PROCESSING AND PROPERTIES OF NYLON 6 - POLYPROPYLENE BLENDS FROM RECYCLED TOOTHBRUSHES WITH A COMPATIBILIZER AND ADDITIVES

WEAWBOON MINGMAUNG

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หัวข้อวิทยานิพนธ์	กระบวนการขึ้นรูปและสมบัติของพอลิเมอร์ผสมไนลอน-6 และพอลิพรอพิลีนที่เหลือใช้ในแปรงสีฟันกับสารช่วยผสมและสารเติมแต่ง
นักศึกษา	นางสาวแววบุญ มิ่งเมือง
รหัสประจำตัว	40065100
ปริญญา	วิทยาศาสตรมหาบัณฑิต
สาขาวิชา	เคมีประยุกต์ (เทคโนโลยีพอลิเมอร์)
พ.ศ.	2543
อาจารย์ผู้ควบคุมวิทยานิพนธ์	ผศ.ดร.สมศักดิ์ วรมงคลชัย

บทคัดย่อ

งานวิจัยนี้ศึกษากระบวนการขึ้นรูปพอลิเมอร์ผสมระหว่างพอลิพรอพิลีนและไนลอน-6 จากแปรงสีฟันที่เหลือใช้ โดยอาศัยการผสมแบบสองลูกกลิ้ง แบบสกรูเดี่ยว และแบบสกรูคู่และศึกษาอิทธิพลของสารช่วยผสมและสารเติมแต่ง ที่มีต่อสมบัติเชิงกล สมบัติการไหล สมบัติทางความร้อนและสัณฐานวิทยาของพอลิเมอร์ผสม

พบว่าสภาวะที่ให้ชิ้นงานที่มีสมบัติเชิงกลดีที่สุดสำหรับเครื่องผสมสองลูกกลิ้งผสม คือที่อุณหภูมิ 250°C และเวลา 10 นาที สำหรับเครื่องผสมแบบสกรูเดี่ยวคือที่อุณหภูมิ 240°C และความเร็วรอบ 50 รอบต่อนาที และสำหรับเครื่องผสมแบบสกรูคู่ผสมที่อุณหภูมิ 230°C และความเร็วรอบ 50 รอบต่อนาที โดยที่เวลา อุณหภูมิ และความเร็วรอบที่ใช้ในการผสมมีอิทธิพลต่อสมบัติเชิงกลของพอลิเมอร์ผสม ส่วนปริมาณพอลิพรอพิลีนกราฟท์มาเลอิกแอนไฮดรายด์ (สารช่วยผสม) ที่เหมาะสมและให้สมบัติเชิงกลดีที่สุด คือ 5% โดยน้ำหนัก โดยที่เครื่องผสมแบบสกรูเดี่ยวให้ชิ้นงานที่มีสมบัติเชิงกลและสัณฐานวิทยาดีที่สุด พบว่าถ้าหากเติมแคลเซียมคาร์บอเนตมากเกินกว่า 1% โดยน้ำหนัก จะทำให้พอลิเมอร์ผสมมีสมบัติเชิงกลต่ำมาก ส่วนการเติมใยแก้วจะทำให้สมบัติเชิงกล และสัณฐานวิทยาดีขึ้น แต่ความหนืดและจุดหลอมเหลวของพอลิเมอร์ผสมที่เติมสารช่วยผสมจะมากขึ้นกว่าเดิมเนื่องจากเกิดพันธะเคมีขึ้นระหว่างพอลิเมอร์และสารช่วยผสม

Thesis Tittle	Processing and Properties of Polypropylene-Nylon 6 Blends from Recycled Toothbrushes with a Compatibilizer and Additives
Student	Miss Weawboon Mingmaung
Student ID.	40065100
Programme	Applied Chemistry (Polymer Technology)
Year	2000
Thesis Advisor	Ass. Prof. Dr. Somsak Woramongkolchai

ABSTRACT

This research studied processing of recycled blends from toothbrushes containing nylon-6 and polypropylene using two-roll mill, single-screw and twin-screw extruders. Also the research aimed to examine the influences of compatibilizer and additives on the mechanical, rheological, thermal and morphological properties of the blends.

It was found that the blends with the best mechanical properties were processed at 230°C and milling time of 10 min using two-roll mill, 240°C and 50 rpm using single-screw extruder and 230°C and 50 rpm using twin-screw extruder. Milling time, screw speed and mixing temperature had significant effects on mechanical properties. The 5% PP-g-MA (compatibilizer) gave superior mechanical properties of all blends. The results showed that compatibilized blends preparing with single-screw extruder had the best mechanical and morphological properties, compared to other techniques. The addition of calcium carbonate exceeded 1% by weight decreased the mechanical properties were decreased as the morphology of recycled blends were improved with glass fibers. The viscosity and melting point of compatibilized blends were greater than those of non-compatibilized blends because of the chemical bonding between the polymer and compatibilizer.

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Weawboon Mingmaung

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CHAPTER I

INTRODUCTION

1.1 Research Motivation

Of the 500 billion pounds per year of municipal solid waste, it is estimated that about 8% by weight (20 % by volume) is plastics [1]. Plastics impact the environment starting with raw material processing, parts manufacturing, post-consumer recycling, and eventually disposal.

Recycling efforts for post-consumer plastic waste have mostly concentrated on sortation, separation and reprocessing of polymer materials. The development of effective methods for the recycling of mixed-plastic waste has been very limited and in most cases the product is of such quality that is only suitable for low value or specialized applications for example, timber replacement. As a result of the rapidly developing compatibilization technologies for multi-component polymer blends, the production of value-added compounds from modified plastics waste does not appear unrealistic. Potential applications could possibly compete with those of virgin resins.

Finding appropriate markets for reclaimed plastic is one of the most difficult tasks for plastic recyclers. It is anticipated a continuous increase in legislated requirements for recycled resin level in packaging up to 25 % or more. Key factors to the success of recycled materials are their quality and relative price to those of the virgin resin. It is clear that federal and state legislation as well as the requirements of our environment will result in a sharp growth in recycling.

In recent years it has been much interested in the development of alloys based on engineering polymers such as polyamides. Although polypropylene and polyamide have excellent mutually compensating properties that are in great demand in the industry, they are inherently immiscible. Thus they must be blended with a compatibilizer in order to produce finished products with favorable mechanical, thermal, and rheological properties.

1.2 Objectives of the Research

In this research, we focus on processing and properties of nylon-6 and polypropylene blends from recycled toothbrushes with a compatibilizer and additives. Optimum processing conditions and the compatibilizer would be expected to improve the properties of recycled blends. The objectives of this research are:

1. to study the possibility of recycled toothbrushes in Thailand,
2. to study the effect of processing conditions on mechanical, thermal and morphological properties of the blends, and,
3. to study the effect of a compatibilizer and additives on mechanical, rheological, thermal and morphological properties of the blends.

1.3 Scopes of the Research

1. Study the optimum processing conditions of nylon-6 and polypropylene blends with two-roll mill, single-screw and twin-screw extruder.
2. Study the optimum quantity of a compatibilizer and additives of nylon-6 and polypropylene blends with two-roll mill, single-screw and twin-screw extruder.
3. Study the effect of a compatibilizer and additives on properties of polypropylene and nylon-6 blends with two-roll mill, single-screw and twin-screw extruder.

CHAPTER II

THEORETICAL CONSIDERATIONS AND LITERATURE REVIEW

2.1 Polymer Blends

2.1.1 Theory of Polymer Blends

Polymer blends are mixtures of at least two macromolecular species, i.e., polymers and/ or coplymers. For practical reasons, the name *blend* is given to a system only when the minor component content exceeds 2 % wt. Depending on the sign of the free energy of mixing, blends are either miscible or immiscible. The polymer/polymer miscibility is always limited to a "miscibility window" range of independent variables, such as composition, molecular weight, temperature, and pressure [2].

Morphology of immiscible blends depends on thermodynamics, interphase, and flow history. At high dilutions and low flow rates, the morphology of polymer blends is controlled by the three micro-rheological dimensionless parameters: (i) the viscosity ratio, $\lambda = \eta_1 / \eta_2$ where η_1 is the viscosity of the dispersed liquid and η_2 is that of the matrix; (ii) the capillary number, $K = \sigma_{12} d / \nu_{12}$, where σ_{12} , d , and ν_{12} are the shear stress, the initial drop diameter, and the interfacial tension coefficient, respectively; and (iii) the reduced time, $t^* = t\dot{\gamma} / K$, where $\dot{\gamma}$ is the deformation rate, and t is its duration [4]. Thus, for binary systems the interfacial and rheological properties are the keys for the morphological development in polymer blends and their performances.

Equilibrium-phase behavior of mixtures is governed by the free energy of mixing which consists of enthalpy (ΔH) and entropy (ΔS) parts, depending on composition and temperature (equation 2.1). For a miscible blend [3], ΔG_{mix} must be negative and satisfy the additional requirement which ensures stability against phase segregation (equation 2.2).

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \tag{2.1}$$

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial \phi_i^2}\right)_{T,P} > 0 \qquad (2.2)$$

The volume fraction ϕ_i of component i is employed here, but any other measurement of mixture concentration could be used. In Figure 2.1a, when T_1 more than T_2 so T_c is an upper critical solution temperature (UCST), whereas in Figure 2.1b, when T_2 more than T_1 so T_c is a lower critical solution temperature (LCST). These T - ϕ planes define the liquid-liquid phase diagram for a two-component mixture. More complex diagrams, including those with both a UCST and LCST, are possible [2]. The area dividing the single-phase and two-phase regions, for example, the locus of all points B and B', is called the binodal curve. The inflection points S and S' on the free-energy curve for T_2 define the spinodal curve, shown as S - S' lines on the T - ϕ planes. The critical point where the binodal and spinodal curves touch may not always lie at the extreme limit of the binodal. The binodal defines the equilibrium-phase behavior, whereas the spinodal is significant with respect to the mechanisms and kinetics of phase-separation processes. Figure 2.1(c) shows the dependence of the free energy of a mixture on composition at three temperatures. At T_1, the above two conditions are fully satisfied miscible and single-phase mixtures occur for all compositions at this temperature. At T_2, equation 2.2 is not satisfied for all compositions and mixtures between the points B and B ' separate into two phases with these compositions. This results in a total free energy falling on the dashed line. There is lower than that of the homogeneous phase (B - B' line). The curve for an intermediate temperature T_c has been drawn in a manner satisfying the conditions of a critical point at C [3].

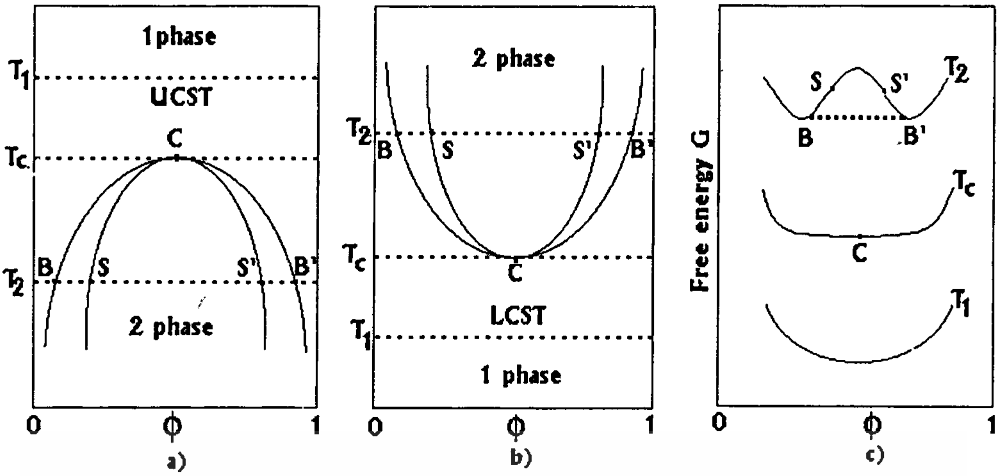

Figure 2.1 Phase diagrams for mixtures: (a) upper critical solution temperature (UCST); (b) lower critical solution temperature (LCST); (c) composition dependence of the free energy of the mixture (on an arbitrary scale) for temperatures above and below the critical value [3].

Under microscopic inspection, a miscible polymer blend consists of a single phase. On a molecular level, polymer-A molecules intermingle with polymer-B molecules, as shown in Figure 2.2 (a). Because a miscible polymer blend has only one phase, it is much like a random copolymer in properties and processing. In order to be miscible, some attractions between the two polymers must be present to overcome partially the intramolecular cohesive forces of the individual polymer. Interpolymer attractions result from specific interactions between functional groups on polymer A with different functional groups on polymer B. This condition, however, rarely occurs and only few polymer blends are totally miscible.

A second possible morphology for polymer blends is shown in Figure 2.2 (b), where polymer A forms a separating phase from polymer B. This is the morphology of an immiscible blend, which is far more common than the one-phase miscible blend. The polymer present in the lower concentration usually forms a discontinuous or discrete phase (domain), whereas the polymer presented in the higher concentration forms a continuous phase. Other factors, such as relative viscosity and blend-preparation procedure, also help to determine blend morphology.

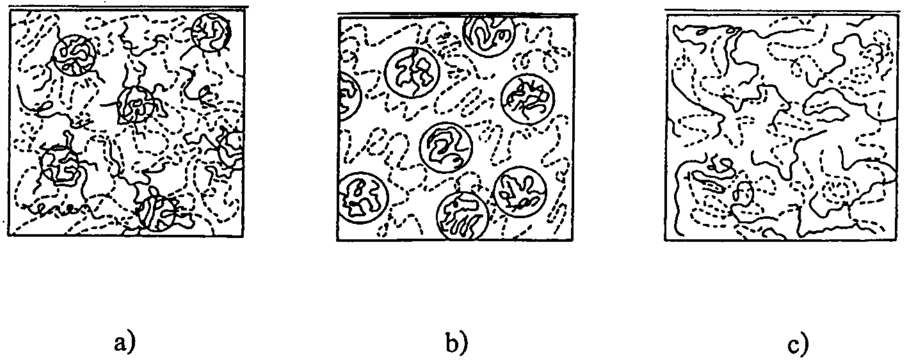

Figure 2.2 a) Miscible blend b) Immiscible blend and c) Partially miscible blend [3].

Frequently, a blend of two polymers is neither totally miscible nor totally immiscible, but falls somewhere in between. A blend of this type is partially miscible which may form completely miscible blends when either polymer is present in small amounts. However, as the ratios progress toward equality, the phases separate. At compositions where a partially miscible polymer blend is in two phases, the phases may not have a well-defined boundary since polymer-A molecules can significantly penetrate into the polymer-B phase and *vice-versa,* as depicted in Figure 2.2 (c). The molecular mixing that occurs at the interface of a partially miscible two-phase blend can stabilize the domains and improve interfacial adhesion which in turn explains why these two-phase blends generally have good bulk properties. The abundance of blends in this category and their good properties have made them perhaps the most common of the commercial blends.

To ascertain high performance of immiscible blends, usually compatibilizers are needed to be added. There are three aspects of compatibilization, i.e.,

(1) reduction of the interfacial tension, in which facilitates dispersion,

(2) stabilization of the morphology against changes during the following processing steps, and

(3) enhancement of adhesion between the phases, in which facilitates the stress transfer and hence improves the mechanical properties of the product.

There are two basic strategies of compatiblization, i.e., (i) addition of a compatibilizer and (ii) reactive compatibilization. Within the first category one may distinguish addition to 35 wt % of a multi-component ingredient. Usually, the first copolymer is specifically designed to have one part miscible with one polymeric phase and the other part with another polymeric phase. Furthermore, to ascertain stabilization effects on the generated morphology, the central part of copolymer is a random copolymer that creates a thicker interphase for better protection of the dispersed phase. The second type of additives is usually a general purpose compatibilizer and impact modifier. Most often, this is either a core-shell or multi-layered copolymer containing reactive groups attached to either elastomeric or rigid part. These materials are commonly based on acrylics and vinyls. In engineering and special resins blends may not have adequate thermal stability. The reactive compatibilization is designed to *in-situ* generate the desired quantity of either block or graft copolymers that forms chemical bonds across the interface.

It is to be expected that different compatibilization strategies generate different morphologies, hence different sets of the physical properties. For example, an addition of block copolymer may decrease the interfacial tension, but the system will remain sensitive to stress. An addition of a core-shell coplymer compatibilizer toughens the brittle and immiscible blends, but it may increase the thermal sensitivity.

2.1.2 Polymer Blend Characterization

2.1.2.1 Scanning Electron Microscopy (SEM)

Fine details of the microstructure can not be resolved by optical microscopy, but electron microscopy can resolve details smaller than 1 nm. Electro-optical imaging can be achieved in different ways. The electron beam is controlled by lenses consisting of magnetic fields. Rotational symmetric electromagnets focus the electron beam in the same way as convex lenses do in optical microscopes. The acceleration voltage used in scanning electron microscopes is considerably lower, typically about 15 kV. Scanning electron microscopy provides information about the topography of a specimen. The electrons that hit the surface of the specimen yield secondary electrons (used for the image), backscattered electrons (used for the image), Auger electrons (50-2000 eV) and X-ray radiation. The secondary electrons have relatively low energies, less than 50 eV, with an average value close to 4 eV. Polymer specimens to be examined by SEM are coated with a thin layer of electrically conductive material. The electrons which hit the specimen are partly scattered and subsequently recorded by the detector and partly conducted to the grounded electrode. The coating is achieved by vacuum evaporation or sputtering of a heavy metal (e.g. Au or Pd) or carbon. The specimen is often glued with an electrically conductive adhesive to a metal-base specimen holder to achieve good electrical contact with the grounded electrode [4].

2.1.2.2 Differential Scanning Calorimetry (DSC)

Thermal analysis of polymers is effectively done using the technique of differential scanning calorimetry (DSC). In general terms, this test method provides a measurement of some materials responded to a programmed change of temperature. The parameter monitored can be mass, dimension, or an optical or acoustical property of the material. The DSC provides a measure of heat capacity (C_p). This property is important to polymers because the processing history, or any mechanical and/or thermal treatment, essentially confers its own "fingerprint" on the arrangement of polymer chains in the final product. This implies that the energy of the system is unique. Hence the change or integral of C_p with respect to a well-defined reference state such as the molten polymer characterizes the prior history of the sample [5].

The directly measured quantity can be either a differential power or temperature between two cells, where one cell contains the polymer sample and the other a thermally inert reference. In the case of a differential power instrument, each cell has its own heater and the differential quantity measured is the difference between the power input that is needed to maintain the same programmed temperature in each cell. If the sample is at its melting point, T_m, for example, the sample heater output must increase significantly as heat of fusion is supplied. When the instrument is based on a differential temperature measurement, both cells are regulated by a common power source. The sample temperature will remain constant at ΔT until all the heat of fusion has been supplied. Since no such applies to the reference cell, the quantity $\Delta T = T_s - T_R$ becomes quite negative in this region. Figure 2.3 illustrates the differential signal for a sample undergoing phase change. Both differential power and temperature instrument signals are similar, however, for the latter the sign is opposite.

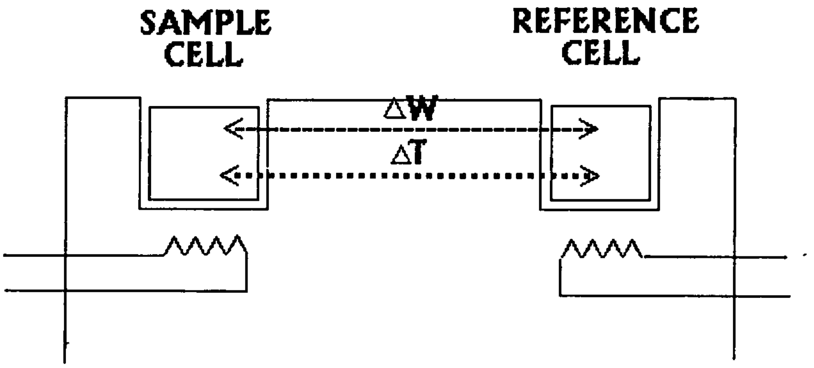

Figure 2.3 Operation of differential power (dashed line) and differential temperature (dotted line) differential scanning calorimetry [5].

Note that the abscissa of the signal response plot is either time or temperature. For all practical purposes the two are essentially synonymous. The signal from either type of DSC instrument is proportional to the difference in heat capacity between the sample cell and reference. Operation requires three experiments with the sample cell, which contains first an empty pan, the second, pan and sample, and the third, pan and calibrant. Throughout the experiment the reference cell is left undisturbed. DSC normally contains an empty pan, whose purpose is to balance roughly the effect of the pan in the sample cell.

2.2 Properties of Polymer Blends

2.2.1 Thermal Properties of Polymer Blends

2.2.1.1 Thermal Degradation and Stabilization [7]

The most important properties of polymers result from their high molecular weights. Grassea and Seotied [7] found that if the molecular weight was reduced by chain scission, important properties of polymers would be lost. During processing operations under considerable shearing of the polymer melt, the polymer chains can undergo homolytic scission at the carbon-carbon bonds with the formation of macro-alkyl radicals. Although this is not frequently encountered, the macro-alkyl radicals which are like to lower molecular weight radicals can initiate the radical chain reaction as shown by, equations 2.3 to 2.5.

$$R_2 \rightarrow R^{\bullet} + R^{\bullet} \qquad (2.3)$$

$$R^{\bullet} + O_2 \rightarrow 2\,ROO^{\bullet} \qquad (2.4)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (2.5)$$

2.2.1.2 Polymer Melting and Crystallization [8]

There are four main effects that have influence on the melting and crystallization of the polymers.

1). Effect of molecular weight on melting point

At a very high molecular weight, there is a tendency for the melting point to increase due to strains within the crystallites and their imperfections caused by chain entanglements and the high melt viscosity which impedes crystal growth. However, Khanna, *et.al.* [9] found that the crystallization temperature upon cooling from the molten state, T_C , changed only 1 oC per 10,000 change in the nylon-6 molecular weight. This was small compared to the changes in T_C values of variously processed nylon-6.

2) Effect of branching on melting point

Branching and the formation of network structures disrupt molecular order and chain regularity, thereby reducing both crystallinity and the melting point.

3) Effect of polymer-polymer blending on melting point

Polymers are rarely miscible with one another eventhough some crystallization occurs when two semi-crystalline polymers are mixed. In general, the crystal phases remain separate with the melting temperature of each component shifted slightly. In some blends which are partially miscible due to interaction occurring, such as the PC/PETP system, the transition temperatures of both components seem to merge into a single transition with heat treatment. But some are not compatible eventhough grafting has been incorporated, such as, in the system of PA6/EPM/EPM-g-SA and the PA6/EPDM system.

4) Effect of orientation on crystallinity

The polymer chains may be aligned during processing. Molecular orientation affects many properties. They depending on direction of flow. Orientation has a very large effect on both crystalline morphology and rates of crystallization. It induces nucleation growth along the flow line by shear or elongational stress. The nucleation growth occurs from these nuclei.

The melt crystallization behaviors of nylon-6 can be controlled by processing variables. The parameters such as thermal treatment, mechanical treatment, monomer and oligomer content, product homogeneity, moisture and additives are not responsible for the observed changes in crystallization bohavior upon processing.

Khanna, *et.al.* [9] found a big difference of 20 °C in the T_C of the virgin and extruded nylon-6. This change did not occur in a polyolefin system of different molecular weights, thus the drastic change in T_C in the nylon-6 should not be the result of disentanglement of the molecular chains. The following work [10] reported that the melt elasticity and melt viscosity of the virgin and extruded nylon-6 were similar. This confirmed that shearing did not obviously affect the disentanglement in the nylon-6. The intermolecular force, H-bonding was suggested to play a dominant role in molecular orientation of the nylon-6, thus high shear stress was required to overcome this bonding. It can be seen that the high shear stress processing systems, such as, solution precipitation, melt extrusion and freeze-grinding were subjected to this phenomena and again molecular arrangement was stabilized by H-bonding. A more ordered environment is responsible not only for the irreversible memory effect but also for the generation of nucleation centers so that a big difference in T_C from the origin nylon-6 were obtained.

The effect of processing history on crystallization rate of polymers depends on the degree of intermolecular forces, i.e. the polarity of polymer molecules. On the other hand, non-polar polymers were not influenced in terms of crystallization bohavior from the processing history.

2.2.1.3 Thermal Expansion and Contraction

When heat energy is applied to a polymer, it usually expands. The degree of expansion depends on polymer structure that causes the anisotropy in the system. There are four main factors that affect thermal expansion,i.e., crystallinity, crosslinking, fillers and orientation [8].

The level of crystallinity is an important variable affecting expansion and contraction which generally occur in the amorphous phase. Thereby, the higher the crystallinity, the lower the expansion and contraction of the material was observed [8]. The crosslinking effect reduced the expansion of the materials. It might be further reduced by the high thermal expansion and contraction by adding fillers: particulate and fibrous fillers. Oriented polymers would show an anisotropy in their expansion bohavior and this will be lower in the orientation direction. It is generally found that similar consideration applies to oriented crystalline plastics and to the shrinkage observed on crystallization.

2.2.2 Rheology of Polymer Blends [11]

Rheology can be defined as the science of the flow and deformation of materials. In polymer processing techniques must be studied in order to :

1) understand processing faults and defects,
2) select the best polymer or polymer compound, and
3) obtain information on molecular structure.

Rheological properties depend upon shear rate, temperature, polymer structure, molecular weight and molecular weight distribution.

2.2.2.1 Effect of Shear Rate and Temperature

The polymer melts have non-Newtonian behavior whereby the apparent viscosity (η_a) decreases as the rate of shear increases. Non–Newtonian behavior is of tremendously practical importance in polymer processing because [11]:

1) The decreased viscosity makes the molten polymer easier to process.

2) Increased shear rate results in an increase orientation in the melt and hence a greater potential for elastic recovery that leads to an increase in die swell.

The viscosities of polymer melts are influenced by the shear rate and temperature. Firstly, with increasing shear rate, the rate of chain orientation is higher than the rate of re-entanglement, and hence the number of chain entanglements decreases. Therefore, the viscosity decreases with increasing rate of shear as shown in Figure 2.4. Secondly, by increasing the temperature, the molecular energy and the thermal motion. The molecules have higher energy to overcome the forces that lead to entanglement. Hence, they may slide passed one another more easily. Consequently viscosity is lower as shown in Figure 2.5.

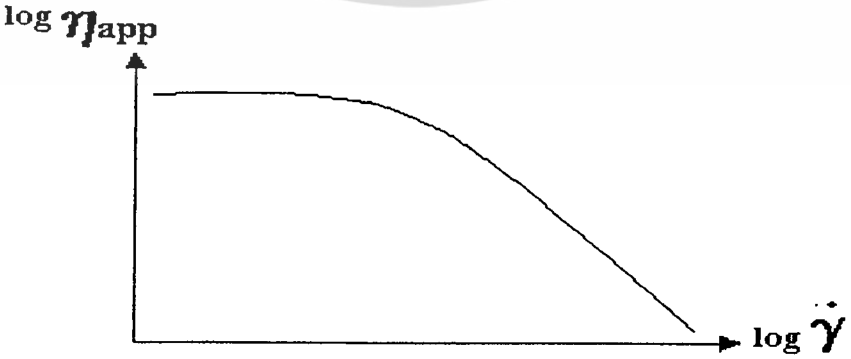

Figure 2.4 The variation of apparent viscosity with shear rate [11].

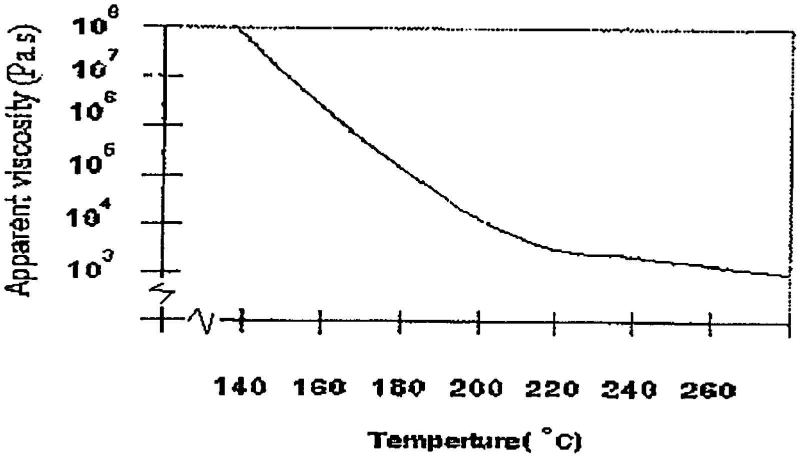

Figure 2.5 Temperature dependence of viscosity at low shear rate [11].

2.2.2.2 Effect of Molecular Weight [11]

Molecular weight $(\overline{M}_w)$ is the main factor that determines flow behavior of polymer. Melt viscosity becomes constant at low shear rates. The viscosity in this region is known as the zero shear, or Newtonian viscosity (η_o). For low molecular weight polymers in which chain entanglement is not a factor, the zero shear viscosity is directly proportional to the polymer's molecular weight. However, above a critical molecular weight, chains begin to entangle and the zero shear viscosity depends much more strongly on molecular weight, proportional to about the 3.4 power of the molecular weight [11].

2.2.2.3 Effect of Molecular Weight Distribution and Structure

Polymers with a broad molecular weight distribution tend to thin at lower shear rates than those with a narrow distribution at the same $\overline{M}_w$ [11]. Some important consequences of this are that molding and extrusion can be made easier by broadening of polymer molecular weight distribution. Polymer chain branches can vary in number, length, flexibility and distribution along the main chain. Increasing the number, the size, or the flexibility of the branches can change the melt viscosity but if the branches are few and long enough to entangle, melt viscosity will be higher at low shear rates.

2.2.3 Morphology of Polymer Blends

The morphology of the dispersed phase in immiscible polymer blends plays an important role in the determination of the final physical properties. Immiscible polymers form multiphase systems with deformable phases and consequently have wide ranges of sizes and shapes of the phases that are generated during processing. It is of fundamental importance to understand how a droplet of one polymer suspended in another polymer is deformed and broken up in a flow field. Several basic parameters have been reported to be important [11].

2.2.3.1 Effect of Shear Stress on Polymer Blends

Shi studied the deformation of liquid drops in flow fields [12]. The stretching action of the flow field is counteracted by the interfacial tension, which tries to restore the ellipsoid to sphere. In polymer melts, the elastic modulus may be the major factor in place of interfacial tension in resisting deformation. At high shear rates the drop deforms into a liquid cylinder and may breakup. Under equilibrium conditions, the deformation of the drop is given by equation 2.6, the orientation angle is in equation 2.7 and the capillary number is in equations 2.8 to 2.9, respectively. Figure 2.6 represents the deformation of a droplet of liquid in shear field.

$$D = (L-B) / (k/2) \, [\, (19\lambda+16) / (16\lambda+16) \,] \qquad (2.6)$$

$$\alpha = \pi/4 \qquad (2.7)$$

$$K = \sigma d/\nu_{12} \qquad (2.8)$$

$$\sigma = \eta_m \gamma \qquad (2.9)$$

Where D is the deformation of the drop

K is the capillary number

λ is the viscosity ratio

α is the orientation angle

L and B are the major and minor axes of the deformed droplet, respectively.

σ is the local shear stress

ν_{12} is the interfacial tension coefficient

γ is the shear rate

η_m is the shear viscosity of the matrix

d is the drop diameter

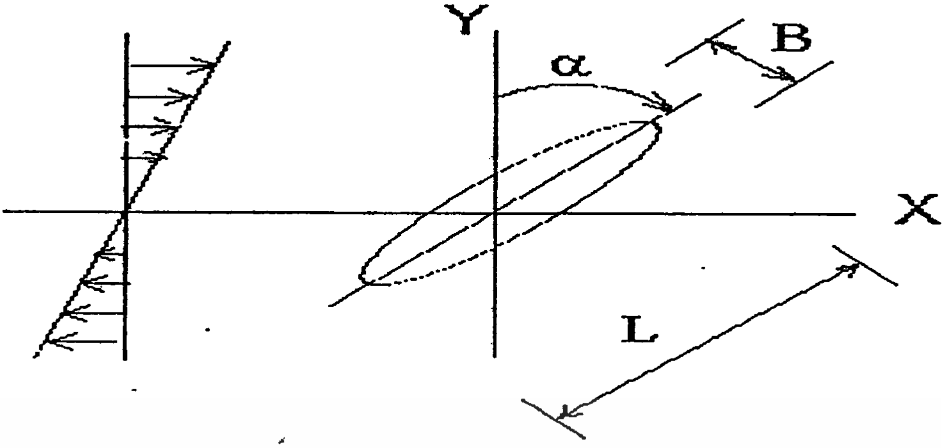

Figure 2.6 The deformation of a droplet of liquid in a shear field [12].

2.2.3.2 Effect of Viscosity and Interfacial Tension

The viscosity ratio has been shown to be one of the most important variables in controlling blend morphology [12]. Generally, a high viscosity ratio results in a coarse morphology, while matching the viscosity ($\lambda \approx 1$) results in a fine morphology.

$$\phi_1/\phi_2 = \eta_1/\eta_2 = \lambda \qquad (2.10)$$

Where ϕ_i and η_i are the volume fraction and shear viscosity of the component, respectively,

λ is the viscosity ratio,

1,2 is the dispersed and matrix phases, respectively.

Wu [13] showed that for polyamide/rubber systems, viscoelastic drops can break up during extrusion when the viscosity ratio, λ (viscosity of dispersed phase/viscosity of the matrix), is greater than 4. He suggested that as the viscosity ratio increased above unity or decreased below unity the dispersed particles became larger. He also found that the decrease in the dimensions of the minor phase of a chemically modified rubber system compared to the unmodified case was significant and was closely related to the decrease in the interfacial tension.

2.2.3.3 Effect of Droplet Coalescence

During mixing the dispersed phase progressively breaks down until a minimum drop diameter is reached. However there is operating mechanism that is the reverse of droplet break-up called coalescence. Coalescence occurs when two or more small dispersed phase particles collide and combine forming one larger particle. The coalescence may be accelerated by the same factors that favor droplet breakup, i.e. higher shear rate and reduced dispersed phase viscosity.

2.3 Technology of Recycled Plastics

World production of plastics has increased from 1 x 10^6 tons to 1000 x 10^6 tons over the last half-century. The current concern regarding the disposal of industrial and post consumer waste in diminishing landfill sites and the general impact of waste on the environment has drawn attention to developing effective reclaimation and recycling policies. The high visibility of waste products arising from plastic packaging which accounts for about 30% of total plastic consumption has contributed to the perception of plastics as a major environmental problem.

Therefore, the plastic industry, including resin suppliers, equipment manufacturers, processors, and distributors, must pay attention to this situation. The recycling of plastics is at an embryonic stage. Hence, the development of appropriate collection and separation infrastructures, recycling techniques, and markets for recycled products will be required in the future to meet the current recycling targets [14].

As both the industrial and municipal solid waste crisis worsen with further industrial growth and population expansion, new studies continue to demonstrate the adverse environmental impact of old-fashioned dumping methods and post consumer plastics must be recycled for transforming into useful applications. However, for the recycling of plastics to succeed, four distinct phases need to be considered: collection of post consumer plastics, sorting by type, reclaimation (recovery of material into salvaged and usable form), and end-use (a way for the recovered material to be used again).

Of the above four interrelated phases, from the technical viewpoint, reclaimation is the most important. In this regard, polymer blending technology holds bright promise because of the following factors [15]:

1. Blends are more economical to produce and generally have a lower technical risk than developing a new polymer or polymeric grade. They offer a cost-effective means to fill the gap in performance of existing materials.

2. Blends usually improve the critical properties required for end-use.

3. Blends often increase revenue/sales without major expenditure or capital investment.

4. Blends offer commodity plastic producers an easy way to enter the lucrative specialty segment of the business.

5. Waste plastic materials (both primary and secondary) may be turned into useful products by blending them with similar or different resins/plastics.

6. Polymer blending technology has the potential to produce plastics with various degrees of stability.

Despite the above advantages, if polymers (virgin or post consumer) are blended based on operational experience, but not following scientific study, both product qualities and effective recycling will suffer.

The plastic products found in municipal solid waste are primarily made by extrusion, blow molding, and injection molding processing techniques. Extrusion is used to produce plastic pipe, vinyl and other profiles. Blow molding is employed to make plastic detergents and beverage bottles and containers. Injection molding is used to manufacture caps, closures, and plastic pipe fittings.

Each of the above mentioned processes requires different melt flow characteristics. For example, high melt flow index resins are more suitable for injection molding while low melt flow index plastics are used for blow molding. Consequently, even if the same type of plastic (i.e., HDPE) is used to make the base cap for beverage bottles and for drinking water, the difference in their melt flow would require their separation for some recycling operations. Weak adhesion between phases of incompatible polymers results in blends with poor mechanical properties. For example, blends of PET and HDPE are difficult to process because their incompatibility results in severe die swelling and low melt strength during extrusion. Compatibilizers, impact modifiers and reinforcing agents are frequently used to improve mechanical properties of incompatible blends.

Material testing is of particular importance for recycled plastic materials due to the variability in their constitutions. Design specifications require that materials meet certain property requirements and designers often use manufacturer data as a guide. Due to the enormous cost of running testing facilities, most current recycling companies are unable to generate sufficient information about the properties of their reprocessed materials. This often precludes the use of these materials as their properties are not known, nor can they be guaranteed [16].

2.4 Toothbrushes

2.4.1 Polypropylene

Polypropylene is a high-volume commodity polymer processing characteristics of special materials and has a history of technical innovation. This polymer has numerous grades for specific end uses. Because of its inception, polypropylene usage has grown rapidly. A major advantage has been its versatility since it can be molded or extruded easily and it is easily oriented into high-strength films or fibers. There are four types [2]:

- Homopolymers are polymers of propylene only; (there properties were shown in Table 2.1).
- Random copolymers are polymers of propylene and small quantities of a comonomer, usually ethylene, inserted randomly throughout the PP chain;
- Impact copolymers are matrices of isotactic polymers of propylene with low-to-substantial amounts of olefin copolymer rubber, usually ethylene propylene rubber, formed in a later stage of the polymerization and dispersed within the matrix ;
- Filled and reinforced versions of the above.

Table 2.1 Properties of polypropylene homopolymers [2]

Properties	Standard	Unit	Value
Melt flow rate	ASTMD 1238	g/10 min	4
Flexural modulus	ASTM D 790	MPa (K Psi)	1720(250)
Izod impact	ASTM D 256	J/m (ft-lb/in)	43(0.8)
Heat deflection	ASTM D 648	deg °C	97
Hardness	ASTM D 2240	Rockwell R	99

2.4.2 Nylon-6

Nylons are semi-crystalline materials. They are the combination of ordered crystalline regions and more random amorphous areas. Nylon-6 having a much lower concentration of hydrogen bonding. This semi-crystalline structure gives rise to the good balance of properties. The crystalline regions contribute to the stiffness, strength, chemical resistance, creep resistance, temperature stability, and electrical properties. The amorphous areas contribute to the impact resistance and high elongation. The crystallinity can be disrupted by substituents on the chains that interfere with the alignment process.

The presence of the polar amide groups allows hydrogen bonding between the carbonyl and NH groups in adjacent sections of the polyamide chains. In particular, the relatively high tensile strength and stiffness, together with good toughness, high melting point (and therefore temperature stability) and good chemical resistance, all combin to allow a wide range of applications. The material soon comes to be seen as an engineering plastic that can be used for metal replacement in structural or semi-structural end uses [2]. Properties of the more common nylons are shown in Table 2.2.

Table 2.2 Properties of common nylons [2]

Properties	**Nylon-6**
Specific gravity	1.13
Water absorption, wt%	
- 24 h	1.6
- equilibrium at 50% reative humidity	2.7
- saturation	9.5
Melting point, °C	215
Tensile yield strength, Mpa	81
Elongation at break, %	50-150
Flexural modulus, Mpa	2800
Izod impact strength, J/m	55-65
Rockwell hardness, R scale	119
Deflection temperature under load, °C	
- at 0.5 Mpa	185
- at 1.8 Mpa	75
Dielectric strength, kV/mm	
- short time	17
- step by step	15
Dielectric constant	
- at 60 Hz	3.8
- at 10^3 Hz	3.7
- at 10^6 Hz	3.4

2.5 Additives

Additives are used in both thermosets and thermoplastics to change a performance of resin system, process, or cost parameters. A filler can be a simple resin extender low-cost bulk that does not have a debilitating effect on the properties needed for the application. Some phenolic compounds, for instance, include wood "flour" ground from hardwoods and crushed nut shells. Other fillers provide a measured improvement in the performance of the compound and/or finished part. For example, calcium carbonate improves the surface gloss of rigid PVCs and talc improves the heat deflection temperature of polypropylenes [16]. Both these fillers see widespread use because of their low cost and their abilities to be used at high filler loadings.

2.5.1 Calcium Carbonate Filler [17-18]

The stable form of calcium carbonate at an ordinary temperature is calcite (hexagonal), exemplified by limestone, chalk marble, iceland spar and onyx. Calcite is formed when crystallization occurs below 30°C. The other form, aragonite polymorph (orthorhombic), is rare and metastable at low temperatures.

2.5.1.1 Manufacture

Calcium carbonate filler is produced by either chemical methods or the mechanical treatment of the natural varieties of calcium carbonate, such as limestone and chalk. Precipitated calcium carbonate is distinguished by a finer, more uniform particle size, a narrower size range 0.03 to 15 μm and higher degree of chemical purity. It occurs in both calcitic and aragonitic form by control of temperature, rate of precipitation and concentrations of the reactants.

Three common methods for manufacturing precipitated calcium carbonate are the by-product process, the calcium chloride process and the carbonation process. The carbonation is commercially used today because it is the simplest and most direct process using the most readily available and lowest cost raw materials. The production uses the following procedure. The carbon dioxide that is driven off during calcination of the limestone is replaced by the reaction of calcium carbonate with the milk of lime suspension, until neutrality is reached. The equation for reaction is shown in equation 2.11 to 2.13.

$$CaCO_3 \xrightarrow{\Delta\ 900\,^{\circ}C} CaO + CO_2 \qquad (2.11)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (2.12)$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (2.13)$$

2.5.1.2 Chemical Properties

The main chemical reactions of calcium carbonate are:

1) Calcium carbonate is slightly soluble in water, it dissolves in water that contains carbon dioxide; the latter converts the carbonate to the soluble bicarbonate, equation 2.14

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2 \qquad (2.14)$$

2) Carbon dioxide is evolved when heated or reacted with acids, equation 2.15 to 2.17

$$CaCO_3 \xrightarrow{\Delta\, 900\,^{\circ}C} CaO + CO_2 \qquad (2.15)$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O \qquad (2.16)$$

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2 \qquad (2.17)$$

3) In nature dissolved calcium tends to combine with carbon dioxide from the air and precipitate as calcium carbonate. The typical chemical compositions of purified calcium carbonate are shown in equation 2.18 and Table 2.3.

$$Ca^{2+} + H_2O + CO_2 \longrightarrow CaCO_3 + 2H^{+} \qquad (2.18)$$

Table 2.3 The typical chemical compositions of purified calcium carbonate [19]

Chemical Compositions	Percentage (%)
$CaCO_3$	98.20
$MgCO_3$	1.20
SiO_2	0.25
Al_2O_3	0.12
Fe_2O_3	0.06
H_2O	0.10
Cu	None
Heavy metal	< 20 ppm

Formula weight : 100.09

2.5.1.3 Physical Properties

The important physical properties of three forms of calcium carbonate are shown in Table 2.4

Table 2.4 Physical properties of calcium carbonate [17]

Physical properties	**Calcite**	**Aragonite**	**Dolomite**
Formula	$CaCO_3$ Most stable form	$CaCO_3$ Converts to Calcite	$CaCO_3$- $MgCO_3$ (45% $MgCO_3$ by weight)
Specific gravity	2.60-2.75	2.92-2.94	2.80-2.90
Hardness (Mohr)	3.0	3.50-4.0	3.5-4.0
Solubility (grams in100 parts water at 18°C)	0.0013	0.0019	0.032
Decomposition Temperature (°C)	900 (Melting at 1339°C at 1025 atm)	825 (to calcite> 400°C)	730-760
Formation temperature (°C)	Below 30°C	Above 30°C	-
Formation	Limestone, marble, chalk, eggshells	Shell of molluska and corals	-

2.5.2 Glass Fibers

2.5.2.1 Types and Forms of Glass Fibers

A number of glass compositions are commonly used for the production of glass fibers. The most important one is E-glass, whereas for special applications other compositions can be used. Where higher mechanical performance is required R- or S-glass can be used. For acid and alkali resistance ECR and AR glasses can be used respectively. C-glass is also available for chemically resistant general purpose (GRP). However, it is generally only available as a veil for the reinforcement of a lining on a structural composite manufactured from E-glass or ECR continuous fibers roving. Some typical glass compositions for fibers drawing are given in Table 2.5.

The fibers are drawn form a bushing below a molten glass reservoir and immediately cooled in a spray of water. Since the presence of surface defects largely determines the strength of glass fibers, the fibers are immediately coated with a protective aqueous size solution [19].

Table 2.5 Typical compositions and properties of various glasses used for fiber formation [19]

				Composition (wt%)			
	A	C	E	ECR	R	S	AR
SiO_2	72.0	64.6	52.4	58.4	60.0	64.4	61.0
Al_2O_3	1.2	4.1	14.0	11.0	25.0	25.0	0.5
CaO	10.0	13.4	17.2	22.0	9.0	-	5.0
MgO	25	3.3	4.6	2.2	6.0	10.3	0.05
Na_2O, K_2O, Li_2O	14.2	9.6	0.8	0.9	-	-	14.0
B_2O_3	-	4.7	10.6	0.09	-	-	-
BaO	-	0.9	-	-	-	-	-
ZnO	-	-	-	3.0	-	-	-
ZrO_2	-	-	-	-	-	-	13.0
TiO_2	-	-	-	2.1	-	-	5.5
Fe_2O_3	0.3	-	0.4	0.26	-	-	0.5
Specific gravity	2.45	2.45	2.56	2.6	2.58	2.49	2.74
Refractive index	1.512	1.520	1.548	-	-	1.523	1.56
Single fibers tensile strength (GPa)	3.1	-	3.6	3.4	4.4	4.5	2.5
Single fibers tensile modulus (GPa)	72.0	-	76.0	73.0	85.0	86.0	80.0
Softening point (°C)	700	690	850	900	990	1000	860

The size whose composition is the most commercially sensitive aspect of glass fibers manufacture, is applied by rubber roller before the fibers are wound up on to a bobbin to form a strand. The size or finish is crucial to the handleability of the fibers and their compatibility with matrix resins. This aspect is examined in detail in the following article [19].

A strand consists of a number of tows. A tow is the unitary element which represents the number of fibers drawn from a single bushing, typically 200. An assembley of strands is called a roving. In new plants, this process occurs at the bushing and the products, called direct rovings, are used in applications where the incidence of a twist in the roving can be significant. Otherwise, the strands are assembled into rovings in a separate process. A slight twist is incorporated into the roving to improve its handleability. For continuous fibers composites, the selection of conventional of direct rovings depends on the nature of the fabrication process and the degree of perfection required in the fibers alignment. The number of filaments in a roving is defined by the tex, typically 600, 1200, 2400, etc. (1 tex is equal to g/1000 m). Other textile processes are used to prepare woven rovings with differing texture. These cloths offer convenience of drape and multidirectional in-plane reinforcement. The rovings can also be chopped and deposited randomly to produce chopped strand mat (CSM), held together by an additional polymer binder. The binder is chosen to provide controlled wet out during resin impregnation so that the random orientation of the discontinuous fibers can be maintained. Furthermore, the binder should be selected to suit the application of the material. For example, the environmental durability of CSM based GRP can be strongly affected and for chemical resistance powder bound mat rather than general purpose emulsion bound mat should be chosen.

Continuous random mats (CRM) are also available in which continuous rather than chopped fibers in a random form is bound into a mat with superior drape, i.e. ability to be layed onto a curved mould without serious fibres distortion.

Chopped fibers at different lengths are also available for incorporation directly into molding granules and compounds. The chopped fibers length tends to be significantly longer for CSM (at >20 mm) than those incorporated in molding materials. Furthermore, the fibers are generally longer for dough molding compounds (DMC) compared to molding granules. Apart from the differing consistencies and processing requirements, the fibers in thermosetting materials are generally longer than those incorporated into thermoplastics. Textile processing has recently become more popular for the production of three-dimensional reinforcements for using in structural reaction injection molding (RIM) and resin transfer molding (RTM).

2.5.2.2 Glass Fiber Manufacturing

There are several basic methods employed for obtaining glass fibers from hot melts to yield products which have some role in reinforcing plastics. These include:

-- continuous filament fibers;

-- staple fibers;

-- blown fibers for mats;

-- mechanically drawn fibers for mats.

Continuous filament glass fibers are usually produced by a marble melt process or a direct melt process. The marble process is the older one and in this technology glass is melted in a separate furnace and formed into marbles, which are partially annealed and graded. Then they are fed into heated platinum bushings, where they are remelted and transformed into filaments, being drawn away rapidly at speeds approaching 4000 m/min. There is nothing magical about marbles, except that they are easily formed mechanically and roll by gravity through grading and feeding contrivances.

As technology improved, the remelting step was superseded by installing in-line fibers-producing bushings in the appropriately designed forehearths of a glass tank furnace and the process known as direct melt glass fibers production evolved. Figures 2.8 and 2.9 illustrate, schematically, the marble melt and direct melt processes, respectively.

Whereas marble bushings were originally capable of 3-4 kg/h, production from larger direct melt bushings may now approach 45 kg/h. Continuous glass filaments produced commercially range from 2-3 μm to 25 μm in individual fibers diameters. Marble processes are still utilized, being more satisfactory for fabrication of finer filaments. They also permit use of glass marbles and the quality and production efficiency of which have been predetermined and thus poor or undesirable glass can be eliminated.

The direct melt process is preferred because it eliminates the remelting step necessary in marble melt, but by comparison, marble bushings obviously favor easy changes to glasses of different composition. The fineness of a continuous filament is expressed in a special unit known as denier, or strand length to weight relationship, hence filament diameter is determined by the following [20]:

- glass composition;
- viscosity of the melted glass;
- number of tips or filaments;
- drawing temperature;
- efficiency of cooling;
- winding speed.

For processing composites, glass fibers have to undergo some special treatments. They are treated with two distinct and separate classes of sizing materials:

(a) A starch-oil emulsion type which has humectant properties, absorbing water to provide lubrication plus resistance to abrasion ;

(b) A plastic emulsion cross-link type of sizing, generally for direct use in composites.

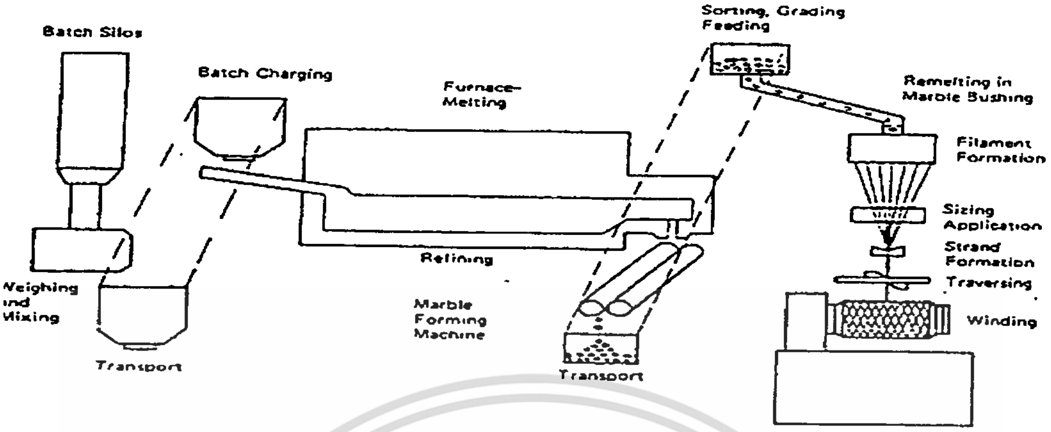

Figure 2.7 Schematic diagram of marble process [20].

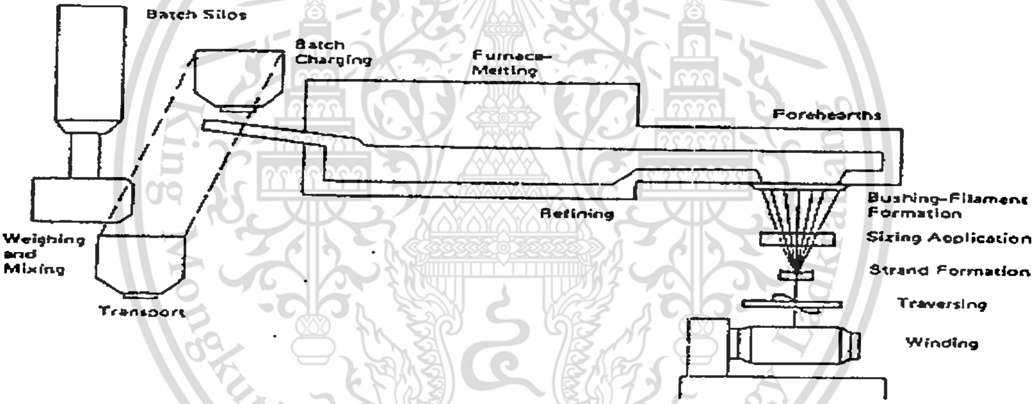

Figure 2.8 Schematic diagram of direct melt process [20].

2.5.3 Requirement of Fillers

The main requirements for the properties of fillers and reinforcements are [21]:

1) Low moisture absorption and high bulk density. They should preserve their properties during storage prior to compounding;

2) Wettability by the polymer;

3) Fillers particles should have low surface energy and absorptivity, assuring low viscosity during compounding;

4) A high compounding speed is obtained with fillers having low specific heat and high capacity for thermal conductivity.

2.5.4 Advantages and Disadvantages of Fillers

The advantages of filled compounds are:

-Improved heat distortion temperature,

-Increased modulus,

-Reduced molding shrinkage,

-Increased tensile strength,

-Cost reduction.

The disadvantages of filled compounds are:

-Reduced resin stability,

-Increased matrix voiding,

-Often decreased impact,

-Opaque product,

-Increased moisture uptake.

2.5.5 Effects of Fillers on Processing

The term 'agglomeration' describes the binding together of small particles to form a larger body. Agglomeration is undesirable because it leads to points of weakness in the finished material. Efficient mixing involves size reduction (dispersive mixing) followed by distribution of the fragments (distributive mixing). The break-up of the dispersed phase involves stresses at the interface acting against various cohesive forces, depending on the type of agglomerated filler. The factors influencing dispersive mixing in mineral filled thermoplastics are shown in Figure 2.9.

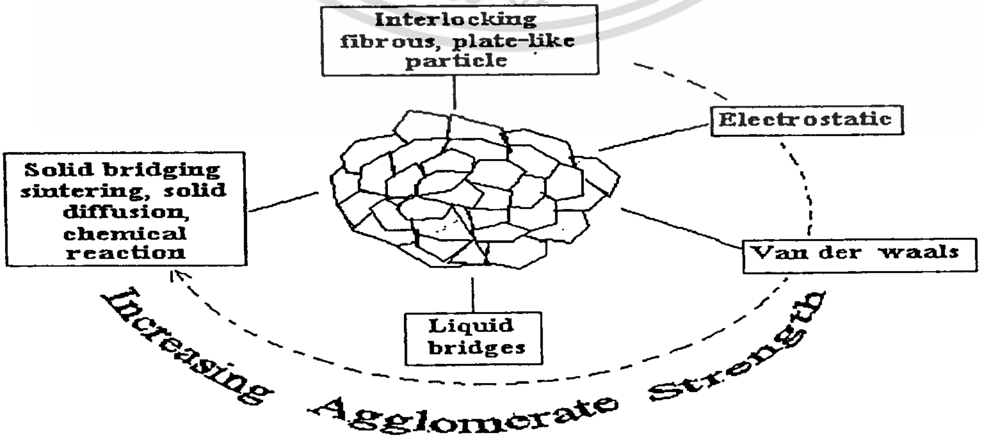

Figure 2.9 Principle adhesion force in agglomeration of filler [21].

Several mechanisms of bonding may occur in inorganic powders.

1) Electrostatic forces originating from accumulated charges, which tend to be greater in non-conducting than conducting fillers.

2) Van der Waals forces which originate from fluctuating dipoles existing in materials, are one order of magnitude greater than electrostatic forces.

3) Liquid-bridging forces are generally about four times larger than Van der Waals forces and will occur in most agglomerates at a level dependent on the degree of liquid saturation in the total pore volume of the agglomerate.

4) Solid bridges can be formed between particles on crystallizing from solution or by sintering, resulting in extremely strong interactive forces.

2.5.6 Effects of Fillers on Viscosity

2.5.6.1 Effects of Filler Types

All filled systems exhibit higher viscosities than pure polymers at all shear rates. Bhagawan et. al. [21] studied the effects of fillers on the rheological behavior of thermoplastic 1,2 polybutadiene rubber (PBD) through capillary rheometry. They reported that among the filled systems, silica filled 1,2 PBD shows the highest viscosity at all shear rates and clay shows the lowest. Carbon black filled 1,2 PBD exhibits intermediate values at all shear rates, as shown in Figure 2.10.

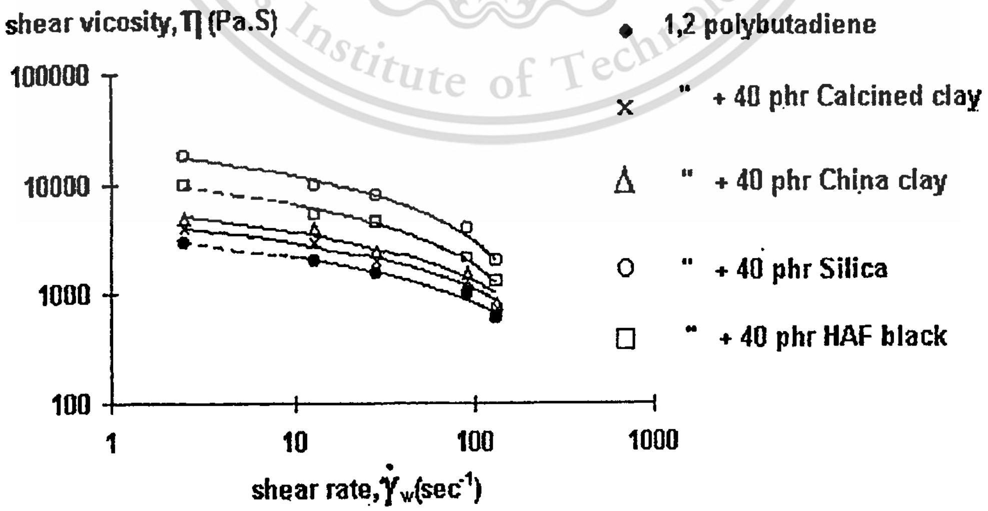

Figure 2.10 Viscosity-shear rate plots showing the effect of filler on 1,2 polybutadiene at 150 °C [22].

Interestingly, at very high shear rates all these systems posses merely the same viscosity. This implied that at high rates of shear the particles are oriented in the direction of flow, resulting in lower viscosity.

2.5.6.2 Effects of Filler Loading

The viscosity increases with increasing filler loading in all cases due to the flow being more restricted. The concentration effect on the viscosity of dispersed particulate systems is defined by Einstein's equation 2.19 [23]:

$$\eta = \eta_1 (1+K_E\phi) \tag{2.19}$$

where K_E is the Einstein coefficient which depends on aspect ratio and degree of agglomeration,

ϕ is the filler volume fraction,

η and η_1 are the viscosities of the compound and matrix, respectively.

The Einstein equation is valid only at very low concentrations. However at higher concentrations, the Mooney equation [23] seems to give a good fit to the real data as shown in equation 2.20.

$$\ln(\eta/\eta_1) = \frac{K_E\phi}{1-\phi/\phi_m} \tag{2.20}$$

where ϕ_m is the maximum packing fraction given by equation 2.21

$$\phi_m = \frac{\text{true volume of filler}}{\text{apparent volume of filler}} \tag{2.21}$$

2.5.7 Effects of Fillers on Mechanical Properties

Many mineral fillers are used in various polymer systems to enhance physical or mechanical properties. There numbers of scientific literature showing the effects of fillers on polymer properties [24]. Mechanical properties of filled polymers are indeed dependent on some parameters, i.e., matrix properties, particle characteristics (nature, size, shape, and size distribution), constituent volume fraction and matrix-filler interaction.

2.5.7.1 Modulus

The higher contents of fillers in the sample leads to an increase in the initial tangent modulus. Figure 2.11 shows the stress-strain curve for an uncoated calcium carbonate filled polypropylene and it can be seen that the modulus increases with filler loading.

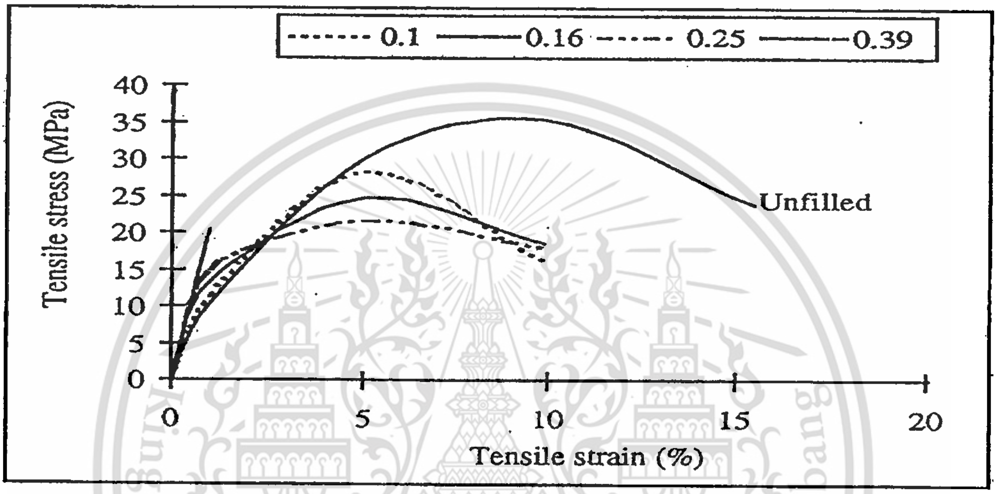

Figure 2.11 Typical stress-strain curve for uncoated calcium carbonate filled polypropylene and calcium carbonate concentration [25].

Yilmazen and Farris [26] examined the behavior of polyurethane filled with glass beads. They found that the higher the filler loading, the greater the modulus of the sample. The effects of fillers on modulus have been modeled with the modified Kerner and Nielsen equations 2.22-2.25.

$$\frac{E_c}{E_m} = \frac{(1+ABV_f)}{(1-B\Psi V_f)} \tag{2.22}$$

In this equation,

$$A = K_E - 1\ ; \tag{2.23}$$

$$\Psi = \frac{1+(1-P_f)V}{(V_f)^2} \tag{2.24}$$

$$B = \frac{(E_f/E_m)-1}{(E_f/E_m)+A} \quad , \tag{2.25}$$

where E_c and E_m are moduli of the composite and matrix, respectively,

K_E is the Einstein coefficient accounts for the shape of the filler particles and possion's ratio of the matrix,

P_f is the maximum packing fraction of the filler by volume,

V_f is the filler volume fraction.

The shape of the particles, especially high aspect ratio, influences the modulus but may cause stress concentration in the region of their sharp edges, which will facilitate failure under impact conditions.

2.5.7.2 Tensile strength

Tensile yield stress (σ_{yc}) depends on the filler content and mechanical properties of the filler constituents, shape and space packing of the filler particles, and the degree of interfacial adhesion. The tensile yield stress of compounds is generally reduced with increasing filler volume fraction [25]. Filler reduces the effective cross sectional area of the matrix and hence reduces its load bearing capacity. This leads to an increase in internal stress, at any given external loading, compared with the unfilled matrix. Stress concentrations caused by the filler also contribute to the internal stress. Microvoid deformations occur around particles facilitates damage of the material at lower external load, compared with the unfilled matrix. The theory of Niclolais and Nicodemo [27] predicted the following relationship.

$$\sigma_c = \sigma_m (1 - a\phi^b) \tag{2.26}$$

where ϕ is the volume fraction of filler,

σ_c and σ_m are the filled composite and the matrix strength, respectively,

a is related to stress concentrations,

b is related to geometry of the filler.

Rigid fillers in polymer matrices generally decrease the impact resistance of the polymer by dewetting and crazing phenomena as displayed in Figure 2.12. A tensile stress produces a type of stress concentration that results in dewetting and cavitation at the poles of a spherical particle. With dewetting, a change in stress concentration takes place that leads to crack or craze formation at the equator of the particle.

where G_1 = shear modulus of polymer matrix

G_2 = shear modulus of rigid filler

σ_o = shearing force

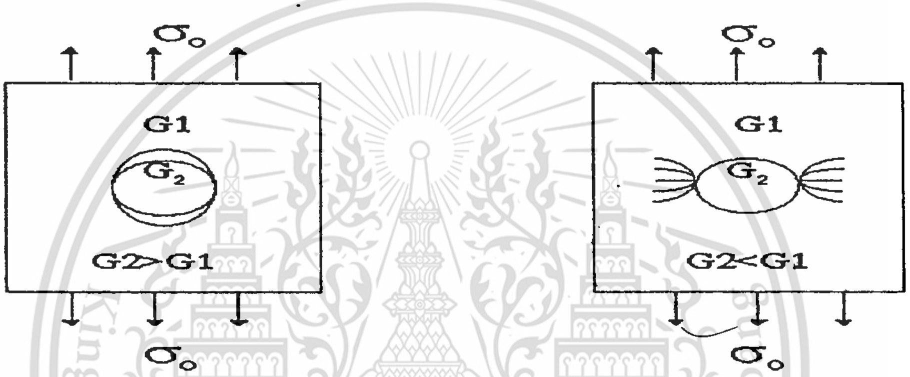

Figure 2.12 (Left) Dewetting of a rigid filler particle in a matrix of lower modulus. (Right) Crazing of polymer around of filler particle (or void) when the matrix has higher modulus than the filler particle [28].

2.5.7.3 Impact Strength

The higher contents of filler in the sample lead to a decrease in impact strength. The mechanical properties of filled polymers depend strongly on the effect of crystallization. The filler particle acts as nucleating agent that induces crystallization in the matrix. Good bonding between filler and matrix inhibits the plastic flow of the ductile matrix so the fracture energy of filled polymers are less than that of the unfilled polymers. Furthermore, the agglomeration of filler may affect the impact strength. Extensive agglomeration leads to insufficient homogeneity and lower impact strength. Agglomerated filler particles act as crack initiation sites in impact specimens. The impact resistance increases with decreasing particle size because large size particle acts as flaw. The large aspect ratio of the filler results in increased stress concentration.

2.6 Processing Technology

2.6.1 Two - Roll Mill

The two-roll mill consists of two opposite rotating parallel rollers placed close to one another with the roll axes lying in a horizontal plane, so that a relatively small space or nip between the cylindrical surfaces exists. Material reaching the nip is deformed by friction forces between itself and the rollers flowing through the nip in the direction of roll motion (Figure 2.13). Liquid plasticizers or finely divided solid ingredients also are placed in the nip and are incorporated into the resin through shearing action. Strip cutters are used to cut ribbons of stock from the roll for feeding to a cooling tank and dicer.

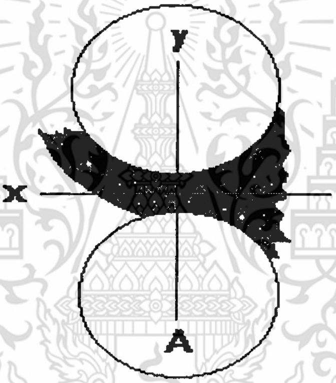

Figure 2.13 The rotation of two-roll mill. (Rolls act on thin, flowing wedge of material simultaneously compressed and forced to flow through the roll nip. Rolls rotate in opposite directions. Material leaving the nip adheres to either roll if rolls rotate at equal speeds) [29].

The two-roll mill operation is essentially a process involving laminar flow with heat transfer in a roll system. Typical outputs include desired roll dimensions, roll speeds, separation of rolls, temperature profiles in the processed material, roll-suspension force and required power. The apparent shear rate is given by:

$$\gamma^{\bullet} = \frac{4Q}{\pi R^3} = \frac{2U}{h_0} \qquad (2.27)$$

where $\gamma^{\bullet}$ is the apparent shear rate, **Q** is the volumetric calendering rate, **R** is the calendering roll radius, **U** is the operating speed of the roll and h_0 is the roll separation.

Usually, by adjusting the roll temperature the compound can be made to adhere to one of the rolls as a relatively thin sheet. The rolls are heated or cooled by a heating or cooling medium introduced into their hollow cores. They are usually rotated at different speeds to facilitate the formation of a sheet or band on one of them. During mixing, the band frequently is cut and manually pulled loose from the roller. The gap between the rollers generally may be adjusted manually by means of hand-driven or motor-driven screws. [29]

Roll mills vary greatly in size from very small laboratory machines with rollers about 1 inch in diameter and driven by fractional-horsepower motors to very large mills with rollers nearly 3 feet in diameter and 7 or 8 feet in length and driven by motors of over 100 hp.

Special-purpose roll mills are available with three, four, or five rolls, in which the material is caused to pass from one nip to the next, in succession. Likewise, rolls may be arranged in pairs within a single frame, each independently adjustable in clearance. Material is led through the various pairs in tandem in a cascade arrangement for continuous mixing.

2.6.2 Single-Screw Extruder

The single-screw extruder is the ideal multi-purpose equipment for polymer processing [30]. The basic function of this type of extruder is to accept material in the feed section of the screw and convey this material along a flighted screw enclosed in a barrel. The conveying is forced by the rotation of the screw via a drive motor and gear reducer. The material usually must be melted (plasticated) along the path through the extruder screw. The melting of the polymer is aided by heaters that tightly encapsulate the barrel's outside diameter and are seperated on the barrel into zones. These zones can be set at different temperatures as appropriate for the particular process involved. The screw must develop enough pumping efficiency to force material through the die system. Typically the die pressure levels encountered are in the 14 to 34 MPa range [31].

As solid material is conveyed from the feed throat and traveled through the feed section of the screw, some compactions take place. When they reach the heated barrel, melt film immediately forms on the barrel inner diameter. The melt film grows in thickness as the material moves down the barrel until it is thicker than the screw flight clearance with the barrel. Then the melt begins to collect at the rear of the screw channel. As the melt film goes through this thickness growth, transporting forces are developed by the shearing of the melt fim. This conveying mechanism is termed viscous drag. The shearing of the melt film creates most of energy for melting of the material at moderate to high screw speeds. The higher the viscosity of the melted material, the more heat is generated via melt film shearing [31].

Pumping of the material against the die resistance can begin back near the screw's feed section, especially when the die pressure levels are high. Melting starts early on the screw in most cases and pressurization of the melt can begin there. In actuality the three basic functions of the extruder solids conveying, melting, pumping cannot be separated into three discrete regions along the extruder. The functions intermesh so strongly that they all must be studied together. As the material advances down the screw toward the die, more melt is present. The prediction of the pumping capacity of simple metering section against no die resistance (drag flow) and the output-reducing tendencies of the die resistance (pressure flow) is given by:

$$Q = AN - \frac{B\Delta P}{\eta} \tag{2.28}$$

$$Q = \frac{\pi^2 D^2 h \sin\phi \cos\phi}{2t} N - \frac{\pi D h^3 \sin^2}{12L} \frac{\phi\Delta P}{\eta} \tag{2.29}$$

where Q is the net volume rate of discharge, N is the screw speed, ΔP is the extruder head pressure, n the apparent viscosity of material in the metering section, A and B are screw characteristics, D is the diameter of the screw, h is the depth of the metering channel, ϕ is the screw helix angle, L is the length of the metering zone and t is the screw lead ($t = \pi D\tan\phi$). This estimation of the output pumping of a screw is applied to the shallowest section of the screw because the region that limits the screw's output [31].

When the melt moves in a direction parallel to fixed surface, such as the extruder barrel, or die wall, it is subject to a shearing force. As the screw speed increases, so does the shear rate. The shear rate in the metering zone is approximated by:

$$\dot{\gamma} = \frac{\pi DN}{h} \tag{2.30}$$

Since single-screw extruders generally provide poor mixing, mixing elements are often added to the screws. These are usually divided into three categories: distributive, dispersive and static mixing elements. Distributive and static mixing elements interrupt the laminar flow and divide the melt stream into many partial streams whereas dispersive elements break up agglomerates and shear unmelted resin particles. However, all three types of elements tend to increase the pressure inside the extruder. They may trap polymer in the mixing section.

Static mixing devices are added to the end of the screw (just prior to the die) Consequently, pressure flow is responsible for their throughput. However, these elements produce high pressure drops and require relatively fluid melts or the addition of pressure generating devices such as gear pumps.

2.6.3 Twin-Screw Extruder

Twin-screw extruders consist of two parallel screws in a single barrel. The screws can rotate in the same direction (co-rotating) or opposite to each other (counter-rotating). In addition the flights and channels of the screws may mesh or be separated. In contrast, intermeshing twin screws have flights with similar sizes and shapes that fit snugly in the other screw's channel with negligible clearance while partially intermeshing screws fit loosely together and provide greater clearance between the screws [32].

Non-intermeshing twin-screw extruders are similar to single-screw extruders and the polymer is conveyed by (viscous) drag flow. Thus, output and head pressure increase with screw speed and the output can be determined by Equation 2.31. However, with fully and partially intermeshing twin-screw extruders, the polymer is transferred from the channel of one screw to the next channel of the other screw. Since the extruders are usually starve fed, output is determined by the feeding rate and screw speed.

In counter-rotating intermeshing twin-screw extruders, the polymer travels in a narrow channel between the two screws. Although there are some leakages flowing back down the channel, positive conveyance provides the forward movement of the polymer. Thus, the output (Q) for a counter-rotating intermeshing twin-screw extruder is estimated from:

$$Q = 2iNV_c = 2iN \frac{\pi DhW}{\cos\phi} \tag{2.31}$$

where i is the number of thread starts, N is the screw speed, V is the volume of the "C chamber" which is the polymer-filled area between the two screws, D is the average screw diameter, h is the polymer chamber depth, W is the channel width and ϕ is the helix angle. Since the chamber is never filled, shear is minimal and heating is by conduction from the barrel walls. This allows the shear rate to be approximated by:

$$\gamma^{\bullet} = \frac{\pi DN}{h} \tag{2.32}$$

With co-rotating intermeshing twin-screw extruders, the polymer follows a "figure-8" path around the two screws. Since portions of this path are filled with polymer, viscous drag is the primary means of conveyance. However, other sections of the "figure-8" contain no polymer. Thus, the output of a co-rotating intermeshing twin-screw extruder may be approximated by [33]:

$$\mathbf{Q = \phi AN,} \tag{2.33}$$

where ϕ is the degree of fill for the screw, A is the screw characteristic and N is the screw speed. Shear is controlled by screw speed and feed rate.

Unlike single screws, twin screws usually consist of two rods which small elements are placed. Thus, twin screws can be programmed to vary conveying efficiency, throughput rate, mixing and shear. This permits tighter control of shear.

Co-rotating screws (intermeshing or not) are primarily used for compounding and mixing because of their ability to disperse additives, such as carbon black which have very small particle sizes. Counter-rotating and fully intermeshing flight extruders are used primarily for low-shear extrusion of polymers such as rigid polyvinyl chloride and ultra high molecular weight polyethylene. The controlled shear and the ability to add materials downstream in the extrusion process also makes twin-screw extruder idea for compounding of glass-filled polymers.

2.6.4 Injection Molding

Injection molding is a major processing technique for converting thermoplastic materials. In this process, the thermoplastic resin is softened or melted, formed under pressure and hardened by cooling. When the process in adapted for thermosetting resins, the two components of the thermosetting system are mixed in or just prior to the mold. In gas-assist injection molding, gas is inserted into the melt stream, while in co-injection molding two materials are melted separately and then injected sequentially into the same mold.

The most common injection molding machine is the single-stage reciprocating screw injection molder. This machine has two sections, the plasticating unit which is a modified single-screw extruder and the clamping unit which holds the injection mold. Thermoplastic resin is fed from the hopper into the plasticating unit. The rotating screw melts the material and conveys the resin to the end of the screw. As in a single-screw extruder, approximately 60-70 % of the heating results from viscous dissipation with the remainder conducted from the barrel walls. However, in the injection molding machine, the material melt does not immediately exit the plasticating unit, but is trapped between the blocked nozzle and a non-return valve on the end of screw.

At the beginning of a molding cycle, this melt is forced through the nozzle and into the injection mold by the forward (linear) movement of the screw. Once in the mold, the melt is cooled by conduction through the cooled walls of the mold. When the plastic is cool enough to hold its shape, the mold opens and the plastic part is ejected from the mold. During cooling of the part, the screw rotates to convey more material. This material forces the screw back (linearly) in preparation for the next molding cycle.

Each plastics material differs in its ability to flow under heat and pressure. Typically resin suppliers suggest melt and mold temperature ranges and drying conditions for a particular resin. From these conditions, the machine parameters of shot size (melt volume), injection velocity, pressures and times are experimentally determined for each molding machine/mold/resin combination. Injection (filling of the mold) is controlled by either ram (screw) velocity or the hydraulic pressure behind the screw. Packing and holding (which force more material into the mold to compensate for shrinkage) are also controlled by the hydraulic pressure behind the screw. Switch-over from injection to packing is usually controlled by time, hydraulic pressure, screws position or pressure in the mold cavity. Switch-over from packing to holding and from holding to cooling in controlled by times.

Injection molding is a high shear process with shear rates of 1,000 to 10,000 S^{-1} Which is typical for conventional molding and exceeding 40,000 s^{-1} for thin-wall and high speed injection molding. Rapid injection produces high shear which increases the melt temperature and degrades the polymer. Slow injection causes excessive cooling of the melt resulting in higher injection pressures, high shear stresses in the molded part and incomplete filling of the part. While material touching the mold wall cools rapidly in an oriented and stressed state, the polymer adjacent to this frozen layer is dragged along the frozen material, this produces more orientation and frozen-in stress. Material in the center of the part cools slowly and so is less oriented and stressed. Since pressures decrease with the distance from the gate, orientation and frozen-in stresses are highest near the gate.

The shearing during injection molding alters the morphology within the injection molded part. Researchers [34] have found that injection speed affects the morphology of slowly crystallizing polymers such as syndiotactic polystyrene and polyethylene naphthenate. With polypropyiene/polyethylene elastomer blends [35] the segregation of the component polymers occurring in the surface layers affects the paintability and physical properties of the blends even though the morphologies of the parts' centers are similar.

2.7 Literature Reviews

Polymer blending is a well-recognized method for the design of macromolecular materials with properties defined for specific applications, and in the majority of cases, it is a more versatile and economic alternative to the synthesis of new polymeric materials. For this reason, there is a great deal of interest in the industrial development of blended polymer systems.

It is accepted that due to the low entropy of blending. The product resulting from a blend of two polymers. Immiscible system composed of two phases. The higher concentration component forms the continuous matrix and the other component is heterogeneously dispersed in small domains. These systems present high surface tension and poor adhesion, resulting in poor mechanical properties. To improve the properties of this type of blend, a series of compounds denominated compatibilizing agents are added to the blends. These compounds generate interfacial interactions between the components, resulting in a reduction in the energy between the distinct phases and an increase in adhesion and improved mixing during the blending process [36].

Blends of isotactic polypropylene and polyamide have received much attention over recent years. They combine the environmental moisture-stability and ease processing. Unfortunately, both polymers are incompatible because of their different polarities and crystalline morphologies. In an attempt to increase the compatibility between these polymers, different compatibilizing agents have been employed as a third component in the blend. These compounds are generally based on polypropylene functionalized with acrylic acid, maleic anhydride, other modified polar thermoplastics such as ionomers or functionalized styrene block copolymers [37].

Among these, Ide and Hasegawa [34] studied the effect of maleic anhydride grafted polypropylene on polypropylene/nylon-6 blends. The structural stabilty and morphology of the blends were improved greatly by polypropylene/nylon-6 grafted copolymers that were formed by the *in situ* reaction of anhydride groups with amino end groups of nylon. Recently, Holsti *et. al.* [36] used various functionalized copolymers with maleic anhydride as compatibilizers and reported that the blends compatibilized with maleic anhydride grafted styrene-ethylene-butylene-styrene block copolymer possessed more enhanced impact strength than those with other copolymers. For polypropylene/nylon-6 blends compatibilized with polypropylene grafted maleic anhydrided, the blend properties were strongly dependent on the degree of *in situ* reaction between maleic anhydride and amine groups of nylon-6 and the concentration of the *in situ* formed copolymers polypropylene grafted maleic anhydride along the phase interface. So far as we know, only few publications considered the reaction and diffusive transport of *in situ* formed copolymers toward the interface of the blends. In order to examine the interplay between the chemical reactions forming copolymers and the diffusive transport in a ternary blend system, the blends prepared by single-step mixing have to be compared with those by two-step mixing in which one of the polymers is premixed with the compatibilizer before the final mixing with the other polymer. Cimmino *et al.* [37] considered the effect of mixing procedure on the compatibilized blends of ethylene-propylene random copolymer and nylon-6 with the same ethylene-propylene random copolymer functionalized by insertion of anhydride groups onto the chains. They utilized two kinds of mixing processes; namely, single-step mixing of the three components and two-step mixing in which the pre- mixture of two rubbers ethylene-propylene random copolymer and ethylene-propylene random copolymer grafted maleic anhydride blended with nylon-6. The results showed that the blends obtained by the two-step mixing possessed very fine morphologies and excellent impact property compared with those made by the single-step mixing procedure. Similar observations were made by Willis and Favis [38] for polypropylene/nylon-6. Nylon-6 blends compatibilized with an ionomer [poly(ethylene-methacrylic acid-isobutylacrylate terpolymer)]. In this case, the two-step blending process with premixing of polypropylene and the ionomer produced much finer morphology than the single-step mixing.

Chang and Hwu [39] selected two types of reactive compatibilizers, styrene-maleic anhydride random copolymer and styrene glycidyl methacrylate in polyblends of polystyrene and nylon-6,6 to examine their dispersed morphologies and correlation with their physical properties for various multistep blending processes. Their results showed that the compatibilized blend with the highest content of styrene glycidyl methacrylate/nylon-66 copolymer in the nylon-66 phase and along the interface did not possess the best impact toughness. This was because the toughness of blends depended on the competition between the enhancement induced by better adhesion and dispersity. Relatively brittle styrene glycidyl methacrylate caused the loss of inherent toughness of the blend components. Obviously, the blending processes that yield enhanced interfacial adhesion and finer phase morphology do not always guarantee improved physical properties. In particular, for poylpropylene/nylon-6 blends, the strong hydrophilicity of nylon-6 requires an effective blending procedure that reduces property degradation caused by moisture absorption.

Dagli [40] studied on the reactive compatibilization of nylon-6 and polypropylene blends through a functionalized polypropylene. A graft copolymer was formed *in situ* by reacting an acid modified polypropylene with nylon-6 during blend compounding. There was a substantial increase in initial reaction rate, as the rotor speed was increased. Increasing the temperature did not significantly affect the reaction rate. Process parameters which are important for such a reactive compatibilization process were identified by statistically designed experiments in a co-rotating intermeshing twin-screw extruder. Screw speed, presence of venting, and sequence of feeding were shown to have a noticeable effect on the reactive compatibilization process during continuous compounding. Wu [41] used a twin-screw extruder examined the effects of molecular weight of nylon and the effects of different types of compatibilizing agents on the phase morphology and the properties. Three different types of compatibilizers, including maleic anhydride modified polypropylene, acrylic acid modified polypropylene, and ethylene glycidyl methacrylate copolymer, were used to examine their effects. It seemed that blends compatibilized with polypropylene graft maleic anhydride exhibited the most homogeneous phase morphology and superior mechanical properties among the three. It was shown that the properties of the composites relied on the phase morphology which, in turn, was affected by both the molecular weight of nylon and the compatibilizing agents.

Wu [41] showed that compatibilized blends prepared by the single-step process exhibited improved phase morphology, thermal stability, and mechanical properties for dried conditions, compared with other blend types. Finally, the water absorption test indicated that the added compatibilizer yielded enhanced water resistance in spite of the strong intrinsic hydrophilicity of nylon-6. In particular, two-step blending with reactive premixing was the most effective method in improving water resistance and reducing degradation of mechanical properties after moisture absorption.

Sathe [42] found that addition of 2.4% (W/W) PP-g-BA compatibilizer in binary polypropylene/nylon-6 blends resulted in more regular and finer dispersions of the two phases and improved mechanical properties. Campoy [43] found that the crystallization kinetics of blends have been systematically. The isothermal crystallization of the nylon-6 component was influenced by the presence of polypropylene, reducing the crystallization rate due to the diluent effect originated by this polymer. On the contrary, the crystallization rate of polypropylene, in the blends is higher than the corresponding value for pure polypropylene. This effect was higher in the blends without compatibilizer. This behavior is related to the nucleating activity by the nylon-6 component.

Gonzalezmontiel [44] indicated that the morphology of the blends was found to be dependent on the ratio of polypropylene and polypropylene grafted maleic anhydride. By changing this ratio it was possible to induce drastic changes of morphology, going from a continuous nylon-6 phase to a continuous polypropylene phase at a fixed composition. The mechanical properties of these blends were found to be dependent on their morphologies. Rosch [45] investigated by blending 70 vol% polypropylene, with 30 vol% nylon-6 in the presence of compatibilizers such as maleic anhydride-grafted polypropylene and maleic anhydride-grafted rubber. Compatibilizer volume fraction and molecular architecture gave control of nylon-6 dispersion and interfacial adhesion between polypropylene and nylon-6.

Toughened versions of both nylon-6 and polypropylene have become important industrial products. Nylon-6 has been successfully toughened by the use of active rubbers grafted with functional groups that react during melt processing with the end-groups of nylon-6. The nylon-rubber copolymer formed during melt blending increases the interfacial adhesion between the rubber and the polyamide and provides the control of rubber particles. Both of which are believed to be essential for promoting toughness. Polypropylene can be toughened either by melt blending with an olefinic rubber (usually ethylene-propylene rubber) or by copolymerization, where ethylene is introduced into the reactor feed at the end of the main propylene polymerization process. Toughened polypropylene materials formed by a reactive scheme similar to the one employed for the polyamides have also been recently reported.

Maleated olefinic rubbers are especially effective impact modifiers of nylon-6. Therefore, they are a primary choice for impact modification of nylon-6/polypropylene blends. An additional benefit of using these reactive rubbers is the affinity of the olefinic rubber for the polypropylene. Even though polypropylene and the rubber are not miscible, there is a certain affinity that leads to good adhesion between the phases. Thus, the rubber may serve as a compatilibizer in addition to being an impact modifier. Recent literature has focused on the use of functionalized styrenic block copolymers and ethylene-propylene copolymers as modifiers for nylon6/polypropylene blends [46].

The use of various mineral fillers in polyolefins, especially polypropylene, has become widespread. Fillers such as talc, calcium carbonate and mica generally improve physical properties (i.e, flexural modulus) in addition to lowering raw material cost. Much effort is placed on improving the interaction of the filler surface with the polymer. However, fillers may have an adverse effect on the heat and light stability of the polyolefin matrix. In order to extend the service life of filled polyolefins, antioxidants and light stabilizers are used to inhibit and/or reduce polymer deterioration.

CHAPTER III

EXPERIMENTALS DETAILS

3.1 Materials

The materials used in this study were toothbrushes, compatibilizers and additives. Some properties of materials are shown in Table 3.1.

Table 3.1 Some properties of the materials

Materials	**Properties**		
	Suppliers	**MFI (g/10min)**	**Others**
Recycled polypropylene**	First Thai Brushes LTD.	12	T_m 169.7 °C, T_c 123.2 °C
Recycled nylon-6**	Thai Brushes Industry LTD.	13	T_m 225.1 °C, T_c 180.9 °C
PP-g-MA*	TOA Uni Royal Chemical	50	1.5 % Maleic anhydride, T_m 157°C, density 0.91 g/cc
Calcium Carbonate**	N/A	-	Diameter8.09µm, non-coated Surface area 1.10 m^2/g
Glass Fiber**	N/A	-	Diameter 10 µm ,non-treat E type, length1 cm,

* data from the manufacture

** data from the measurement

3.2 Instruments

The instruments used in this research are listed below:

1) Internal intensive batch mixer (NEMA 600)
2) Single-screw extruder machine (Axon ab BX-18)
3) Two-roll mill (Lab Tech)
4) Twin-screw extruder (Collin ZK-25)
5) Injection molding (Cosmc 'TI 220/80)
6) Tensile tester (LLOYD LR 30)
7) Impact tester (Yasuda Seiki 258)
8) Hardness tester (Yasuda)

8) Hardness tester (Yasuda)
9) Scanning electron microscope (JEOL JSM - 6400)
10) Differential scanning calorimeter (Perkin Elmer DSC 7)
11) Deflection temperature under load (Yasuda)
12) Particle size analyer (Masterizer X)

3.3 Preparation of Materials

Toothbrushes which were off-specification from the manufacturing factory were ground into 2-5 cm in particle size with the grinding machine. After the metal chips and other impurities were separated from ground tooothbrushes by using a 2 mesh sieve analysis equipment, the ground toothbrushes were dried for two hours in an oven at 80 °C for removing the moisture. Then the treated ground toothbrushes were ready for each process.

3.4 Processing

3.4.1 Blending using the Two-Roll Mill

The recycled toothbrushes were blended under 18 sets of processing conditions. Temperature and time were varied from 210 °C to 230 °C and 6, 8 ,10 minutes, respectively. Table 3.2 shows the operating conditions for each run.

The mill was preheated at least half an hour to reach the set temperature. Mixed toothbrushes were dried at least two hours at 80 °C. The material was fed into the counter-rotating two-roll mill which was set to operate at specified temperatures and times. The screw speed and gap were fixed at 10 rpm and 1.2 mm, respectively. When the specified time was reached, the sample was removed with the cutting tool and set out to cool down. The sample was then ground with internal intensive batch mixer for injection molding. The rolls were cleaned with stearic acid.

3.4.2 Blending using the Single-Screw Extruder

The recycled toothbrushes were blended under 18 sets of processing conditions in the single-screw extruder. Temperatures and screw speeds were varied from 180 °C to 240 °C and 30 to 70 rpm, respectively. Recycled blends were compounded in Axon ab BX-16 single-screw extruder with 25D. Table 3.3 shows the operating conditions in each run.

The screw was cleaned and purged with polyethylene. The extruder was preheated at least half an hour to reach the set temperature. The sample was cooled down with water and air, and then passed through the pelletizer to be ready for injection molding.

3.4.3 Blending using the Twin-Screw Extruder

The recycled toothbrushes were blended under 18 sets of processing conditions in the twin-screw extruder. Temperatures and screw speeds varied from 165 °C to 230 °C and 30 to 50 rpm, respectively. Recycled blends were compounded in a Collin ZK-25, co-rotating laboratory twin-screw extruder which has 25 mm x 30 D in size. Table 3.4 shows the operating conditions in each run.

The screw was cleaned and purged with polyethylene. The extruder was preheated at least half an hour to reach the set temperature. The mixed toothbrushes were cooled down with water and air, and then passed through the pelletizer to be ready for injection molding.

Table 3.2 The operating conditions for the two-roll mill

Temperatures:			
Front Roll (°C)	210	220	230
Rear Roll (°C)	220	230	240
Time : (min.)	6, 8, 10	6, 8, 10	6, 8, 10
Gap (mm.)	1.2	1.2	1.2
Speed (rpm)	10	10	10

Table 3.3 The operating conditions for the single-screw extruder

Temperature Zones (°C)			
Zone 1	190	200	210
Zone 2	200	210	220
Zone 3	210	220	230
Zone 4	220	230	240
Screw Speed (rpm)	30, 50, 70	30, 50, 70	30, 50, 70

Table 3.4 The operating conditions for the twin-screw extruder .

Temperature Zones (°C)			
Zone 1	165	165	165
Zone 2	180	190	200
Zone 3	200	210	220
Zone 4	220	230	240
Screw Speed (rpm)	30, 50, 70	30, 50, 70	30, 50, 70
Die Melt Temperature (°C)	223	233	244

3.4.4 Effect of Compatibilizer

The optimum processing conditions for each process were investigated. The effect of compatibilizer was studied by adding 1, 3 and 5 % wt to the blend. For each optimum processsing technique, the characterization of the blends was completed.

3.4.5 Effect of Additives

After the optimum processing conditions and optimum amount of the compatibilizer for each techniques were found. The effect of additives (chopped glass fiber and calcium carbonate) were studied by adding 3, 5 and 10 % wt of the filler to the blends. For each optimum technique, the characterization of the blend was carried out.

3.5 Molding Test Specimens

The Cosmo injection molding machine (model ITI 220/80) was used to make molded with dumbbell and Izod bars. The machine was preheated at least one hour to reach the set temperatures. A range of processing conditions (Table 3.5) was used. The barrel, nozzle and mold were cleaned and purged with polyethylene.

Table 3.5 The operating conditions for injection molding

Control Parameters	Values
Barrel Temperature (°C): Zone 1	120
Zone 2	130
Zone 3	140
Die Temperature (°C)	160
1st Stage Injection Pressure (bar)	40
2nd Stage Injection Pressure (bar)	35
3rd Stage Injection Pressure (bar)	30
1st Injection Time (sec)	20
2nd Injection Time (sec)	15
Die Close/Open Time (sec)	60
Speed (rpm)	40

3.6 Physical Property Testing

The polypropylene and nylon-6 blends were examined for the properties of tensile strength, tensile modulus, impact strength, flexural strength, hardness, and heat deflection temperature. The mechanical property test methods of the blend are shown in Table 3.6.

Table 3.6 Mechanical property test methods

Mechanical properties	Test methods	Units
Tensile Strength	ASTM D 638	MPa
Tensile Modulus	ASTM D 638	MPa
Flexural Strength	ASTM D 790	MPa
Impact Strength	ASTM D 256	kJ/m
Hardness	ASTM D 2240	Shore D
Heat Deflection Temperature	ASTM D 648	°C

3.6.1 Tensile Strength and Tensile Modulus

The test specimens were prepared by injection molding machine, with rectangular bar form. The tensile bar size of 10.4 mm wide x 2.5 mm thick x 151 mm long was tested on LLOYD Instruments Co., Ltd.. Ten specimens were tested at the maximum load cell of 30 kN, crosshead speed of 5 mm/min and gauge length of 7 cm. This method was carried out according to ASTM D 638. All data were recorded by computer acquisition software connected to the testing machine.

3.6.2 Flexural Strength

Flexural properties were measured according to ASTM D 790, Procedure A. The LLOYD instruments was used. The 1.38 mm bar was moved with a crosshead speed of 2 mm/min and span length of 10 cm were used. At least seven samples were tested and all data were recorded by computer acquisition program connected to the testing machine.

3.6.3 Impact Strength

According to ASTM D 256, V - notch type Izod impact test specimens were injected with the injection molding machine. Impact strength was measured with Yazuda impact tester model 285 - PC , linked with a computer. The test results were analyzed using a software. Notched Izod impact strengths of ten specimens were measured at a temperature of 23 ± 2 °C and reported as an average value for each run.

3.6.4 Hardness

The hardness value was measured from the durameter hardness tester of Shore D type according to ASTM D 2240. The samples from injection molding were laid down on the stand and were then pressed under 5 kg of load for 3 seconds under the specific condition. The results can be read from the dial.

3.6.5 Heat Deflection Temperature Under Load

Heat deflection temperature under load was measured according to ASTM D648. The specified load of 0.5 MPa was used under operating condition. The temperatures under specified load were recorded by the data acquisition program. At least ten samples were tested.

3.7 Characterizations of Blends

The characterization of the blends of polypropylene and nylon-6 were investigated using scanning electron microscopy (SEM) and differential scanning calorimetry techniques.

3.7.1 Scanning Electron Microscopy

A scanning electron microscope was used to study the morphology of the blends. The test samples were obtained from fracturing surface specimen. The samples were coated with a thin film of gold by using a sputter coater. The coated samples were then examined under a scanning electron microscope (JEOL JSM- 6400).

3.7.2 Differential Scanning Calorimetry

Differential Scanning Calorimeter directly measured the heat flow of a sample as a function of temperature. A sample was weighed 5 to 10 mg on a sample pan and heated at a time and temperature controlled manner. The test temperature ranged from 20 °C up to 250 °C with a heating rate and cooling rate of 10 °C/min. Melting and glass temperatures were recorded by the data acquisition program.

3.7.3 Viscosity Measurement

The ground samples were used to measure viscosity following ASTM D 3835-90. The tests were done on Instron Capillary Rheometer model 3213 with 25 kN load cell and long die. Shear rate were 3000, 4500, 6000 and 7500 s^{-1} with die speed 100, 150, 200 and 250 mm/min respectively. L/D ratio of the capillary die diameter was 16 mm and the working temperature was 230 °C. Viscosity was recorded by the data acquisition program.

CHAPTER IV

RESULTS AND DISSCUSSION

After the ratio of PP/PA was chosen, the processing conditions were varied. The polar thermoplastics, 11% nylon-6, would probably form dispersed domains in the polypropylene matrix with a variety effect on properties. The recycled toothbrushes were proceeded in two-roll mill, single-screw extruder and twin-screw extruder. The purposes of this research were to study the optimum processing conditions to fabricate the recycled blends and the effect of a compatibilizer and additives on the properties of the blends.

4.1 Effect of Processing Conditions on Mechanical Properties

4.1.1 Two-Roll Mill

Increasing milling temperature and time favored a better mixing, but caused degradation. Consequently, temperature and time had to be balanced against each other. Increasing rotational speed of the roll produced greater shear, which also favored mixing and increased frictional heating.

Figures 4.1 to 4.5 showed the effect of mixing temperature and mixing time of the two-roll mill on tensile strength, modulus at 3% strain, impact strength, hardness and flexural strength of the PP/PA blends. Mixing parameters were first investigated in order to find the optimum conditions for preparing the blends prior to the study of other effects. Mixing temperature and mixing time were varied in the range of 220 to 240 °C and 6 to 10 min, respectively.

Tensile strength, modulus at 3% strain and impact strength of PP/PA blends (Figures 4.1, 4.2 and 4.3) generally increased with milling time. The higher milling time (10 min) yielded the blends with better properties. The tensile strength, modulus at 3% strain and hardness of PP/PA blends at the mixing temperature of 230°C were higher than these of 220 °C and 240°C (Figures 4.1, 4.2 and 4.4). Milling time had less significant effect on flexural strength of PP/PA blends (Figure 4.5). Therefore, temperature of 230°C and milling time of 10 min were chosen for all mixing conditions on two-roll mill for preparing the blends for other tests.

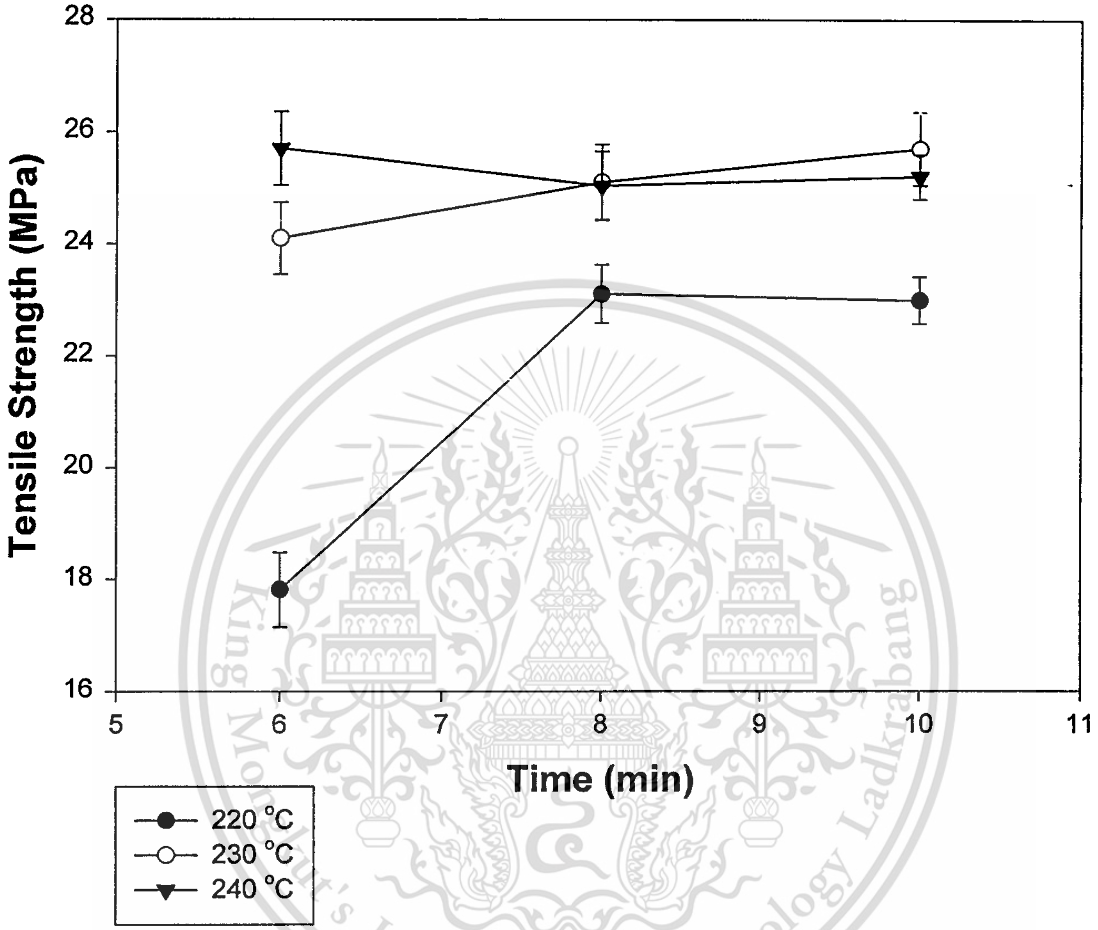

Figure 4.1 Tensile strength of PP/PA blend compounded using two-roll mill at 220, 230 and 240 °C at different times.

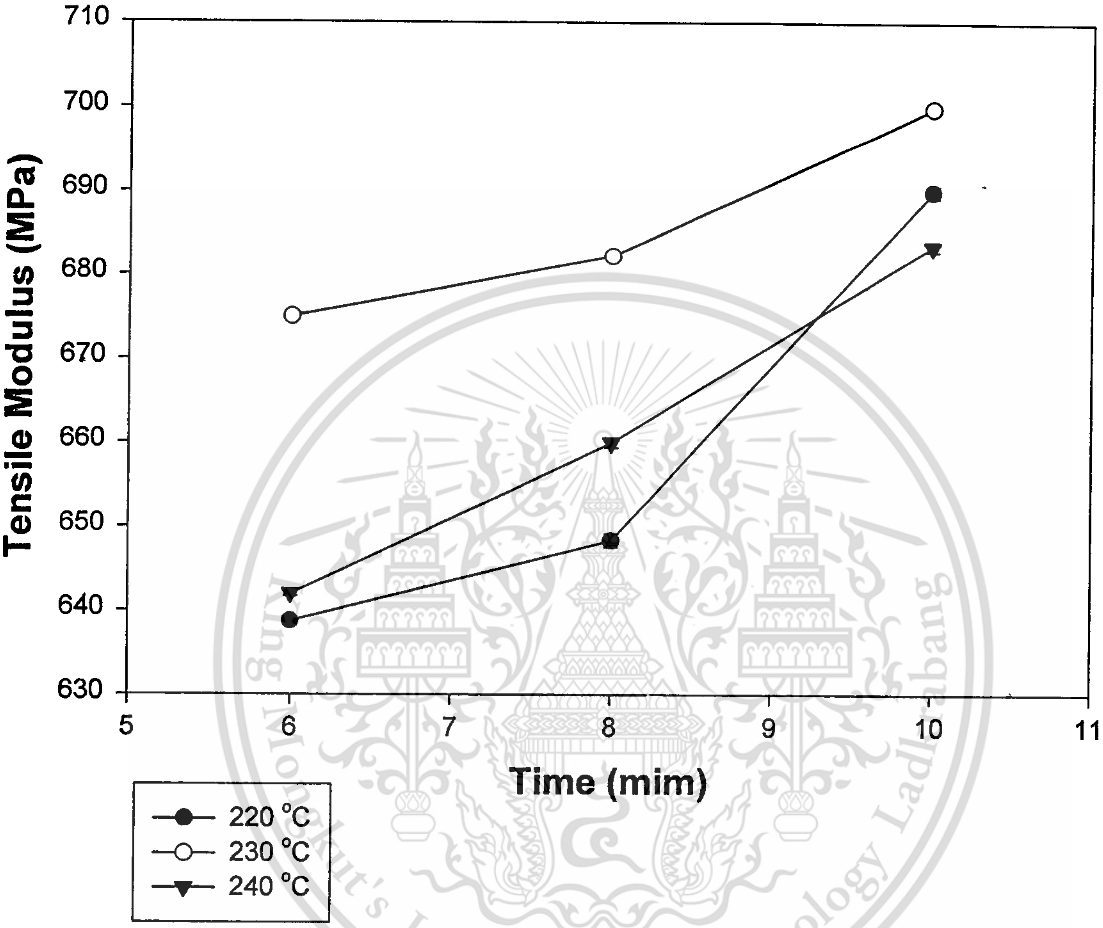

Figure 4.2 Modulus of PP/PA blend compounded using two-roll mill at 220, 230 and 240 °C at different times.

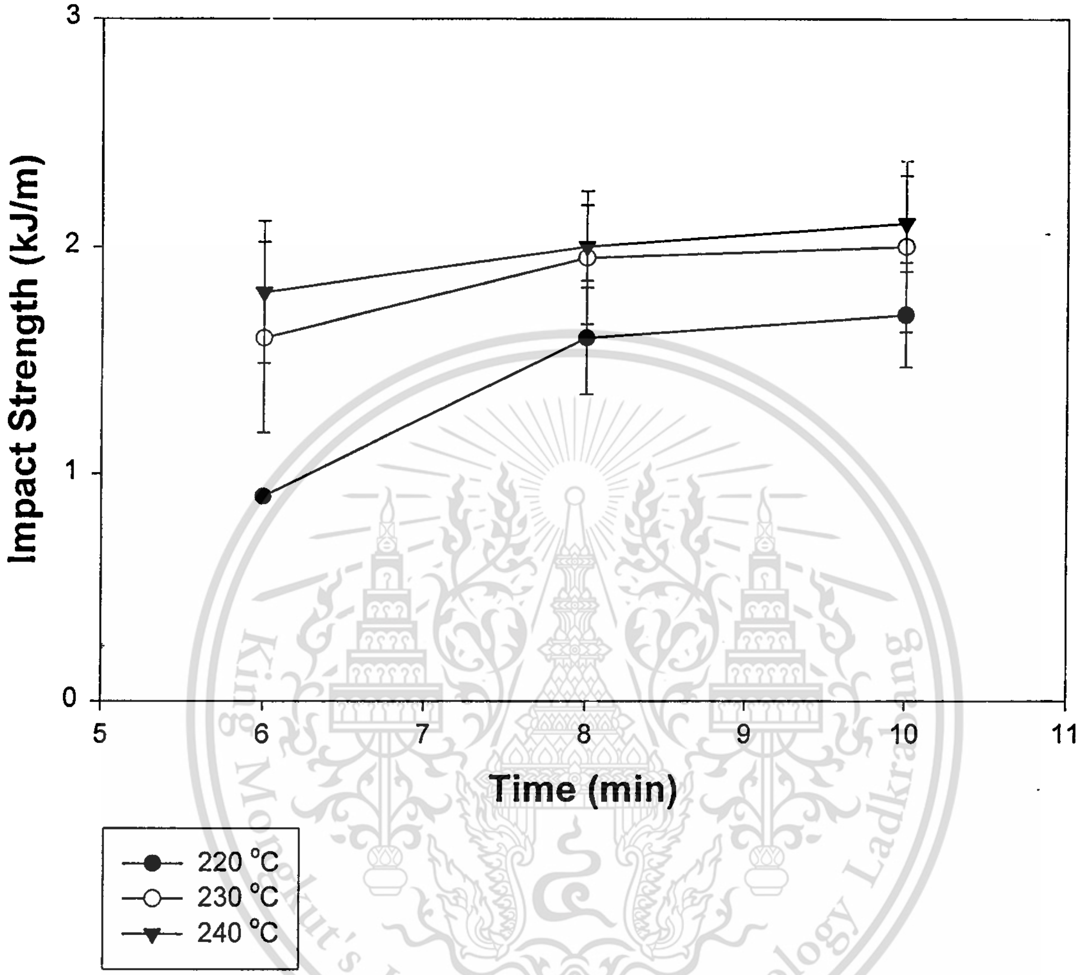

Figure 4.3 Impact strength of PP/PA blend compounded using two-roll mill at 220, 230 and 240 °C at different times.

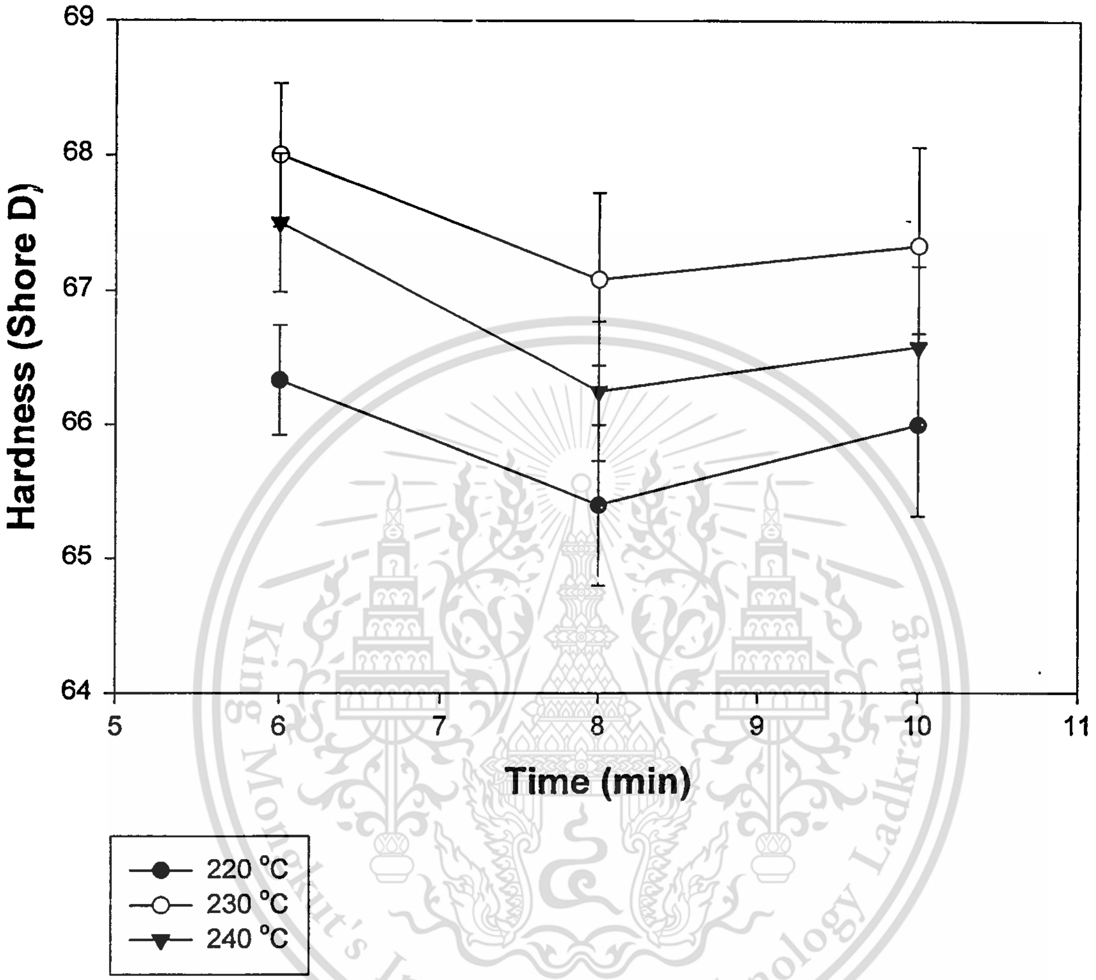

Figure 4.4 Hardness of PP/PA blend compounded using two-roll mill at 220, 230 and 240 °C at different times.

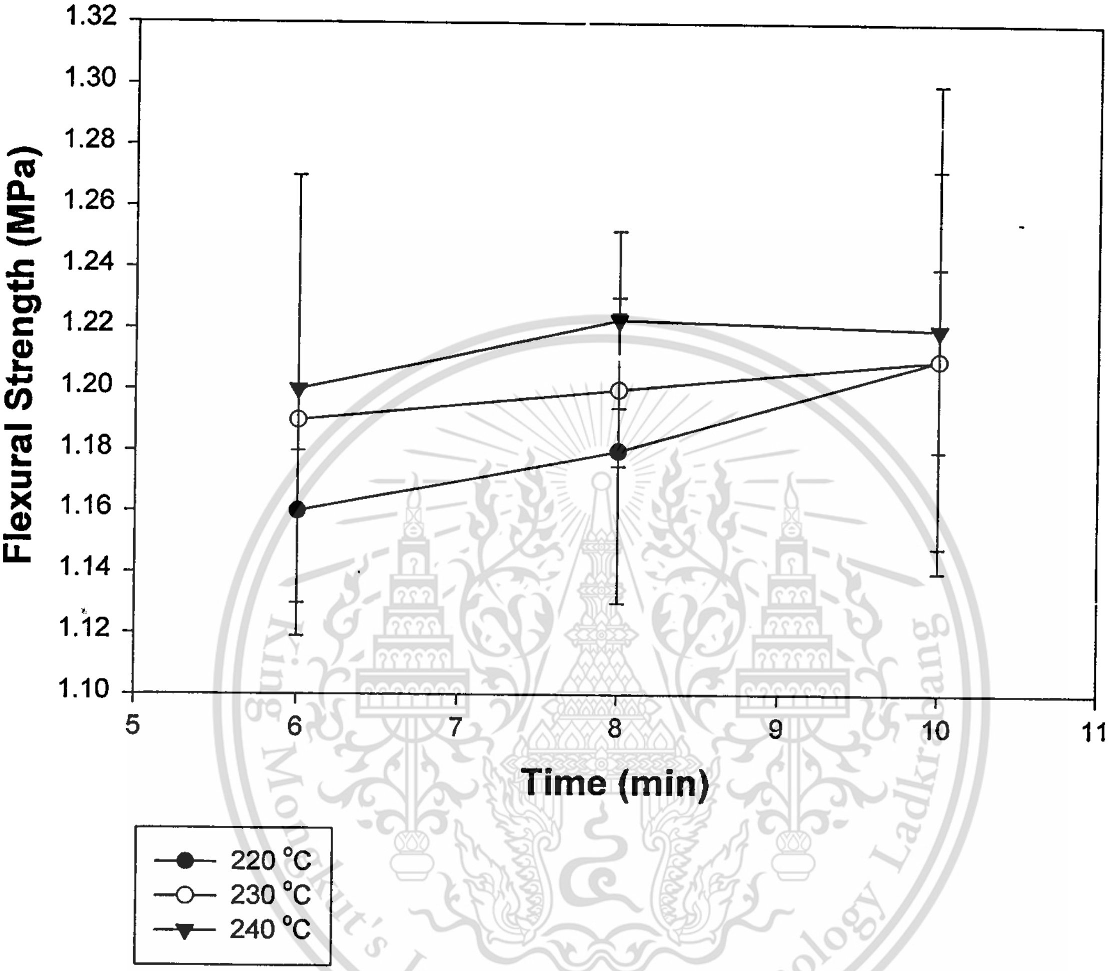

Figure 4.5 Flexural strength of PP/PA blend compounded using two-roll mill at 220, 230 and 240 °C at different times.

4.1.2 Single-Screw Extruder

Mixing temperature and screw speed were varied in the range of 220 to 240°C and 30, 50 and 70 rpm, respectively. In general, it might be expected that lower temperature would favor greater shear mixing, while higher temperature would favor lower viscosity for mixing. Slow screw speeds also produce longer residence time in the extruder while higher screw speed provided higher shear mixing. Effect on properties may be considered with respect to those process conditions.

Tensile strength, tensile modulus, impact strength, hardness and flexural strength of PP/PA blends compounding using single-screw extruder (Figures 4.6 to 4.10) generally increased with mixing temperature because nylon-6 did not fully melt at the low processing temperature. Higher temperature would also permit better mixing of nylon-6 and polypropylene. Tensile strength and modulus at 3% strain of PP/PA blends were dependent on screw speed. The tensile strength and modulus at 3% strain of PP/PA blends were highest at the middle screw speed (50 rpm). Impact strength of PP/PA blends increased with screw speed but hardness decreased with screw speed (Figures 4.8 to 4.9) because the higher screw speed destroys the interfacial thickness between polymer chains. Flexural strength (Figure 4.10) was unaffected by screw speed. Therefore, temperature of 240°C and screw speed of 50 rpm were chosen for all mixing conditions on single-screw extruder for preparing the blends of other tests. The overall properties were also slightly higher than those obtained from two-roll mill processing.

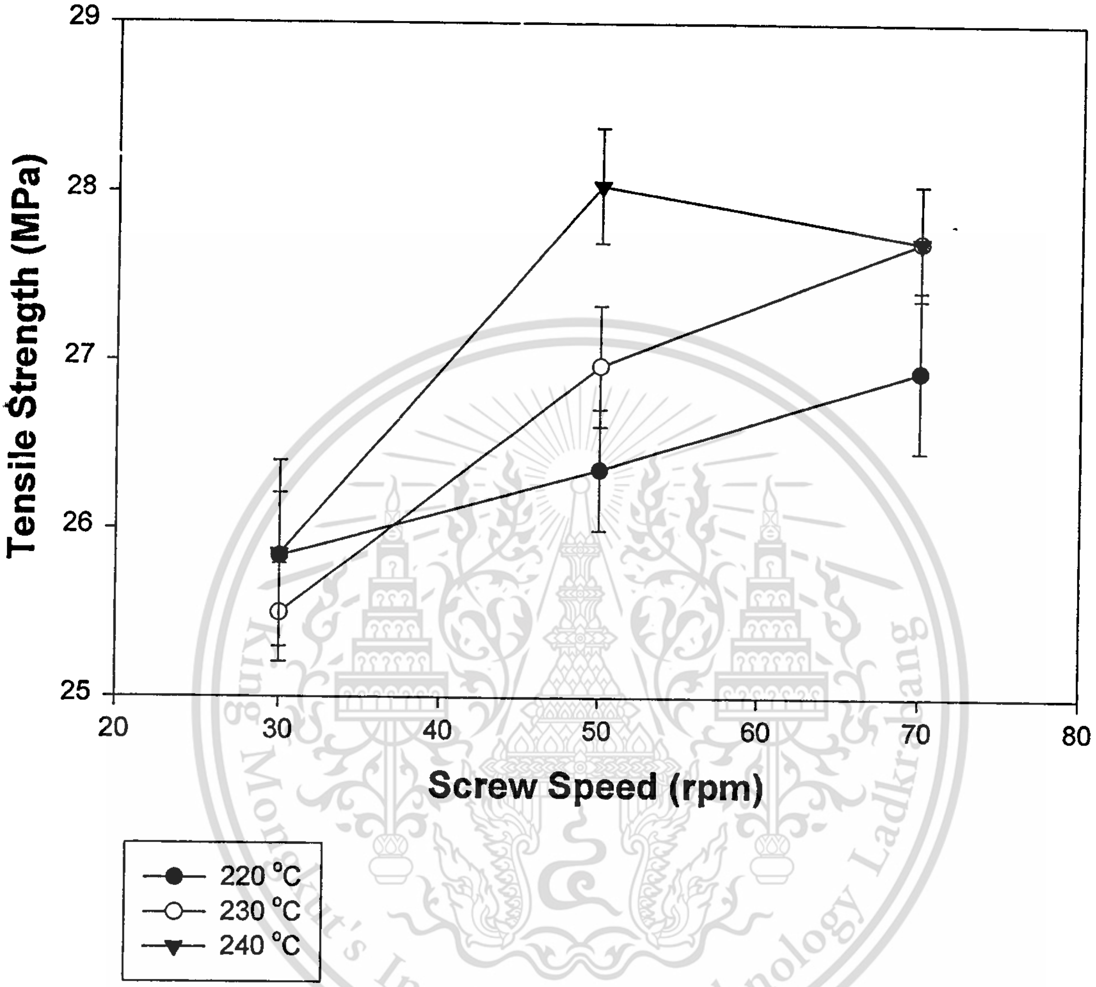

Figure 4.6 Tensile strength of PP/PA blend compounded using single-screw extruder at 220, 230 and 240 °C at different screw speeds.

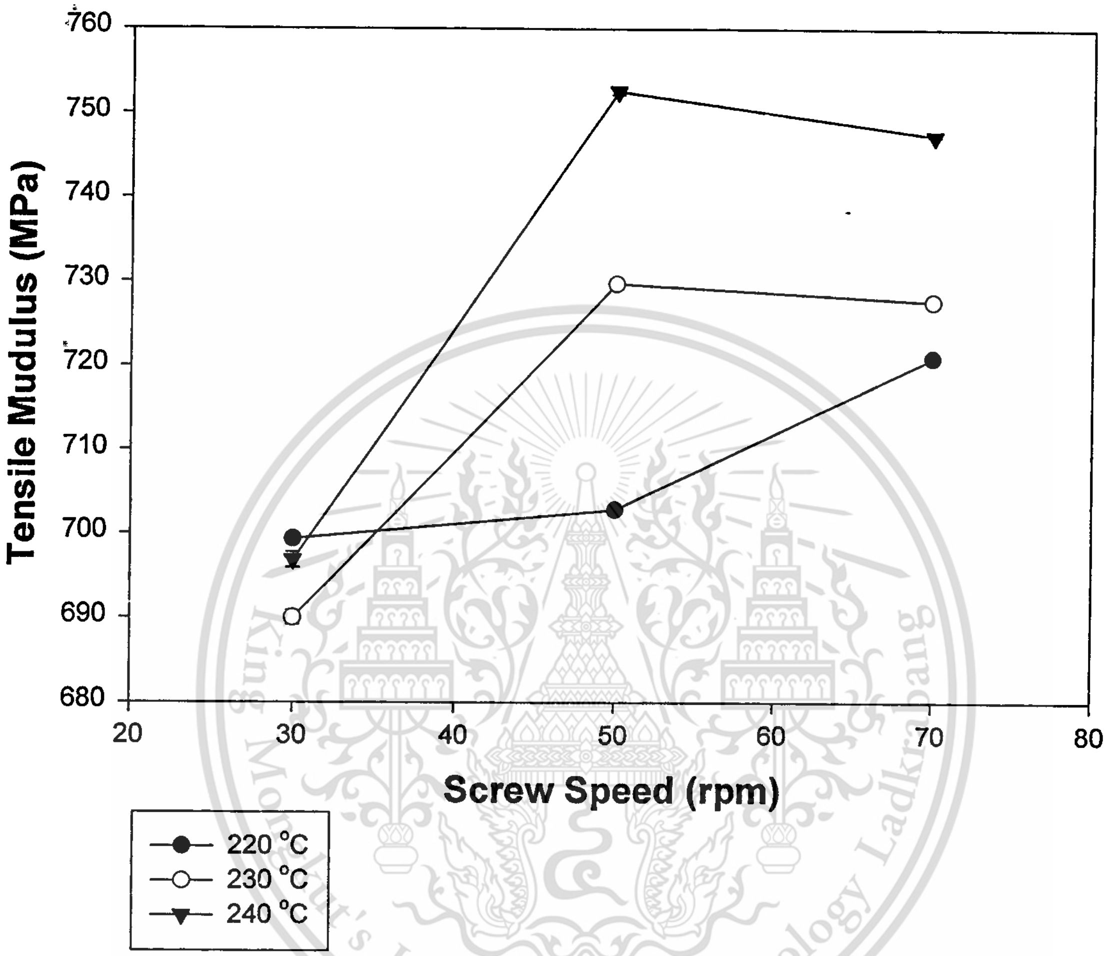

Figure 4.7 Modulus of PP/PA blend compounded using single-screw extruder at 220, 230 and 240 °C at different screw speeds.

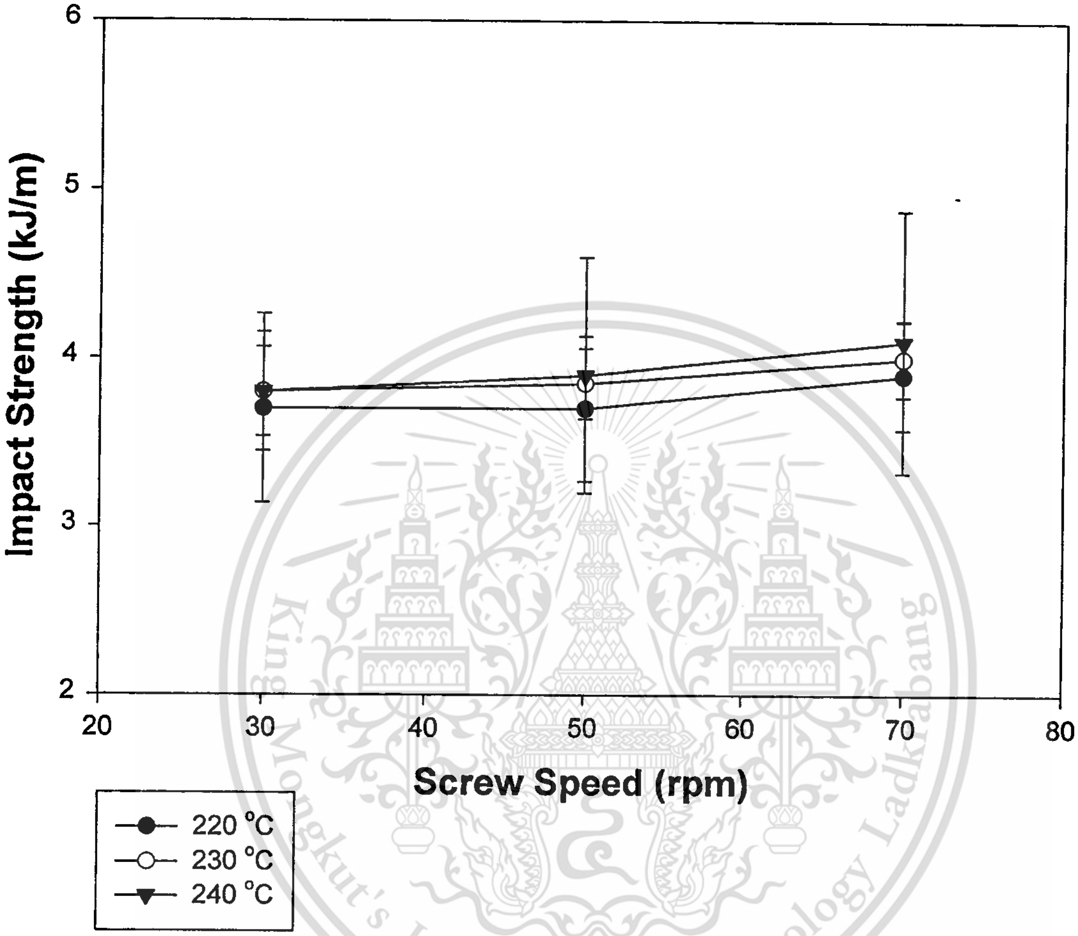

Figure 4.8 Impact strength of PP/PA blend compounded using single-screw extruder at 220, 230 and 240 °C at different screw speeds.

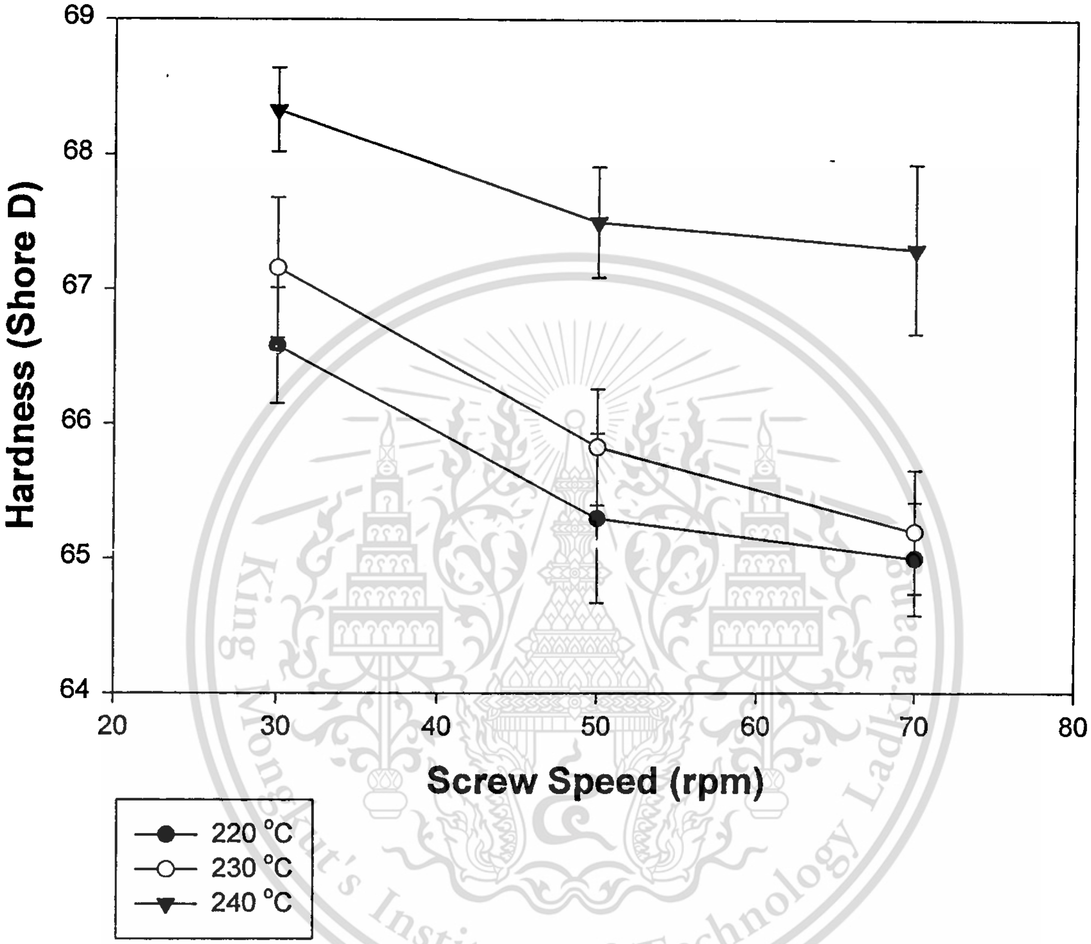

Figure 4.9 Hardness of PP/PA blend compounded using single-screw extruder at 220, 230 and 240 °C at different screw speeds.

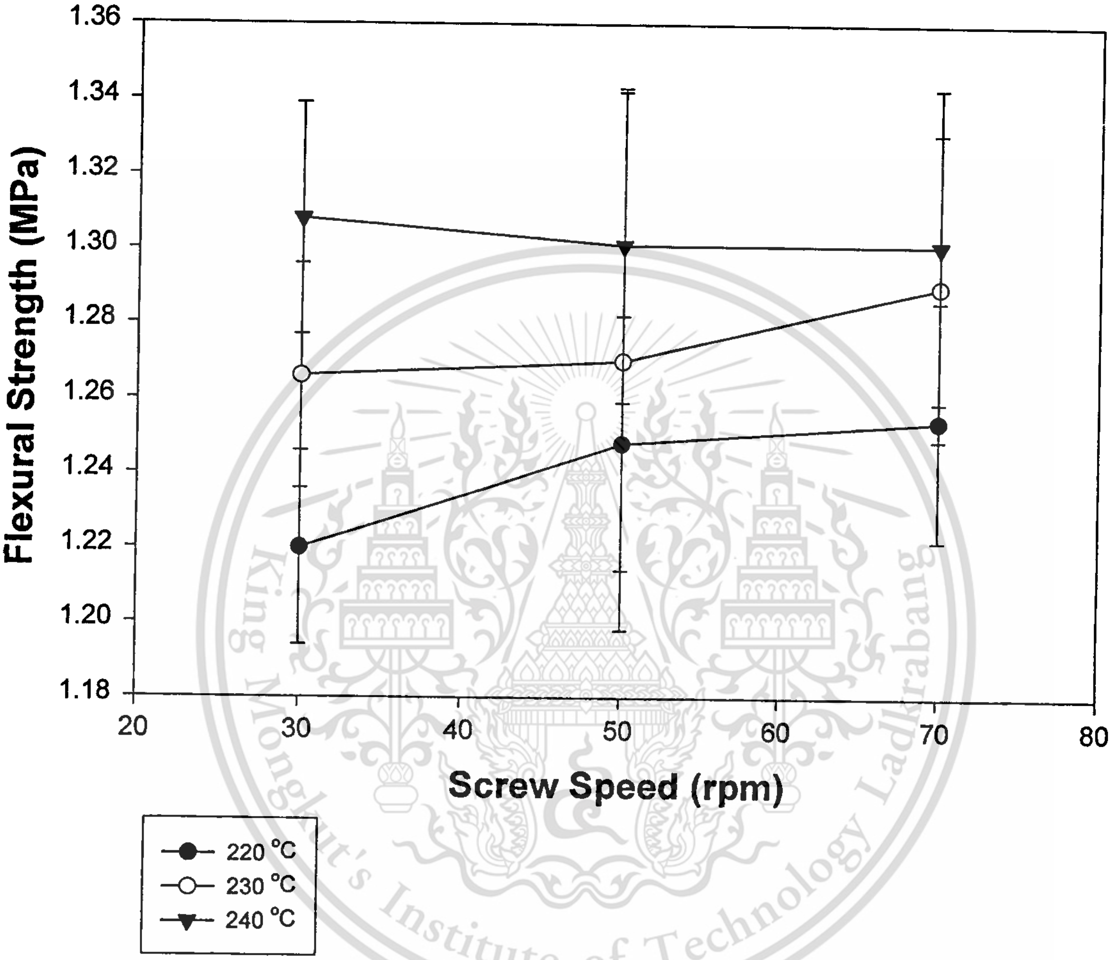

Figure 4.10 Flexural strength of PP/PA blend compounded using single-screw extruder at 220, 230 and 240 °C at different screw speeds.

4.1.3 Twin-Screw Extruder

Mixing temperature and screw speed were varied in the range of 220 to 240°C and 30, 50 and 70 rpm, respectively. The overall properties of twin-screw extruder were also lower than single-screw extruder but slightly higher than two-roll mill. Twin-screw extruder provided improved dispersion, better mixing, lower frictional heating and shorter contact time in the extruder. Typically twin-screw extruder produces better mixing than single-screw extruder. However, the twin-screw extruder used for this study was a co-rotating type with shoter screw length and lower shear.

Figures 4.11 to 4.15 showed the effect of mixing temperature and the screw speed of PP/PA blends compounded using twin-screw extruder. At the middle of the mixing temperature (230°C) and the screw speed (50 rpm), the tensile strength and modulus at 3% strain of PP/PA blends were the highest (Figures 4.11 and 4.12). Impact strength and hardness of PP/PA blends decreased with screw speed according to the excess shearing force by twin-screw extruder (Figures 4.13 and 4.14) breaking the interfacial adhesion of PP and PA. The mixing temperature and screw speed had less significant effect on flexural strength of PP/PA blends (Figure 4.15). For overall balance of properties, it appeared that optimum conditions in twin-screw extruder should be at 230°C and 50 rpm.

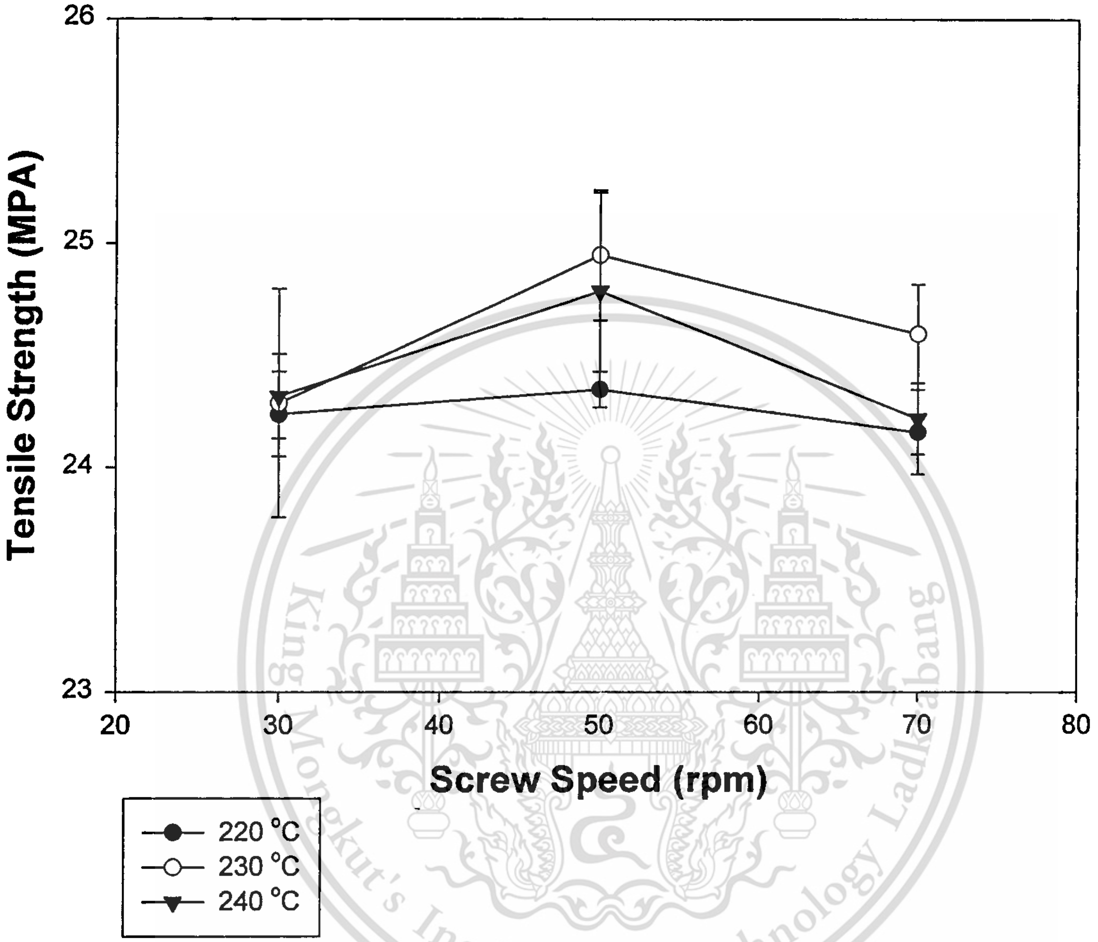

Figure 4.11 Tensile strength of PP/PA blend compounded using twin-screw extruder at 220, 230 and 240 °C at different screw speeds.

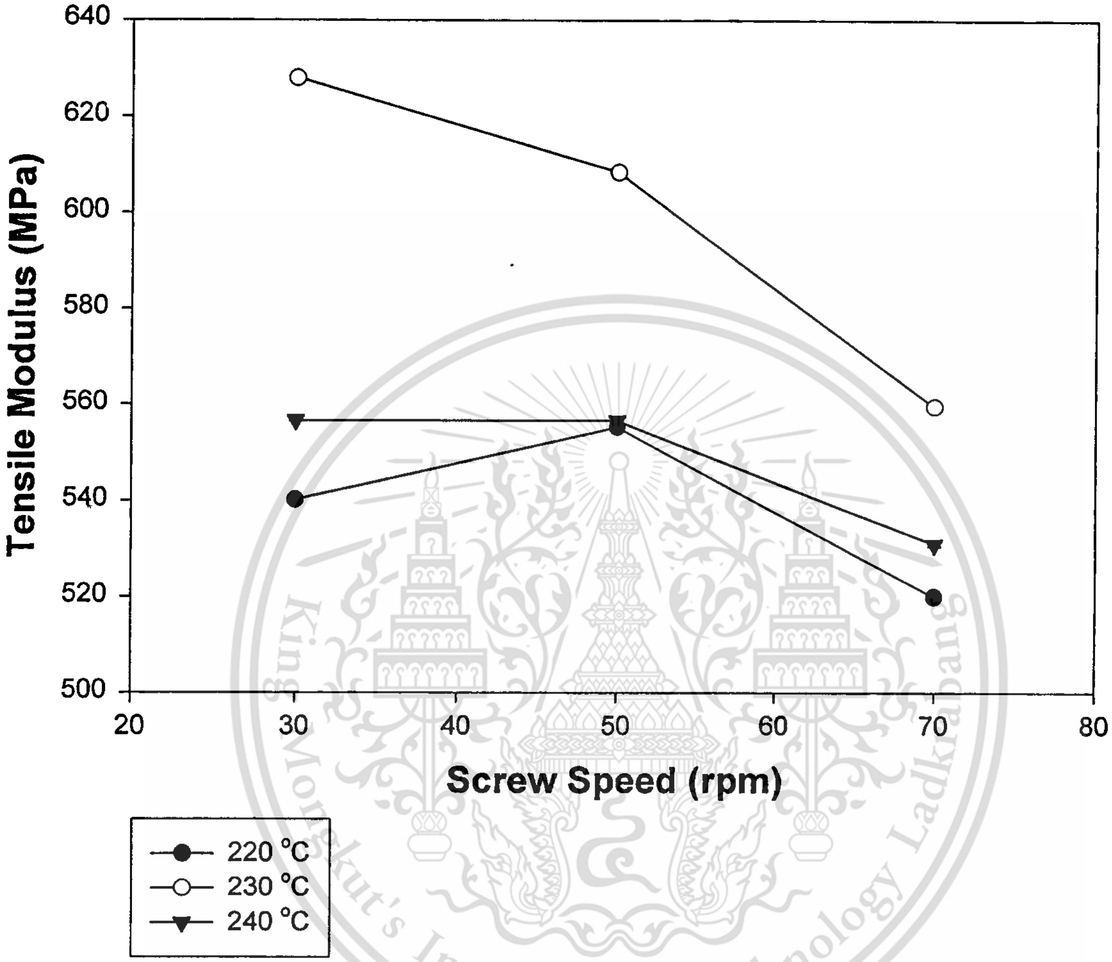

Figure 4.12 Modulus of PP/PA blend compounded using twin-screw extruder at 220, 230 and 240 °C at different screw speeds.

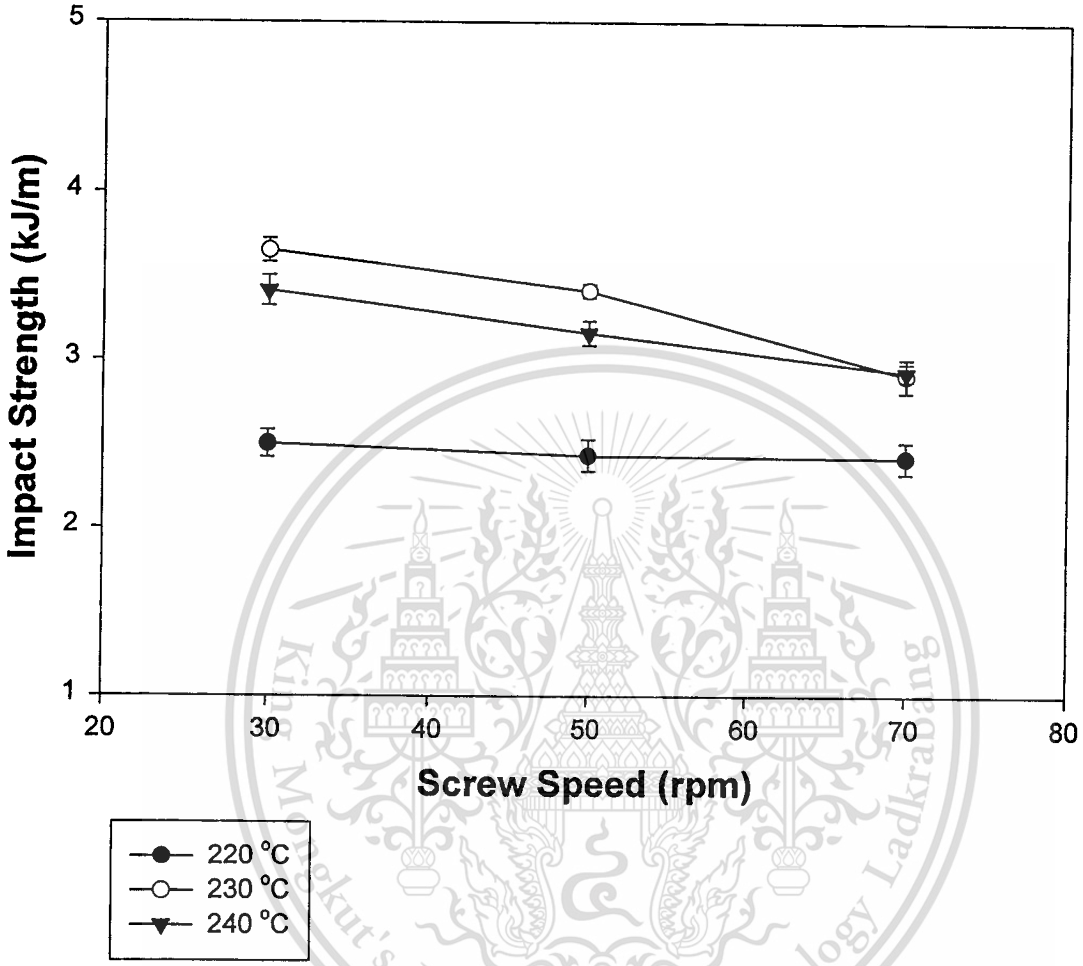

Figure 4.13 Impact strength of PP/PA blend compounded using twin-screw extruder at 220, 230 and 240 °C at different screw speeds.

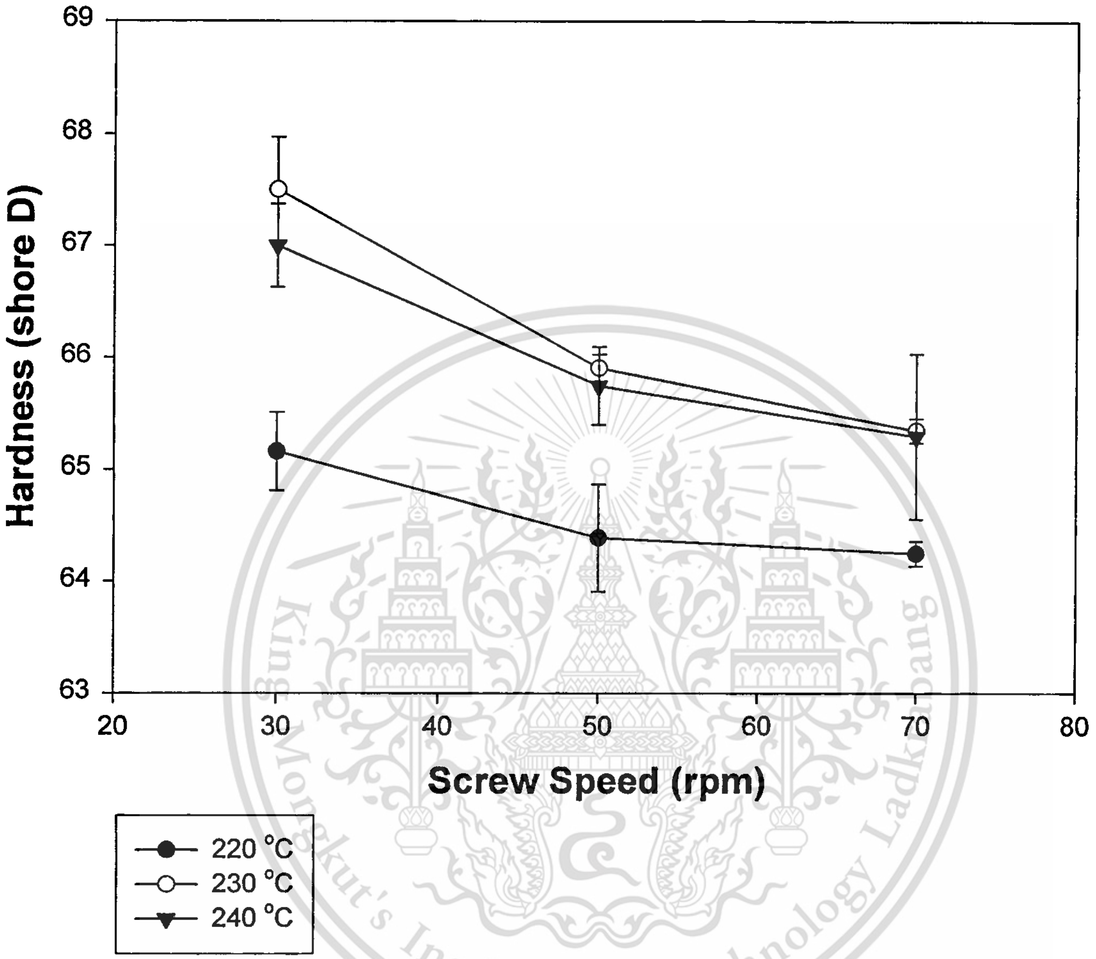

Figure 4.14 Hardness of PP/PA blend compounded using twin-screw extruder at 220, 230 and 240 °C at different screw speeds.

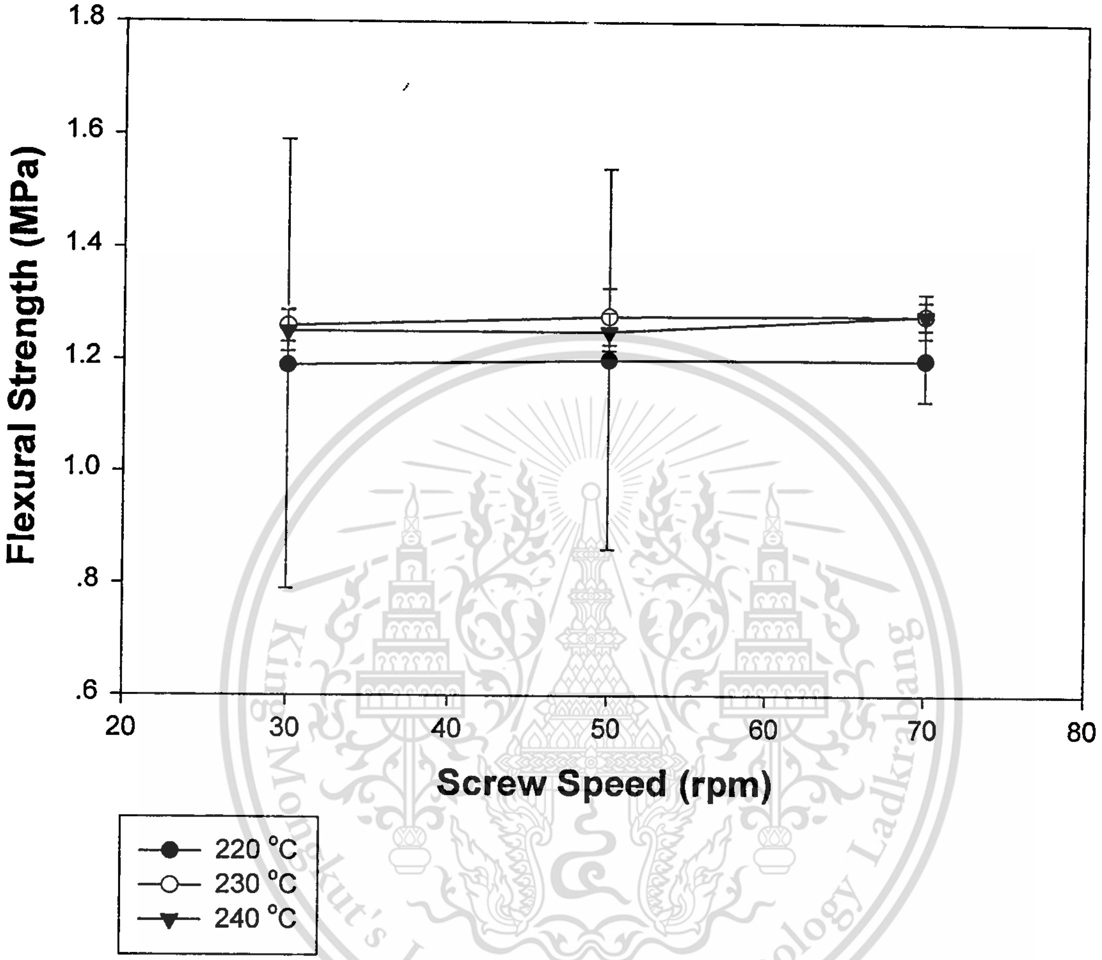

Figure 4.15 Flexural strength of PP/PA blend compounded using twin-screw extruder at 220, 230 and 240 °C at different screw speeds.

4.2 Effects of Compatibilizer on Mechanical Properties

The optimum operating conditions of each technique were further studied by adding a compatibilizer (polypropylene graft maleic anhydride, PP-g-MA or MA). Figures 4.16 to 4.20 show the effect of compatibilizer on tensile strength, modulus at 3% strain, impact strength, hardness and flexural strength of recycled polypropylene and nylon-6 blends. The results showed that the highest percentage of compatibilizer (5%) gave the best results on the properties. The compatibilized blends exhibit much finer dispersed phase than the non-compatibilized blends of inherently immiscible polypropylene and nylon-6 blends. When a compatibilizer was added, the interfacial tension between the two phases reduced and thus enhanced the interphase adhesion. PP-g-MA is the compatibilizer of nylon-6 and polypropylene blends. It gives the strong specific interactions such as H-bonding. The amine end groups of nylon-6 are expected to react with the acid groups of maleic anhydride modified polypropylene with the evolution of water to form a graft copolymer *in-situ*. Under this processing condition, an anhydride/amine reaction is also possible [50]. Both of these reactions in simplified form are shown in Figure 4.21. The reactions can form a graft copolymer by grafting PP molecules onto nylon-6 molecules. Thus, a copolymer having parts common with both the phases could be formed and could act as a compatibilizer. Maleic anhydride modified polypropylene has more than one acid group on each graft since polyacrylic acid oligomers are usually grafted on the PP backbone. This led to multiple reactive sites and multiple graft reactions, including the crosslinking of nylon-6 and anhydride formation. Hardness of compatibilized blends were increased for the blends having the PP-g-MA up to 3% wt and decrease with greater PP-g-MA contents. This concluded that more polypropylene grafted maleic anhydride would improve the tensile properties, but gave less hardness. When added 7% of compatibilizer in the PP/PA blends, most of mechanical properties (except hardness) were only sligthly improved. Hardness of the recycled PP/PA blends with 7% of compatibilizer were decreased. Therefore, 5% of copmatibilizer was selected for all processing techniques for the reason of economic and high performance properties.

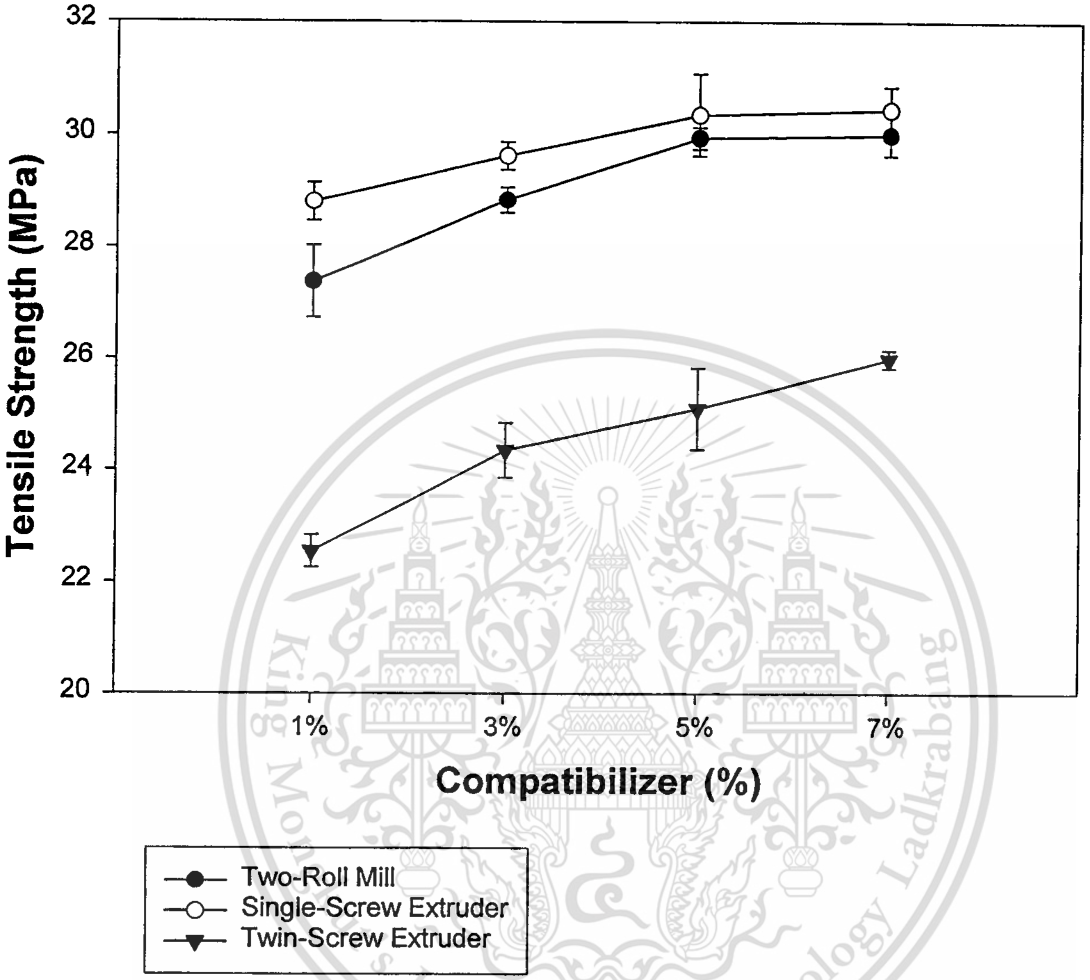

Figure 4.16 Effect of compatibilizer on tensile strength of PP/PA/MA blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

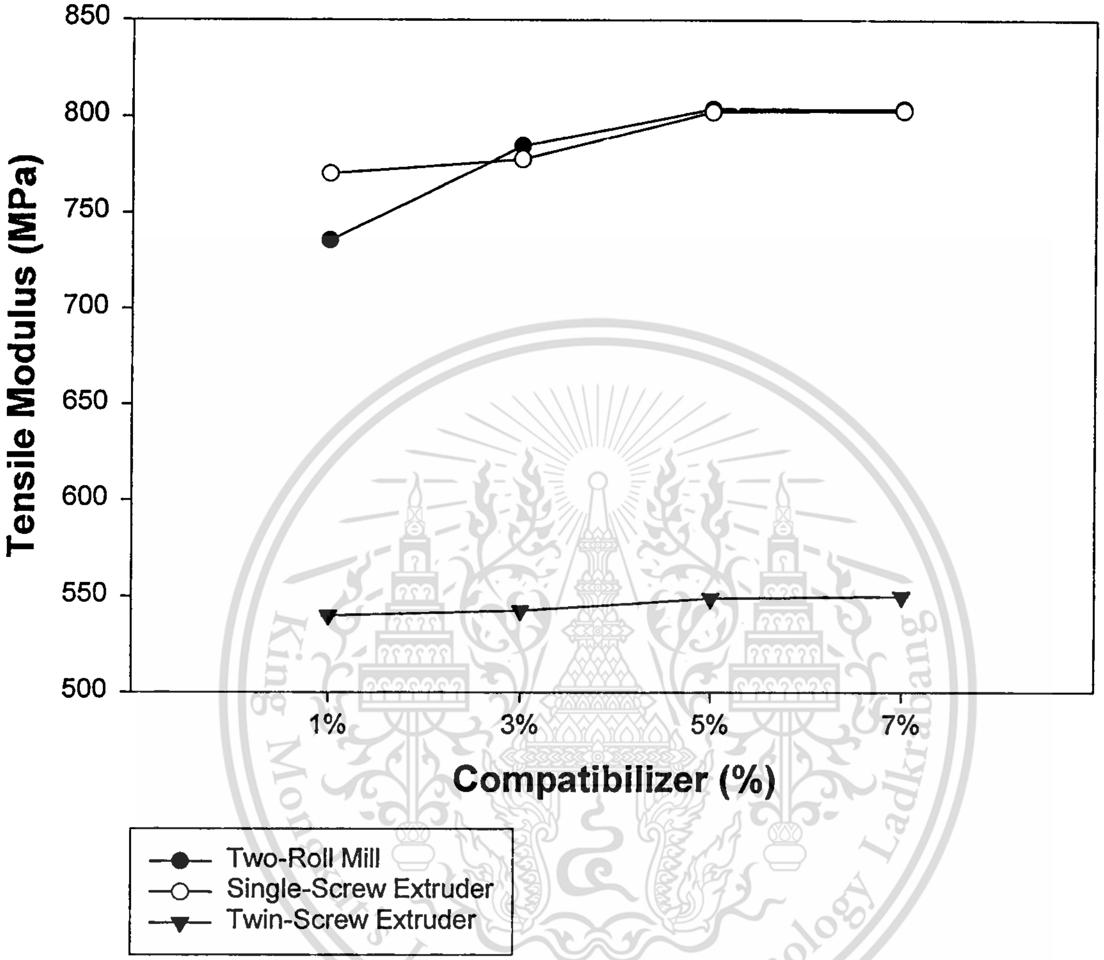

Figure 4.17 Effect of compatibiiizer on modulus of PP/PA/MA blend preparing using two roll mill, single-screw extruder and twin-screw extruder.

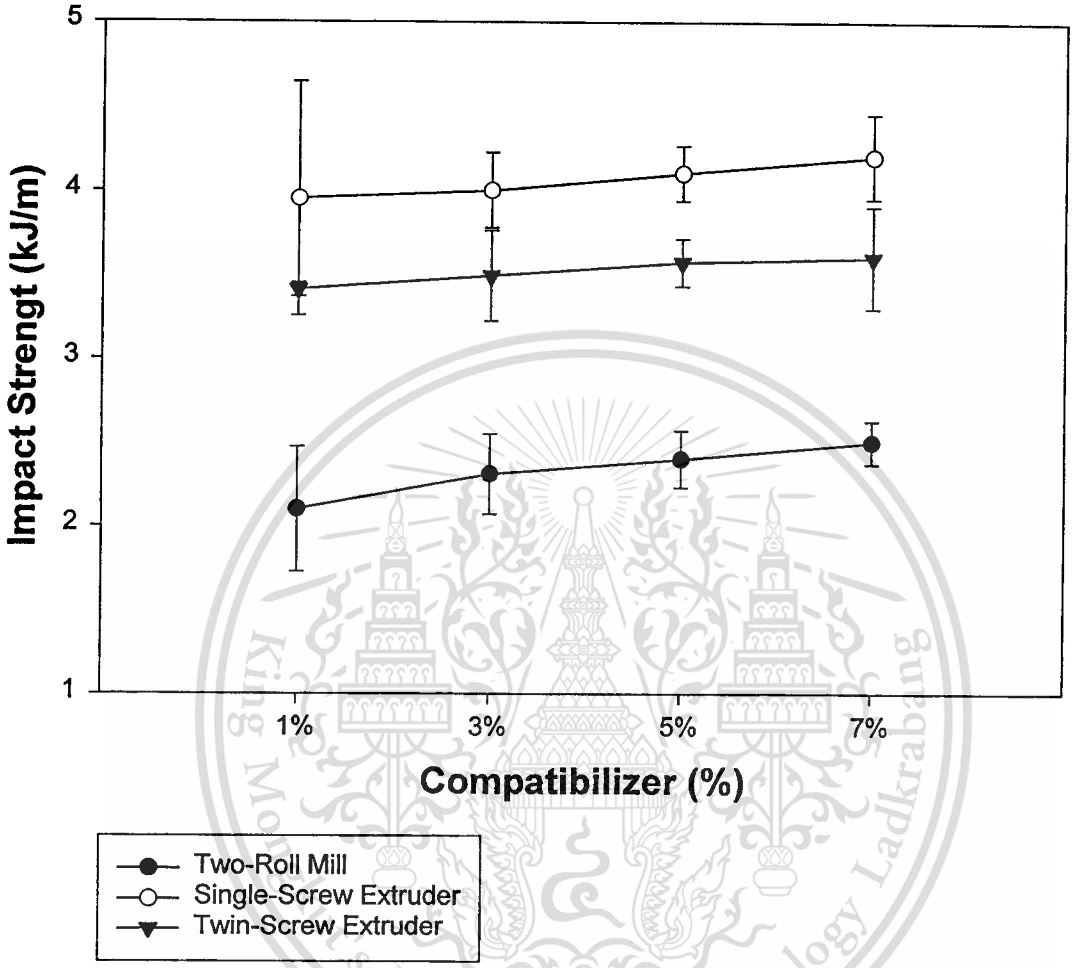

Figure 4.18 Effect of compatibilizer on impact strength of PP/PA/MA blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

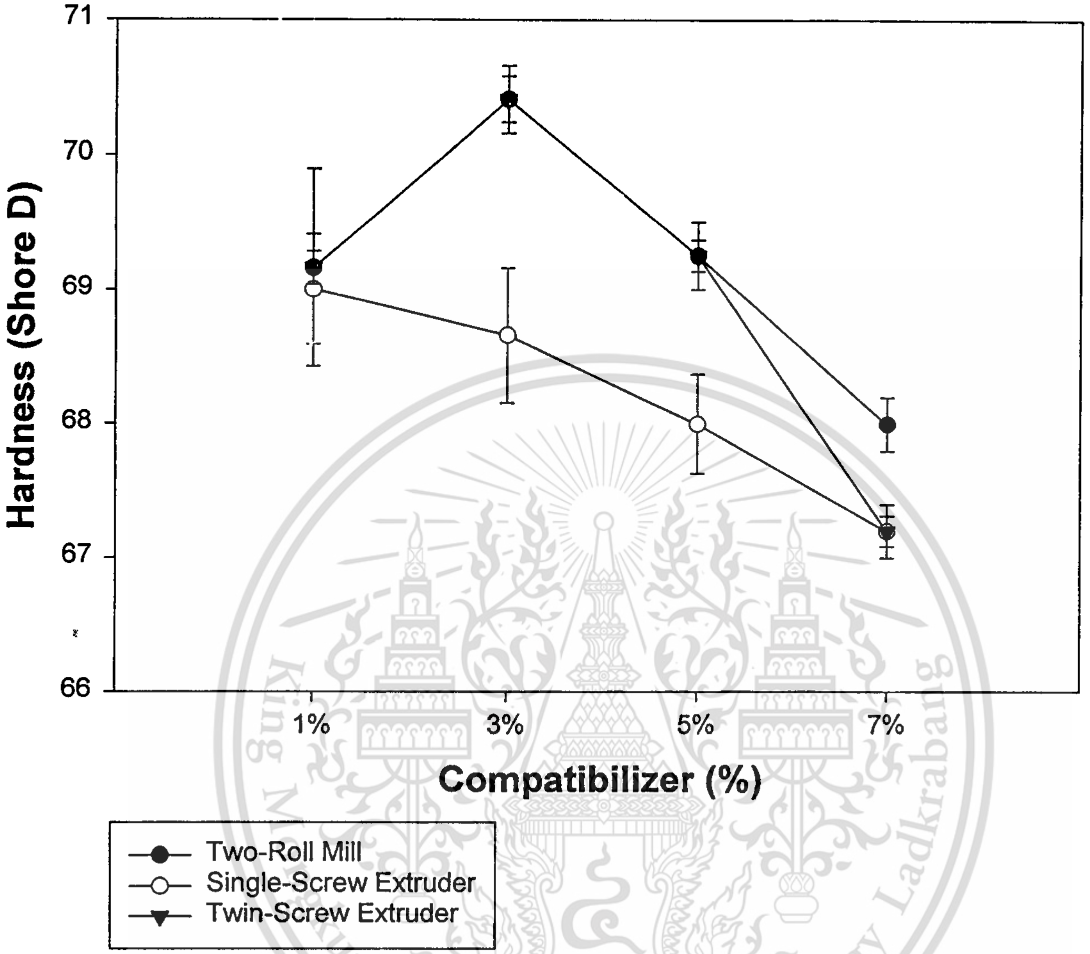

Figure 4.19 Effect of compatibilizer on hardness of PP/PA/MA blend preparing using two-roll mill, single-screw-extruder and twin-screw extruder.

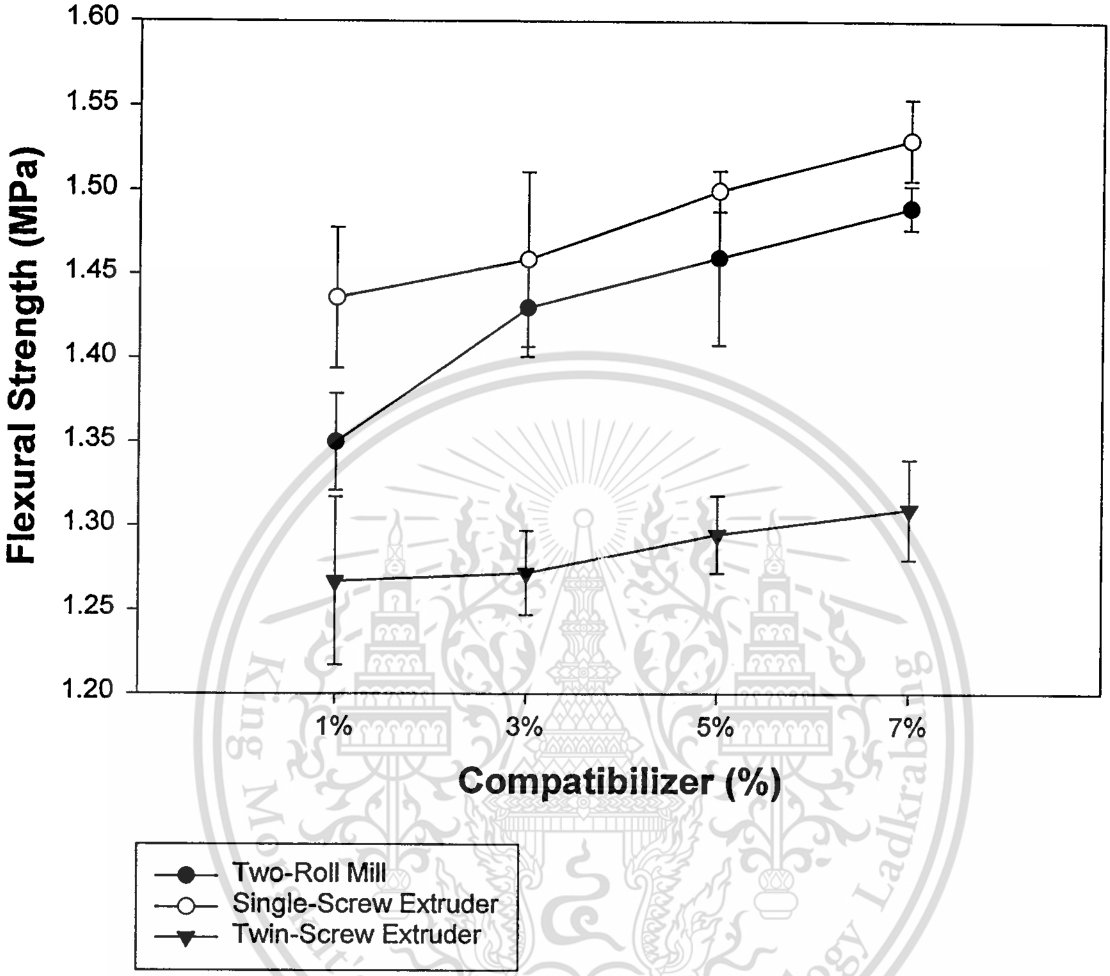

Figure 4.20 Effect of compatibilizer on flexural strength of PP/PA/MA blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

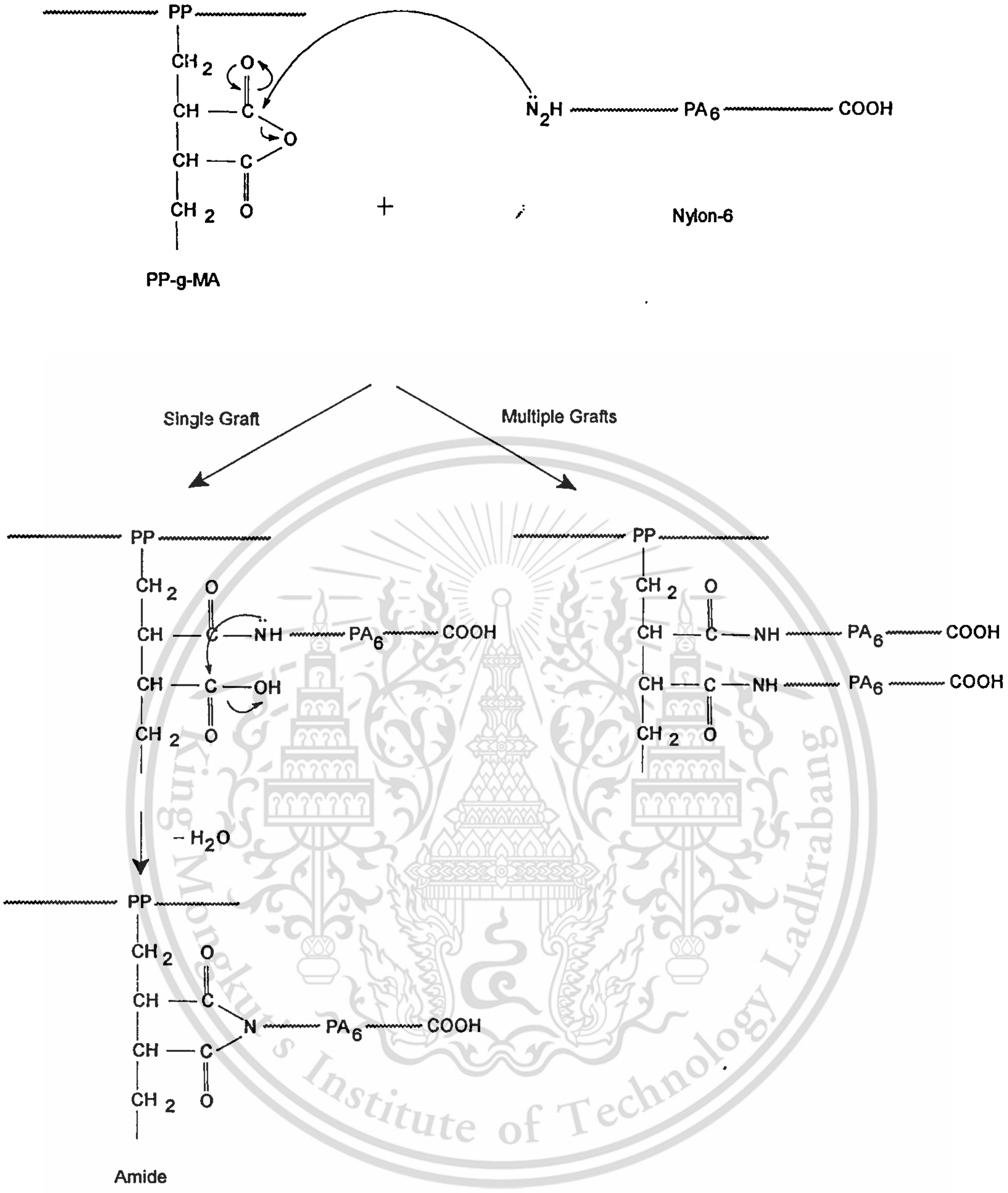

Figure 4.21 Anhydride / amine reaction showing single and possible multiple grafting patterns.

4.3 Effect of Additives on Mechanical Properties

4.3.1 Glass Fibers

Chopped glass fibers (E-typed) with 1-2 cm length were mixed with PP/PA/MA blends using two-roll mill, single-screw and twin-screw extruder. Diameter of glass fiber were 10 μm. Addition of the glass fiber to the recycled polypropylene and nylon-6 blends with the compatibilizer was expected to improve mechanical properties of blends. By varying the percentage of glass fiber loading in the range of 0 to 10% by weight on the blends, most of the blend properties were increased except modulus (Figures 4.22 to 4.26). The tensile strength was increased with increasing glass fibers content in the same maner as the flexural strength, impact strength and hardness because the glass fibers acted as reinforcing fillers for the recycled blends due to large surface areas of the fibrous form. The opposite result was found for modulus at 3% strain, since it decreased with increasing glass fiber content. It has been found that the glass fibers reduced the toughness of the blends. It was expected that the toughness was decreased as the rigidity increased by the addition of glass fibers because the addition of the glass fibers into the blends destroyed the continuity of the matrix and caused premature failure[19]. It also had been known that the more the fibers loading, the more the possibility of poor contact areas between the fibers and the matrices which were the source of premature failure and lower modulus [19].

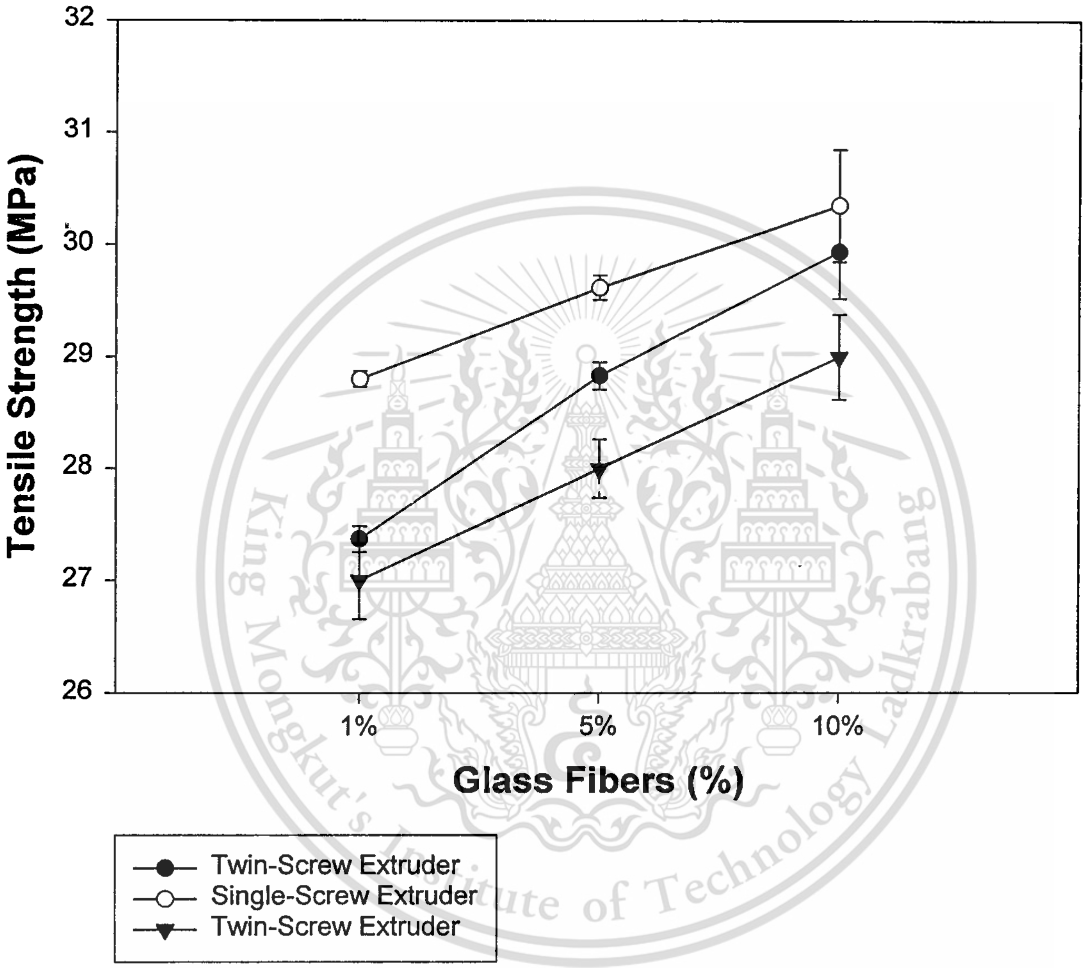

Figure 4.22 Effect of glass fiber contents on tensile strength of PP/PA/MA/glass fibers blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

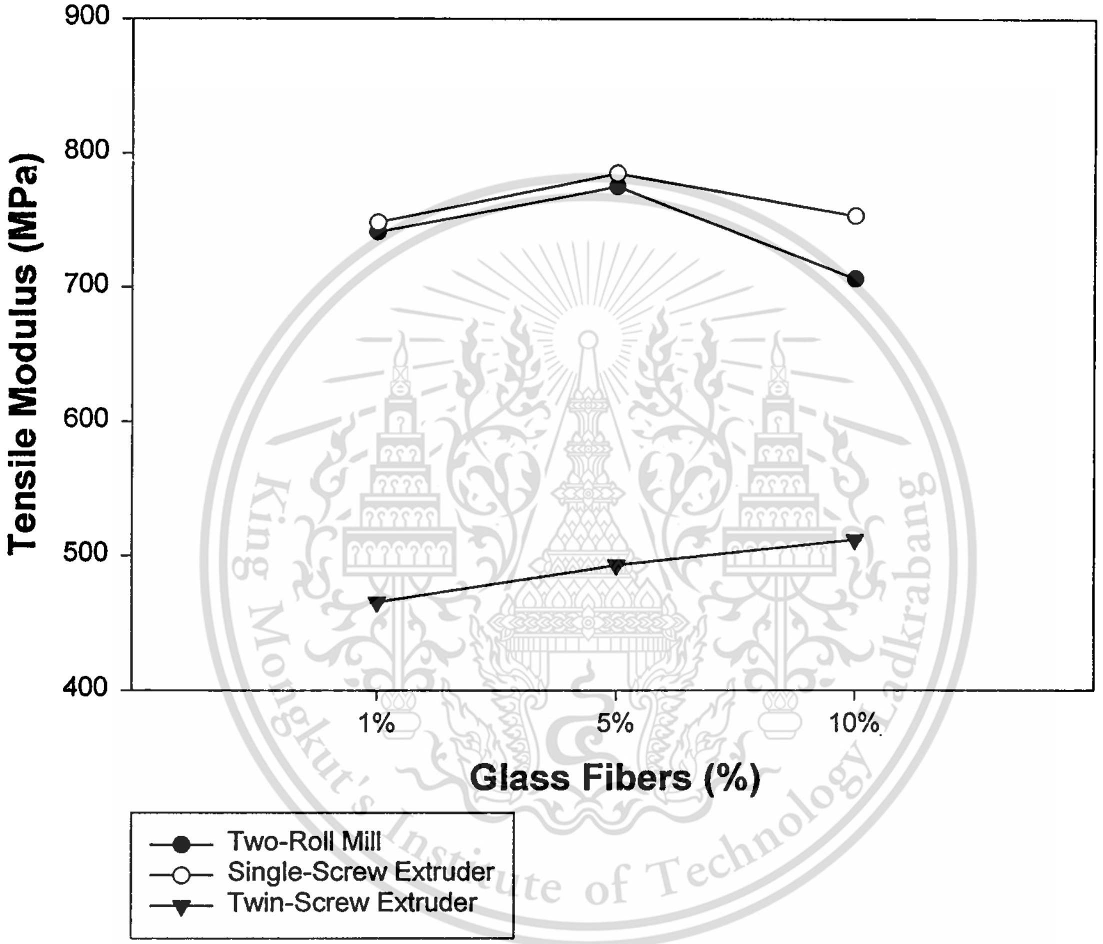

Figure 4.23 Effect of glass fiber contents on modulus of PP/PA/MA/glass fibers preparing using two-roll mill, single-screw extruder and twin-screw extruder.

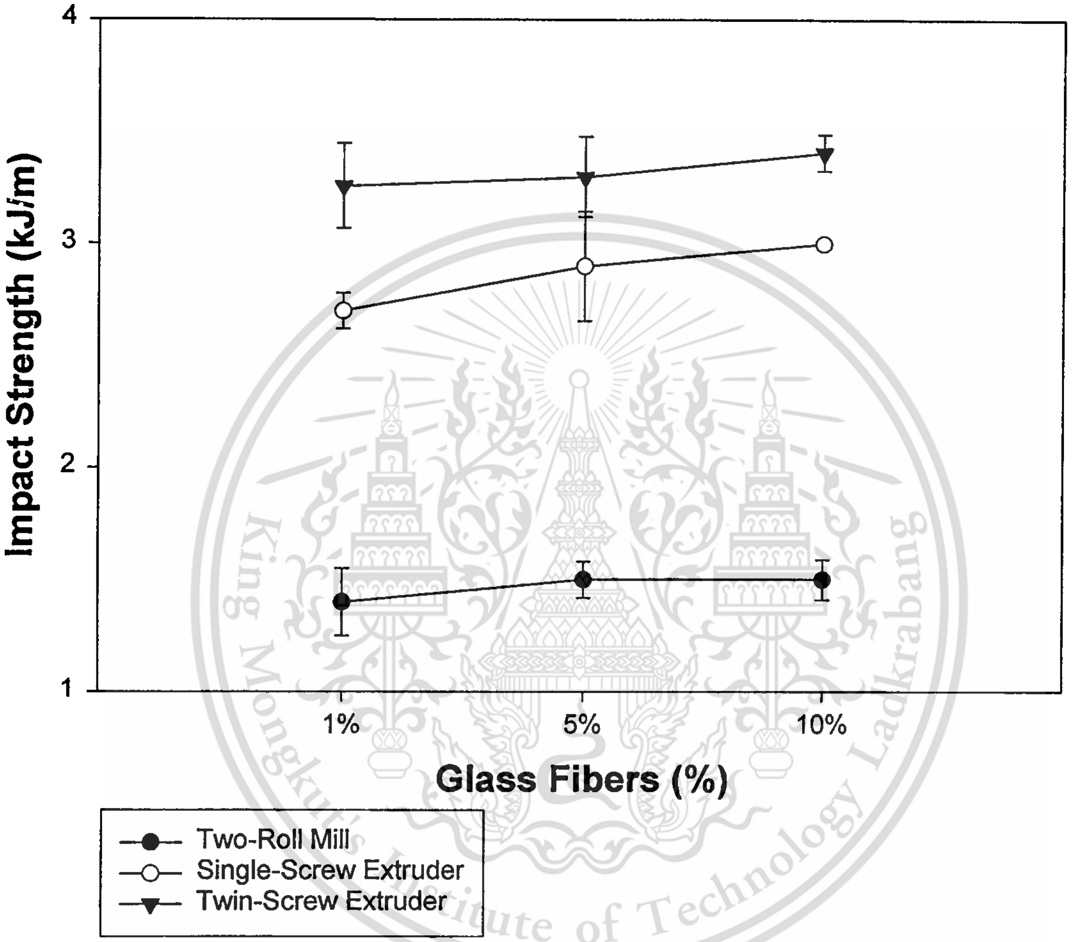

Figure 4.24 Effect of glass fiber contents on impact strength of PP/PA/MA/glass fibers blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

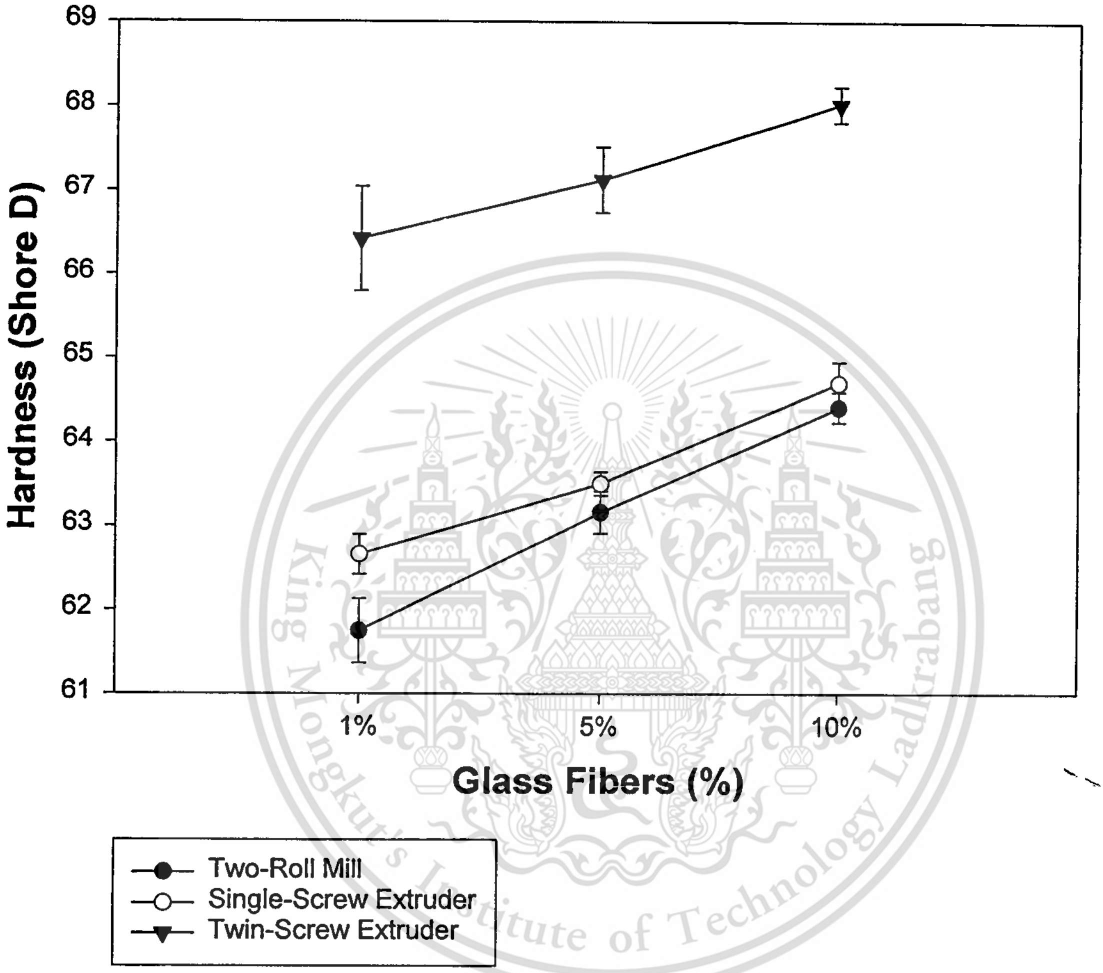

Figure 4.25 Effect of glass fiber contents on hardness of PP/PA/MA/glass fibers blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

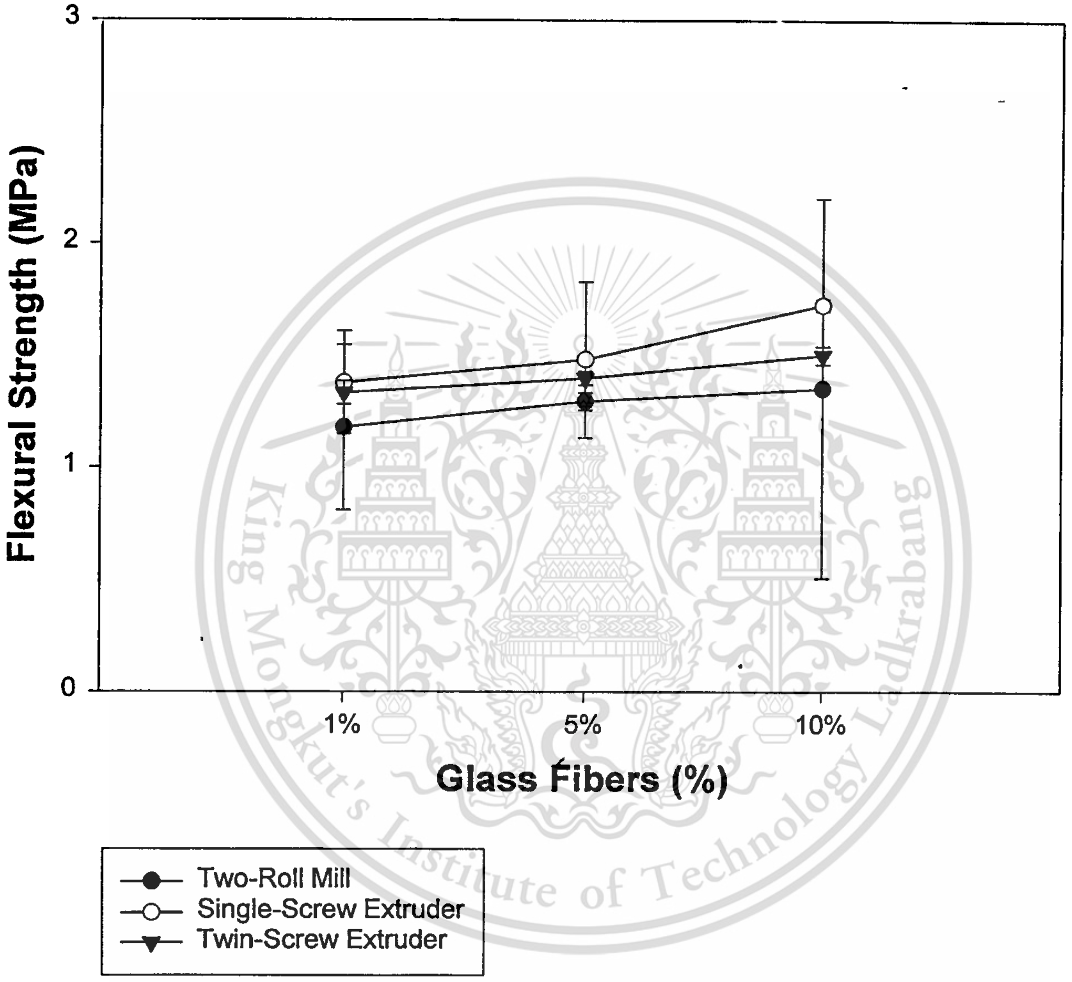

Figure 4.26 Effect of glass fiber contents on flexural strength of PP/PA/MA/glass fibers blend preparing using two-roll single-screw extruder and twin-screw extruder.

4.3.2 Calcium Carbonates

Non-coated calcium carbonates were blends with PP/PA and compatibilizer. Diameter and specific surface area of calcium carbonate were 8.09 μm and 1.1088 m^2/g, respectively. Addition of calcium carbonate to the blends of recycled polypropylene and nylon-6 with the compatibilizer was expected to lowering raw material cost. Calcium carbonates were loaded in the range of 0 to 10% by weight. Properties of the blends were shown in Figures 4.27 to 4.31.

The tensile strength, tensile modulus, impact strength, hardness and flexural strength had the same trend. Each properties was unchanged with addition of the calcium carbonate. The calcium carbonate acted as impurities for the recycled blends of which caused the failure to the blends. It also had known that the high calcium carbonate loading, the more continuity of the matrix was destroyed and caused premature failure [21]. The mechanical properties (tensile strength, tensile modulus, impact strength and flexural strength) of PP/PA/MA/Ca blends from the single-screw extruder were higher than two-roll mill but slightly higher than twin-screw extruder. (Figures 4.27 ,4.28 ,4.29 and 4.31) Because the twin-screw extruder was a co-rotating type which was shorter in screw length and lower shear. This would be lower dispersion, frictional heat and shorter contact time.

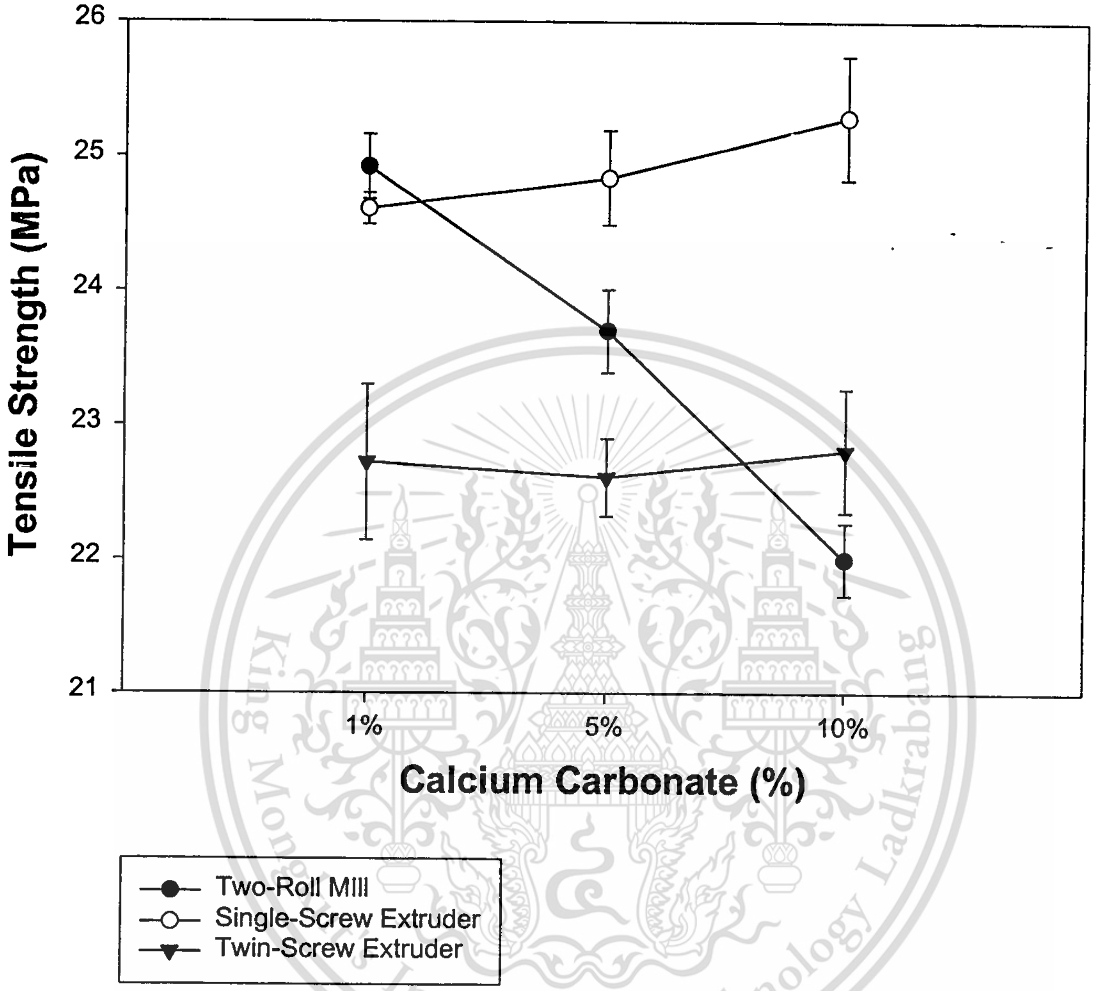

Figure 4.27 Effect of calcium carbonate contents on tensile strength of PP/PA/MA/$CaCO_3$ blend preparing using two-roll mill, single-screw and twin-screw extruder.

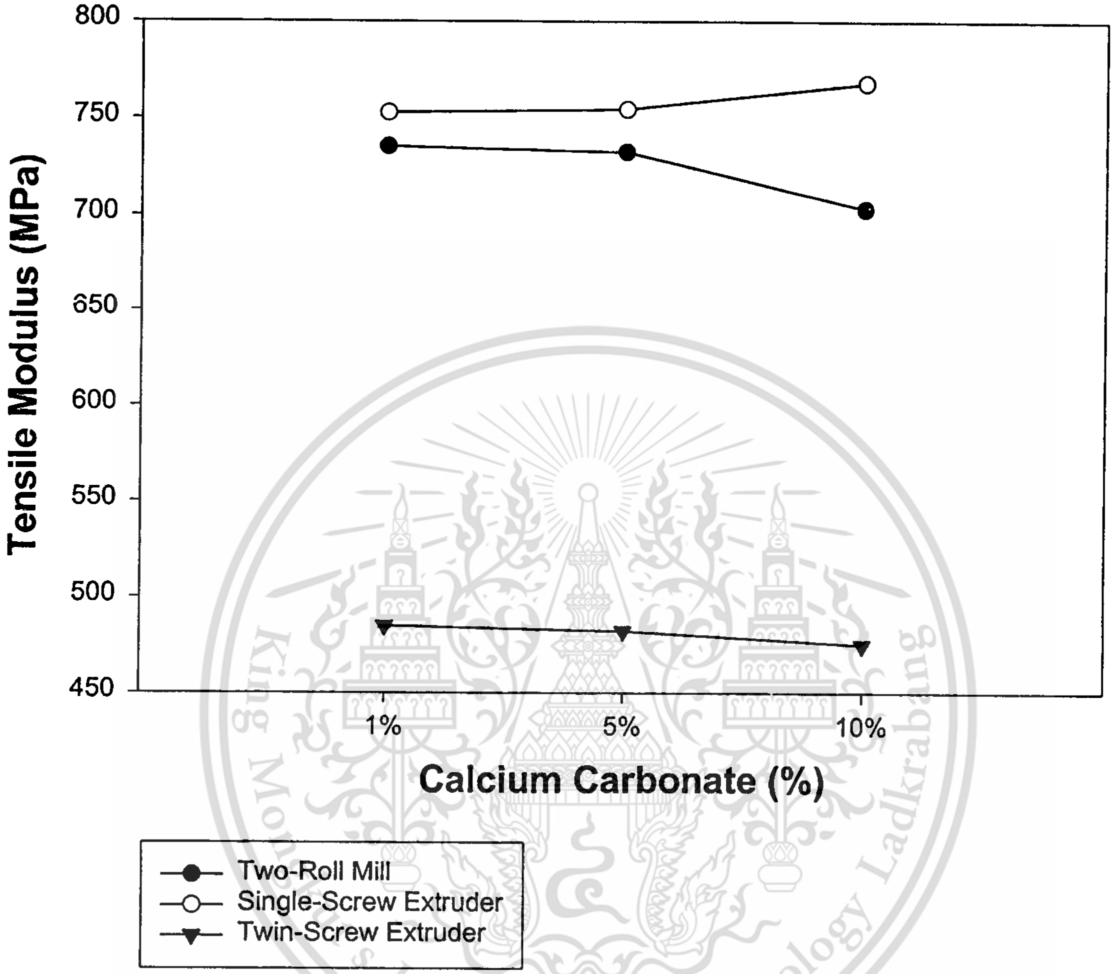

Figure 4.28 Effect of calcium carbonate contents on modulus of PP/PA/MA/$CaCO_3$ blend preparing using two-roll mill, single-screw and twin-screw extruder.

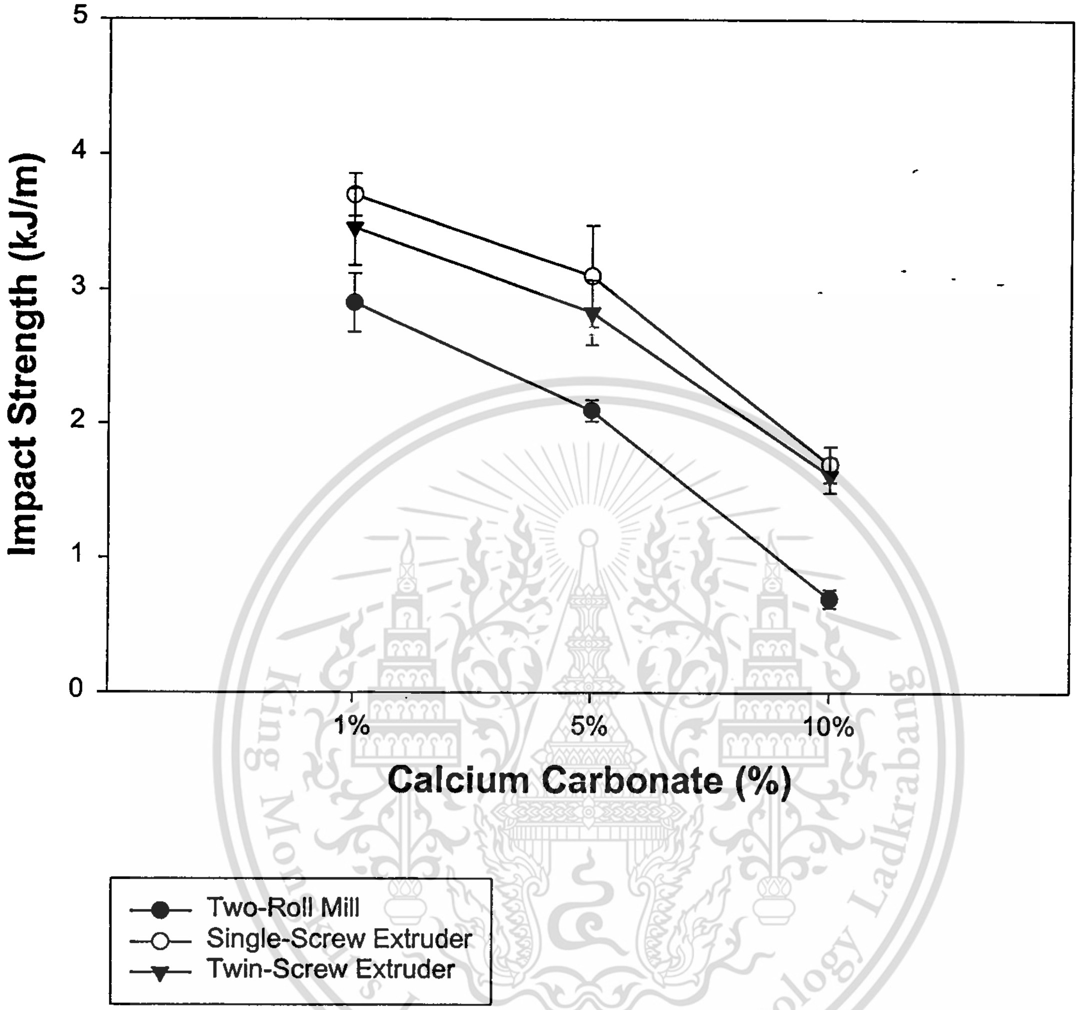

Figure 4.29 Effect of calcium carbonate contents on impact strength of PP/PA/MA/$CaCO_3$ blend preparing using two-roll mill, single-screw and twin-screw extruder.

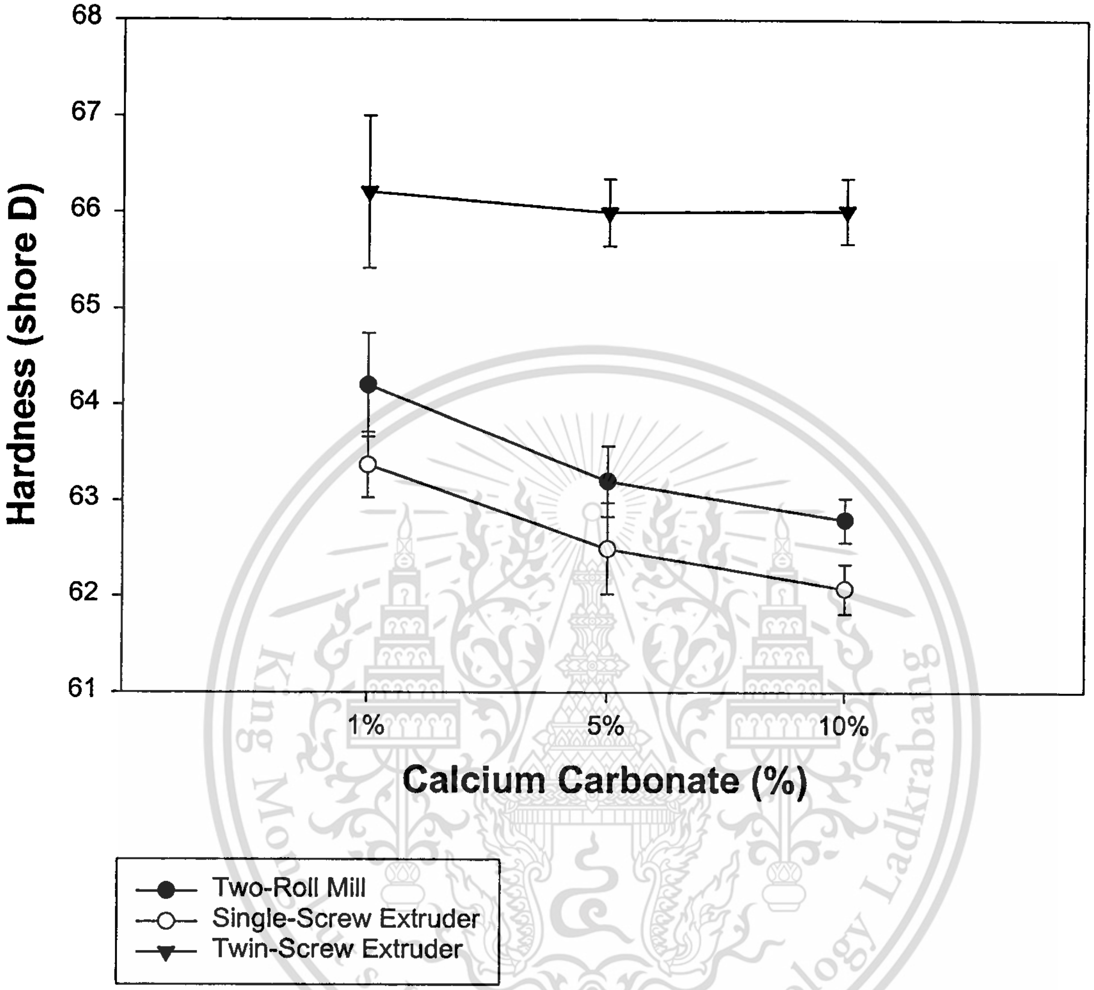

Figure 4.30 Effect of calcium carbonate contents on hardness of PP/PA/$CaCO_3$ blend preparing using two-roll mill, single-screw extruder and twin-screw extruder.

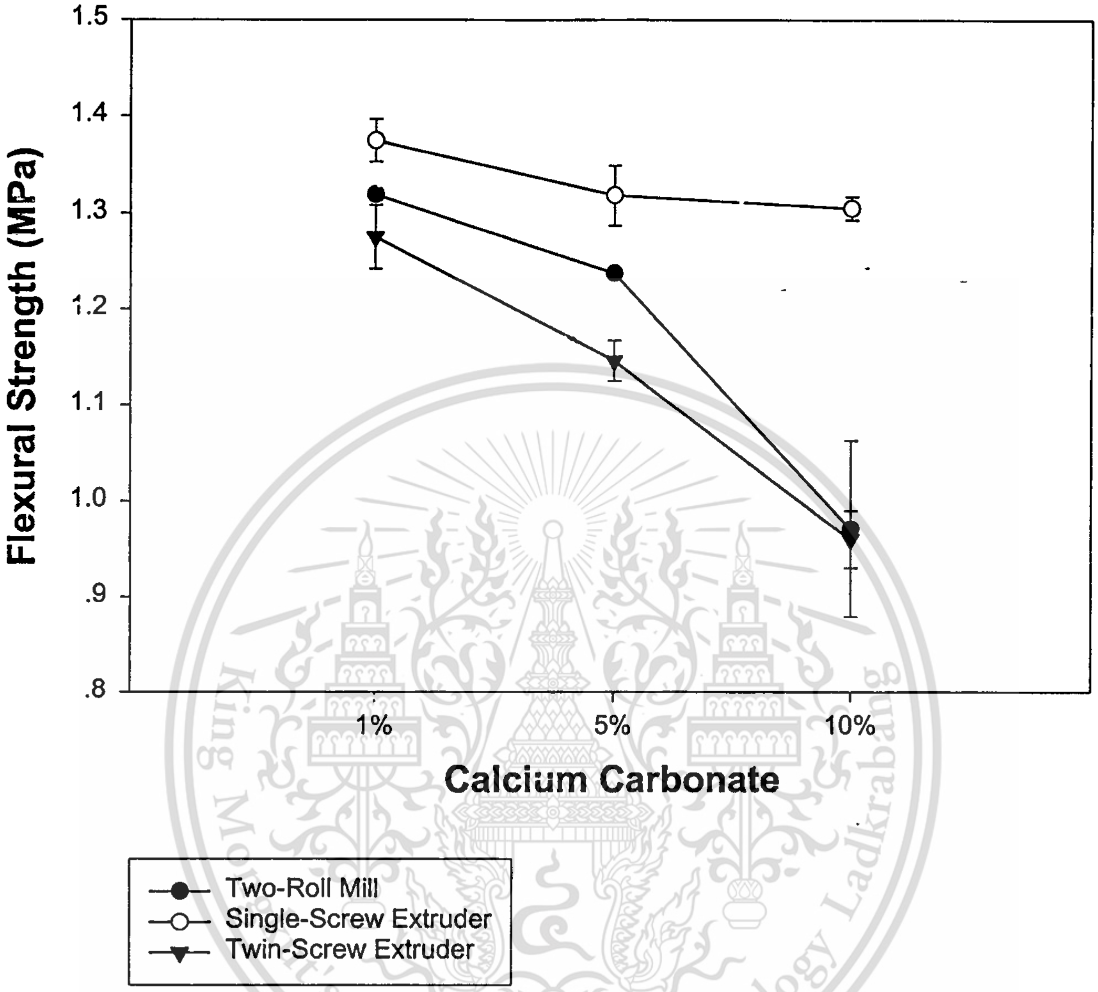

Figure 4.31 Effect of calcium carbonate contents on flexural strength of PP/PA/MA/$CaCO_3$ blend preparing using two-roll mill, single-screw and twin-screw extruder.

4.4 Fundamental Characterization

4.4.1 Morphological Property

A scanning electron microscope was used to study the morphology of the blends. In general, the morphologies of polymer blends depend on shear history in the mixer, viscosity ratio, and the interfacial tension between matrix and minor components. In particular, the interfacial tension between two polymers is very important for phase morphology, and the added compatibilizer play a major role in lowering interfacial tension and thereby forming a finer morphology. The interfacial adhesion between polypropylene and nylon-6 was investigated by scanning electron microscope in order to observe the effect of compatibilizer and additives on two-roll mill, single-screw extruder and twin-screw extruder. The SEM micrographs of recycled blends prepared from each process were shown in Figures 4.32 to 4.47 at a magnification of 2000 times.

Figures 4.32 to 4.35 are the SEM micrographs of recycled PP/PA/MA blend with two-roll mill. Figure 4.32 presents the morphology of non-compatibilized polypropylene and nylon-6 blend with two-roll mill and Figure 4.33 showed the phase morphology of compatibilized blend. The phase morphology of the non-compatibilized polypropylene and nylon-6 blend was very poor since the dispersed phase (nylon-6) was large and coarse due to the inherent immiscibility. The compatibilized blend of polypropylene and nylon-6 exhibits more homogeneous phase structure since polypropylene grafted maleic anhydride aids the compatibility of both polypropylene and nylon-6. The maleic anhydride groups of compatibilizer get along with the amine group of nylon-6 and lead to a cyclic imide bond by the ring opening reaction at processing temperature. The *in situ* formed copolymers (PP-g-PA), which acted as a true compatibilizer, locate mostly along the interface between the two constituting polymer polypropylene and nylon-6. Figures 4.34 and 4.35 show the SEM micrographs of the compatibilized blend with adding calcium carbonate and glass fiber, respectively. They indicated that the strong interfacial adhesion between the glass fiber and the matrix was greater than that between the calcium carbonate and the matrix, according to the nature of each filler capability.

Figures 4.36 to 4.39 showed the morphologies of recycled polypropylene and nylon 6 blend with single-screw extruder. The SEM micrograph of the non-compatibilized blend (Figure 4.36) shows the number of dispersed phase (nylon-6) in the continuous phase of polypropylene which indicats the poor interfacial adhesion between nylon-6 and the matrix. The

SEM micrograph of the compatibilized blend (Figure 4.37) indicats more homogeneous phase structure. The compatibilized blend withs calcium carbonate and glass fiber give the poor interfacial adhesion between additive and the matrix, when compared to that without filler a (Figures 4.38 to 4.39).

Figures 4.40 to 4.43 show the morphologies of recycled polypropylene and nylon-6 blends with twin-screw extruder. The morphology of non-compatibilized blend is very poor since dispersed phase is large and coarse due to the inherent immiscibility (Figure 4.40). On the other hands, the compatibilized blends exhibited more homogenous phase structure (Figures 4.41). Figures 4.42 to 4.43 showed the SEM micrographs of the compatibilized blend with calcium carbonate and glass fiber, which show the same tendency as in single-screw extruder.

Figures 4.44-4.46 showed the fibers pull-out in SEM micrographs. Figure 4.47 shows the calcium carbonate particle in the SEM micrographs at X2000 for twin-screw extruder. This was corespondent to the mechanical properties of PP/PA/MA/Ca in section 4.3.2. The results could be also related to the agglomeration of the calcium carbonate. If the agglomeration of calcium carbonate was found it meant that the point of weakness in finished material was occurred.

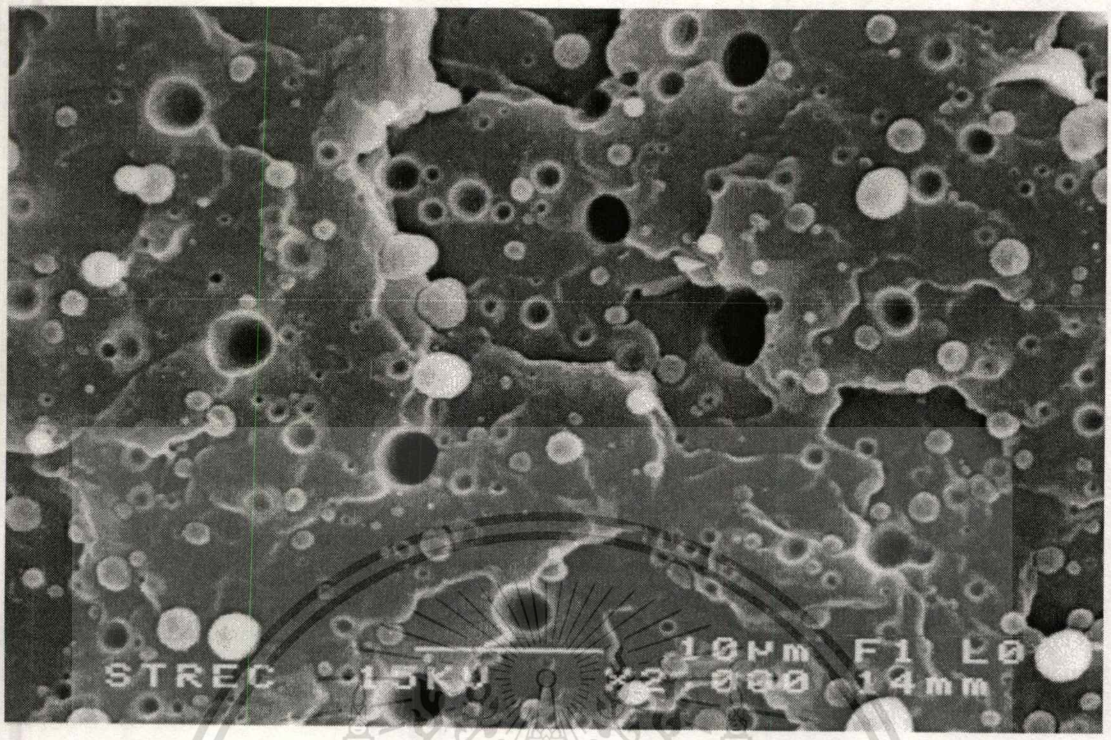

Figure 4.32 SEM micrograph of recycled PP/PA nle d with two-roll mill at X 2,000 (15 KV).

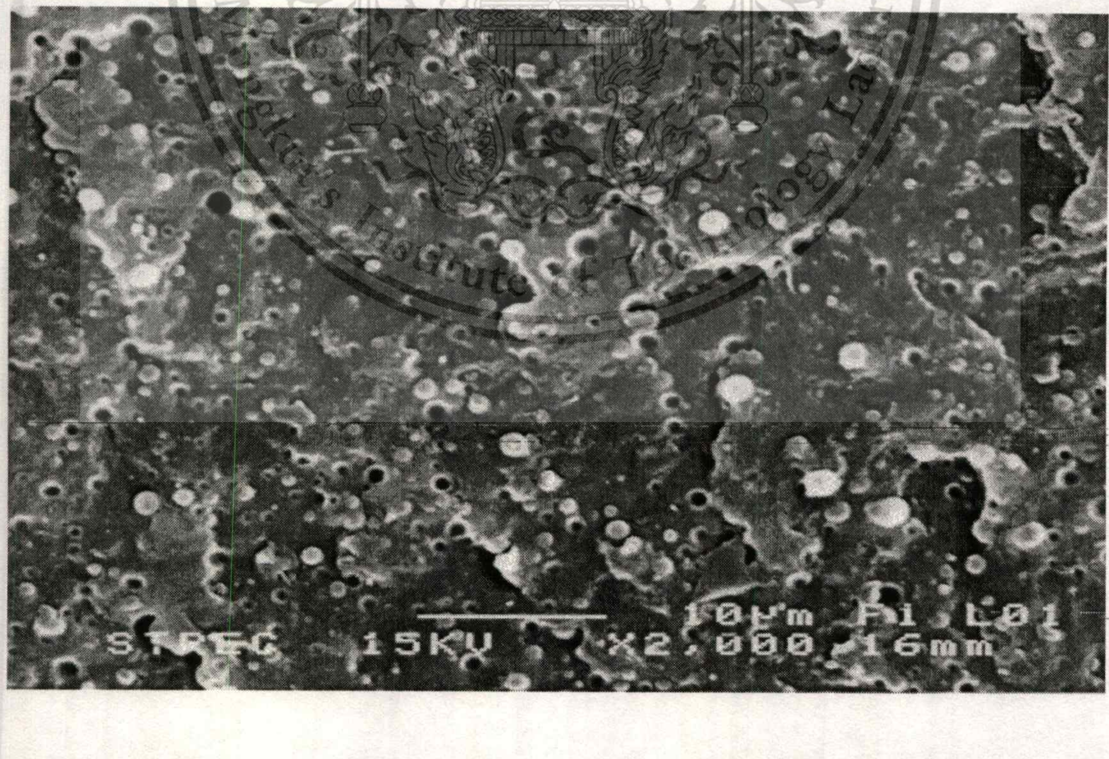

Figure 4.33 SEM micrograph of recycled PP/PA/MA nle d with two-roll mill at X 2,000 (15 KV).

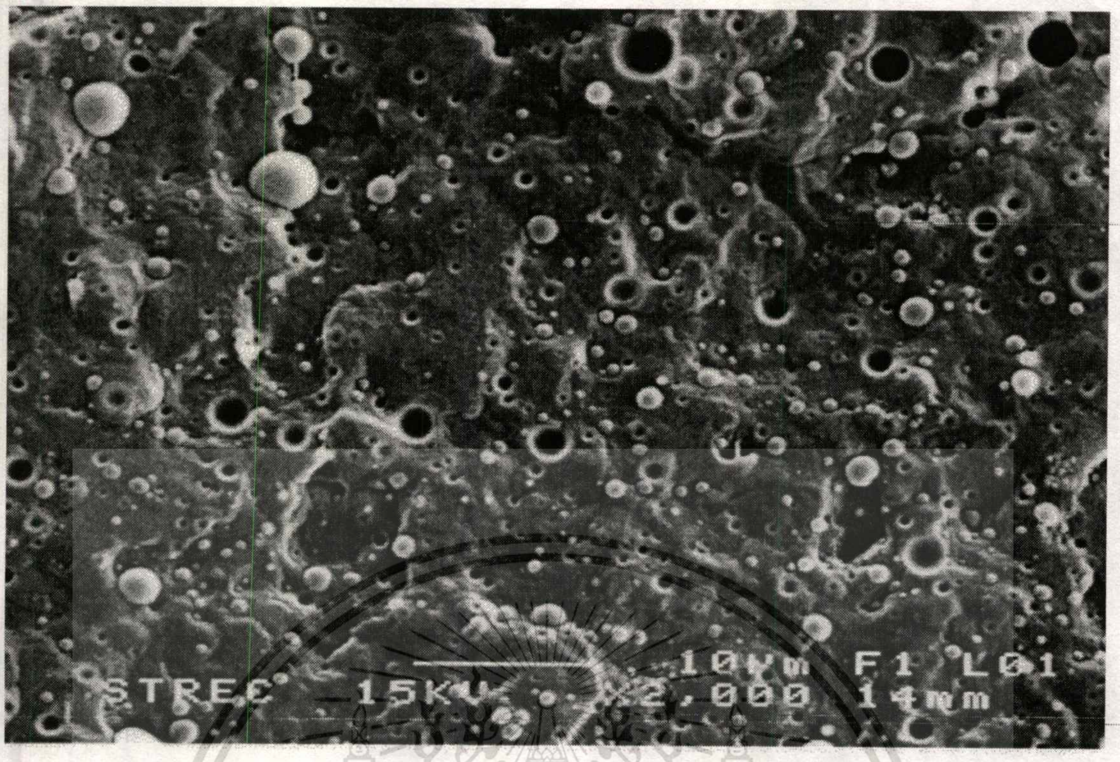

Figure 4.34 SEM micrograph of recycled PP/PA/MA/$CaCO_3$ added blend with two-roll mill at X 2,000 at (15 KV).

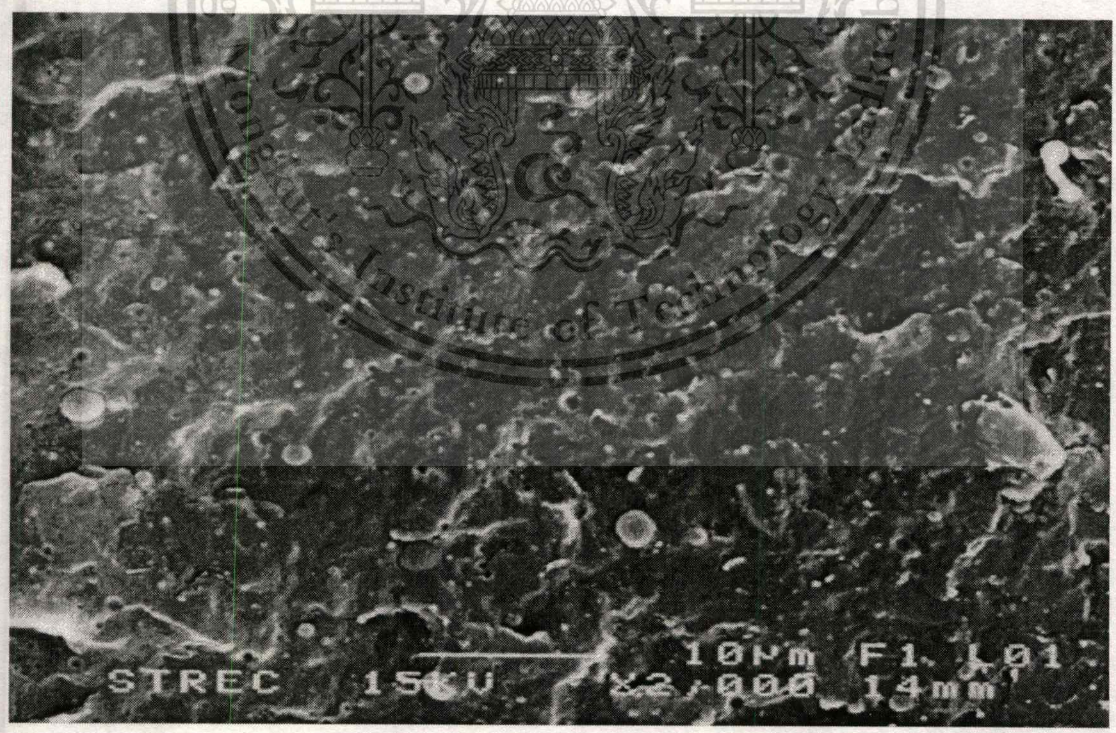

Figure 4.35 SEM micrograph recycled of PP/PA/MA/glass fibers blend with two-roll mill at X 2,000 (15 KV).

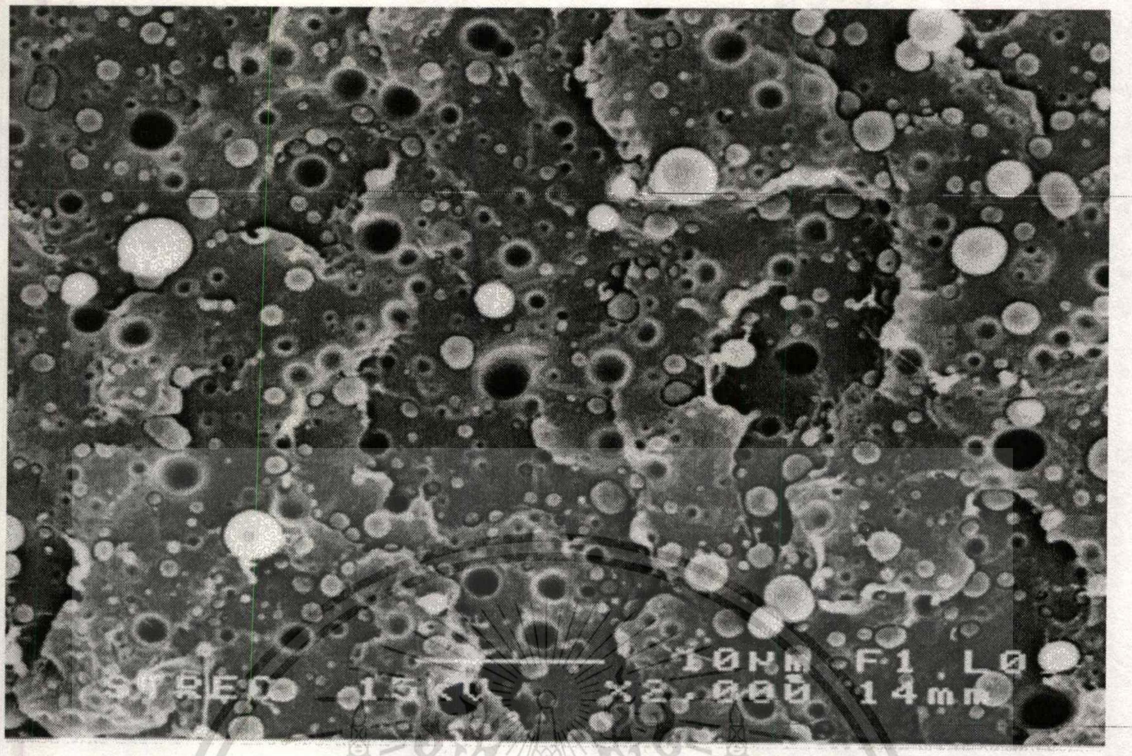

Figure 4.36 SEM micrograph of recycled PP/PA blend with single-screw extruder at X 2,000 (15 KV).

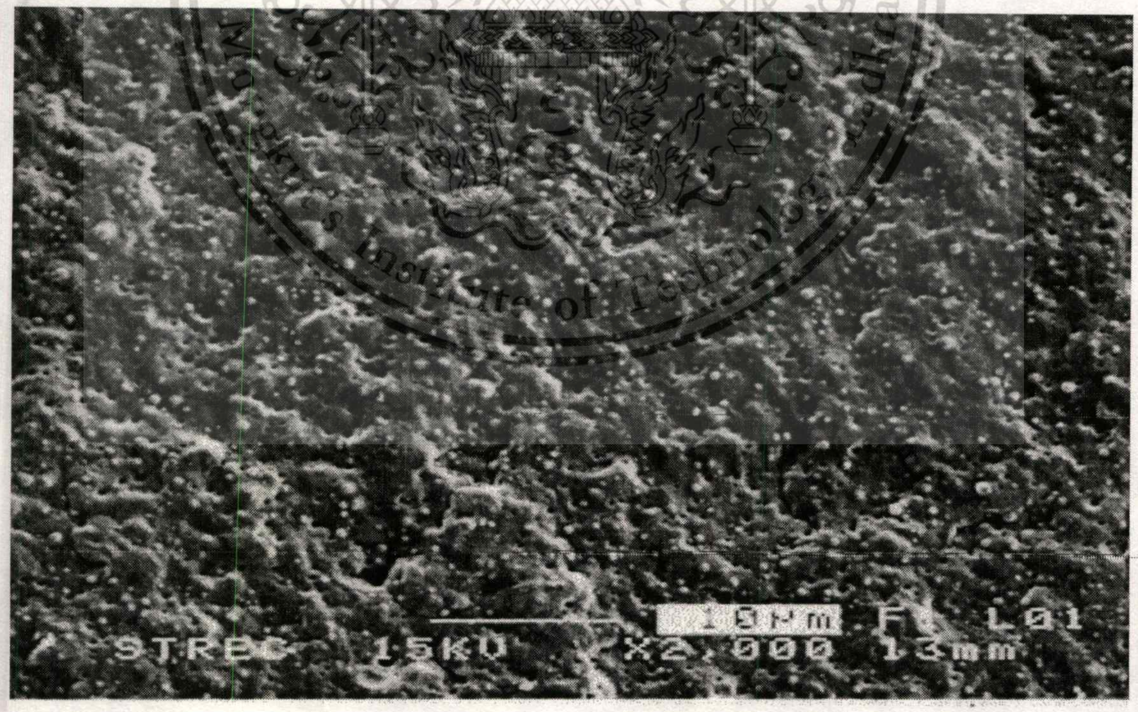

Figure 4.37 SEM micrograph of recycled PP/PA/MA blend with single-screw extruder at X 2,000 (15 KV).

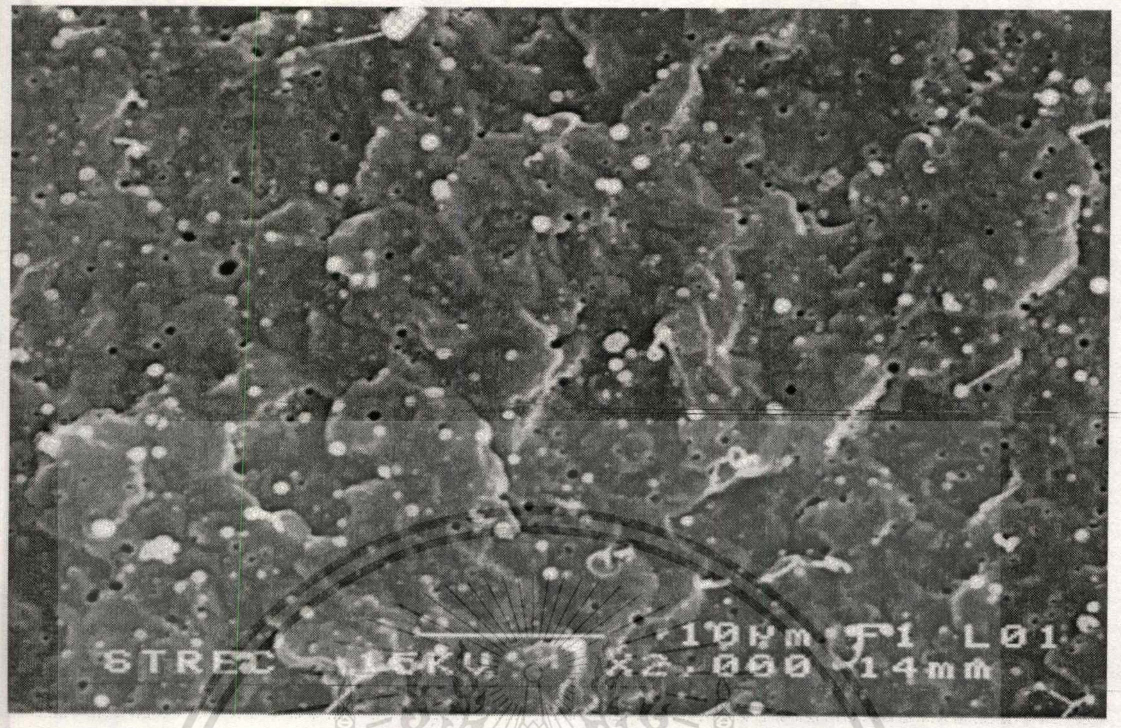

Figure 4.38 SEM micrograph of recycled PP/PA/MA/$CaCO_3$ blend with single-screw extruder at X 2,000 (15 KV).

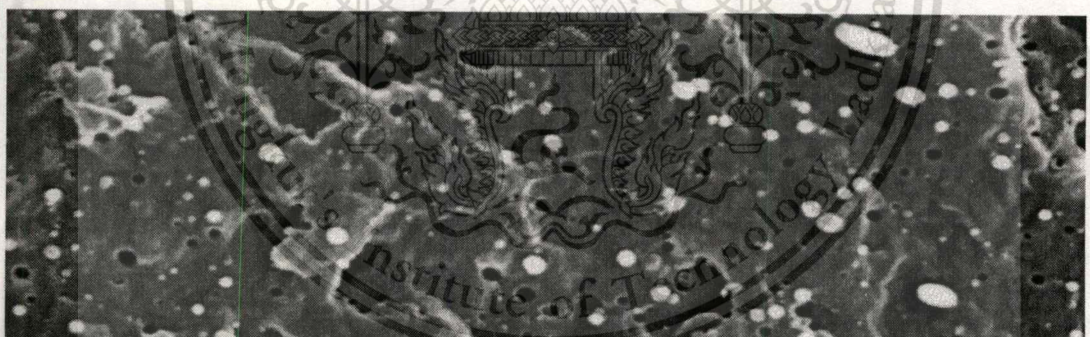

Figure 4.39 SEM micrograph of recycled PP/PA/MA/glass fibers blend with single-screw extruder at X 2,000 (15 KV).

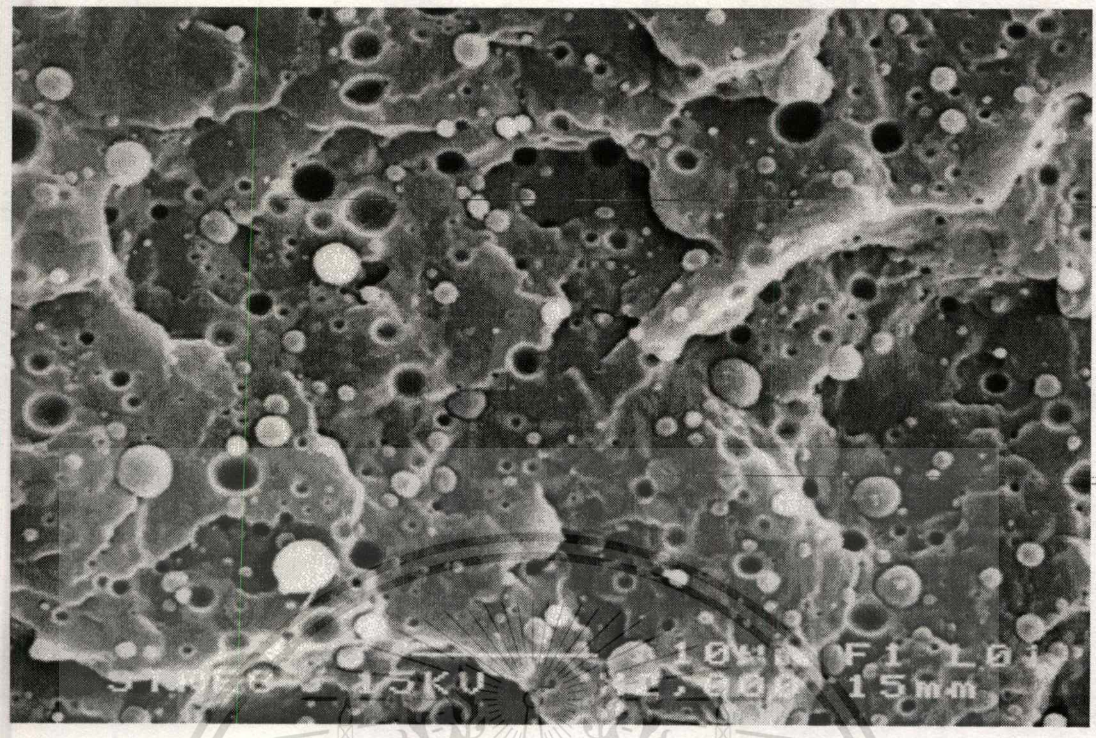

Figure 4.40 SEM micrograph of recycled PP/PA blend with twin-screw extruder at X 2,000 (15 KV).

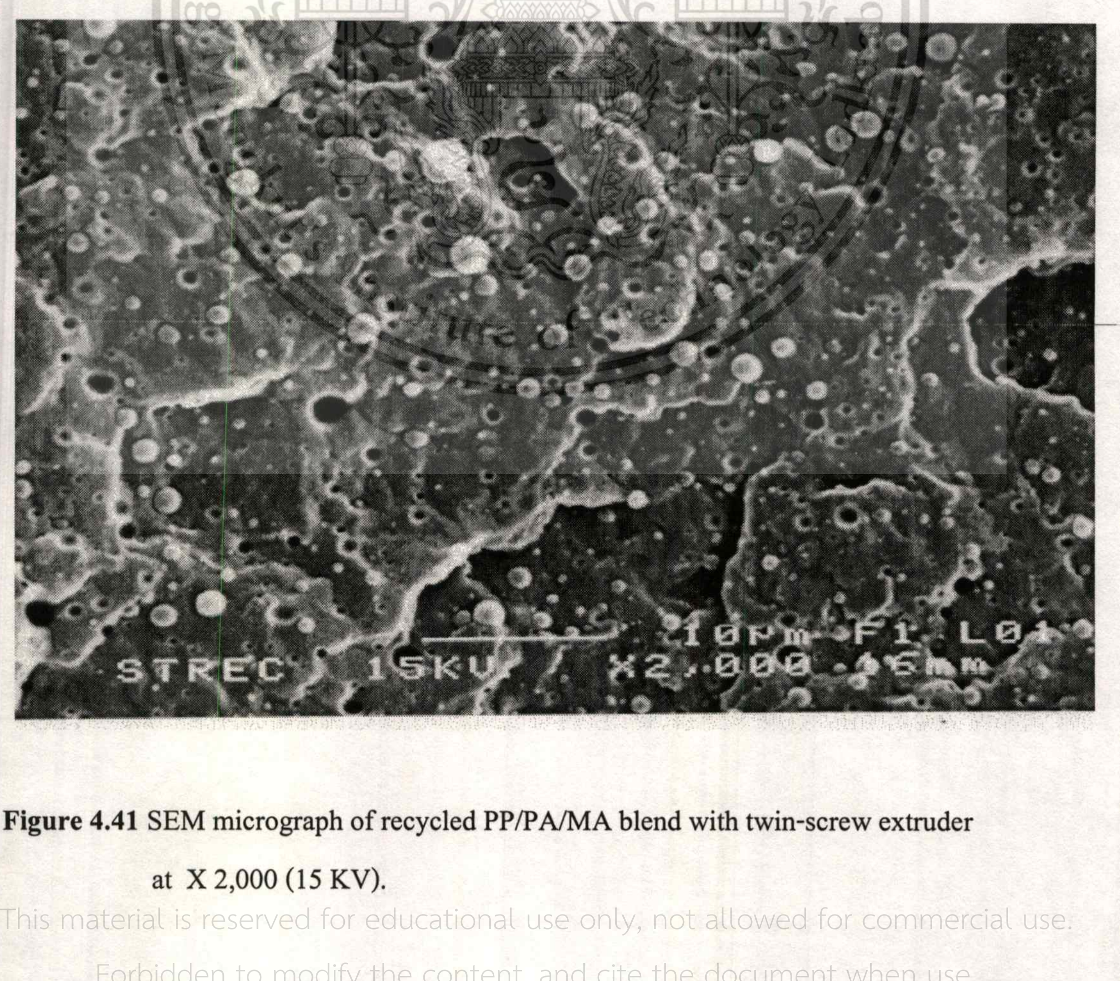

Figure 4.41 SEM micrograph of recycled PP/PA/MA blend with twin-screw extruder at X 2,000 (15 KV).

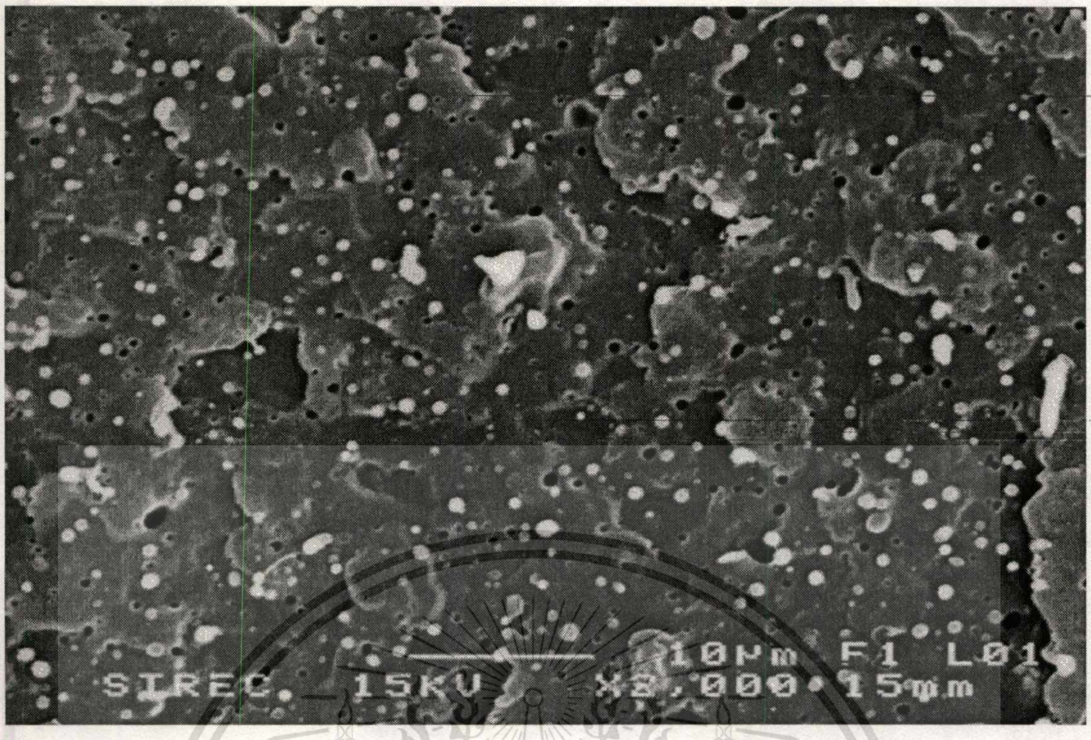

Figure 4.42 SEM micrograph of recycled PP/PA/MA/$CaCO_3$ blend with twin-screw extruder at X 2,000 (15 KV).

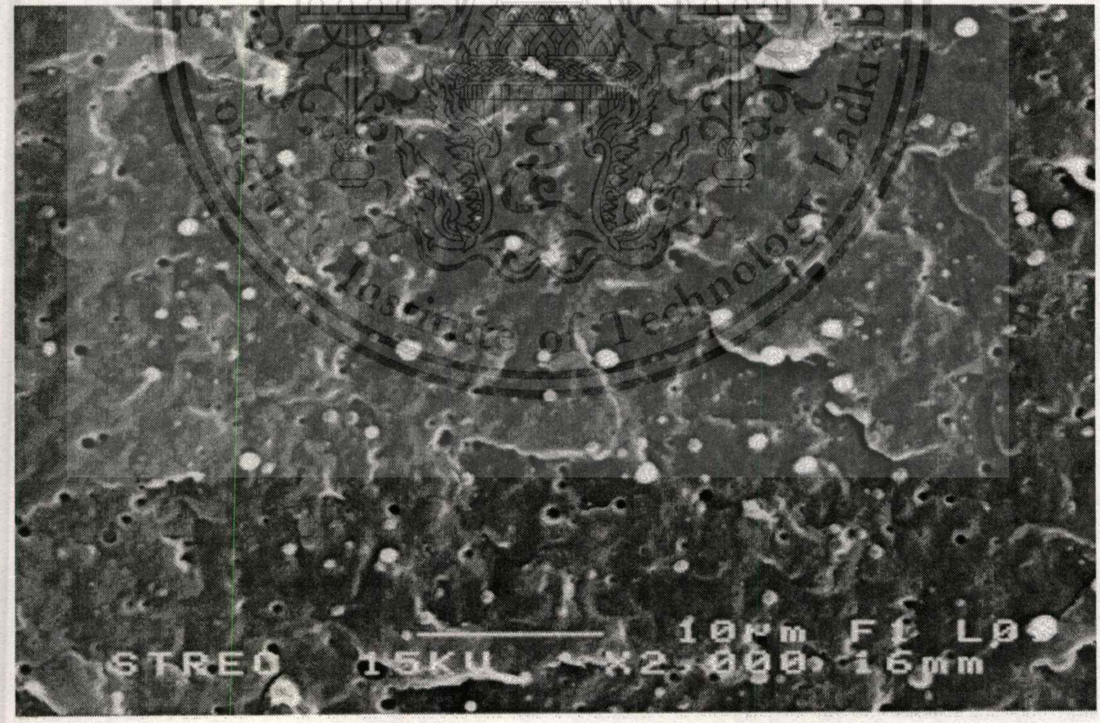

Figure 4.43 SEM micrograph of recycled PP/PA/MA/glass fibersblend with twin-screw extruder at X 2,000 (15 KV).

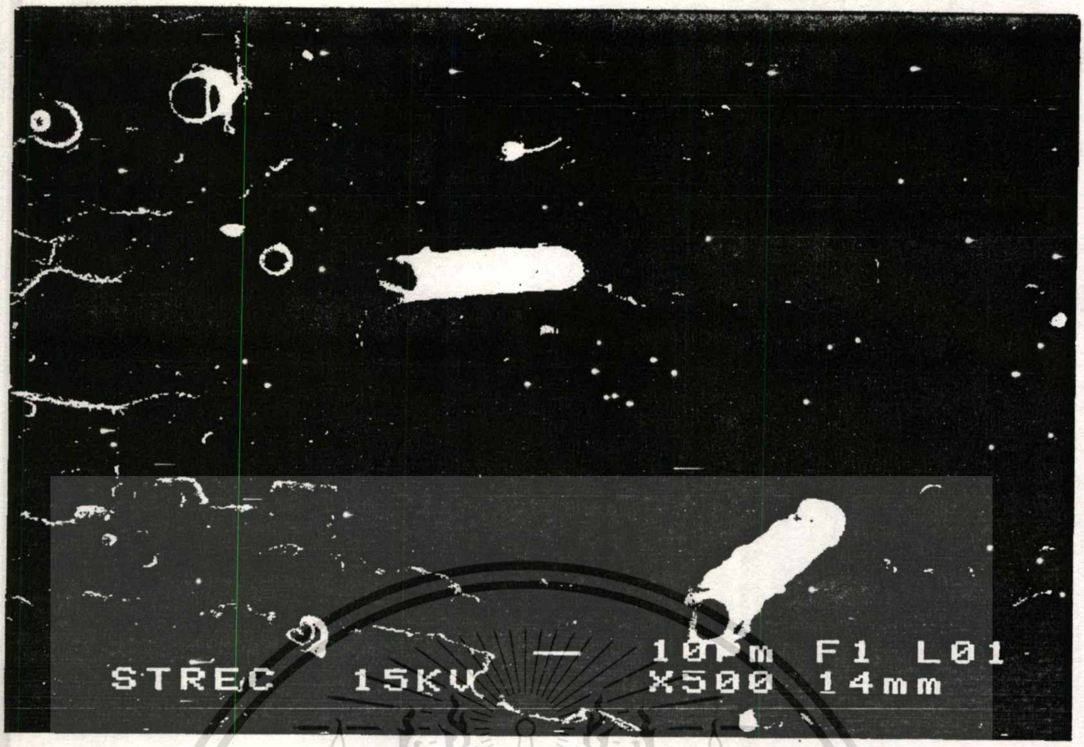

Figure 4.44 SEM micrograph of recycled PP/PA/MA/glass fiber blend with two-roll mill showed the fibers pull-out at X 2,000 (15 KV).

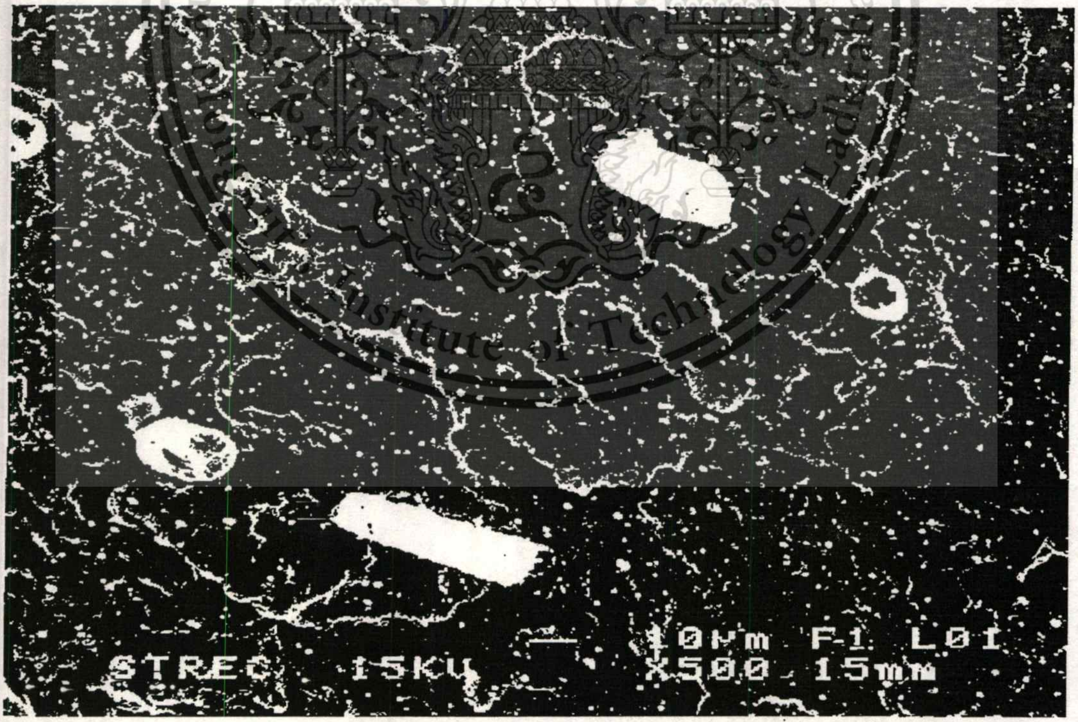

Figure 4.45 SEM micrograph of recycled PP/PA/MA/glass fiber blend with single-screw extruder showed the fibers pull-out at X 2,000 (15 KV).

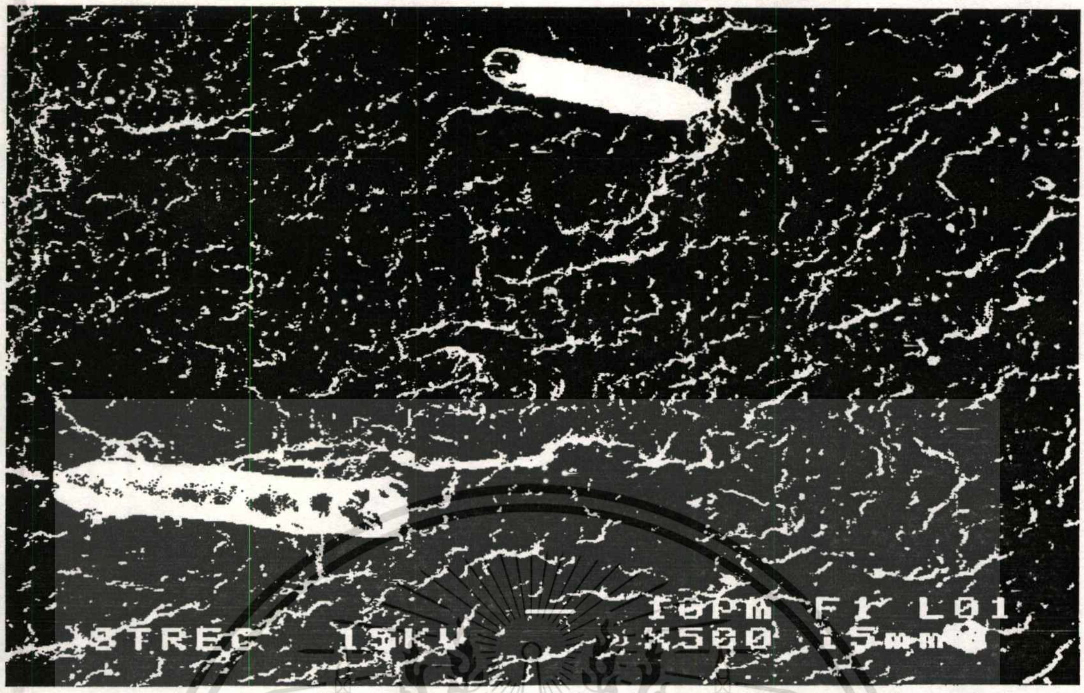

Figure 4.46 SEM micrograph of recycled PP/PA/MA/glass fiber blend with twin-screw extruders showed the fibers pull-out at X 2,000 (15 KV).

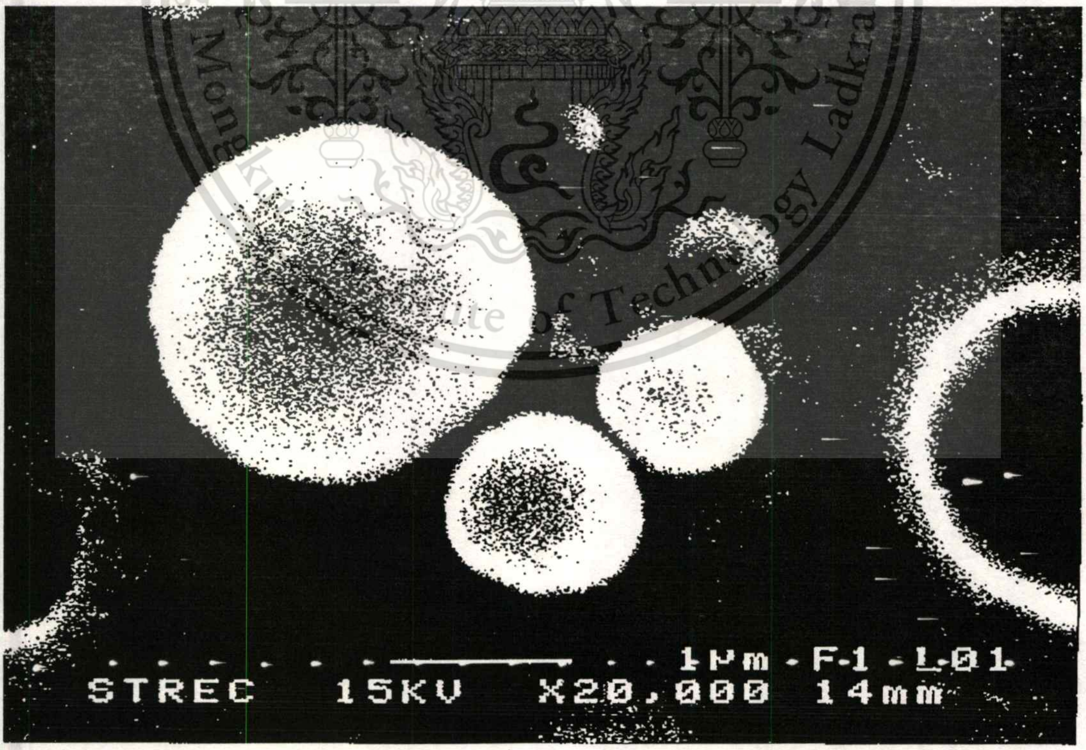

Figure 4.47 SEM micrograph of $CaCO_3$ particles from PP/PA/MA/$CaCO_3$ blend with twin-screw extruder at X 2,000 (15 KV).

4.4.2 Rheological Properties

Figures 4.48 to 4.50 showed the log shear viscosity versus log shear rate for the recycled polypropylene and nylon-6 used in this study. All resins showed the typical pseudoplastic flow behavior, for example, the viscosity of each processing technique decreased with increasing shear rate. This was caused by the fact that the shear flow field oriented the polymers chains and decreased the number of chain entanglement. The polymer with high molecular weight, nylon-6, had higher viscosity than polypropylene because of the effect of the more extensive chain entanglement. It was seen that the values of the viscosity for non-compatibilized blends lay between the pure component. For all processing techniques, the viscosities of compatibilized blends were greater than those of non-compatibilized blends with providing the miscibility between the two components. It was understood that compatibilization could interact in various methods to influence the final blend properties. The first effect of compatibilizing agents was to reduce interfacial tension in the melt, causing an emulsifying effect leading to a fine dispersion. The second effect was to increase the adhesion of the PP/PA phase and the last effect was to stabilize the dispersed phase against growth during annealing.

The flow properties of compatibilized blend with and without filler were compared. It was found that calcium carbonate filled compatibilized blends had a high viscosity at all shear rate for all techniques. Because the calcium carbonate particles disturbed the streamlines of the melt flow. For two-roll mill, the compatibilized blends filled with glass fibers showed a low viscosity because the glass fiber arrangement was in the same direction of the melt flow. For single-screw extruder, the viscosity value of glass fiber filled compatibilized blends was closed to that of non-filler compatitibilized blends. Therefore, it had less significant effect.

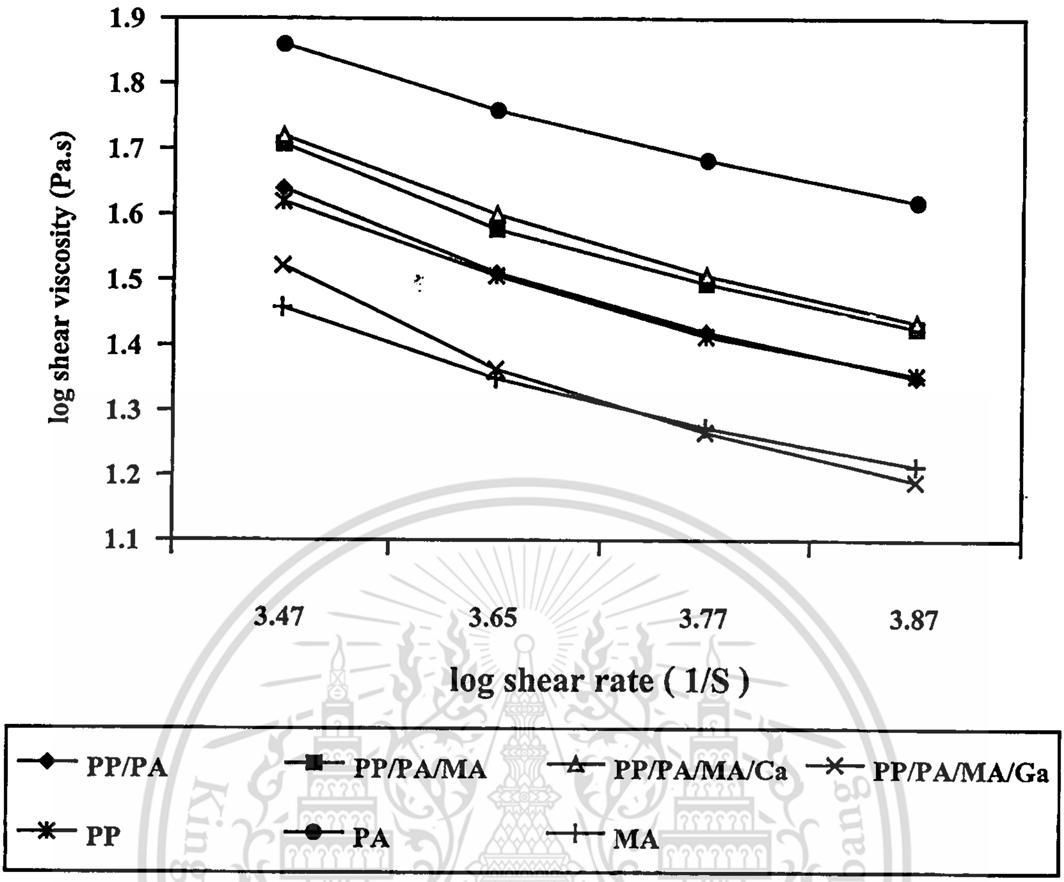

Figure 4.48 Relation between log shear viscosity and log shear rate from two-roll mill. Ca = calcium carbonate, Ga = glass fiber, PP = polypropylene, PA = nylon-6, MA = compatibilizer (PP-g-MA).

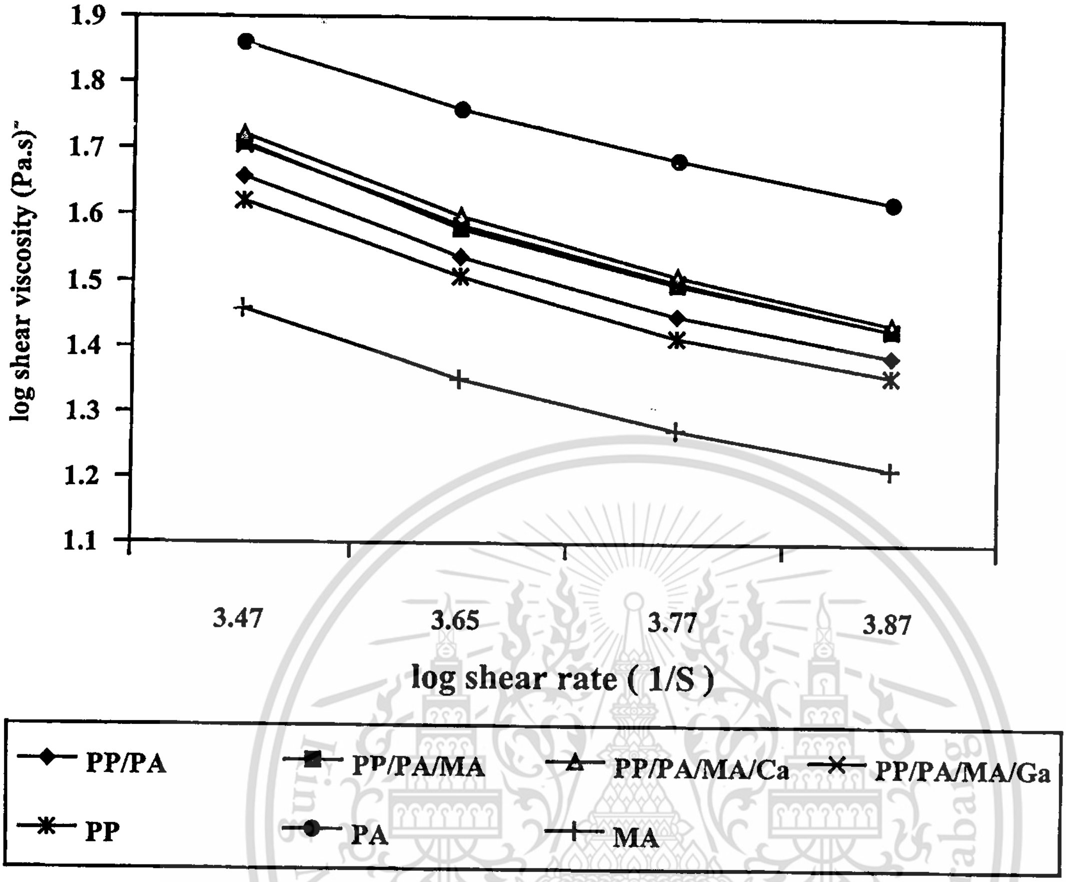

Figure 4.49 Relation between log shear viscosity and log shear rate from single-screw extruder. Ca = calcium carbonate, Ga = glass fiber, PP = polypropylene, PA = nylon-6, MA = compatibilizer (PP-g-MA).

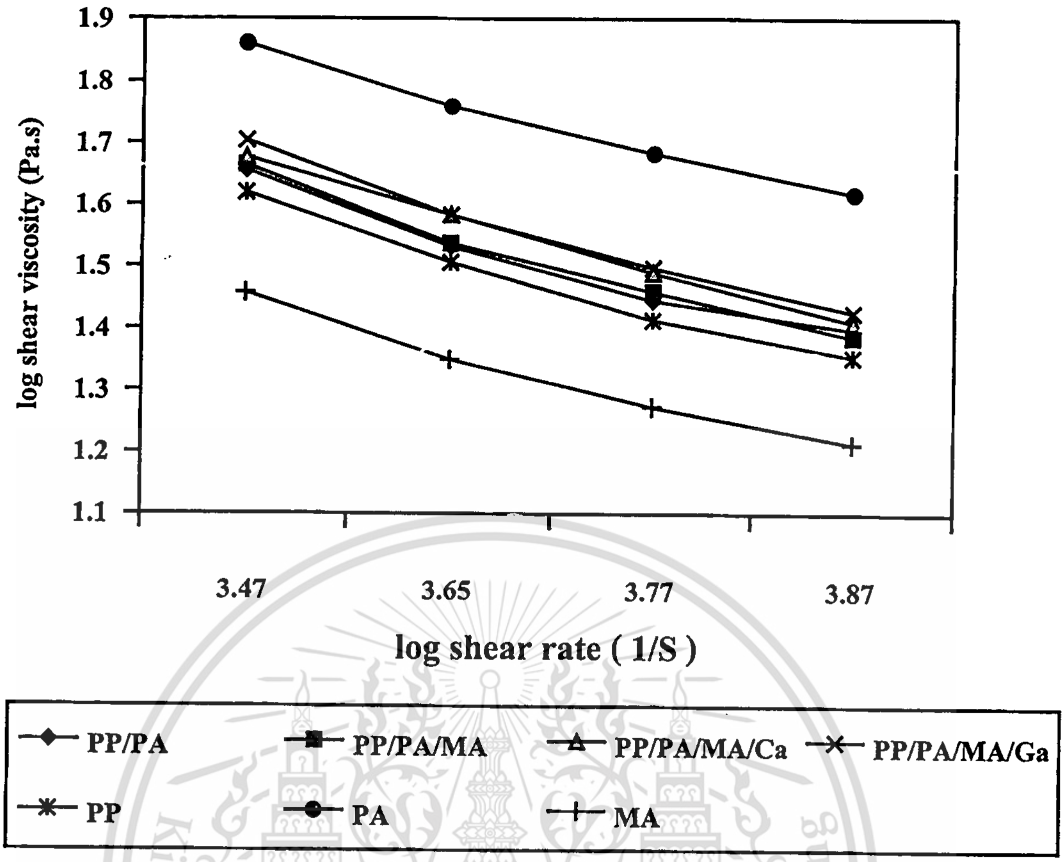

Figure 4.50 Relation between log shear viscosity and log shear rate from twin-screw extruder. Ca = calcium carbonate, Ga = glass fiber, PP = polypropylene, PA = nylon-6, MA = compatibilizer (PP-g-MA).

4.4.3 Thermal Properties

4.4.3.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was the method used to study the thermal behavior of PP/PA blends with compatibilizer and additives. In previous section, compatibilizer and additives showed the effect on mechanical properties of recycled PP/PA blends, thus it is interesting to investigate how compatibilizer and additive will affect thermal behavior of blends. The crystallization and melting temperature and percentage of crystallinity are meaningful for thermal behavior.

The typical thermograms DSC of PP/PA blends for each process are shown in appendix B. From Table 4.1, the crystallization and melting temperature of each polymer in the recycled PP/PA blends were not significantly different from individual. But the percentage of crystallinity was generally decreased because of the two different type blends of polymer and different orientation of molecules for each process (twin-screw extruder allowed higher orientation than two-roll mill and single-screw extruder). When added the compatibilizer to PP and PA blends, the crystallization and melting temperature slightly increased for each process, but the percentage of PA crystallinity in two-roll mill and single-screw extruder process increased. Because the chemical bonding between anhydride and amine group was reduced chain flexibility and increased order of crystallinity. For the same type of polymers blends, they were compatible and increased the percentage of crystallinity [3]. However, the bulky maleic anhydride group in the compatibilizer could disrupted the crystallization of PP and so the percentage of crystallinity of PP were decreased when compatibilizer was added. When the additives (calcium carbonate and glass fibers) were added, the crystallization and melting temperature were not changed significantly. Additived improved the percentage of crystallinity for both PP and PA in the PP/PA/MA/additive system. These phenomena were due to the additives acted as nucleating agents for the blend system of PP/PA/MA.

Table 4.1 Crystallization, melting temperature and percentage of crystallinity of PP/PA blends

	Tm (°C)		Tc (°C)		ΔH_f (Cal/g)		% Crystallinity	
PP	169.7		123.2		379.482		48.853	
PA	225.1		180.9		233.534		26.731	
MA	170.0		120.1		559.320		52.47	
Two-Roll Mill	**Tm (°C)**		Tc (°C)		ΔH_f (Cal/g)		% Crystallinity	
	PP	PA	PP	PA	PP	PA	PP	PA
PP/PA	169.4	217.0	127.5	193.5	299.09	10.962	42.340	11.406
PP/PA/MA	168.8	216.6	129.0	188.7	304.58	30.98	39.211	32.237
PP/PA/MA/Ca	169.5	217.6	128.9	188.6	372.94	20.497	48.011	21.329
PP/PA/MA/Ga	167.3	222.2	128.1	189.0	325.00	25.824	41.839	26.872
Single-Screw Extruder	**Tm (°C)**		Tc (°C)		ΔH_f (Cal/g)		% Crystallinity	
	PP	PA	PP	PA	PP	PA	PP	PA
PP/PA	170.8	219.0	126.5	194.0	356.53	25.584	45.899	26.622
PP/PA/MA	168.4	217.2	129.0	188.0	300.51	27.584	38.687	28.106
PP/PA/MA/Ca	168.6	217.5	127.9	191.9	353.04	11.734	45.449	12.230
PP/PA/MA/Ga	169.6	219.0	129.3	193.5	340.05	19.547	43.777	20.340
Twin-Screw Extruder	**Tm (°C)**		Tc (°C)		ΔH_f (Cal/g)		% Crystallinity	
	PP	PA	PP	PA	PP	PA	PP	PA
PP/PA	169.8	-	127.4	-	351.12	-	44.125	-
PP/PA/MA	172.4	-	129.0	-	293.34	-	41.846	-
PP/PA/MA/Ca	168.4	-	127.3	-	354.14	-	45.961	-
PP/PA/MA/Ga	168.4	-	129.4	-	370.39	-	47.472	-

* PP = Polypropylene, PA = Nylon-6, MA = Compatibilizer (PP-g-MA), Ca = Calcium carbonate and Ga = Glass fibers.

4.3.3.2 Deflection Temperature Under Load

The deflection temperature under load (DTUL) of uncompatibilized recycled nylon-6 and polypropylene blends were higher in single-screw extruder because it showed more homogeneous blend than the other process. When added the compatibilizer and glass fiber, were added the DTUL was improved because the compatibilizer reduced the interfacial tension between two phases and enhanced the interphase adhesion. Then, the glass fiber acted as reinforcing fibers for recycled blends, leading to the greater DTUL in the single-screw extruder. DTUL of PP/PA/MA blend with glass fiber and calcium carbonate filled have the same trend. (Figure 4.51)

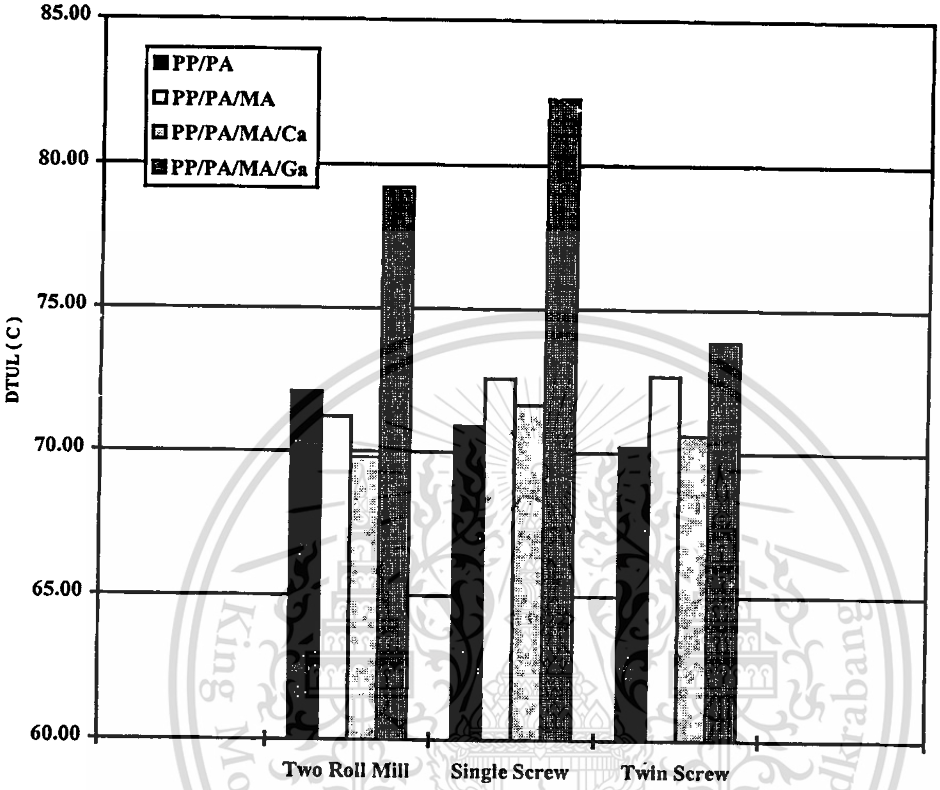

Figure 4.51 Deflection temperature under load of the blends.

CHAPTER V

CONCLUSIONS

This research focuses on processing and properties of nylon-6 and polypropylene blends from recycled toothbrushes with a compatibilizer and additives. From the optimum processing conditions, compatibilizer and additive would be expected to improve the properties of recycled blends.

Tensile strength, flexural strength, modulus at 3% strain and impact strength were generally increased with milling time. The higher milling time (10 min) yielded the blends with higher properties. The mixing temperature 230°C gave higher the tensile strength, modulus at 3% strain and hardness than 220°C and 240°C. As milling time did not have any significant effect on hardness. Therefore, temperature 230°C and milling time 10 min were chosen for all mixing conditions on two-roll mill for preparing the blends.

Tensile strength, tensile modulus, impact strength, hardness and flexural strength were generally increased with mixing temperature because nylon-6 did not fully melt at the lower processing temperature. Higher temperature would also permit better mixing of nylon-6 and polypropylene. Tensile strength and modulus at 3% strain were dependent on screw speed. At 50 rpm the tensile strength and modulus at 3% strain were higher than those at 30 and 70 rpm. Impact strength increased with screw speed but hardness decreased because the higher screw speed destroyed interfacial surface between polymer chain. Flexural strength was unaffected by screw speed. Therefore, temperature 240°C and screw speed 50 rpm were chosen for all mixing conditions of single-screw extruder for preparing the blends.

At the middle of the mixing temperature (230°C) and the screw speed (50 rpm), the tensile strength and modulus at 3% strain were the highest for twin-screw extruder. Impact strength and hardness decreased with screw speed because of higher L/D ratio and higher shear rate. The mixing temperature and screw speed had less significant on flexural strength. For overall balance of properties, it appeared that optimum conditions in twin-screw extruder should be 230°C and 50 rpm.

The results showed that the highest percentage of compatibilizer (5%) gave the highest tensile strength, tensile modulus at 3% strain and flexural strength of blends prepared from each technique. The compatibilized blends exhibited much finer dispersed phases than the non-compatibilized blends of inherently in miscible polypropylene and nylon-6 blends. Compatibilizer (maleic anhydride modified polypropylene) reduced the interfacial tension between the two phases and enhanced the interphase adhesion.

Addition of the non-treated glass fibers to the recycled polypropylene and nylon-6 blends with the compatibilizer improved mechanical properties of blends because tensile strength and modulus were increased. By varying the percentage of glass fiber loading in the range of 0 to 10% by weight of the blends, the tensile strength, flexural strength, impact strength and hardness were increased. This is because the glass fibers acted as reinforcing fibers for the recycled blends due to large surface areas of the fibrous form.

The tensile strength, flexural strength, tensile modulus, impact strength and hardness decreased when calcium carbonate was added because the hydrophilic nature of calcium carbonate restricted its introduction only in polar matrix (nylon-6) and its possible utilization in non-polar polymer (polypropylene). The calcium carbonate acted as impurities for the recycled blends which caused the failure to the blends. The higher calcium carbonate loading, the more premature failure occurs.

The phase morphology of the non-compatibilized polypropylene and nylon-6 blends was very poor. The dispersed phase was large and coarse due to the inherent immiscibility. On the other hand, the compatibilized blends of polypropylene and nylon-6 exhibited more homogeneous phase structure since polypropylene grafted maleic anhydride aided the compatibility of both polypropylene and nylon-6. The maleic anhydride groups of compatibilizer got along with the amine group of nylon-6 and led to a cyclic imide bond by the ring opening reaction at processing temperature. The *in situ* formed copolymers (PP-g-PA), acted as a true compatibilizer, located mostly along the interface between the two constituting polypropylene and nylon-6. SEM micrographs indicated that the strong interfacial adhesion between the glass fiber and the matrix was greater than the calcium carbonate according to the nature of each filler and the reinforcement capability.

For all processing techniques, the viscosities of compatibilized blends were greater than non-compatibilizing blends providing the miscibility between PP and PA. For the flow properties of compatibilized blends with and without filler, it was found that the compatibilized calcium carbonate filled blends had a higher viscosity at all shear rate for all techniques because the calcium carbonate particles disturbed the streamlines of the melt flow. For two-roll mill, the compatibilized glass fiber filled blends had a lower viscosity because the glass fiber arrangement was in the same direction of the melt flow. For single-screw extruder, the viscosity values of compatibilized glass fiber filled blend were closed to compatitibilized blends. Therefore, it has less significant effect on single-screw extruder for the rheological properties.

The crystallization and melting temperature of PP/PA blends in two-roll mill, single-screw extruder did not change too much from the virgin PP and PA. The deflection temperature under load of uncompatibilized nylon-6 and polypropylene blends were higher in single-screw extruder because the optimum shear enhanced the more miscible blends. For calcium carbonate and glass fibers filled recycled blends gave the same results.

CHAPTER VI

RECOMMENDATIONS

The properties of the recycled polypropylene and nylon-6 blends are not acceptable. Therefore, the further research should be studied as follow:

1) The processing of single-screw and twin-screw extruder should be reexamined with the same L/D ratio screw for clearly results of properties.

2) The particle size and particle size distribution of the blends should be investigated to understand the effect of dispersion.

3) The content and the acid groups of maleic anhydride in the blends should be varied and determined for enhancing the miscibility.

4)The types and forms of glass fiber and calcium carbonate should be varied for studying the optimum type and form of additives.

5) The other types of additive such as natural polymers could be included for the application on biodegradation polymer.

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APPENDICES

Appendix A Physical properties of recycled blends.

Table A1 Effect of processing condition on physical properties of recycled polypropylene and nylon-6 blends for two-roll mill.

Milling time	6 minutes		8 minutes		10 minutes	
Tensile strength (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	17.82	0.99	23.11	1.09	24.07	0.86
230°C	24.1	1.12	25.1	1.02	25.7	1.21
240°C	22.83	0.90	25.04	1.14	25.2	1.41
Modulus (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	638.72	3.18	648.33	3.04	690	32.1
230°C	675	3.41	682.26	3.19	699.91	31.8
240°C	642	2.85	660	3.07	683.46	31.1
Impact strength (kJ/m)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	0.9	0.40	1.6	0.36	1.7	1.77
230°C	1.6	0.13	1.95	0.38	2	3.01
240°C	1.8	0.25	2	0.25	2.1	0.59
Hardness (shore D)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	66.33	1.23	65.4	0.56	66	1.34
230°C	68	0.98	67.08	1.47	67.33	0.97
240°C	67.5	1.17	66.25	1.09	66.58	0.46
Flexural Strength (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	1.16	1.65	1.19	0.91	1.2	0.87
230°C	1.18	1.49	1.2	1.46	1.223	1.04
240°C	1.21	2.01	1.21	0.47	1.22	0.75

Table A2 Effect of processing condition on physical properties of recycled polypropylene and nylon-6 blends for single-screw extruder.

Screw speed	30 rpm		50 rpm		70 rpm	
Tensile strength (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	25.84	0.46	26.35	0.46	26.94	0.94
230°C	25.5	0.36	26.97	0.28	27.21	0.45
240°C	25.85	1.05	28.04	1.23	27.71	0.71
Modulus (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	699.33	23.5	702.86	23.01	721.06	22.94
230°C	690	21.4	729.73	23.17	727.66	22.31
240°C	696.86	23.7	752.59	22.08	747.33	23.40
Impact strength (kJ/m)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	3.7	0.21	3.7	0.24	3.9	0.91
230°C	3.8	0.37	3.85	0.37	4	0.97
240°C	3.8	0.09	3.9	0.51	4.1	0.94
Hardness (shore D)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	66.58	1.02	65.3	1.37	65	1.90
230°C	67.16	1.34	65.83	0.91	65.2	0.86
240°C	68.33	0.45	67.5	0.76	67.3	0.67
Flexural Strength (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	1.22	1.27	1.248	0.64	1.254	0.47
230°C	1.266	1.90	1.27	0.54	1.29	1.46
240°C	1.308	2.08	1.301	0.92	1.305	1.23

Table A3 Effect of processing condition on physical properties of recycled polypropylene and Nylon-6 blends for twin-screw extruder.

Screw speed	30 rpm		50 rpm		70 rpm	
Tensile strength (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	24.24	0.98	24.35	0.87	24.35	1.02
230°C	24.29	0.37	24.95	0.49	24.95	0.49
240°C	24.32	0.61	24.79	2.03	24.79	1.05
Modulus (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	540.21	23.1	540.21	24.1	520	20.13
230°C	627.95	22.4	627.95	22.6	559.68	21.4
240°C	556.62	20.7	556.62	20.1	531	21.9
Impact strength (kJ/m)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	2.5	0.98	2.433	1.3	2.42	1.40
230°C	3.65	0.32	3.41	0.49	2.91	0.82
240°C	3.41	0.51	3.16	0.47	2.93	1.03
Hardness (shore D)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	65.16	1.02	64.39	1.01	64.25	1.06
230°C	67.5	1.91	65.91	0.67	65.35	0.54
240°C	67	0.34	65.75	1.05	65.3	0.64
Flexural Strength (MPa)						
	Mean	S.D	Mean	S.D	Mean	S.D
220°C	1.19	1.20	1.2	1.02	1.201	0.91
230°C	1.26	1.06	1.277	0.31	1.28	1.45
240°C	1.251	0.48	1.25	0.91	1.28	1.23

Table A4 Physical properties of compatibilized, recycled nylon-6 and polypropylene blends.

Weigth of Compatibilizer (%)	0%		1%		3%		5%	
Tensile strength (Mpa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	25.7	0.64	27.37	0.64	28.83	0.64	29.94	0.56
Single-screw extruder	28.04	0.87	28.8	1.37	29.62	0.91	30.35	1.21
Twin-screw extruder	21.9	0.93	22.55	1.23	24.35	1.81	25.1	1.07
Modulus (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	699.91	23.5	735.49	20.14	784.71	19.23	803.88	21.08
Single-screw extruder	752.59	25.1	770.44	21.21	777.99	20.4	802.33	20.49
Twin-screw extruder	500	21.4	540	20.34	542.67	20.6	549	19.4
Impact strength (kJ/m)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	2	0.65	2.1	1.81	2.31	1.18	2.4	0.76
Single-screw extruder	3.9	0.73	3.95	1.07	4	0.83	4.1	1.29
Twin-screw extruder	3.41	0.91	3.41	1.39	3.49	0.72	3.57	1.05
Hardness (shore D)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	67.33	.046	69.16	0.92	70.41	0.82	69.25	1.16
Single-screw extruder	67.75	1.09	69	0.67	68.66	1.6	68	1.67
Twin-screw extruder	67.33	1.05	69.16	0.34	70.41	1.07	69.25	0.64
Flexural Strength (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	1.23	1.39	1.35	0.54	1.43	1.09	1.46	1.08
Single-screw extruder	1.308	1.47	1.436	1.09	1.459	0.97	1.5	0.94
Twin-screw extruder	1.2	0.28	1.267	1.08	1.272	0.34	1.295	0.75

Table A5 Physical properties of calcium carbonate filled and recycled blends.

Weigth of $CaCO_3$ (%)	0%		1%		3%		5%	
Tensile strength (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	25.7	0.64	27.37	0.27	28.83	1.97	29.94	0.67
Single-screw extruder	28.04	1.37	28.8	0.64	29.62	1.08	30.35	1.06
Twin-screw extruder	24.85	0.47	27	1.09	28	0.82	29	1.04
Modulus (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	803.88	22.5	741.33	21.90	775.52	21.08	706.64	23.50
Single-screw extruder	802.3	21.03	748.67	22.34	785.26	22.07	753.73	22.01
Twin-screw extruder	608.38	22.09	465.28	20.14	493.02	20.14	512	23.0
Impact strength (kJ/m)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	2.4	0.63	1.4	0.76	1.5	0.28	1.5	1.04
Single-screw extruder	4.1	0.43	2.7	1.07	2.9	1.07	3	0.76
Twin-screw extruder	3.41	0.91	3.26	1.20	3.3	0.46	3.41	0.46
Hardness (shore D)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	69.25	1.34	61.75	1.24	63.16	0.73	64.41	1.09
Single-screw extruder	69.5	1.07	62.66	0.82	63.5	0.13	64.7	1.04
Twin-screw extruder	65.91	0.46	66.42	0.31	67.12	0.49	68.02	1.34
Flexural Strength (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	1.46	0.78	1.179	2.09	1.297	1.07	1.355	0.76
Single-screw extruder	1.301	0.67	1.38	1.67	1.483	1.05	1.73	1.64
Twin-screw extruder	1.277	1.07	1.335	1.34	1.4	1.64	1.503	0.37

Table A6 Physical properties of glass fiber filled, recycled nylon-6 and polypropylene blends.

Weigth of Glass fiber (%)	0%		1%		3%		5%	
Tensile strength (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	29.94	0.34	24.92	0.19	23.7	0.34	22	1.02
Single-screw extruder	30.35	0.34	24.61	0.64	24.84	0.28	25.29	1.06
Twin-screw extruder	24.35	0.37	22.72	1.37	22.61	0.91	22.81	0.59
Modulus (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	803.88	22.1	735.05	22.06	732.2	20.43	702.88	20.49
Single-screw extruder	802.3	22.40	752.54	21.07	754.4	20.37	767.99	21.09
Twin-screw extruder	542.7	21.06	484.84	21.09	482.28	21.09	475.06	21.06
Impact strength (kJ/m)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	2.4	0.49	2.9	1.09	2.1	0.49	0.7	0.27
Single-screw extruder	4.1	0.34	3.7	0.49	3.1	0.76	1.7	0.43
Twin-screw extruder	3.36	0.12	3.46	0.64	2.83	0.37	1.62	0.27
Hardness (shore D)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	69.25	1.02	64.2	1.04	63.2	0.91	62.8	0.76
Single-screw extruder	69.5	1.07	63.37	1.06	62.5	0.76	62.08	0.46
Twin-screw extruder	66.5	1.04	66.21	1.07	66	0.37	66.02	0.49
Flexural Strength (MPa)								
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	1.46	1.04	1.319	0.37	1.237	1.07	0.9709	1.06
Single-screw extruder	1.355	1.07	1.375	0.94	1.318	0.34	1.305	1.06
Twin-screw extruder	1.272	0.70	1.275	1.04	1.146	0.67	0.96	2.01

Appendix B DSC thermogram of polymer blends.

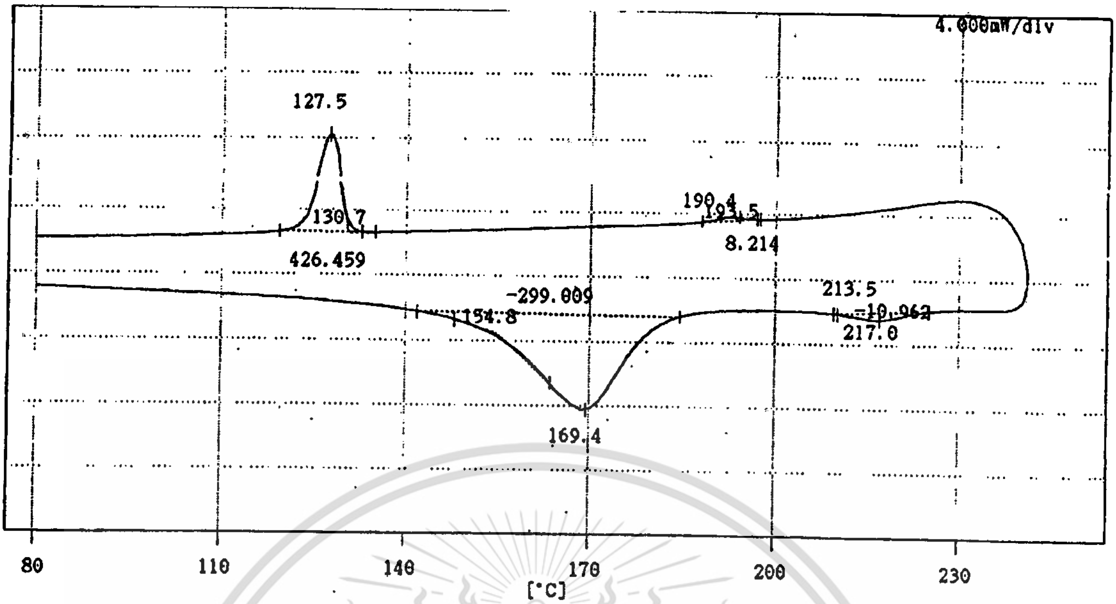

Figure B1 DSC thermogram of PP/PA blend preparing using two-roll mill.

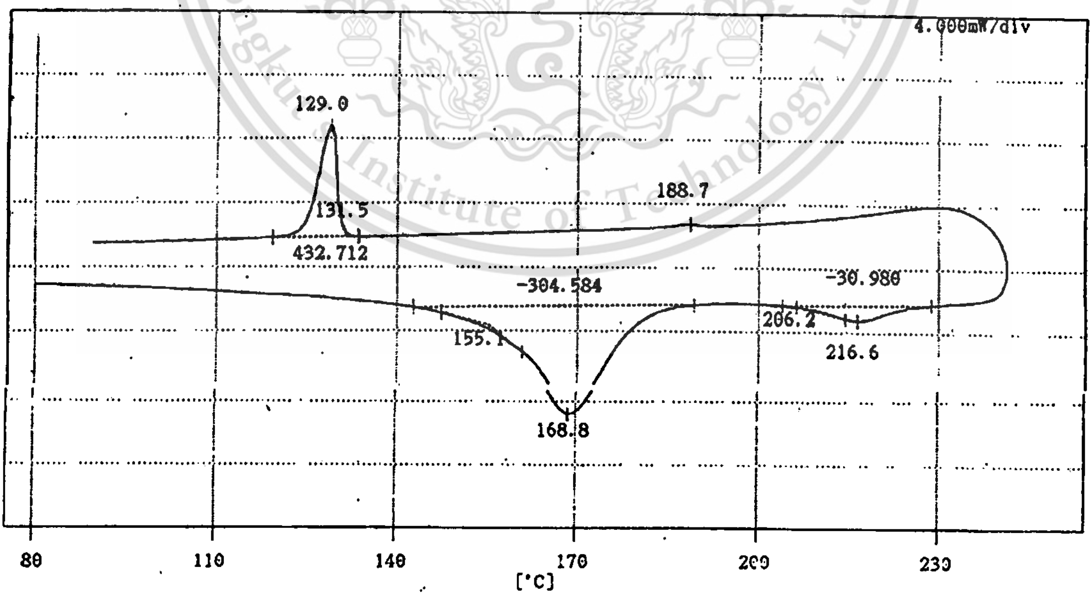

Figure B2 DSC thermogram of PP/PA/MA blend preparing using two-roll mill.

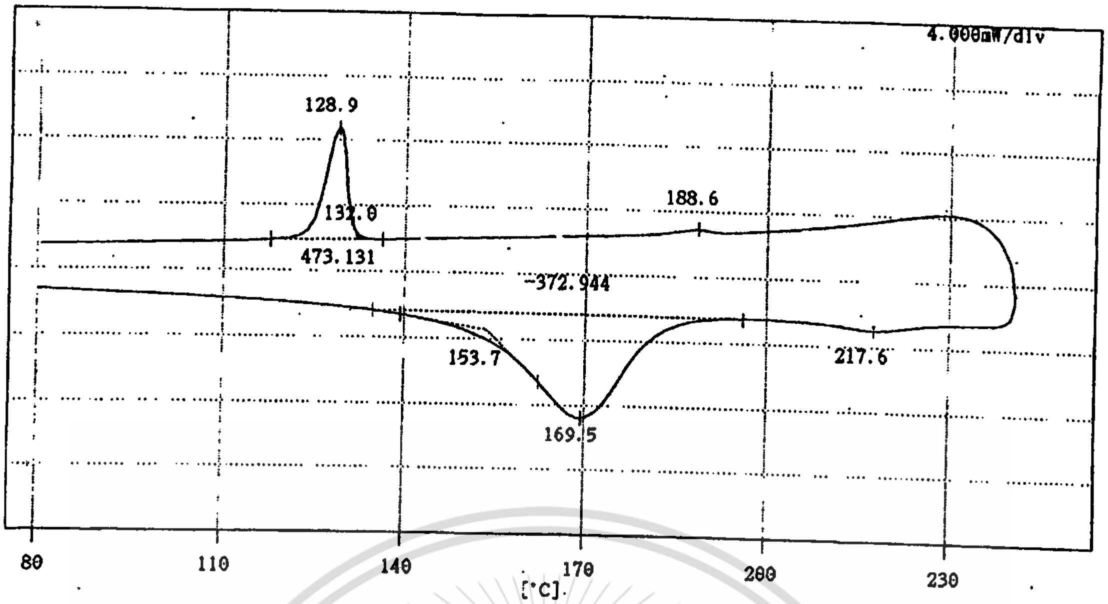

Figure B3 DSC thermogram of PP/PA/MA/calcium carbonate blend preparing using two-roll mill.

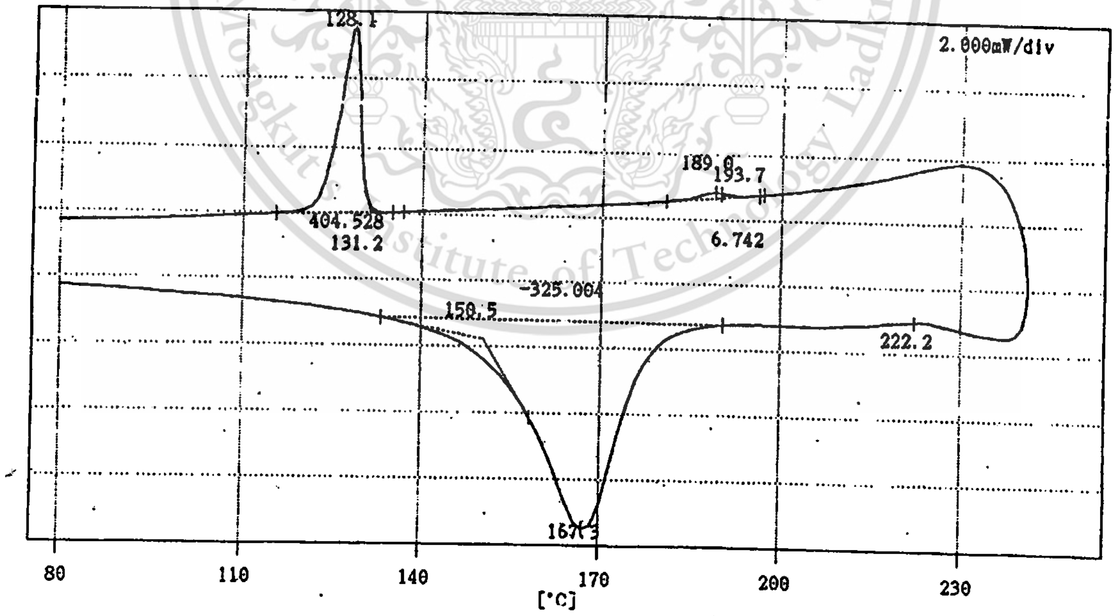

Figure B4 DSC thermogram of PP/PA/MA/glass fiber blend preparing using two-roll mill.

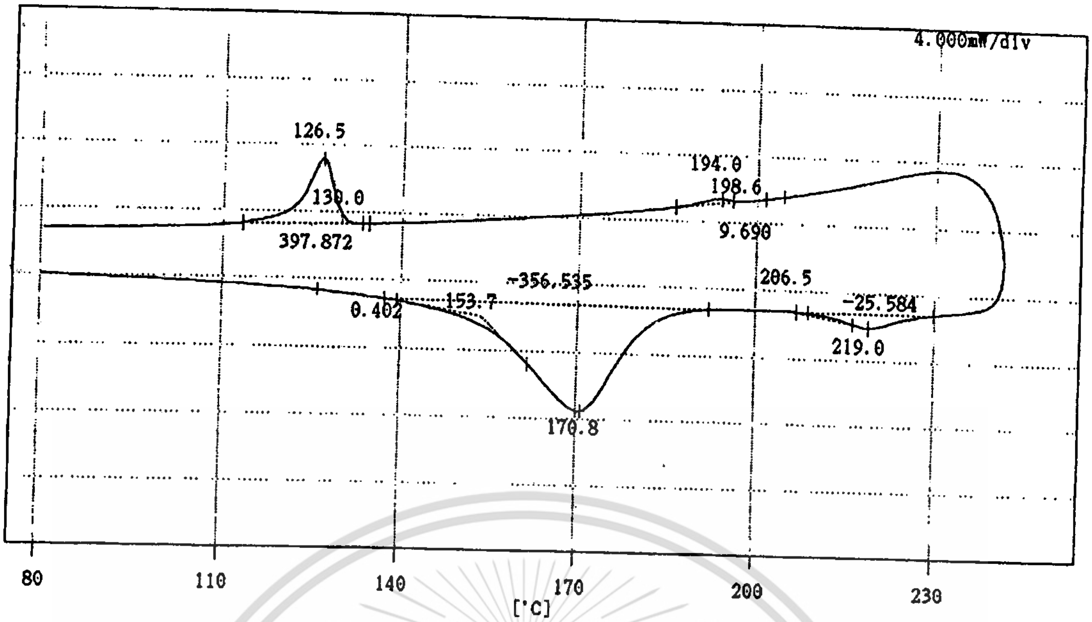

Figure B5 DSC thermogram of PP/PA blend preparing using single-screw extruder.

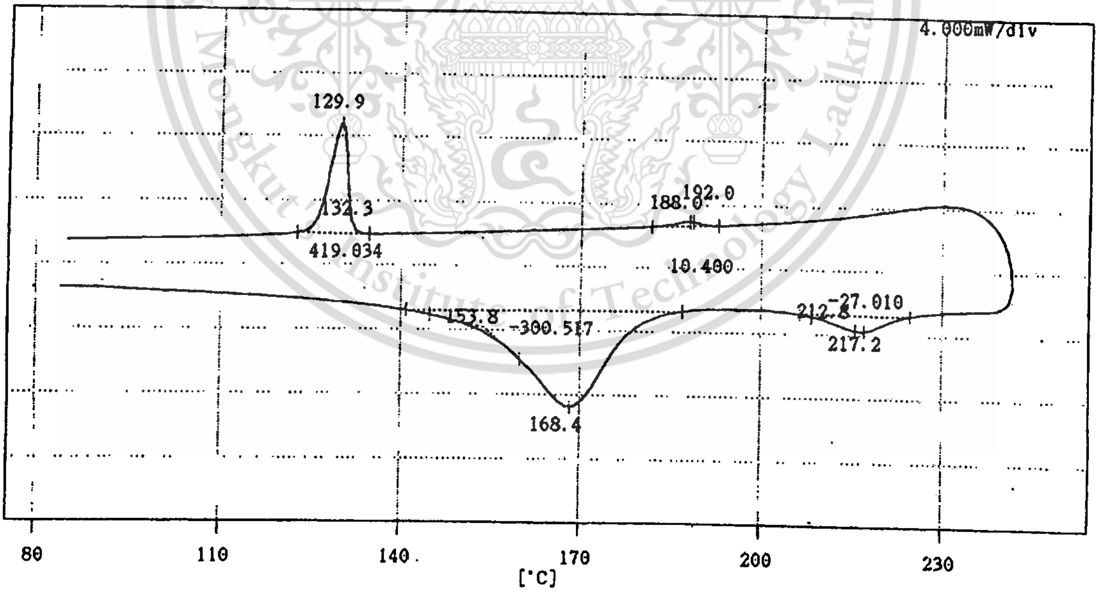

Figure B6 DSC thermogram of PP/PA/MA blend preparing using single-screw extruder.

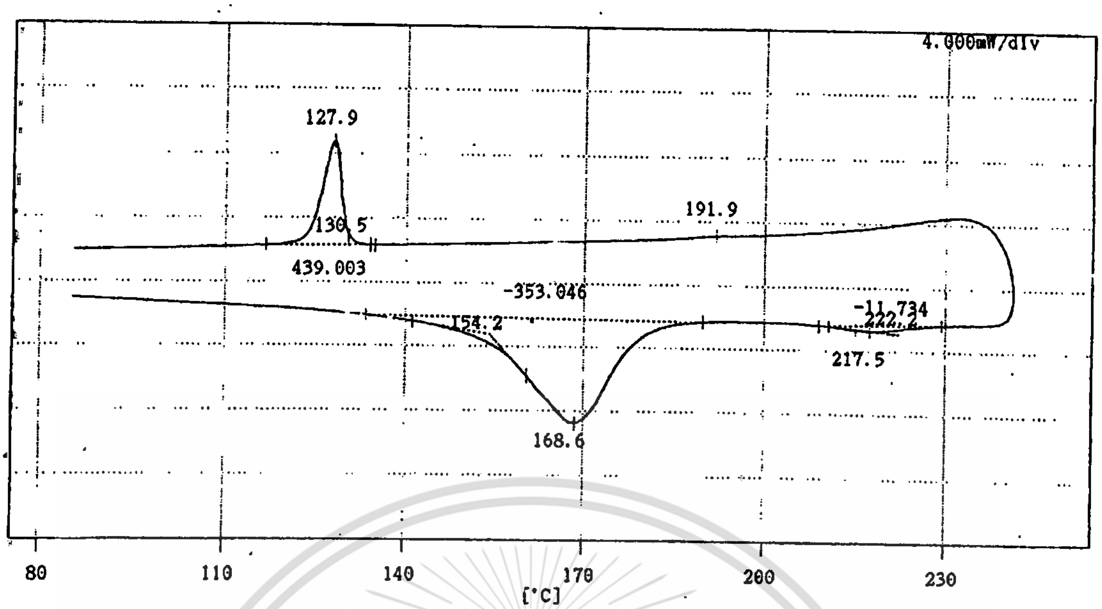

Figure B7 DSC thermogram of PP/PA/MA/calcium carbonate blend preparing using single-screw extruder.

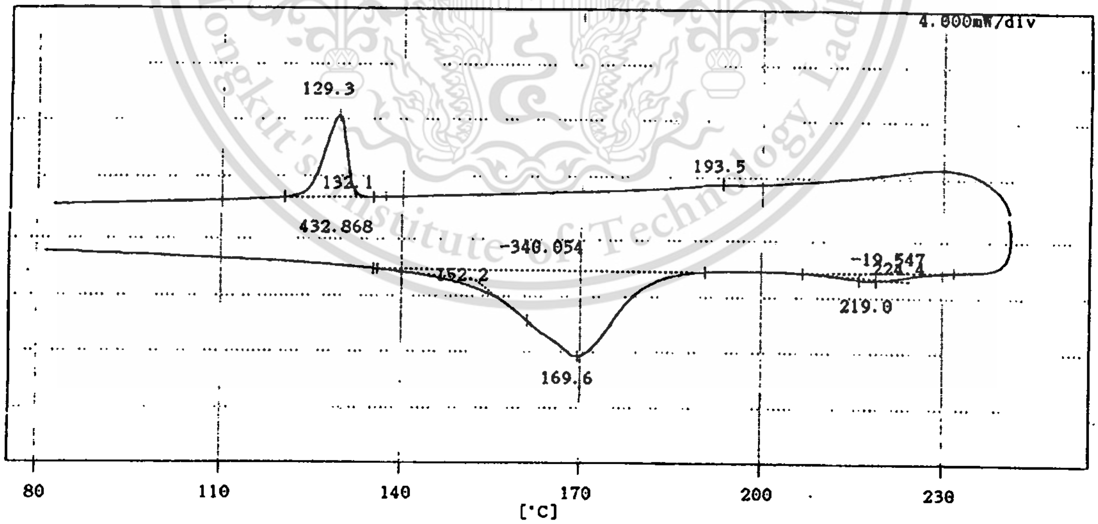

Figure B8 DSC thermogram of PP/PA/MA/glass fiber blend preparing using single-screw extruder

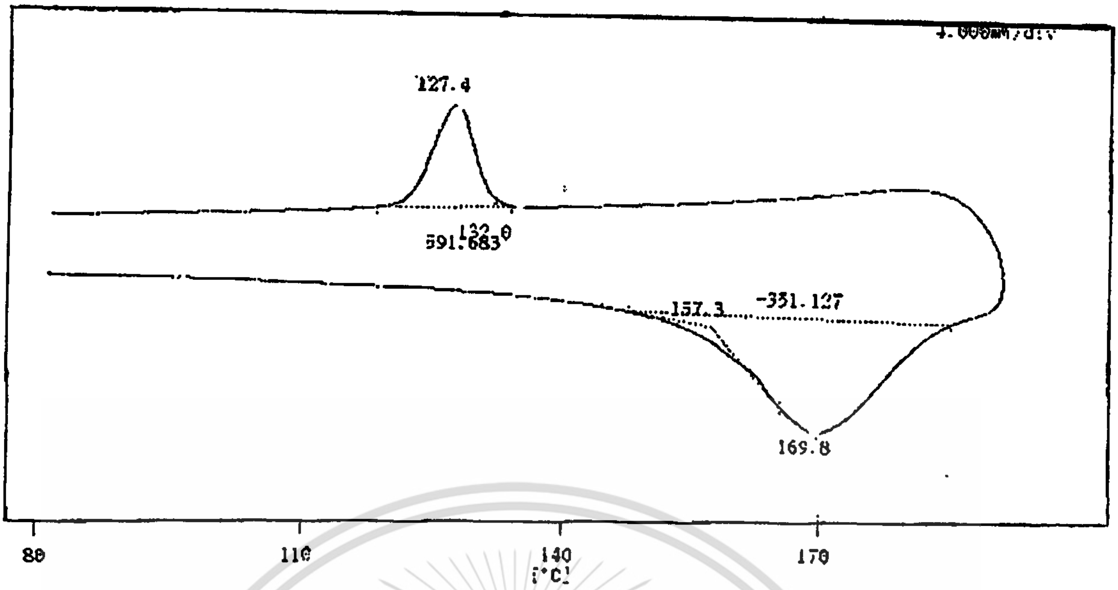

Figure B9 DSC thermogram of PP/PA blend preparing using twin-screw extruder

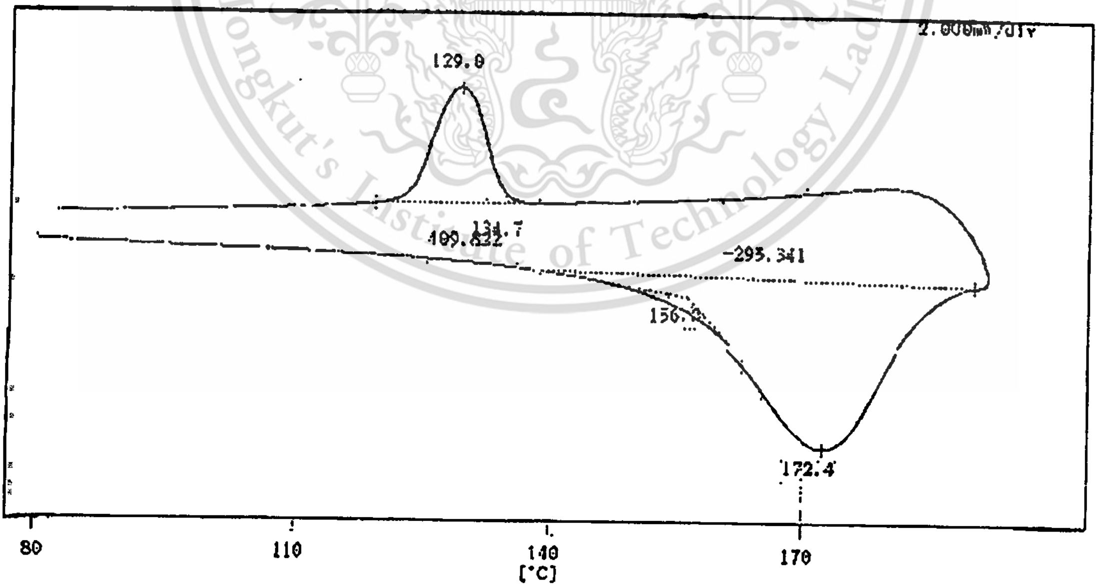

Figure B10 DSC thermogram of PP/PA/MA blend preparing using twin-screw extruder .

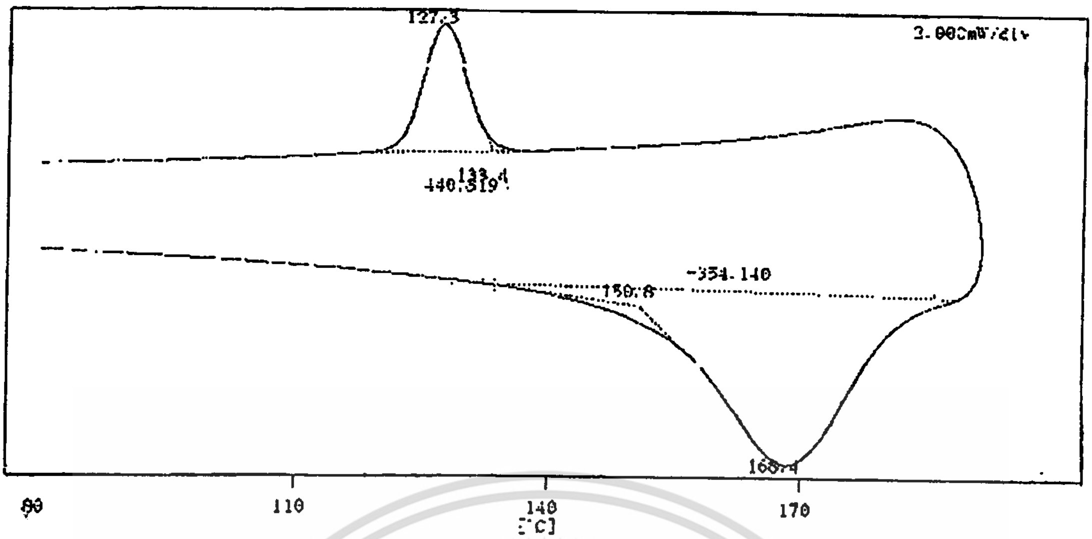

Figure B11 DSC thermogram of PP/PA/MA/calcium carbonate blend preparing using twin-screw extruder .

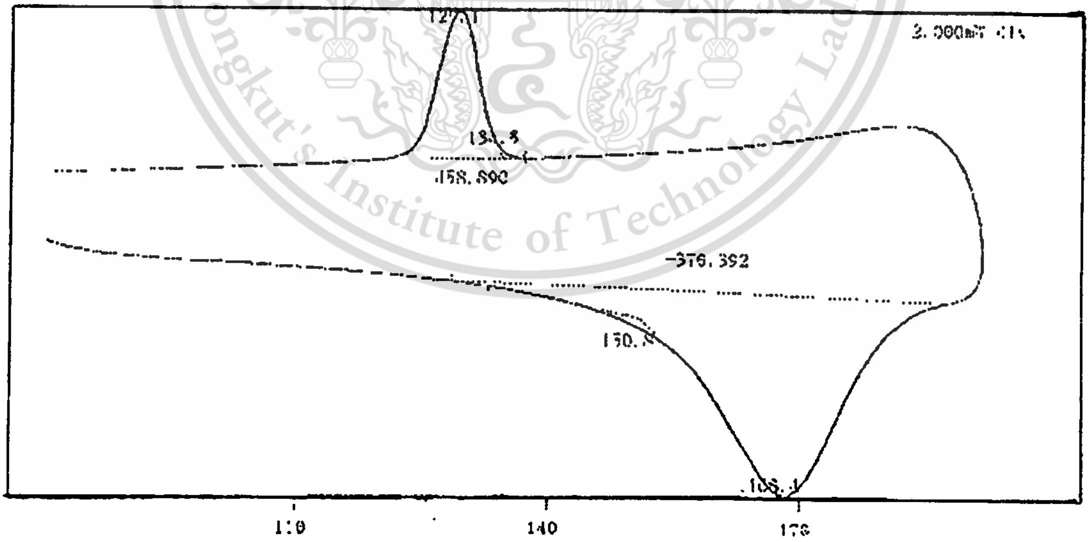

Figure B12 DSC thermogram of PP/PA/MA/glass fiber blend preparing using twin-screw extruder.

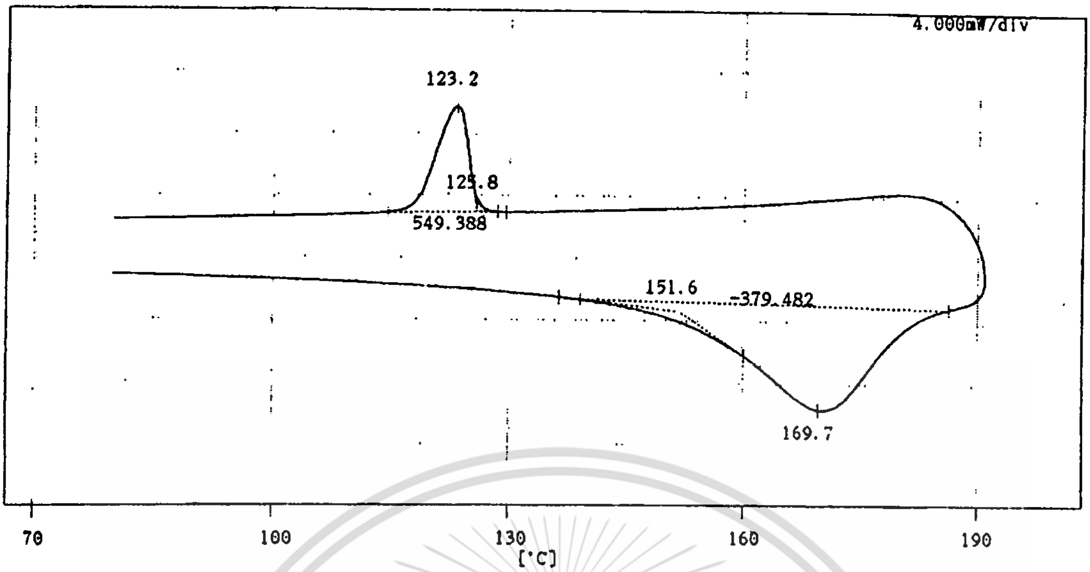

Figure B13 DSC thermogram of recycled polypropylene.

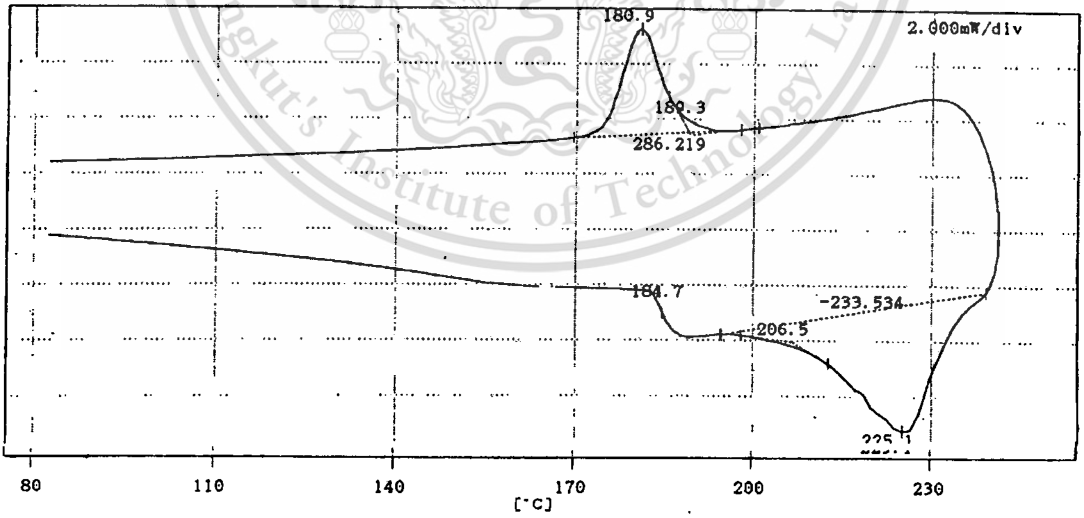

Figure B14 DSC thermogram of recycled nylon-6.

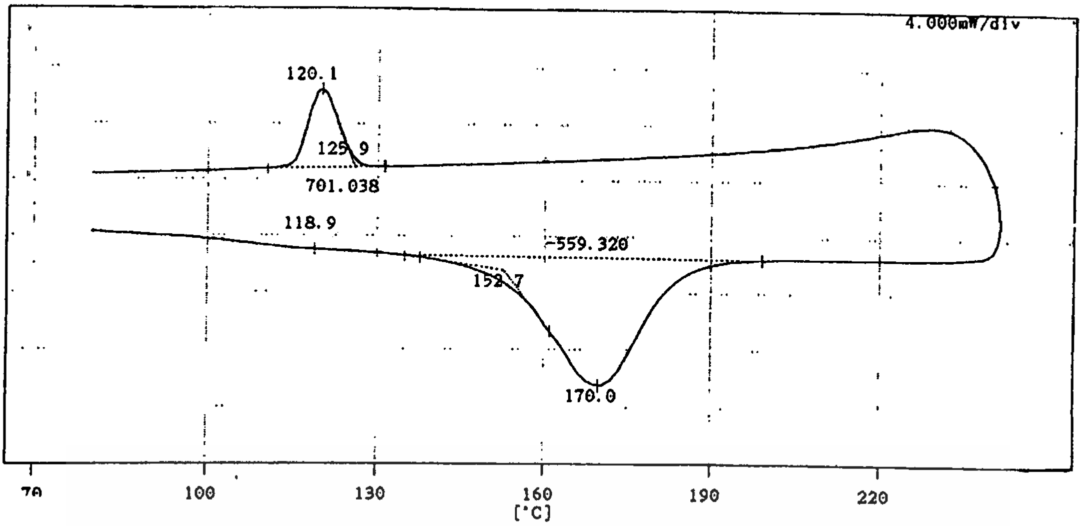

Figure B15 DSC thermogram of polypropylene graft maleic anhydrided.

Appendix C Deflection temperature under load of recycled blends.

DTUL (°C)	Non-compatibilizer		Compatibilized blend		CaCO$_3$Filled		Glass fiber filled	
	Mean	S.D	Mean	S.D	Mean	S.D	Mean	S.D
Two-roll mill	71	1.32	71.2	1.24	69.8	0.34	7.2	1.2
Single-screw extruder	70.9	1.34	72.56	0.47	71.65	0.49	82.3	0.46
Twin-screw extruder	70.2	0.83	72.66	0.67	70.6	1.06	73.85	1.06

Appendix D Calculation method

D1. Tensile strength

From tensile testing, tensile strength was calculated by the equation (D1),

$$\sigma = F / A \tag{D1}$$

where σ = tensile strength (MPa or N/mm^2)

F = force at yield or at breake (N)

A = intitial cross-sectional area of the test specimen (mm^2)

D2. Tensile modulus at 3% strain

Tensile modulus at 3% strain could be calculated by the equation (D2),

$$E = \frac{(F / A)}{(3/100)} \tag{D2}$$

where E = modulus at 3 % strain (MPa)

F = load at 3 % strain (N)

A = intitial cross-section area of the test specimen (mm^2)

D3. Impact strength

The impact strength of each specimen could be calculated from the equation (D3),

$$IS = W / A \tag{D3}$$

where IS = impact strength (kJ/m^2)

W = loss energy

D4. The standard deviation (sd) and mean value were calculated from equation (D4),

$$\overline{X} = \frac{\Sigma x_i}{n} \tag{D4}$$

and

$$sd = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n}} \qquad \text{(D5)}$$

where x_i = values of properties of each sample

n = number of observation

D5. Percentage of crystallinity

Percentage of crystallinity of each sample was calculated by equation (D6) and (D7),

$$\%\,Crystallinity = \left(\frac{\Delta H_f}{\Delta H^0_f} X100\right) X\,(polymer\ fraction)^{-1} \qquad \text{(D6)}$$

and

$$\Delta H_f = \frac{Surface\ Area\ (mJ)}{Sample\ weigth\ (mg)} \qquad \text{(D7)}$$

where ΔH_f = Heat of fusion of sample (J/g)

$\Delta H^0{}_f$ = Heat of fusion of pure polymer (J/g)

* $\Delta H^0{}_f$ of poylpropylene is 208.8 J/g [66].

* $\Delta H^0{}_f$ of nylon-6 is 209.0 J/g [67].

AUTHOR BIOGRAPHY

Name	Miss Weawboon Mingmaung
Date of Birth	September 29,1975
Place of Birth	Sakonnakorn, Thailand
Institute Attended	Khon Khan University, 1994-1997: Bachelor of Science (Chemistry) King Mongkut 's Institute of Technology Ladkrabang, 1997-1999: Master of Science (Applied Chemistry, Polymer Technology)
Research Grant	King Mongkut 's Institute of Technology Ladkrabang