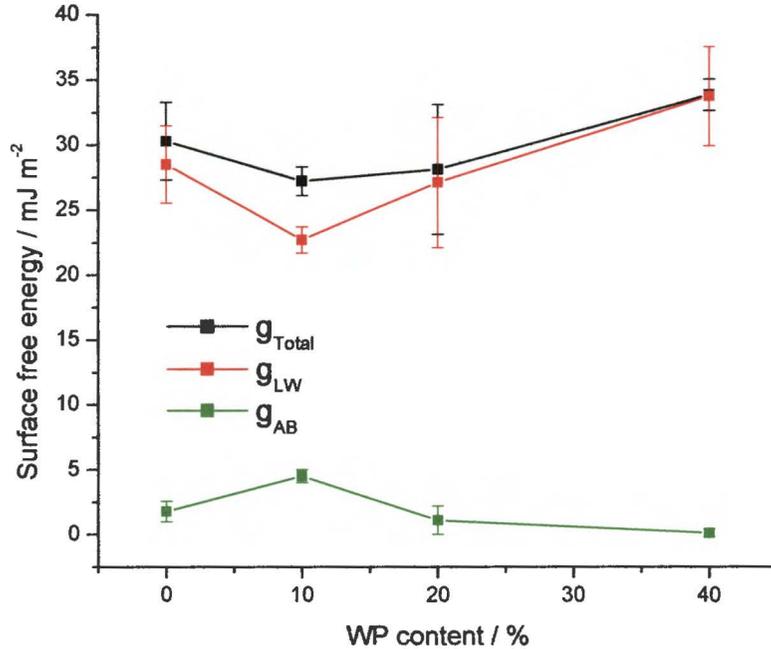


Figure 3.35 Surface free energy as function of WP content of composites with 300 – 600 μm WP particles

In section 3.3.1 it was mentioned that there may have been a possible interaction between the hydroxyl groups in WP and the anhydride groups in MAPP. This would reduce the number of polar groups in WP composites containing 10 % MAPP. The results in Figure 3.37, however, show an increase in the polar part of the surface free energy with increasing WP ($< 38 \mu\text{m}$ particle size) content. Again there is no obvious explanation for this observation. The observations for composites containing larger (300 – 600 μm) WP particles (Figure 3.38) are similar to those for composites containing different WP particle sizes in the absence of MAPP (Figures 3.34 and 3.35). Again there is no logical explanation for this. This observed decrease at higher WP contents may be the result of a reduction in the number of polar groups due to a reaction between the hydroxyl groups in WP and the anhydride groups in MAPP. In the presence of MAPP, an increase in WP particle size gives rise to only a slight increase in the polar part of the surface free energy (Figure 3.39). The general decrease in the polar part of the surface free energy with increasing MAPP content in Figures 3.40 and 4.41 may be the result of a reaction between the WP and MAPP functional groups, leads to a reduction in the number of polar groups.

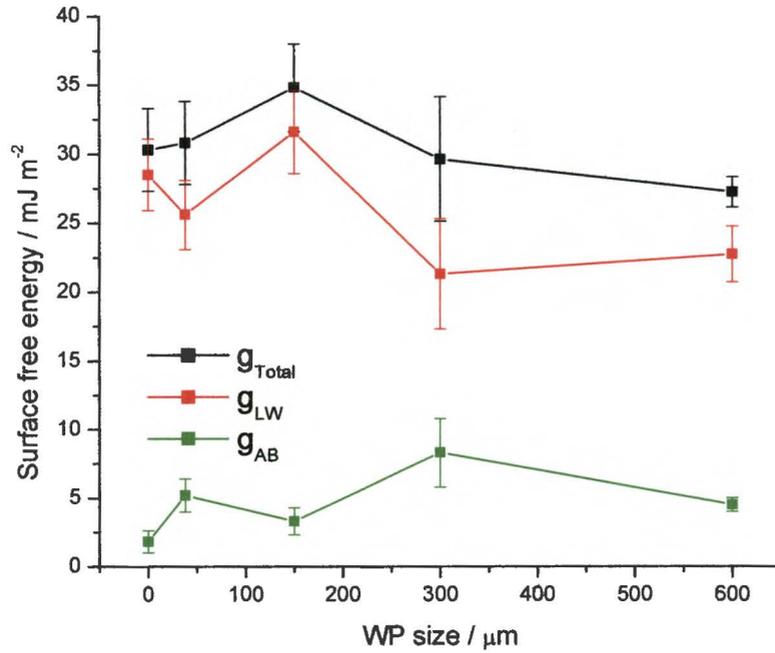


Figure 3.36 Surface free energy as function of WP size for composites containing 10 % WP and 0 % MAPP

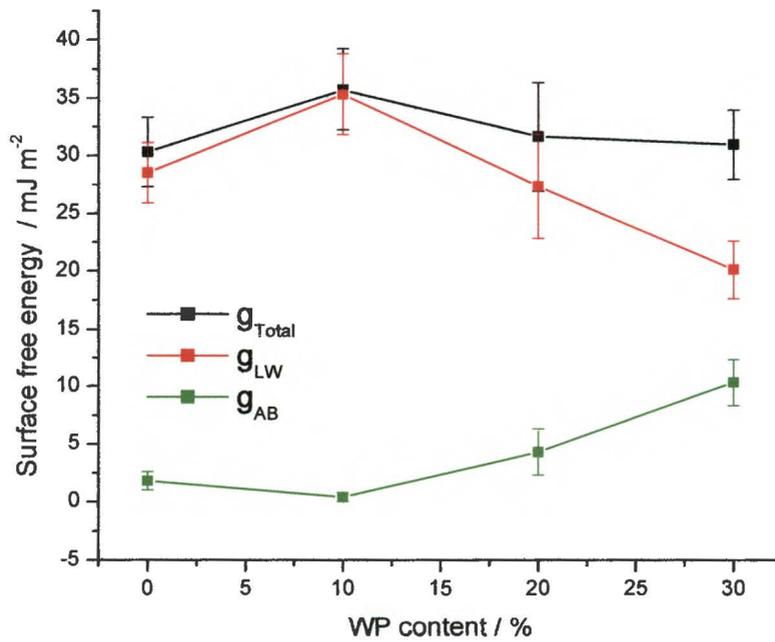


Figure 3.37 Surface free energy as function of WP content for composites with < 38 μm WP particles and 10 % MAPP

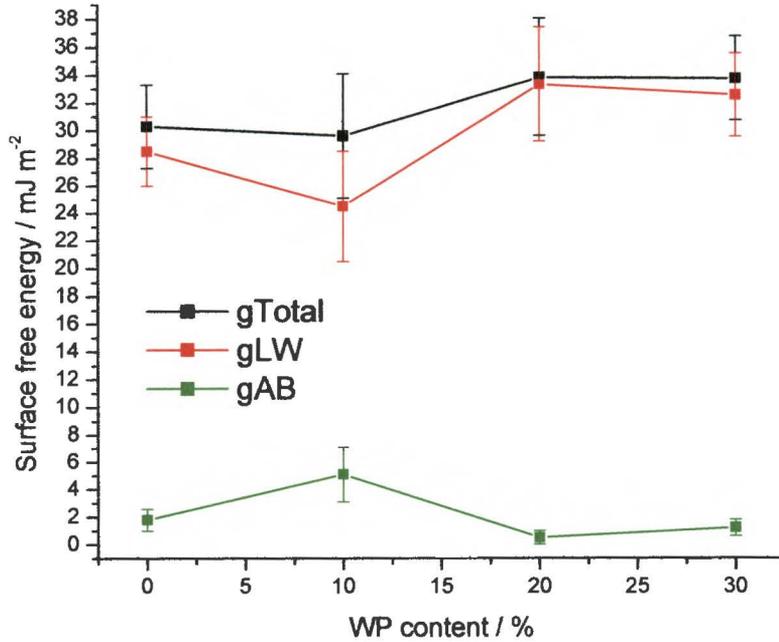


Figure 3.38 Surface free energy as function of WP content for composites with 300 – 600 μm WP particles and 10 % MAPP

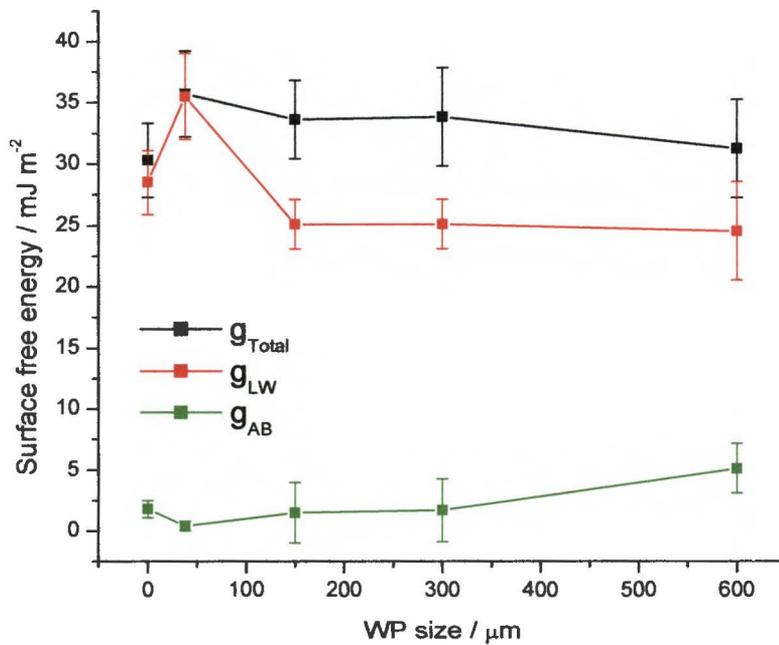


Figure 3.39 Surface free energy as function of WP size for composites containing 10 % WP and 10 % MAPP

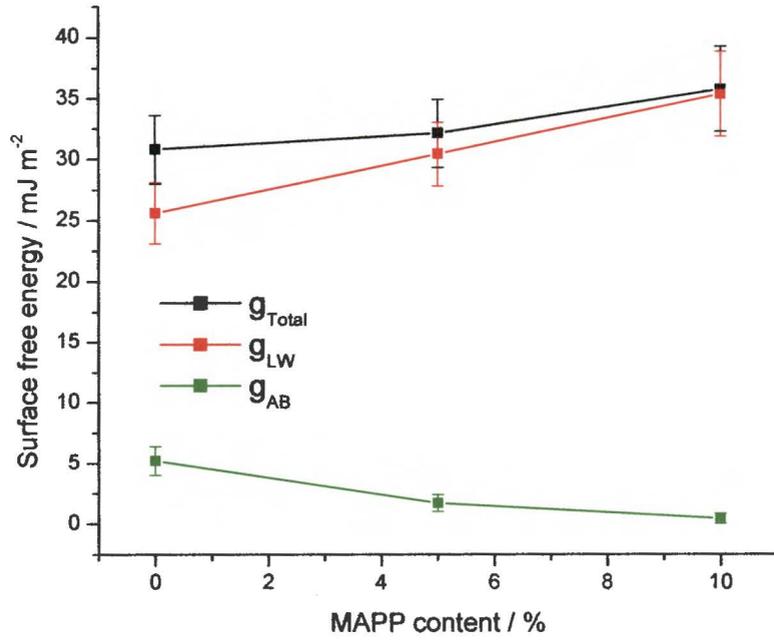


Figure 3.40 Surface free energy as function of MAPP content for composites with $< 38 \mu\text{m}$ WP particles

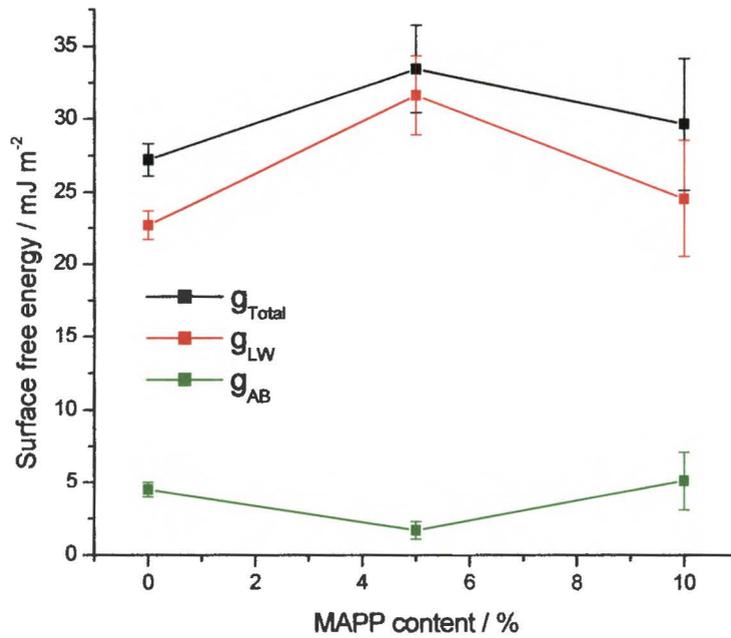


Figure 3.41 Surface free energy as function of MAPP content for composites with $300 - 600 \mu\text{m}$ WP particles

Table 3.3 Summary of surface free energy results

PP/MAPP/WP (w/w)	$g_{\text{Total}} \pm s_{g_{\text{Total}}}$	$g_{\text{LW}} \pm s_{g_{\text{LW}}}$	$g_{\text{AB}} \pm s_{g_{\text{AB}}}$
100/0/0	30.3 ± 3.0	28.5 ± 2.6	1.8 ± 0.8
90/0/10 (< 38 μm WP)	30.8 ± 2.7	25.6 ± 2.5	5.2 ± 1.2
80/0/20 (< 38 μm WP)	36.5 ± 2.0	36.4 ± 2.0	0.1 ± 0.1
60/0/40 (< 38 μm WP)	33.3 ± 4.0	32.6 ± 4.0	0.7 ± 0.6
90/0/10 (300 - 600 μm WP)	27.2 ± 1.1	22.7 ± 1.0	4.5 ± 0.5
80/0/20 (300 - 600 μm WP)	28.1 ± 5.0	27.1 ± 5.0	1.1 ± 1.5
60/0/40 (300 - 600 μm WP)	33.8 ± 3.7	33.8 ± 3.7	0.1 ± 0.3
90/0/10 (38 - 150 μm WP)	34.8 ± 3.2	31.6 ± 3.0	3.3 ± 1.5
90/0/10 (150 - 300 μm WP)	29.6 ± 4.5	21.3 ± 4.0	8.3 ± 2.6
85/5/10 (< 38 μm WP)	32.1 ± 2.7	30.4 ± 2.8	1.7 ± 0.7
80/10/10 (< 38 μm WP)	35.7 ± 3.5	35.3 ± 3.5	0.4 ± 0.4
70/10/20 (< 38 μm WP)	31.6 ± 4.7	27.3 ± 4.3	4.3 ± 2.0
60/10/30 (< 38 μm WP)	30.9 ± 3.1	20.6 ± 2.5	10.3 ± 2.0
85/5/10 (300 - 600 μm WP)	33.4 ± 3.0	31.6 ± 2.7	1.7 ± 0.6
80/10/10 (300 - 600 μm WP)	29.6 ± 4.5	24.5 ± 4.0	5.1 ± 2.5
70/10/20 (300 - 600 μm WP)	40.2 ± 3.5	15.0 ± 2.0	0.5 ± 0.5
60/10/30 (300 - 600 μm WP)	30.3 ± 2.0	27.9 ± 1.7	2.4 ± 0.5
80/10/10 (38 - 150 μm WP)	33.6 ± 3.2	15.1 ± 2.0	18.5 ± 2.5
80/10/10 (150 - 300 μm WP)	33.8 ± 3.5	15.1 ± 2.1	18.7 ± 2.6

g_{Total} – total surface free energy; g_{LW} – disperse part of surface free energy; g_{AB} – polar part of surface free energy

Chapter Four

Conclusions

Modified and unmodified PP/WP composites were used to investigate the influence of WP (filler) and MAPP (compatibilizer) on different properties of the composite material. Results from previous studies showed that WP particle size and content as well as compatibilizer are some of the factors influencing the properties of the composite material. In addition to these, preparation parameters e.g. temperature and pressure can play a significant role in changing the desired properties of the composite material. Due to the differences in polarity between the two components of the composites, the interfacial adhesion was found to be poor. As a result, the use of compatibilizers or surface modifiers was recommended.

In this work, the results were presented in graphs as well as in tables and they were fully discussed. The results point to the fact that WP is settled in the amorphous part of the matrix and create new crystalline phases/zones. SEM micrographs and POM photos show an even distribution of WP in the PP matrix, which contributed to improvements observed in the properties of the material. Different ratios of PP to WP, WP content, WP particle size as well as the presence of MAPP gave rise differing the surface roughness of the samples. It difficult to distinguish the components if the composites due to the homogeneity of the composite mixture.

Hg-porosimetry results indicate that the PP matrix, which has a low pore volume, was incorporated into the WP structure and filled the pores in the WP particles. This reduced the total volume of pores in the PP/WP composites. This observation was also supported by a general decrease in gas permeability of the material.

Thermal analysis results indicate that the presence of both WP and MAPP lead to an increase in enthalpy values of the composites, but also to a decrease in lamellar thickness in the composites containing MAPP. The thermal stability of the composite materials was also improved to a certain extent.

Surface free energy results were difficult to explain, and no solid conclusion could be drawn from these results. There is some indication of a possible reaction between the WP and MAPP functional groups, which leads to a reduction in the number of polar groups

For both unmodified and modified PP/WP composites, there were significant changes in the mechanical properties of the materials. An increase in modulus is a common behaviour for polymer/filler composites, since the fillers are said to have a high stiffness compared to the polymer matrix. Flexibility of polymer chain segments was restricted by the presence of WP and this was

indicated by a decrease in elongation at break. Even though MAPP was employed to enhance interfacial adhesion between the PP and WP in the composite material, it was seen to have a negative impact on the elongation at break of the composites.

There were, however, distinctive differences between the results for composites containing different WP particle sizes, as well as for composites prepared in the presence and absence of MAPP. It is clear from the results that the presence of MAPP generally improves the tensile properties of the composites, probably because of an interaction between the reactive groups in MAPP and WP. Generally the larger WP particles gave rise to better tensile properties, in the presence and absence of MAPP, probably because of better stress transfer between the WP particles and the PP and PP/MAPP matrices.

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