PREPARATION OF CROSSLINKABLE HIGH DENSITY POLYETHYLENE AND POLYPROPYLENE POLYBLENDS

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ABSTRACT

PREPARATION OF CROSSLINKABLE HIGH DENSITY POLYETHYLENE AND POLYPROPYLENE POLYBLENDS

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High density polyethylene (HDPE) and polypropylene (PP) are two commonly used thermoplastic polymers existing in the commodity plastic market due to their developed and easy post-reactor processability characteristics. Although these two polymers can be subjected to reprocessing, they eventually experience critical losses in their main physical and mechanical properties at elevated temperatures. With the aim of preventing these losses in their mechanical and thermal properties in their individual and blended states, this thesis presents a unique way of processing the blends of the sought polymer components incorporated with dicumyl peroxide (DCP). The two polymers were extruded with weight percentages of 30%, 50%, and 70% for each polymer. Followed by the swelling of the pellets in hexane-DCP solution, they were processed into films in a hot-press. The data obtained as a result of tensile testing performed on the specimens taken from the prepared films showed that the Young's moduli of individual PP set incorporated with 1.0% (w/w) DCP, 30HDPE70PP set incorporated with 0.5% (w/w) DCP, and 50HDPE50PP set incorporated with 0.5% (w/w) DCP were increased by 28.5%, 28.4%, and 2.45% compared to their pristine values, respectively. The tensile strength of 30HDPE70PP set at 2.0% (w/w) DCP level experienced a small increase. The percentage elongation of 70HDPE30PP set was increased from its pristine value of 8% to 30%, 44%, and 98% with addition of 0.5% (w/w), 1.0% (w/w) and 2.0% (w/w) DCP, respectively. Upon processing the blends with DCP and applying differential scanning calorimetry (DSC) analysis to their specimens, their percent crystallinities were calculated from the analysis outputs. The mechanical results are mutually explained via the simultaneous interpretation of the calorimetric analysis data.

Keywords: High Density Polyethylene, Polypropylene, Dicumyl Peroxide, Crosslinking, Polyblends

ÖZ

ÇAPRAZ BAĞLANABİLİR YÜKSEK YOĞUNLUKLU POLİETİLEN VE POLİPROPİLEN KARIŞIMLARININ HAZIRLANIŞI

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Yüksek yoğunluklu polietilen (YYPE) ve polipropilen (PP), kolay işlenme süreçlerine sahip olmaları ve gelişmiş özellikleri sayesinde ticari plastik pazarında en sık kullanılmakta olan iki polimer halindedirler. Bu iki polimer her ne kadar yeniden işlenilebilir olsalar da, nihayetinde yüksek sıcaklıklar altında ana fiziksel ve mekanik özelliklerini kaybetmeye başlarlar. Bu tez, söz konusu polimerlerin saf ve karışım hallerinde bahsi geçen mekanik ve termal özelliklerindeki kayıpların önlenmesi amacı ile bu polimer bileşenlerinin dikümil peroksit (DCP) ile birleştirilmiş hallerinin işlenilebilmelerini sağlayan bir yol sunmaktadır. Polimerler, bileşen başına kütlece %30, %50 ve %70 oranlarında ekstruder yardımı ile karıştırılmışlardır. Pelletler dikümil peroksit – hekzan çözeltisinde şişirildikten sonra sıcak pres kullanılarak film haline getirilirler. Filmlerden alınan numunelere uygulanan gerilme sınama testi sonuçları saf PP'nin kütlece %1 DCP, 30HDPE70PP setinin kütlece %0,5 DCP ve 50HDPE50PP setinin kütlece %0,5 DCP ile işlenmiş hallerinin Young's modüllerinde saf değerlerine kıyasla sırası ile %28,5, %28,4 ve %2,45 artış gerçekleştiğini göstermiştir. 30HDPE70PP setinin kütlece %2,0 DCP ile işlenmiş halinin gerilme direncinde küçük artışlar gözlemlenmiştir. 70HDPE30PP setinin kopmada uzama yüzdeleri karışımın saf halde sahip olduğu %8'den, kütlece %0,5, %1,0 ve %2,0 DCP yüzdelerinde sırası ile %30, %44 ve %98'e çıkartılmıştır. Karışımlar DCP kullanılarak işlenip diferansiyel taramalı kalorimetre (DSC) analizine tabi tutulduktan sonra, analiz sonuçlarına göre sahip oldukları kristallilik yüzdeleri hesaplanmıştır. Mekanik sonuçlar, kalorimetrik analiz sonuçları ele alınarak eş zamanlı olarak incelenmiştir.

Anahtar Kelimeler: Yüksek Yoğunluklu Polietilen, Polipropilen, Dikümil Peroksit, Çapraz Bağlanma, Polimer Karışımları

To my family and to those who perished in the search for science and engineering

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LIST OF ABBREVIATIONS

ABBREVIATIONS

ASTM : American Society for Testing and Materials

DCP : Dicumyl Peroxide

DSC : Differential Scanning Calorimetry

g : a means of mass, grams

HDPE : High Density Polyethylene

J : a means of energy, Joules

kN : a means of force, kiloNewtons

LDPE : Low Density Polyethylene

LLDPE : Linear Low Density Polyethylene

MFR : a means of flow ability, Melt Flow Rate

min : a means of time, minutes

mm : a means of length, millimeters

MPa : a means of pressure, megaPascals

PE : Polyethylene

PP : Polypropylene

psi : a means of pressure, pounds per square inch

rpm : a means of rotational frequency, revolutions per minute

SADT : Self Activating Degradation Temperature

XLPE : Crosslinked Polyethylene

CHAPTER 1

INTRODUCTION

The first chapter of this dissertation presents background and historical information about the topic by citing previously conducted scientific studies. The aim of this work and expectations from the study are also explained in this part.

1.1 Polyethylene and Its Types

Polyethylene (PE) is one of the most commonly used and mass-produced conventional thermoplastics in the world. It is a polyolefin with well-developed production processes, and there exists a wide range of post-reactor processing techniques for shaping its final articles of different geometries. Together with a broad history of process design and development, polyethylene can be manufactured in different phases such as high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE). Amongst them, HDPE and LLDPE have linear molecular structure. In those types of polyethylene, chain branching occurs at a lesser degree and the resulting polymeric complex consists of linear, continuous chains of methylene groups. Because HDPE has a less branched and linear structure, its chains are more closely packed, giving it a higher degree of crystallinity than that of LDPE.

HDPE is produced by the polymerization of ethylene gas using the Ziegler-Natta coordination-catalysis that uses a metal salt such as titanium tetrachloride and a co-catalyst involving triethyl- or trimethylaluminum. Most HDPE production plants utilize the slurry phase process which makes use of continuous stirred tank reactors operated at low temperature and under low pressure, working in series or in parallel depending on the desired kinetic chain length of the polymer. On the other hand, LDPE is obtained by the free radical polymerization of ethylene gas by catalyzing the reaction with different types of peroxides. Most of the new designs for LDPE production processes use tubular reactors operating at high pressures, whereas old designs involving autoclave type reactors are still in use.

In spite of the fact that polyethylene is one of the most substantial thermoplastics; its utilization is heavily lessened in some particular practices on the account of its low melting point, proclivity for dissolution and natural inclination to swell in hydrocarbons, and probability of cracking under loads.[1] It is known that the service range of polyethylene is rather narrowed due to its low melt viscosity, which eventually makes it improper for high temperature processes.[2] For the purpose of preserving its pristine characteristics at desired levels below its melting point and to help it show the characteristics of a rubber above that temperature, a process that is called crosslinking which avoids melting and flowing of the polymer upon heating is used.[1]

1.2 Crosslinked Polyethylene and Types of Crosslinking Processes

A commonly employed option for the enhancement of characteristic properties of a polymer is crosslinking. The usage of rubbers and thermosets is a prevalent notion in the case of crosslinking, though the crosslinking of polyolefins is another major focal point.[3] A molecular structure comprised of branches is preferable for crosslinking which in turn necessitates the investigation of cases in which the counterparts with linear molecular structure are used. Whenever the degree of crosslinking is purposely kept low, the produced polymeric material is called “crosslinkable”.[4]

Many pathways of performing a crosslinking process in polyolefins exist. Those include forming macroradicals by thermally decomposing organic peroxides, irradiating the material using highly energetic beams, and grafting of silane groups.[3] In irradiation crosslinking of polyolefins, the reaction proceeds in the solid state so that little to no negative changes are observed in the material’s crystallinity. In silane crosslinking of polyethylene, silane grafts onto the reactive sites on polyethylene chains and crosslinks are formed between the chains using those silane moieties. The reactive sites on the chains, on the other hand, are also initiated by peroxide radicals.[3]

Amongst the three main methods mentioned above, only chemical crosslinking was employed throughout the continuation of this scientific work. It is a method in which initiator molecules are employed with the aim of producing free radicals that would eventually proceed to crosslinking. Chemical crosslinking can involve the use of either peroxide or silane, but by the usage of organic peroxides, greatest and most monotonic degrees of crosslinking can be obtained.[4]

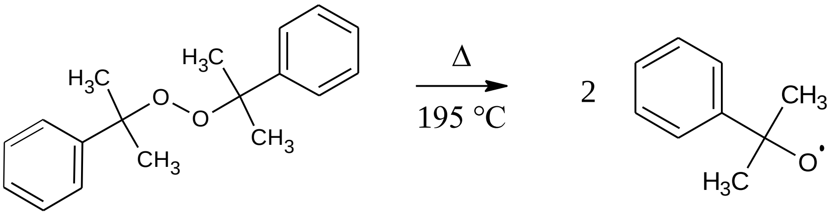
In chemical crosslinking, polyethylene and peroxide are mixed together at temperatures which are lower than the temperature at which the employed peroxide starts decomposing. Once compounding is completed, the process is continued by one or more downstream equipment which operates at substantially higher temperature and pressure. This higher temperature aids in the decomposition of the peroxide to give out a free radical which eventually aims to abstract a hydrogen atom from the main polymer backbone, leading to the creation of a reactive site. This reactive site eventually reacts with another reactive site from the same or a different chain. This reaction proceeds until complete consumption of peroxide occurs or the temperature decreases beyond the decomposition point.[5,6]

Because crosslinked polyethylene builds up a high molecular weight complex, it becomes more resistant to external effects such as impacts, stress cracks, creep and abrasion while keeping its tensile modulus to remarkable extents.[4]

1.3 Choice of Peroxide for Crosslinking

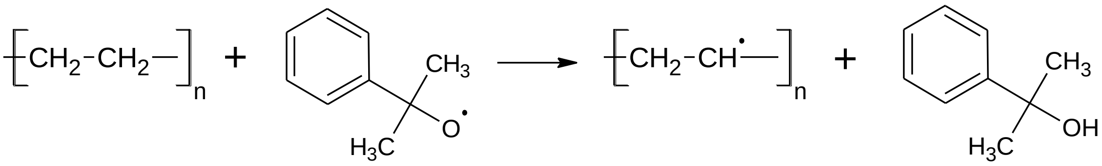
It is stated that an appropriate type of peroxide must be chosen in order to avoid early curing but also to be able to yield enough crosslinking inside the compounding machinery. Although the usage of dicumyl peroxide (DCP) is widely accepted, di-*tert* butyl cumyl peroxide is also employed owing to it being in liquid form which makes it easier in feeding into the extruder with safer operating temperature limits.[1]

It is reported previously that using organic peroxide is preferable because of its economic feasibility and easy control of the initiator's decomposition rate. With the additional advantage of lesser amounts of side products created during the process, the crosslink density of HDPE can be governed more easily by the content of DCP in its molten phase.[7] It is expressed that DCP could be worked in polymeric filaments before processing, which empowers the use of that type of peroxide.[8] The thermal decomposition, i.e. radical formation, of DCP can be easily represented by the following chemical reaction given in Scheme 1.1 as follows;



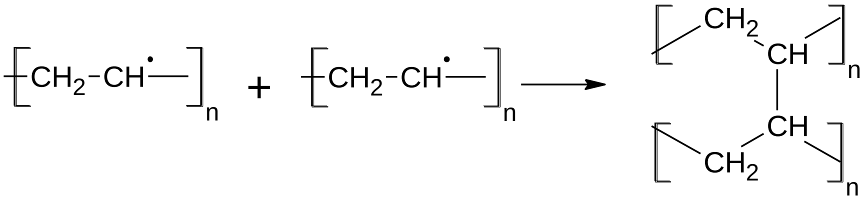
Scheme 1.1: Decomposition of Dicumyl Peroxide

This decomposition process is then followed by the initiation of the radicalization reaction on one or more of the chains which is given in Scheme 1.2 as follows;



Scheme 1.2: Initiation of Polyethylene Chains

Once the initiation step is complete, the crosslinking reaction finalizes the process as given in Scheme 1.3 as follows;



Scheme 1.3: Termination of Crosslinking Reaction

The organic peroxide used in the study was decided to be dicumyl peroxide (DCP) with the side products of cumyl alcohol radicals, cumyl alcohol, acetophenone, and ethane. The underlying reasons for employing that specific type of peroxide were mainly its advantages of affordability and availability.

1.4 Polyblends Composed of Polyethylene and Polypropylene

It is most of the time expensive to separate the waste of plastics into an individual polymeric component, thus the recycling industry often comes across intricate mixtures.[9] These intricate polymeric assortments show bad characteristics in mechanical performance, aging behavior, with decreased resistance towards thermal and chemical effects, mostly due to their incompatible nature.[10,11] It therefore becomes necessary to conduct research on the structure, compatibility, rheological characteristics, and processability of the weak blends of polyethylenes and polypropylenes.[9]

The compounding of PE and PP yields heterogeneous mixtures. In those mixtures of PE and PP, the former takes the role of an impact modifier such that whenever its degree of dispersion in the resulting mixture is high, the mechanical properties are enhanced.[12] The latter, on the other hand, is reported to have a significant role since it affects the interfacial properties between the two polymers.[13] This claim is supported by pointing out that the impact performance of polypropylene is increased when small quantities of ethylene-propylene copolymer or polyethylene are added into polypropylene.[14-16] Additionally, the optical clarity of solid polyethylene is increased when a small quantity of polypropylene is added into polyethylene.[17] Polyethylenes and isotactic polypropylenes are semi-crystalline with the capability of crystallizing with lamellar structure and spherulitic morphology.[9] Despite this fact, the crystals of polyethylene are orthorhombic whereas those of polypropylene are α-monoclinic and β-hexagonal.[18]

The Young’s modulus for isotactic PP is higher than that of HDPE, because the stereoregular arrangement of the repeating units results in a maximization of the Van der Waals forces between its chains. The graph that relates the Young's modulus of the PE-PP blends to their composition is given in Figure 1.1 as follows;

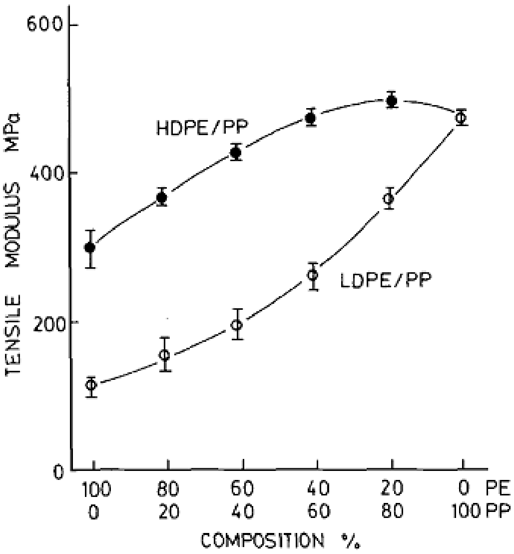


Figure 1.1: Tensile Moduli of PE-PP Blends[19]

The responses of the PE-PP blends in their strains against varying polymer concentrations are given in Figure 1.2 as follows;

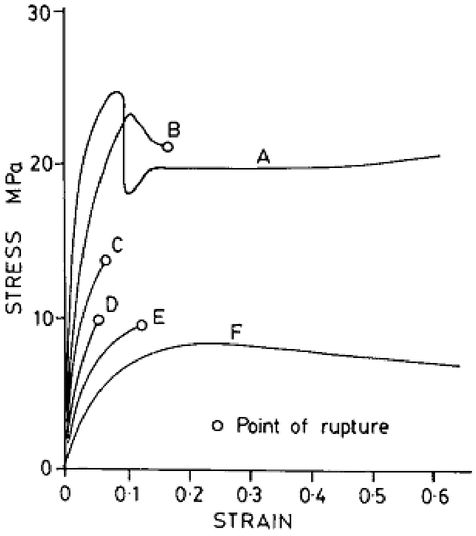


Figure 1.2: Strain Responses of PE-PP Blends[20]

where A is PP, B is 80%PP-20%PE, C is 60%PP-40%PE, D is 40%PP-60%PE, E is 20%PP-80%PE, and F is PE, all by weight percentages. It should be noted that the points of rupture for pure PE and PP are not shown in Figure 1.2, since they can attain strain values of several hundred percent. As shown above, Figure 1.2 can constitute a proof about how the two polymers result in very intricate and weak blends whenever they are mixed in given concentrations.

1.5 Crosslinking in Polyethylene and Polypropylene Polyblends

The investigation of crosslinking of PE-PP polyblends with varying concentrations of PP (10% (w/w) to 90% (w/w) with 10% (w/w) increments) using DCP yielded that for 2.5% (w/w) of DCP, only the PE component is crosslinked which was found to be independent of the concentration of the constituent polymers. The inference from the sought study came out to be that when using small quantities of peroxide, relatively small amounts of PP are incorporated into the polymer network.[12]

There was also a case in which PE-PP blends with 2,5-di-tert-butylperoxy-2,5-dimethylhexane in the melt and in solution were prepared for comparison.[21] It is expressed that in solution, grafting of PP onto PE took place where the degradation of PP smothered and crosslinking of polyethylene was barriered. In the same study, it is found out that in the melt, grafting efficiency was very low and the dominating processes were PP degradation and PE crosslinking.[21]

PP degradation during a peroxide-initiated crosslinking reaction is stated to be hard to overcome since majority of the PP chains tend to undergo chain-scission in the form of a beta-scission reaction.[22] This fact is known to pin down the necessary and effective utilization of a co-agent for the prevention of PP degradation.[23] Whenever PP is tried to be crosslinked, a process involving grafting of silane groups must be used.[4]

1.6 Aim of the Work

The aim of this thesis is to conduct scientific research on the molten state organic peroxide crosslinking of HDPE-PP blends without using co-agents or compatibilizers, and review their responses against varying polymer and peroxide compositions. The main reason for choosing HDPE and PP as the constituents for the blends is that they are of very similar densities which make them harder and less efficient to separate using regular water-alcohol mixtures. Another reason was that they do not structurally involve any chemical groups that could have added some functionality to those polymers, which would have aided in their sorting or mutual-compatibilization. The polymer compositions are chosen as 30% (w/w), 50% (w/w), and 70% (w/w) of each component with the purpose of resembling realistic conditions experienced in the plastic recycling industry. For the same purpose, the crosslinking reaction is decided to be performed in the molten state, since it is not feasible for the industrial applications to dissolve large amounts of polymer in solvents and apply solution phase crosslinking.

The aim also involves, if and whenever possible, the improvement of the mechanical properties of the sought blends. This notion would most probably help the polymer recycling industry to decrease its needs to separate these two very close polymers into individual counterparts, on the grounds that addition of organic peroxides into the HDPE-PP blends followed by molten state processing would yield polyblends of adequate performance that might make a substitute for the usage of a single polymeric compound in different areas of polymer processing. The research and results presented in this work are based on the evaluation of mechanical and thermal properties of the polyblends. For the mechanical part, universal and standardized tensile testing methods are employed with the interest of evaluating the mechanical performance of the polyblends under dynamic loading. For the thermal part, differential scanning calorimetry (DSC) technique is used for the analysis of the enthalpies of fusion and corresponding crystallinity percentages of the prepared polyblends.

CHAPTER 2

EXPERIMENTAL

The second chapter of this dissertation presents the materials and machinery used in the study, the process of preparation of specimens, and the theory of testing and analysis applied to the prepared specimens.

2.1 Materials Used In the Study

The materials made use of in the study and their respective properties are given in this section of the dissertation. Whenever it is felt inadequate about the properties given in the following part, the reader is kindly advised to refer to the product data sheets of the employed materials.

2.1.1 High Density Polyethylene (HDPE)

High density polyethylene (HDPE) used in this study was produced by Petkim Petrokimya Holding A.Ş. (İzmir, Turkey) with the trade name “HDPE S 0464”. This type of HDPE is obtained by the Ziegler-Natta polymerization of polymer-grade ethylene gas at low temperature and under low pressure, making use of hexane as the solvent medium. The powdered polymer leaves the reactor system as the effluent in a slurry phase, which upon further drying, filtering and extruding, is pelletized and batched in bags of 25 kilograms. The melt flow rate (MFR), density, and the tensile strength at break values are supplied by the company as 0.25-0.40 g/10min (by ASTM D1238), 0.959-0.963 g/cm^3 (by ASTM D1505), and 31 MPa (by ASTM D638), respectively.[24]

2.1.2 Polypropylene (PP)

Polypropylene (PP) used in this study was produced by Borealis AG with the trade name “HE125MO”. According to the data supplied by the producer, this type of PP has MFR, density, and tensile stress at yield values of 12 g/10min, 0.905 g/cm^3, and 34 MPa, respectively. It is noted by the company that this PP is extremely rigid with a percentage elongation at yield of only 9%.[25]

2.1.3 Dicumyl Peroxide (DCP)

Dicumyl peroxide (DCP) used in this study is the product of Sigma Corporation (Japan). Although DCP is sold in different physical states in the market, the one used in this study is in the crystalline form with a molar purity of ≥98%. This type of DCP has a self-activating degradation temperature (SADT), safe processing temperature, and typical crosslink temperature of 75^{o}C, 130^{o}C, and 170^{o}C, respectively with a half-life of 0.5 minutes at 195^{o}C.[26,27]

2.1.4 Hexane

Hexane used throughout this thesis study was supplied by Sigma-Aldrich Corporation (Germany) at laboratory reagent grade.

2.2 Preparation of Samples

This section of the dissertation gives information on the theory and process of preparing the samples and specimens that were made use of throughout the study. The sample preparation is given in following parts with an objective manner by presenting the technical aspects of the laboratory devices and machinery used in the processes.

2.2.1 Preparation of Pristine HDPE-PP Blend Masterbatches

Pristine HDPE-PP blends used throughout this thesis study were prepared in weight ratios of 30% (w/w), 50% (w/w), and 70% (w/w) and coded as 30HDPE70PP, 50HDPE50PP, and 70HDPE30PP. The sets were extruded at a speed of 60 rpm with respective hopper and die temperatures of 195^{o}C and 190^{o}C in a Haake extruder equipped with Haake Rheomax OS PTW16 twin-screw system and Haake PolyLab OS RheoDrive 4 drive system, produced by Thermo Electron Corporation.

2.2.2 Preparation of Dicumyl Peroxide (DCP)-Incorporated Sets

Incorporation of DCP was the second and most crucial step of the study, due to the fact that its inadequate or excessive presence would mean less- or over-crosslinking of the prepared sets. This step was started by immersing pure HDPE, PP, 30HDPE70PP, 50HDPE50PP, and 70HDPE30PP sets in hexane for 48 hours, a period decided to be enough for appropriate swelling of the material. This process was performed with the aim of creating a continuous medium of hexane adjacent to the surface and in the pores of the pellets. This continuous medium eventually aided in the dissolution and diffusion process of DCP molecules in solution.

This step of sample preparation was continued by the addition of 0.5% (w/w), 1.0% (w/w), and 2.0% (w/w) DCP into each set, yielding a total number of 15 DCP-incorporated sets. The sets were left to wait in hexane-DCP solution under stagnant conditions at room temperature and under atmospheric pressure until hexane slowly evaporated and complete swelling of the pellets took place. A second addition of hexane into the DCP-incorporated sets was also performed in order to ensure further dissolution and adsorption of leftover DCP onto the surface of the pellets. The sets were then dried at 60^{o}C in a heating oven for a very short period of time, which was enough for maximum evaporation of hexane but meager for the melting of the solidified DCP back into its liquid form.

2.2.3 Preparation of Pristine and DCP-Incorporated Blend Films

Until that point, fifteen different DCP-incorporated and five different pristine sets were obtained. Consecutively, pellets of each set were pressed under a pressure of 6000 psi at a temperature of 195^{o}C with a residence, i.e. curing, time of 3.5 minutes in a hydraulic press produced by PHI Corporation. The pressure differential on the films during the curing time was kept constant, since zeroing out the pressure would result in the stopping of the flowing gel due to crosslinking. Upon completion of the curing time in the hydraulic press, the films were then quench-cooled under regular tap water, so the rate of cooling was considered to be high and equal for each set, which eventually ceased to be a concerning parameter for the mechanical and thermal analysis of samples. The utilization of quench-cooling of the prepared films was decided with the aim of resembling industrial conditions, where polymeric materials in molten states are either water- or air-cooled at very high rates.

2.3 Testing and Analysis of Obtained Films

This part of the dissertation presents to the reader the logic and the process of testing and analysis of the obtained film samples. Additionally, the experimental setups and process parameters adjusted during experimenting are given.

2.3.1 Mechanical Testing

Following the preparation of the films in hydraulic press, dog-bone shaped samples were cut from these films using standard cutter blades and were exposed to tensile loading test in a universal testing machine produced by Lloyd Instruments, coded as LR5K. The tensile testing was applied to each specimen according to the standards of ISO 527-1 and ISO 527-2 at a crosshead speed of 50 mm/min, making use of a 5 kN load cell. The mechanical performance of the samples was determined by the interpretation of their Young’s Moduli (MPa), Tensile Strengths (MPa), Percentage Elongations at Break (%), and Yield Stresses (MPa). It is to the experimenter’s responsibility to inform the readers that no extensometer was used in tensile testing of the materials.

2.3.2 Thermal Analysis

The thermal properties of the specimens were determined via the application of differential scanning calorimetry (DSC), which was performed by a SCINCO DSC N-650 calorimeter. The temperature range and scanning rate were kept constant for each of the specimens between 25^oC and 200^oC, and at 20^oC/min, respectively. The main thermal properties of the specimens exposed to calorimetric analysis used in the evaluation of their thermal performance were the onset temperature of melting (T_{onset}) (^oC), melting temperature (T_M) (^oC), offset temperature of melting (T_{offset}) (^oC), and corresponding enthalpy of fusion (ΔH_{fusion}) (J/g) values. The crystallinity percentages of the specimens were calculated with respect to their measured enthalpies of fusion, which eventually yielded their thermal performance.

The percent crystallinities of the components building up the blend were calculated separately by making use of the thermal data obtained from DSC experiments. A simple yet adequate equation was employed during these calculations shown as follows;

$$X(\%) = \frac{\Delta H_m}{\Delta H_m^o} \times 100 \qquad (Eqn. 1)$$

where X (%) stands for the percent crystallinity of the sought component, ΔH_m (J/g) is the heat of fusion measured through DSC experiment, and ΔH_m^o (J/g) is the heat of fusion of the polymer assuming its 100% crystalline. The enthalpy of fusion value for a fully crystalline HDPE specimen is given as 245.3 J/g, whereas that of PP is presented as 209 J/g.[28]

CHAPTER 3

RESULTS AND DISCUSSION

The third chapter of this dissertation presents the results obtained from mechanical testing and calorimetric analyses, and corresponding discussion.

3.1 Mechanical Testing Results

This section covers the results of the mechanical testing applied to the specimens. The Young's moduli, tensile strengths, percentage elongation at break values, and yield stresses of the specimens are tabulated and discussed objectively.

3.1.1 Young's Moduli of Prepared Sets

Young's moduli of the prepared sets were found to be consistent with the polymer composition of the blends. That is, pristine PP has yielded the highest Young's modulus value, whereas the one with the smallest PP concentration, i.e. HDPE incorporated with 2.0% (w/w) DCP, has yielded the lowest Young's modulus value. The numerical results are tabulated and given in Table 3.1, as follows;

Table 3.1: Young's Moduli of Prepared Sets

Set Code	Young's Modulus (MPa) (Pristine)	Young's Modulus (MPa) (0.5% (w/w) DCP)	Young's Modulus (MPa) (1.0% (w/w) DCP)	Young's Modulus (MPa) (2.0% (w/w) DCP)
PP	890	959	1144	DISINTEGRATED
30HDPE70PP	790	1014	983	812
50HDPE50PP	777	796	779	632
70HDPE30PP	610	455	430	423
HDPE	467	415	399	261

Table 3.1 can be more easily visualized using Figure 3.1 that involves the changes in the Young's moduli of the sets with varying PP composition and DCP percentage;

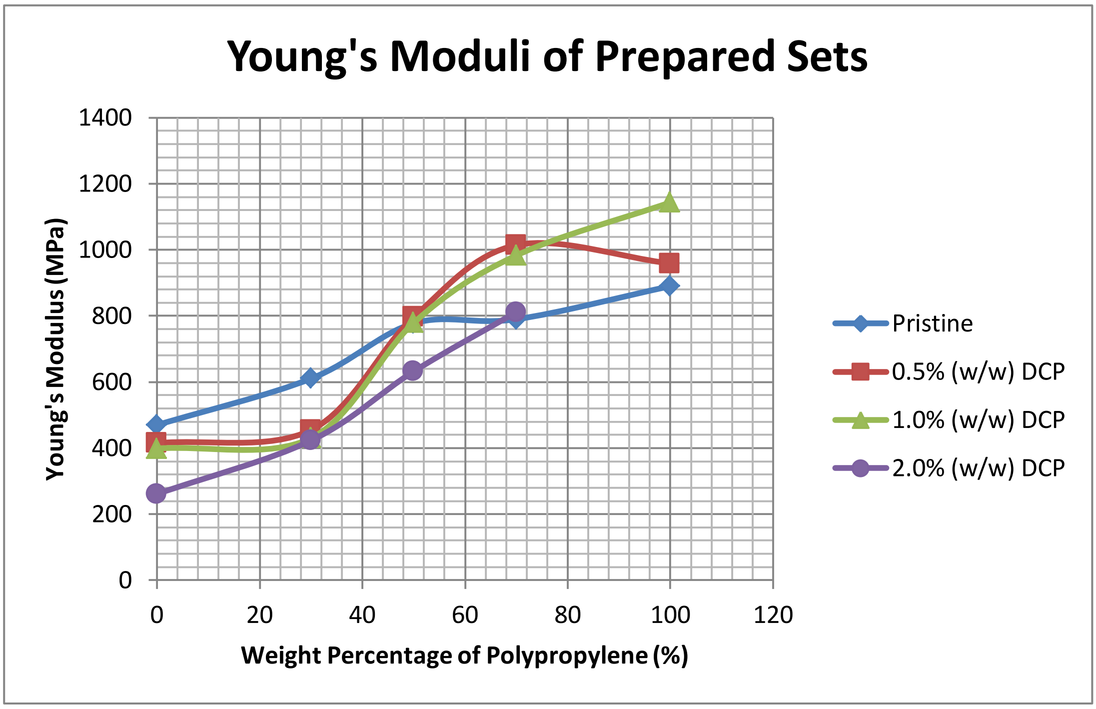


Figure 3.1: Young's Moduli of Sets versus PP Concentration

By analyzing the values in Table 3.1 and Figure 3.1, it is seen that the Young's modulus of individual PP was enhanced using DCP from its pristine value of 890 MPa to a higher 1144 MPa, corresponding to an approximate 28.5% increase. This increase was due to gains of about 70 MPa at each of the 0.5% (w/w) DCP and 1.0% (w/w) DCP marks. Although stiffened at 0.5% (w/w) and 1.0% (w/w) DCP levels, at 2.0% (w/w) DCP the PP film specimens completely degraded during pressing and no usable samples could be taken from the deformed films.

The response of HDPE against increasing weight percentages of DCP was found to decrease its Young's modulus. Despite there exists a common knowledge that crosslinking would increase a materials Young's modulus, i.e. it stiffens the polymer bulk, it was found not true for the case in which crosslinking takes place in the molten state. This happens due to the fact that in the molten state, a period during which the crystalline lamellae of HDPE is disentangled and polymer chains are freely moving, crosslinking takes place immediately and chemical crosslinks are formed between the chains. Once the decomposition of DCP occurs and crosslinking reactions between its radicals and the polymer chains start, the material slowly becomes a gel with no crystalline sites in the molten state. Upon application of quench-cooling, which provides rather high cooling rates, the crosslinked HDPE cannot crystallize back to its previous state due to the lack of time required for that process. Instead, a highly-crosslinked and less-crystalline solid is obtained. Thus, there then exists less numbers of crystalline sites that bond together the polymer complex, resulting in lower Young’s modulus values.

The observed changes in the Young’s moduli of HDPE-PP blends resembled the responses in the Young’s moduli of individual HDPE and individual PP with increasing DCP weight percentages. The specimens taken from 30HDPE70PP and 50HDPE50PP sets experienced maximum increases of 28.4% and 2.45% in their Young’s moduli at a DCP percentage of 0.5% (w/w), respectively. As it is observed from the results of Table 3.1, the increase has been greater in 30HDPE70PP, since the PP composition is 70%, whereas 50HDPE50PP is 50% PP by weight. Whenever the weight percentage of DCP exceeded the 1.0% (w/w) mark, in both sets the increases obtained at 1.0% (w/w) DCP took a downhill turn, which is mainly attributed to the degradation of PP and excessive crosslinking of HDPE in the blend. The 70HDPE30PP set showed a similar characteristic decrease in its Young’s modulus, just as its main constituting component HDPE performed in its DCP-incorporated sets. Since 70% of 70HDPE30PP is HDPE by weight, its Young’s modulus experienced decreases at each weight percentage of DCP.

Thus, as an inference, it can be said that whenever the weight ratio of PP in the blend was greater than or equal to 1:1, the resulting crosslinked blends became stiffer by at least 2.45% to about 28.4% with increasing weight percentages of DCP.

3.1.2 Tensile Strengths of Prepared Sets

Tensile strength values of specimens showed similar trends with the Young’s moduli shown in the previous section. During the experiments, it was found out that the tensile strength values of pristine HDPE and pristine PP were lower than their producers' specifications by about 10 and 8 MPa, respectively.[24,25] This was of no concern about the reliability of the mechanical testing of the samples since they were prepared using hot press machinery under laboratory conditions. Instead of using injection molding followed by slow-cooling, hot pressing and quench-cooling of the samples eventually resulted in lower crystallinity levels which in turn decreased their pristine tensile strengths.

As it was expected, the greatest tensile strength value was the one of pristine PP, and the lowest belonged to HDPE at 2.0% (w/w) DCP. That finding had no contradiction in scientific terms, since it is known that PP is a stronger material than HDPE so that it is eligible to accept greater amounts of uniaxial loads during tensile testing. The tensile strength data obtained via tensile testing is tabulated in Table 3.2 as follows;

Table 3.2: Tensile Strengths of Prepared Sets

Set Code	Tensile Strength (MPa) (Pristine)	Tensile Strength (MPa) (0.5% (w/w) DCP)	Tensile Strength (MPa) (1.0% (w/w) DCP)	Tensile Strength (MPa) (2.0% (w/w) DCP)
PP	26.3	26.0	25.2	DISINTEGRATED
30HDPE70PP	25.5	24.3	22.8	26.0
50HDPE50PP	25.6	22.3	21.3	16.5
70HDPE30PP	23.9	20.9	18.9	17.4
HDPE	20.7	19.5	17.4	14.6

The results of Table 3.2 are plotted in Figure 3.2 as follows;

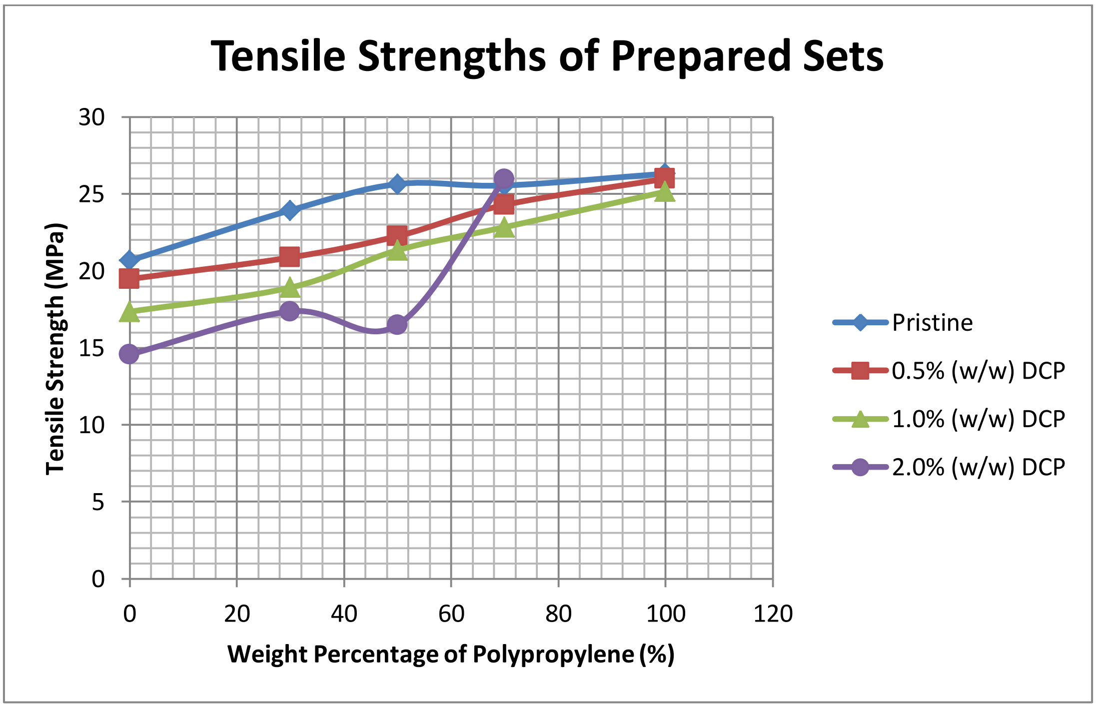


Figure 3.2: Tensile Strengths of Sets versus PP Concentration

As it can be observed in Table 3.2 and Figure 3.2, the highest tensile strength values appeared in pristine PP specimens. Although addition of higher amounts of DCP into PP resulted in lower tensile strengths compared to its pristine tensile strength value, this decrease was found to be particularly small, if not negligible, for PP. That is, PP experienced only about a 4.18% decrease in its tensile strength value when the DCP concentration was at 1.0% (w/w), which was the highest amount of DCP that could be incorporated into PP. The decrease in the tensile strength values of PP with increasing weight percentage of DCP is related with excessive amounts of degradation via chain-scission in the molten state.

In the case of HDPE, results involved interesting findings about the response of its tensile strength to increasing weight percentage of DCP. A previous study conducted on the molten state di-*tert* butyl cumyl peroxide-crosslinking of HDPE yielded increases in its tensile strength values at 0.5% (w/w) and 1.5% (w/w) peroxide concentrations.[1] Contrarily, throughout this thesis study, it was found that the tensile strength values belonging to HDPE were decreased with increasing weight percentages of DCP. At its pristine state, HDPE showed an average tensile strength value of about 21 MPa, whereas this value decreased to a bare 15 MPa at a DCP level of 2.0% (w/w), which corresponds to a decrease of 29%. This decrease in the tensile strength stayed at only 6% at a DCP level of 0.5% (w/w). As in the case of the response of its Young's modulus to increasing weight percentages of DCP, this decrease is correlated with over-crosslinking of the polymeric complex and the disability of the already crosslinked chains to form crystalline lamellae during quench-cooling of the films. Mechanically, the discontinuous interface occurring between the crosslinked network and non-crosslinked chains could not transfer the stress exerted on the specimen, which in turn resulted in lower tensile strength values.[1]

The responses in the tensile strength values of the HDPE-PP blend sets were no surprise when compared with the responses of the individual HDPE and individual PP sets. Upon analyzing the tensile strength values of pristine blends, it is seen that the average tensile strength values increased with increasing PP concentration in the blend, though this increase leveled off whenever the PP concentration in the blend was greater than or equal to 50% by weight.

The tensile strength of each set generally decreased with increasing weight percentage of DCP, some of which are about 27.2% for 70HDPE30PP at 2.0% (w/w) DCP, and 35.5% for 50HDPE50PP at 2.0% (w/w) DCP. An exceptional finding arose in the case of 30HDPE70PP set which was the one that experienced a positive change in its tensile strength value of about 2% at 2.0% (w/w) DCP level. It was mentioned earlier that individual PP degraded completely when it was tried to be processed with 2.0% (w/w) DCP, however in its blend with HDPE in which HDPE weight percentage was 30%, the formed film did not degrade and was suitable for tensile testing.

This small increase in the tensile strength of the sought set can be attributed to the ability of crosslinked polyethylene network to hold degraded PP chains together, which might have aided in carrying and transferring stress, so that there was an occurrence of an increase in the final tensile strength value of the blend.

3.1.3 Percentage Elongations of Prepared Sets

One of the main parameters proving the immiscibility and incompatibility of HDPE and PP was the percentage elongation at break values of their blends. The elongation behavior showed no contradiction with previously conducted studies, in which the researchers gave a stress-strain graph for polyethylene-polypropylene blends for various concentrations of both components.[20]

According to the results obtained from mechanical testing, the HDPE-PP blends were found to perform extremely poorly in terms of elongation ability. The difference in the types of HDPE and PP crystal lattice structures caused the blends to carry stresses lower than or just above the pristine yield stresses of their components. This in turn resulted in the immediate fracture of the blends, i.e. at strain at break values ranging from 5% to 10%. The percentage elongation at break values of HDPE fluctuated between several hundred percent at its pristine phase. On the other hand, pristine PP yielded about an 8% strain.

The percentage elongation at break values of samples obtained as results of mechanical testing are tabulated in Table 3.3 as follows;

Table 3.3: Percentage Elongations of Prepared Sets

Set Code	Percentage Elongation at Break (%) (Pristine)	Percentage Elongation at Break (%) (0.5% (w/w) DCP)	Percentage Elongation at Break (%) (1.0% (w/w) DCP)	Percentage Elongation at Break (%) (2.0% (w/w) DCP)
PP	8.1	5.7	6.8	DISINTEGRATED
30HDPE70PP	7.6	5.0	5.7	8.2
50HDPE50PP	5.8	6.9	9.2	3.2
70HDPE30PP	9.9	30.2	44.3	98.1
HDPE	288.5	368.1	296.5	111.6

The results tabulated in Table 3.3 are plotted in Figure 3.3 as follows;

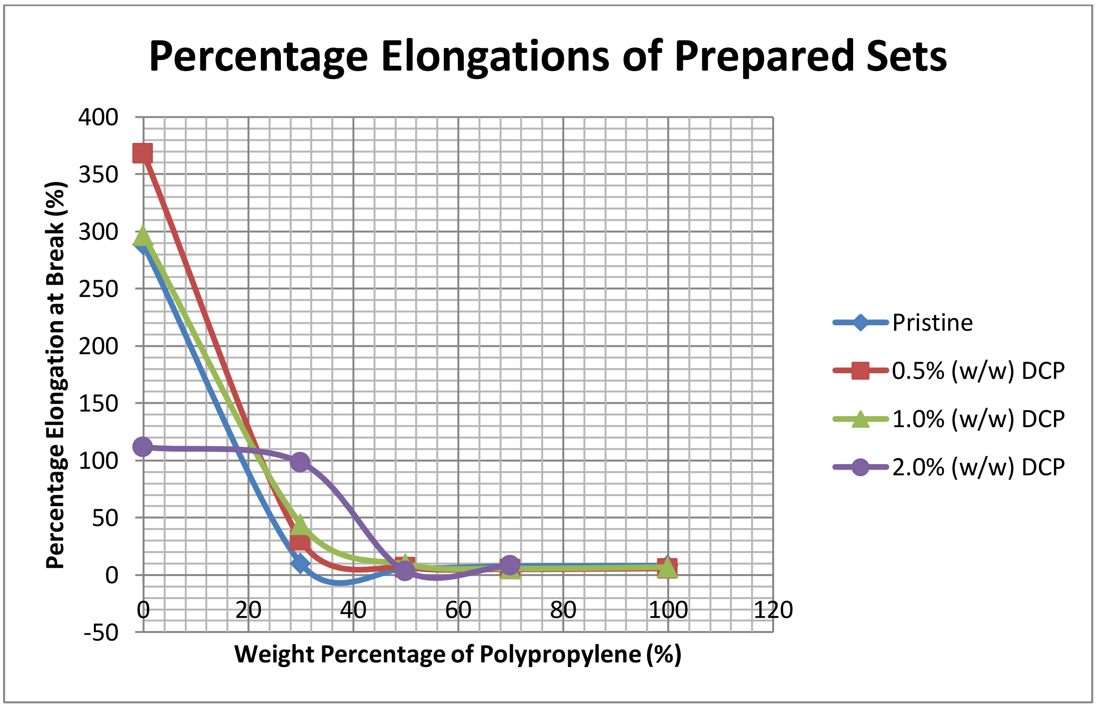


Figure 3.3: Percentage Elongations of Sets versus PP Concentration

The findings for pristine PP resembled the strain values supplied by the producer company.[25] Since that type of PP is a highly rigid polyolefin, percentage elongation at break values fluctuating between 5% and 9% were found to be consistent.

In its pristine form, HDPE had yielded a percentage elongation at break value of 289%, which is about one thirds of the producer's specifications.[24] This difference can be regarded as usual, since processing the polymer at high temperatures and under high pressures which are followed by quench-cooling the final article result in a lowered degree of crystallinity which yields differences in the mechanical properties of the polymer bulk. However, the results for DCP-incorporated HDPE gave rise to a new finding. Although the opposite was expected, DCP-incorporated HDPE sets showed greater percentage elongation at break values than that of the pristine set. At a DCP level of 0.5% (w/w), HDPE elongated by a staggering 368%, corresponding to an increase of 27.6% from its pristine value. At the 1.0% (w/w) DCP mark, this positive change stayed at only 2.8%. At 2.0% (w/w) DCP, over-crosslinking obviously prevailed, and a negative change of 61.3% emerged. The increase of the percentage elongation at break value of HDPE at 0.5% (w/w) DCP level was thought to have two probable reasons. The first possible reason was the possibility of having worked with film specimens of higher crystallinity, which was eventually debunked when the results of DSC analysis came up. The second possibility involved the ability of appropriate crosslinking occurring at the 0.5% (w/w) DCP level to create crosslinked polyethylene sites which could have incorporated the non-crosslinked and non-crystalline polyethylene chains into themselves, so that the resulting polymer bulk become more ductile at the final stage. Although no conclusive decision can be stated for this phenomenon at this stage, the reproducibility of greater elongations during testing supported the correctness of the latter argument.

It was stated earlier that the ability of elongation in HDPE-PP blends is extremely reduced due to the incompatibility of the constituting polymers. The results of the mechanical testing proved exactly that, which can be analyzed by observing the numbers obtained for the pristine sets. Each of the pristine blends showed percentage elongation at break values ranging between 5% to 10%, which were agreeing with similar works performed before.[9,19] Any effect of increasing weight percentage of DCP on the percentage elongation at break values of 30HDPE70PP and 50HDPE50PP sets was not of adequate significance to make comments about.

On the other hand, a behavior in the percentage elongation at break value of 70HDPE30PP similar to the case in DCP-incorporated HDPE set was observed. With increasing DCP concentration, the blend became more ductile and showed greater elongation ability. This was attributed to the incorporation of degraded PP chains into the crosslinked and non-crosslinked polyethylene network, so that the devastating effect of having different incompatible crystalline lattice types in a HDPE-PP blend was overcome. In addition to that probability, it can also be said that degraded and shortened PP chains had shown a plasticizing effect on the polymer bulk.

3.1.4 Yield Stresses of Prepared Sets

Determination of the yield stress values was one of the trickiest parts of this thesis study. Since incompatible polymer blends are known to not always show yielding, which is due to the presence of different lattice types in the polymer matrix, it was not easily traceable, let alone being detectable. Individual HDPE and individual PP were exceptional cases in that sense.

The samples taken from the HDPE-PP blends were observed to experience breaks immediately after yielding, if yielding took place at all. That is, HDPE and PP did not show any synergism in their blends. Additionally, it can be said that whenever the dispersion of PP in the blend was higher, the blend started yielding at greater stress levels.

It is to the experimenters responsibility to state that the yield stress values presented in the following Table 3.4 and Figure 3.4 are averages of only a fraction of specimens which showed yielding behavior. Therefore, some of those values might contradict with the tensile strength values presented in Table 3.2.

Table 3.4: Yield Stresses of Prepared Sets

Set Code	**Yield Stress (MPa) (Pristine)**	**Yield Stress (MPa) (0.5% (w/w) DCP)**	**Yield Stress (MPa) (1.0% (w/w) DCP)**	**Yield Stress (MPa) (2.0% (w/w) DCP)**
PP	26.3	NO YIELDING	NO YIELDING	DISINTEGRATED
30HDPE70PP	23.0	24.3	23.1	27.0
50HDPE50PP	NO YIELDING	21.5	21.3	16.4
70HDPE30PP	23.5	20.7	18.9	16.9
HDPE	21.0	17.3	17.0	14.3

Values given in Table 3.4 are plotted in Figure 3.4 for a better comprehension of the changes in yield stress values experienced by the sets as follows;

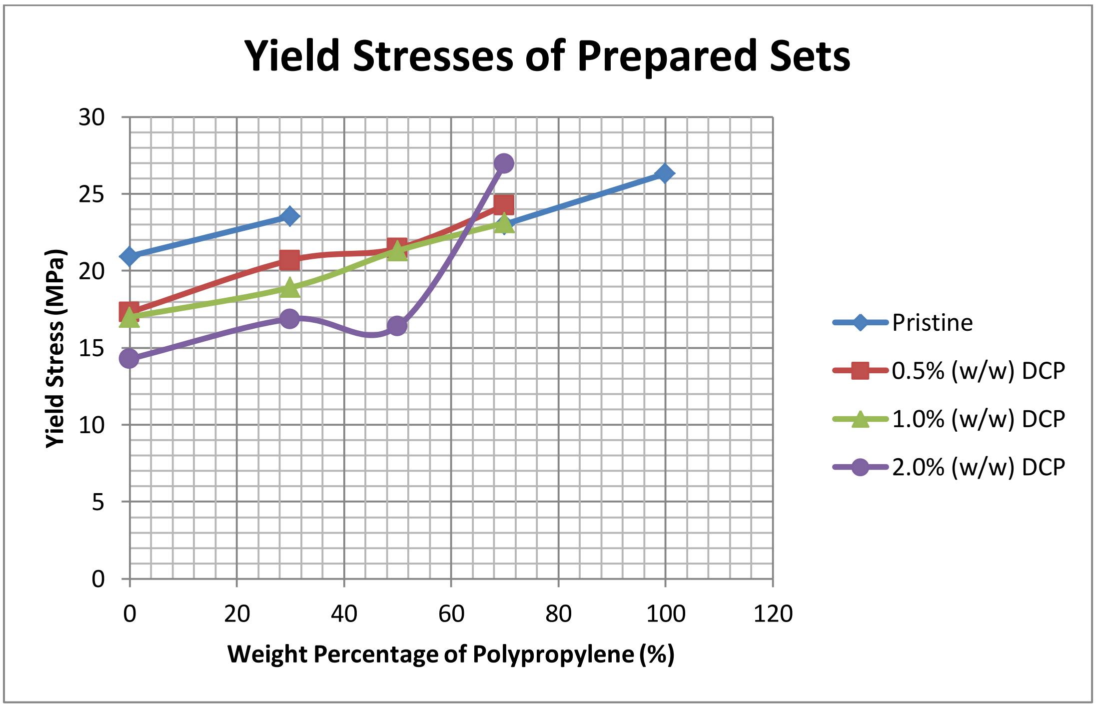


Figure 3.4: Yield Stresses of Sets versus PP Concentration

It is seen in Figure 3.4 that PP showed yielding only in its pristine state when no DCP was present in the polymer bulk. That way, PP was able to preserve its main characteristics and its mechanical results became reliable. However, addition of only 0.5% (w/w) DCP was found to result in enough degradation so that the polymer showed no yielding at all. Although the positive change in the Young's modulus of PP was a significant achievement, this change brought alone with itself the disability of the polymer to flow, i.e. an inclination to break without yielding.

The yield stress value for pristine HDPE was determined to be very close to its tensile strength value. However, yielding was observed to start at lower stress levels with increasing weight percentage of DCP. Individual HDPE suffered a total decrease of 31.9% in its yield stress value at a DCP level of 2.0% (w/w). This decreasing trend showed a plateau at 0.5% (w/w) and 1.0% (w/w) DCP levels, where the losses in the yield stress were 17.6% and 19.0%, respectively.

The responses of the blends in their yield stresses against the application of tensile forces showed up as expected. The lack of ability of HDPE-PP blends to show yielding is a well-known subject and it was proven repeatedly during mechanical testing of the specimens. Many of the specimens of the blends did not yield, and broke suddenly with increasing stress levels. This inability leaped out in the case of 50HDPE50PP set which was the one consisting of 50% HDPE and 50% PP by weight. This resulted in a conclusive argument that whenever the weight fraction of one of the components reached 0.5, in other words whenever the weight ratio of the components became 1:1, the devastating effects of immiscibility and incompatibility dominated the system, resulting in the complete loss of yielding of the material. At HDPE weight percentages of 30% and 70%, i.e. at PP weight percentages of 70% and 30%, a minority of the specimens showed tendency of yielding. This was due to the fact that there was one component that had a greater weight ratio than the other, so that the yielding behavior could be governed by the presence of that component with the greater weight ratio.

3.2 Thermal Analysis

In any of the specimens taken from the films of masterbatches 30HDPE70PP, 50HDPE50PP, and 70HDPE30PP, two very significant peaks were read, each of which belonged to either individual HDPE or individual PP. This result also proved the incompatibility of the polymer components present in the polyblends. Upon exposing the specimens taken from the prepared sets to calorimetric analysis, final and conventional information about the thermal performance of the blends and their individual components could be obtained.

3.2.1 Variation of the Melting Points of Prepared Sets

The variation of the melting points measured during calorimetric testing showed expected results. The melting points measured for any of the polymer components approximated their pristine value as that component’s weight percentage in the blend was increased. Generally, it was observed that increasing weight percentages of DCP diminished the melting point of both components in the blends.

3.2.1.1 Variation of the Melting Point of HDPE

The melting point of HDPE showed a decreasing trend with increasing weight percentages of PP and DCP, respectively. The decrease in the melting point of HDPE is attributed to the over-crosslinking of the polyethylene network which decreased the amounts of crystalline sites. The values obtained as results of the DSC experiment are given in Table 3.5 as follows;

Table 3.5: Melting Points of HDPE in Prepared Sets

Set Code	T_m (°C) (Pristine)	T_m (°C) (0.5% (w/w) DCP)	T_m (°C) (1.0% (w/w) DCP)	T_m (°C) (2.0% (w/w) DCP)
HDPE	135.74	133.89	132.64	125.49
70HDPE30PP	133.19	132.40	130.34	130.18
50HDPE50PP	131.98	132.61	129.86	129.49
30HDPE70PP	131.72	129.52	128.33	124.45

The values given in Table 3.5 are plotted in Figure 3.5 as follows;

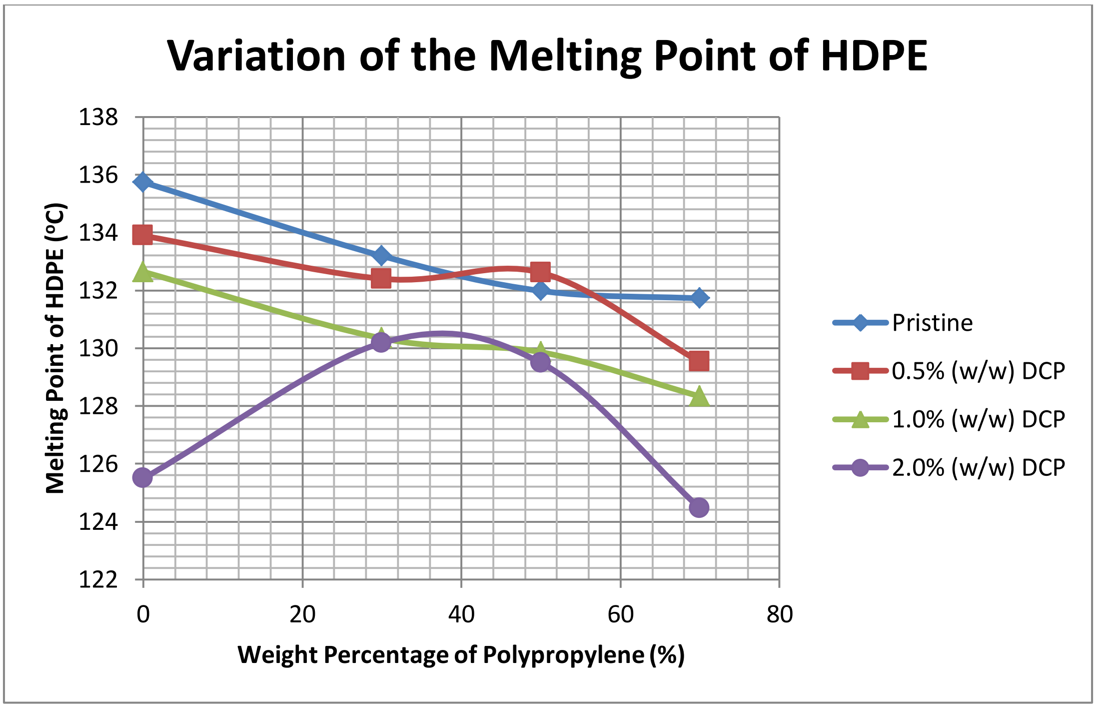


Figure 3.5: Melting Point of HDPE versus PP Concentration

Upon analyzing Table 3.5 and Figure 3.5, it is observed that the melting point of HDPE component in the blend decreased with increasing DCP and PP weight percentages. For individual HDPE samples incorporated with DCP, the decrease in the melting point was found to be about 10.3°C, which corresponded to 7.55% of its pristine melting point. Additionally, this downhill pace was observed to speed up when crossing the 1.0% (w/w) DCP mark, since at 2.0% (w/w) DCP level the polymer melted at its lowest measured temperature. This is attributed to the over-crosslinking of the polymer at its molten state and creation of smaller percentages of crystallinity in the resulting quench-cooled films.

Increasing weight percentages of PP in the blends had also a similar effect on HDPE's melting point. For the pristine sets, a simple overview of Table 3.5 shows that as the PP concentration in the blend increased, the melting point of HDPE decreased by about 4°C, which corresponds to a loss of approximately 2.96% in magnitude. Upon further discussion, this decrease was attributed to the inability of the dispersed HDPE crystals to hold together due to the existence of their incompatible PP crystal counterparts in the polymer bulk, so that they melted at lower temperatures.

In the blends, the results yielded similar characteristics. For 70HDPE30PP, 50HDPE50PP, and 30HDPE70PP blends at their 0.5% (w/w) and 1.0% (w/w) DCP marks, the melting point of the HDPE component in the blend decreased with increasing PP and DCP weight percentages, respectively.

A surprising result, on the other hand, showed up at the 2.0% (w/w) DCP mark for the case of 70HDPE30PP. The melting point of the blend was found to be about 5°C higher than the individual HDPE crosslinked with 2.0% (w/w) DCP. This was thought to be related with the fact that the scission-degraded PP chains to hold together the over-crosslinked HDPE complex together so that the blend melted at a higher temperature than individual HDPE at the same DCP level.

3.2.1.2 Variation of the Melting Point of PP

The variation of the melting point of PP with varying HDPE and DCP weight percentages in its blends resembled the previous case in which HDPE was examined thoroughly. However, there were again interesting findings about the thermal behavior of PP with changing HDPE and DCP concentrations.

Although a general declining trend in the melting point of PP could be talked about; there also existed a different discussion based on the increased ability of PP to better preserve its thermal characteristics at different HDPE and DCP concentrations than its counterpart, i.e. individual HDPE.

The results for the melting point of PP obtained from the calorimetric analysis are given in Table 3.6 as follows;

Table 3.6: Melting Points of PP in Prepared Sets

Set Code	**T_m (^oC) (Pristine)**	**T_m (^oC) (0.5% (w/w) DCP)**	**T_m (^oC) (1.0% (w/w) DCP)**	**T_m (^oC) (2.0% (w/w) DCP)**
PP	164.43	160.66	159.72	158.29
30HDPE70PP	162.52	158.01	159.4	157.39
50HDPE50PP	160.66	163.82	161.71	160.65
70HDPE30PP	162.14	162.05	160.13	160.2

The results listed in Table 3.6 are plotted in Figure 3.6 for an easier grasp of concept as follows;

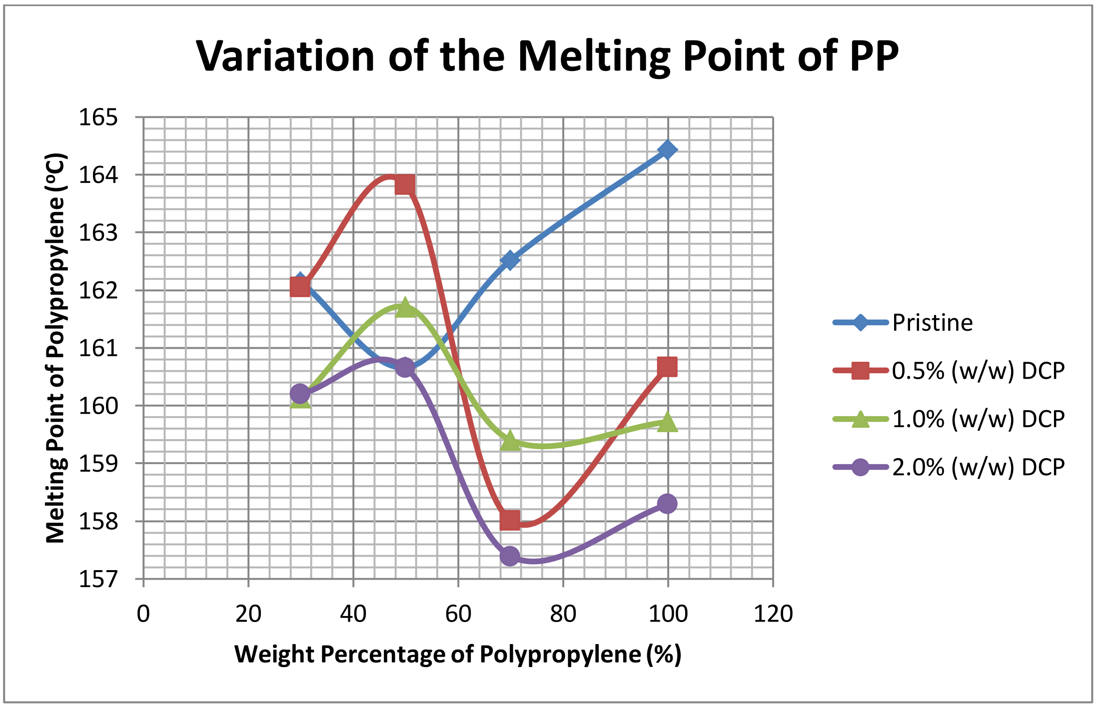


Figure 3.6: Melting Point of PP versus PP Concentration

An analysis of Table 3.6 and Figure 3.6 helps the reader see that individual PP incorporated with DCP experienced a decrease of about 6^{o}C in its melting point, corresponding to approximately 3.73% of its pristine melting point as the DCP level reached 2.0% (w/w) mark. This decrement in the melting temperature of PP was only about 50% of the one belonged to individual HDPE incorporated with DCP which was mentioned earlier. Apart from its blends, this finding yielded that the thermal performance of individual PP reacted with DCP was better in preserving its melting temperature when compared to individual HDPE reacted with DCP.

Addition of HDPE into PP yielded a similar trend in the evaluation of the melting point variation of PP in its blends. At HDPE weight percentages of 30% and 50%, which were the cases in sets of pristine 30HDPE70PP and pristine 50HDPE50PP, the melting point of PP lessened by decrements of about 2^{o}C at each mark, respectively. However, at a HDPE weight percentage of 70%, that was the case of pristine 70HDPE30PP set, the melting point showed a positive change of about 2^{o}C from the pristine 50HDPE50PP set. This unexpected behavior in the melting point of PP could be explained by observing the weight percentages of the components. Whenever the weight ratio of the constituting polymers of the blend was 1:1, their molecular incompatibility dominated the bulk of the material which resulted in greater magnitudes of the loss of thermal performance of PP, so that it reached its lowest temperature of melting. Whenever the weight percentage of any of the polymers in the blend was greater or less than 50%, the PP component was able to withstand its thermal performance in terms of its melting point.

Amongst the cases of DCP-incorporated 30HDPE70PP, 50HDPE50PP, and 70HDPE30PP blends, the 30HDPE70PP set showed the lowest melting points, regardless of the weight percentages of DCP used. This phenomenon was related to the smaller amounts of HDPE existing in the blend, only about 30% (w/w), whose crosslinking could not efficiently help preserve the thermal performance of its PP counterpart. At a DCP level of 0.5% (w/w), the melting point of PP decreased by about 4^oC with respect to its pristine value. At 1.0% (w/w) DCP mark, the melting temperature took its greatest value of 159.4^oC which was about 3^oC lower than its pristine value. At a DCP mark of 2.0% (w/w), over-crosslinking of HDPE and chain-scission PP governed the polymer bulk, so that the melting temperature of PP took its lowest value of 157.4^oC amongst any of the prepared sets during the experiments. Although some particular trending can be obtained by the investigation of Table 3.6 and Figure 3.6, further research and experimenting can be conducted solely on the thermal performance of PP in its blends with HDPE.

3.2.2 Variation of the Enthalpies of Fusion of Prepared Sets

Determination of the enthalpies of fusion of the prepared sets was of essential significance for the evaluation of the thermal performance of the blends and their individual components. Because the enthalpy of fusion of the blends was directly proportional with their crystallinities, the changes in the heats of melting of the components during calorimetric analysis had massive impacts on the final decision-making process about the thermal characters of the polyblends. As the main result of calorimetric testing, it is determined that in their blends the enthalpies of fusion of both HDPE and PP plummeted when compared to the enthalpies of fusion of their individual states.

3.2.2.1 Variation of the Enthalpy of Fusion of HDPE

During the analysis, HDPE lost a significant amount of its enthalpy of fusion with increasing weight percentage of PP in the blend. This trend was found to be coherent and concurrent with any of the sets at any DCP weight percentage. Table 3.7 below gives the results for the measured enthalpies of fusion of HDPE component in the prepared sets as follows;

Table 3.7: Enthalpies of Fusion of HDPE in Prepared Sets

Set Code	ΔH_m (J/g) (Pristine)	ΔH_m (J/g) (0.5% (w/w) DCP)	ΔH_m (J/g) (1.0% (w/w) DCP)	ΔH_m (J/g) (2.0% (w/w) DCP)
HDPE	210.52	181.71	186.65	165.01
70HDPE30PP	124.01	111.46	82.83	107.97
50HDPE50PP	94.93	67.05	76.45	64.82
30HDPE70PP	49.98	37.24	39.04	37

The results of Table 3.7 are plotted in Figure 3.7 as follows;

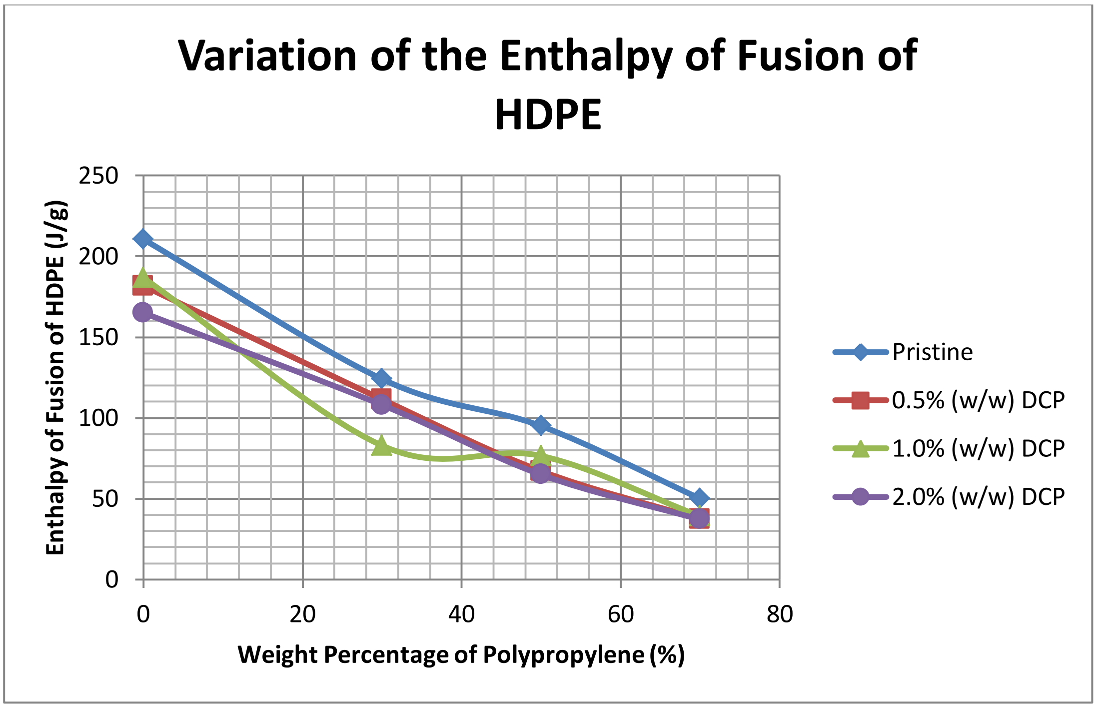


Figure 3.7: Enthalpy of Fusion of HDPE versus PP Concentration

As it can be clearly seen in Table 3.7 and in Figure 3.7, the enthalpy of fusion of individual HDPE decreased as a result of the addition of DCP. HDPE took its lowest enthalpy of fusion value of 165 J/g at the 2.0% (w/w) DCP level, which corresponded to a negative change of 21.6% in magnitude from its pristine value. One thing to note in this trend was that the decrease somehow leveled off at 0.5% (w/w) and 1.0% (w/w) DCP levels, the values of which came up as 181.7 J/g and 186.7 J/g, respectively. That is, pure HDPE was crosslinked via the usage of only 0.5% (w/w) and 1.0% (w/w) DCP by sacrificing an approximate 15% of its enthalpy of fusion. As mentioned, 2.0% (w/w) DCP would carry this loss to above 20%, which might not be desirable for the cases in which the resulting polymer would be used in heat-intensive processes.

In its pristine blends, the enthalpy of fusion values of HDPE suffered major decreases with increasing PP weight percentages, which was expected and stood to be another proof of the incompatibility of the two components. The measured enthalpies of fusion of HDPE component resembled and imitated its weight concentration in the pristine blends. That is, the enthalpy of fusion value of HDPE approximated 70%, 50%, and 30% of its pristine value whenever its weight percentage was 70%, 50%, and 30% in the blends. This phenomenon can be visualized by checking the DSC outputs given in Appendix B of this thesis.

In its DCP-incorporated blends, the decreasing fashion in the enthalpy of fusion values of HDPE with increasing amount of PP retained. In the set coded as 30HDPE70PP, the enthalpy of fusion value of HDPE fluctuated at 37 J/g, 39 J/g, and 37 J/g at 0.5% (w/w), 1.0% (w/w), and 2.0% (w/w) DCP levels, respectively. That is, even though the DCP presence quadrupled in amount, similar values of heat of melting at different DCP weight percentage levels were obtained.

In the set coded as 70HDPE30PP, where the PP concentration was 30% (w/w), the heat of melting value of HDPE decreased while going from 0.5% (w/w) DCP to 1.0% (w/w) DCP. That was thought to be related with the fact that the major process taking place during pressing was the polyethylene crosslinking and decreasing of the number of crystalline lamellae after quench-cooling of the film. When 2.0% (w/w) DCP mark was reached, PP degradation took over and the formed shorter chains somehow barriered the excessive crosslinking of the polyethylene network, allowing a higher enthalpy of fusion value for HDPE than the one at 1.0% (w/w) DCP mark.

3.2.2.2 Variation of the Enthalpy of Fusion of PP

The change in the measured enthalpies of fusion of PP component in the blends was found to be similar and coherent with the trend observed in the case of HDPE. The drastic decrease in the enthalpy of fusion value of PP was obvious and the magnitude of the measured values was directly proportional with the amount of PP present in the blends. The enthalpy of fusion values belonging to PP component are given in Table 3.8 as follows;

Table 3.8: Enthalpies of Fusion of PP in Prepared Sets

Set Code	**ΔH_m (J/g) (Pristine)**	**ΔH_m (J/g) (0.5% (w/w) DCP)**	**ΔH_m (J/g) (1.0% (w/w) DCP)**	**ΔH_m (J/g) (2.0% (w/w) DCP)**
PP	105.51	86.4	101.48	96.01
30HDPE70PP	49.42	38.4	47.45	47.48
50HDPE50PP	35.81	29.45	33.42	28.61
70HDPE30PP	16.92	18.19	14.03	16.59

The values listed in Table 3.8 are plotted in Figure 3.8 for ease of comprehension as follows;

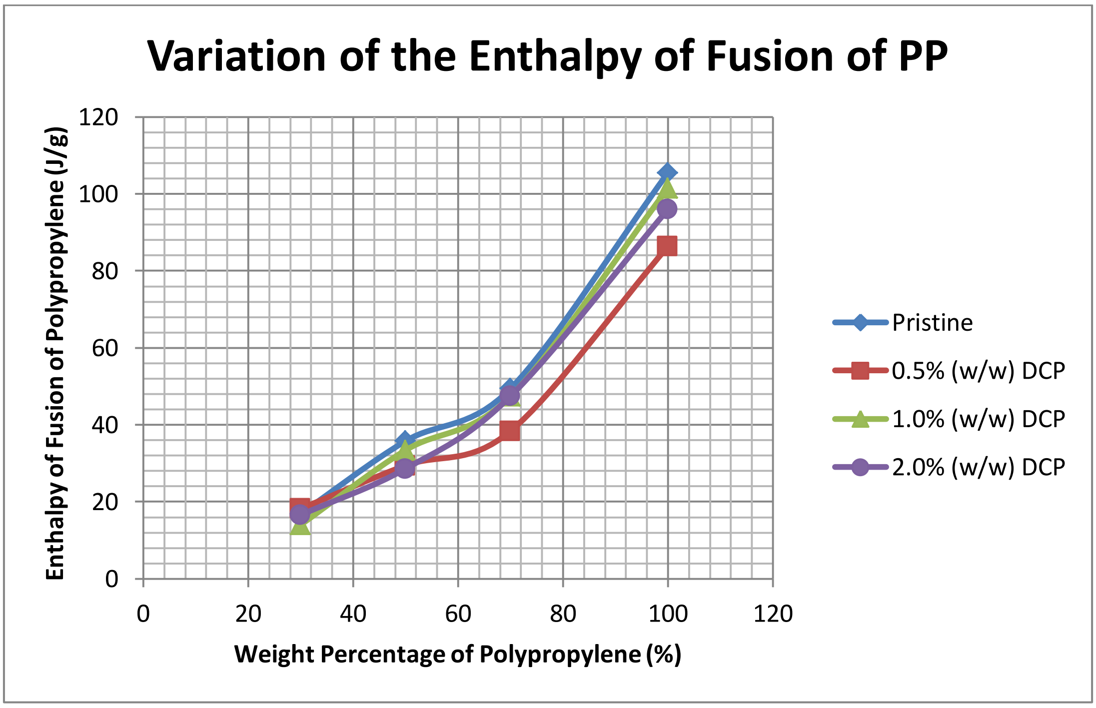


Figure 3.8: Enthalpy of Fusion of PP versus PP Concentration

Individual PP samples showed fluctuating responses in their enthalpies of fusion against increasing DCP weight percentages. The smallest value for the enthalpy of fusion of PP was come across in the case when it was treated with 0.5% (w/w) DCP at 86.4 J/g, whereas at 2.0% (w/w) DCP level the result was a merely higher 96.01 J/g. Interestingly, the highest value for the enthalpy of fusion of PP showed up when it was treated with 1.0% (w/w) DCP amongst the other DCP-incorporated individual PP sets. Since these values were fluctuating about more or less the same magnitudes, the responses of PP were thought to stem from the experimental measurements.

Increasing the weight percentage of HDPE in the pristine HDPE-PP blends resulted in sharp decreases in the enthalpy of fusion values of PP. As in the case of HDPE which was mentioned before, the enthalpy of fusion of the pristine blends measured during calorimetric analysis followed a similar, proportional way with the weight percentage of PP in the blends.

The effect of changing the weight percentage of DCP on the enthalpies of fusion of PP component in the sets was found to be minor when compared to the effect of changing the blend composition with respect to weights of individual components.

The sets, 30HDPE70PP, 50HDPE50PP, and 70HDPE30PP, showed little deviations in the values of enthalpy of fusion of PP, amongst which the greatest change was only about a positive 9 J/g while crossing from 0.5% (w/w) to 1.0% (w/w) DCP in the 30HDPE70PP set.

3.2.3 Variation of the Percent Crystallinities of Prepared Sets

After having obtained the heats of fusion of the polymers making up the blends, the most important feature that was determined through calorimetric analysis of the test specimens was the percent crystallinity of the components. Since crystallinity affected both resulting mechanical and thermal performance of the blends, it was of utmost importance to the experimenter during the study. Therefore, the following sections of this dissertation present the crystallinities of the components with respect to their previously measured enthalpies of fusion.

3.2.3.1 Variation of the Percent Crystallinity of HDPE

The calculated results for the percent crystallinities of HDPE component in the blends obtained via employing Equation 1 are given in Table 3.9, as follows;

Table 3.9: Percent Crystallinities of HDPE in Prepared Sets

Set Code	X (%) (Pristine)	X (%) (0.5% (w/w) DCP)	X (%) (1.0% (w/w) DCP)	X (%) (2.0% (w/w) DCP)
HDPE	85.8	74.1	76.1	67.3
70HDPE30PP	50.6	45.4	33.8	44.0
50HDPE50PP	38.7	27.3	31.2	26.4
30HDPE70PP	20.4	15.2	15.9	15.1

The tabulated results of Table 3.9 are plotted in Figure 3.9 as follows;

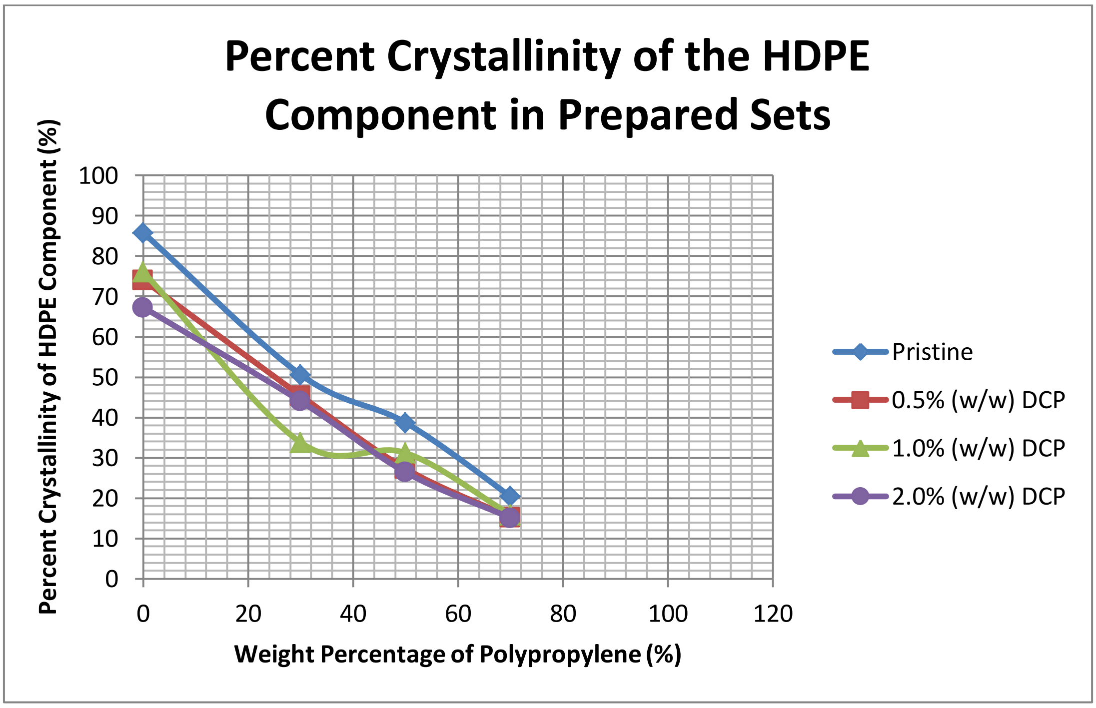


Figure 3.9: Crystallinity of HDPE Component versus PP Concentration

The change in the crystallinity percentage of HDPE in its individual state yielded decreases with increasing weight percentage of DCP, as it can also be observed from the decrease in its enthalpy of fusion values given in Table 3.7. After processing the pristine HDPE pellets in hot press, their crystallinity levels were calculated to be about 86%, which stemmed from the linear molecular structure of the polymer giving it the ability to crystallize even after it was quench-cooled. At a DCP level of 0.5% (w/w), the crystallinity of individual HDPE decreased, as expected, to about 74% in the bulk. This lowered level of crystallinity, i.e. the increased number of amorphous and crosslinked networks developed in the bulk was found to aid in the polymers elongation ability. This phenomenon was attributed to the incorporation of the non-crosslinked HDPE chains into the crosslinked networks, so that there were lesser numbers of amorphous barriers in front of the crystal lattices, thus the polymer could take and transfer stress, and flow more easily and yielded higher degrees of percentage strain. When the 2.0% (w/w) DCP mark was reached, the enthalpy of fusion of HDPE took its lowest value as seen in Table 3.7, so its crystallinity decreased to about 67%. This sharp decrease in the crystallinity of HDPE compared to its pristine state, along with over-formation of crosslinked networks in the bulk, resulted in the polymer to lose its ability of elongation.

When the results given in Table 3.9 and Figure 3.9 are analyzed, it is seen that the crystallinity percentage of the HDPE component yielded a sharp decrease in magnitude as its weight percentage in the blend decreased. In other words, as the weight percentage of PP in the blend increased the percent crystallinity of the other component responded inversely proportionally against that increase. This was an expected situation due to the fact that increasing number of PP chains resulted in an inefficiency of the HDPE chains to meet each other so that they could not build up crystals. This was due to the phase separation of the two components in their solid phases, although no phase separation was observable to the naked eye.

Addition of even a small 0.5% (w/w) DCP into the blends yielded a negative change of at least about 5% in the percent crystallinity of the HDPE component. This was due to the formation of HDPE crosslinks across the polymer matrix which eventually decreased the crystallinity of the HDPE component in the blend. However, a major inference can be made by analyzing the results in Table 3.9 that increasing the weight percentage of DCP over 0.5% (w/w) did not drastically alter the resulting crystallinity value of the HDPE component in the blend.

3.2.3.2 Variation of the Percent Crystallinity of PP

Upon performing the same calculations using the measured enthalpies of fusion of PP given in Table 3.8, the numerical results for its percent crystallinities in the blends obtained via Equation 1 are given in Table 3.10, as follows;

Table 3.10: Percent Crystallinities of PP in Prepared Sets

Set Code	X (%) (Pristine)	X (%) (0.5% (w/w) DCP)	X (%) (1.0% (w/w) DCP)	X (%) (2.0% (w/w) DCP)
PP	50.5	41.3	48.6	45.9
30HDPE70PP	23.6	18.4	22.7	22.7
50HDPE50PP	17.1	14.1	16.0	13.7
70HDPE30PP	8.1	8.7	6.7	7.9

The results given in Table 3.10 are plotted in Figure 3.10 as follows;

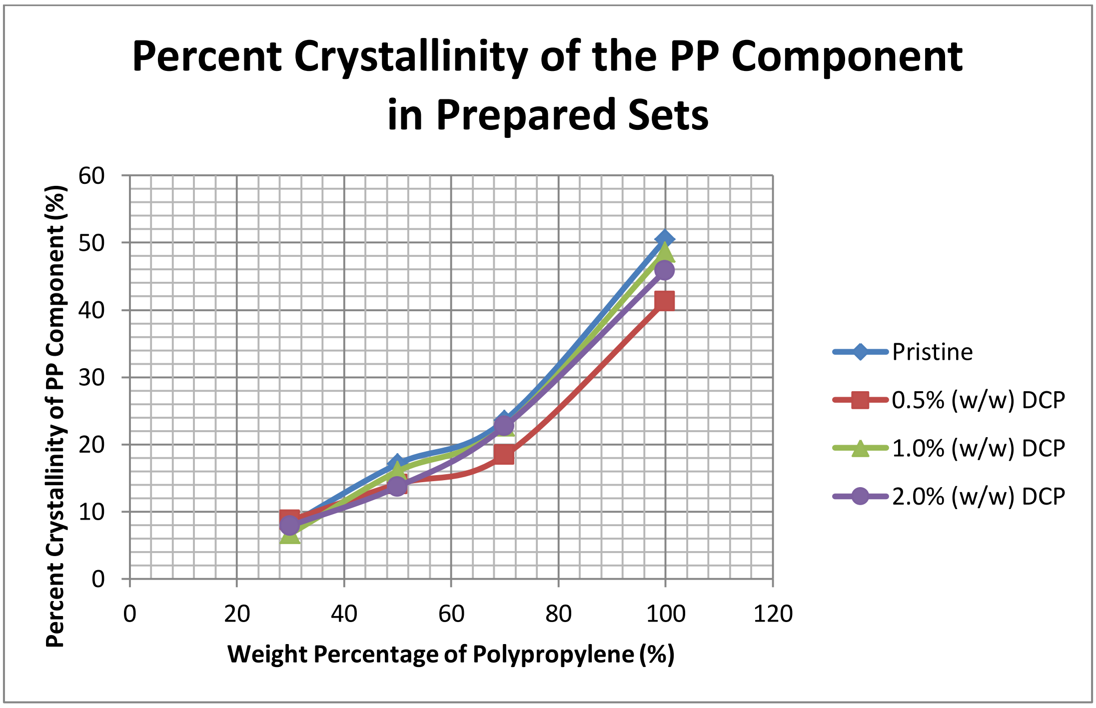


Figure 3.10: Crystallinity of PP Component versus PP Concentration

In its pristine state, individual PP yielded a crystallinity percentage of only about 51%. At DCP levels ranging from 0.5% (w/w) to 2.0% (w/w), PP crystallinity fluctuated about more or less the same value, which can also be observed from the enthalpies of fusion given in Table 3.8. That was attributed to the ability of the PP chains in the crystals to preserve their geometry, while their non-crystalline counterparts suffered excessive degradation via chain-scission, finally resulting in complete deformation of the films processed at 2.0% (w/w) DCP level.

As it was the same case for HDPE, the crystallinity of individual PP decreased whenever its concentration in the blend was lowered. In the set 70HDPE30PP, the crystallinity of the PP component stayed at a bare 8%, which also explained the increased ability of the blend in terms of its elasticity with increasing amount of DCP as it can be observed in Table 3.3. Since the crystallinity of the PP component was too low, the blend’s elongation values resembled the ones of pure HDPE. It can be speculated that as the number of crystals of different lattice types in the blend decreased, i.e. PP crystallinity fluctuated between 6% and 8% while HDPE crystallinity was always about and beyond 40%, the degraded PP chains acted as plasticizers. Simultaneously as the non-crosslinked HDPE chains were incorporated into the crosslinked HDPE matrix, the blend eventually yielded higher degrees of elongation. Whenever the weight ratios of the PP component were greater than 1:1, the incompatibility of the polymers dominated and the final elongation stayed at very low values. This phenomenon was one of the most interesting findings listed in this work.

The response of the PP component in HDPE-PP blends did not contain major changes, either positive or negative, when going from 0.5% (w/w) DCP to 2.0% (w/w) DCP level. The crystallinity stayed somehow the same, resulting in an inference that degradation of PP took place in its non-crystalline parts. Thus, the crystallinity was preserved at roughly the same levels.

CHAPTER 4

CONCLUSIONS

The last chapter of this dissertation presents the inferences and conclusions drawn from the experimental study conducted. The conclusions expressed in this part are given with respect to the continuation of the thesis.

During the preparation of this work, the characteristic behaviors of pristine HDPE, pristine PP, pristine HDPE-PP blends in polymer weight ratios of 30%, 50%, 70% and their responses against DCP levels of 0.5% (w/w), 1.0% (w/w), and 2.0% (w/w) were analyzed. The complete research was based on universal tensile testing and differential scanning calorimetry analysis of the specimens. The processing and testing parameters were kept same for all the specimens for the reliability and reproducibility of the analysis.

The main parameters analyzed in mechanical testing of the specimens were their Young's moduli, tensile strengths, percentage elongation at break values, and yield stresses. Other secondary parameters of any kind were of no significance in the evaluation of the mechanical performance of the specimens exposed to mechanical testing. Thus, whenever there is additional need felt by the reader for that type of evaluation, it must be stated that further exclusive work can be conducted in terms of mechanical testing. The calorimetric analysis involved the evaluation of the main parameters of the blends such as their melting points and enthalpies of fusion. Onset and offset temperatures of melting aided only in the determination of the enthalpies of fusion of the specimens, conducted all via the calorimeter device. Making use of the measured enthalpies of fusion of the specimens, their percent crystallinities were reached.

Since the mechanical and thermal performance of the immiscible, i.e. incompatible, blends were known to be of poor properties, literature did not provide a thorough coverage of the properties of the sought blends. The literature and scientific studies that were presented in this area tended to be aged, and scientific interest in the enhancement of the mechanical properties of incompatible polyblends without using compatibilizers seemed to be of insignificant magnitudes. An investigation making use of larger weight percentages of HDPE and PP together with the usage of DCP as the organic peroxide to be used as chemical crosslinking agent was not come across during the literature review performed until the submission of this work. Thus, whatever presented scientifically in this work might stand as a result of a governing study in its area.

When it was tried to be crosslinked using DCP, PP of isotactic stereochemistry started degrading during processing. At a weight percentage of 2.0%, DCP caused excessive degradation of PP, which eventually resulted in complete deformation of the prepared films.

The Young's modulus of PP was increased by 28.5% at the expense of a negative change of 4.18% in its tensile strength at the 1.0% (w/w) DCP mark. Since a very rigid type of PP was employed in this study, its percentage elongation stayed under 10% for any DCP weight percentage.

The Young's moduli of 30HDPE70PP and 50HDPE50PP sets were increased by a staggering 28.4% and a mere 2.45% whenever their DCP concentrations were held at 0.5% (w/w). These positive increments were obtained at the expense of small losses in their tensile strength values. Whenever stiffer blends of approximate weight ratios on which smaller dynamic loads would be exerted are needed to be used, these blends would stand as a substitute on the grounds that they are chemically crosslinked with DCP.

The ultimate tensile strength values of each blend experienced decreases with increasing weight percentage of DCP. However, it was found that the tensile strength of the 30HDPE70PP set at the 2.0% (w/w) DCP level was increased when compared to its pristine value. This increase was attributed to the ability of the degraded PP chains to act as plasticizers by filling the free volume created between the phase boundary of HDPE and PP, so that the stress exerted on the specimen in dynamic loading could be better transferred in a more continuous medium.

The percentage elongation at break values of HDPE at the 0.5% (w/w) DCP level was increased by about 28% compared to the value it showed at its pristine state, although the contrary situation in which a decrease in the elongation was expected. This phenomenon did not take place at 2.0% (w/w) DCP level where the over-crosslinking of the material resulted in breakages that took place earlier when compared to the ones taking place in the pristine state of the material.

The elongation ability of the 70HDPE30PP set at each of its increasing DCP weight percentage marks was increased. The set experienced a nearly 90% increase in its probable strain at break value at the 2.0% (w/w) DCP level. In that set the weight percentage of PP was 30%, the smallest of three blended sets, which eventually decreased the ability of PP chains to form crystalline lamellae. Addition of increasing amounts of DCP into the blend and high temperature processing resulted in excessive degradation of PP chains by chain-scission which in turn yielded shorter and higher numbers of PP chains. These shortened PP chains acted as plasticizing particles across the polymer matrix. Additionally, at 2.0% (w/w) DCP level, it was inevitable that a majority of the HDPE chains were crosslinked, which might have incorporated some of the degraded PP chains and non-crosslinked HDPE chains into themselves. Intercalarily, even at a high DCP concentration as 2.0% (w/w), HDPE was able to have a crystallinity of 44%. Thus, it can be speculated that a combination of all the probable states listed above might have yielded a case in which the specimen could successfully take and transfer the stress exerted on itself, eventually giving higher percentage elongation at break values. So, whenever a HDPE-PP blend of similar concentrations is to be worked with, it is proposed to use DCP as the crosslinking agent to enhance the elongation ability of the material by compromising some of its Young’s modulus and tensile strength.

The effect of incorporation of DCP into HDPE was found to decrease the melting point of the polymer. When crosslinked with 2.0% (w/w) DCP the melting point of HDPE decreased by about $10^{o}C$ when compared to its pristine melting point. At 0.5% (w/w) and 1.0% (w/w) DCP marks the decrease in the melting point was only about 2°C and 3°C for HDPE. This decreasing trend in the melting point of HDPE was attributed to the formation of crosslinked sites which decreased the amount of crystalline zones in the polymer bulk.

The response of the melting point of PP against the incorporation of DCP was similar to that of HDPE. Addition of only 0.5% (w/w) DCP was enough to decrease the polymer's melting point by about 5°C. This decrease can be said to have leveled off while crossing 1.0% (w/w) and 2.0% (w/w) DCP marks for PP. The decrease in the melting point of PP was attributed to the degradation via chain-scission in the polymer bulk.

In the pristine blends, the melting points of constituting HDPE and PP were determined to be lower than the values belonging to their pristine and individual values. That is, the components melted at lower temperatures whenever their weight fractions in the blends were decreased. PP was found to perform better in that sense by yielding smaller negative changes in terms of its melting point.

In the blends incorporated with DCP, the melting points of constituting HDPE and PP generally decreased with increasing weight percentages of DCP. However, the effect of the weight fraction of the polymers on the melting points of the two components was determined to be more dominant when compared with the effect of the DCP concentration in the blend.

The enthalpies of fusion of constituting HDPE and PP were found to get affected heavily by the concentration, i.e. weight fraction of each constituting polymer in the blend. Whenever one component's weight fraction decreased in the blends, so did its enthalpy of fusion. The effect of weight percentage of DCP on the resulting enthalpy of fusion values of the constituting polymers was insignificant when compared with the effect of the polymer concentration in the blend.

The crystallinities of the constituting polymers in the blends get affected majorly by the polymer composition of the films. Just as in the case of enthalpy of fusion, the crystallinity of a constituent decreased as its degree of dispersion in the blend was lowered. The effect of addition of higher weight percentages of DCP into the blends did not have an effect on the resulting crystallinity as powerful as the polymer concentration had in the first place.

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APPENDIX A

MECHANICAL TESTING DATA

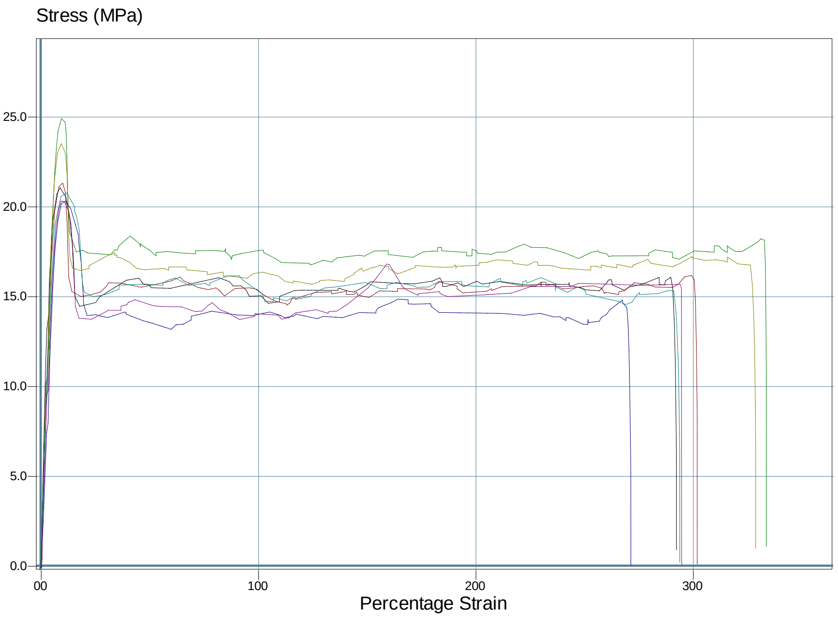


Figure A. 1: Stress-Strain Graph of HDPE

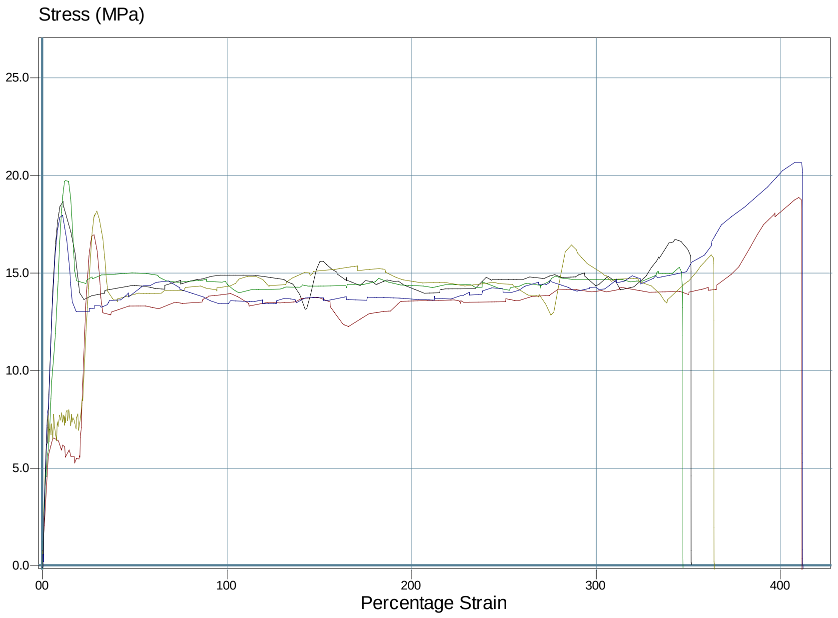


Figure A. 2: Stress-Strain Graph of HDPE 0.5% (w/w) DCP

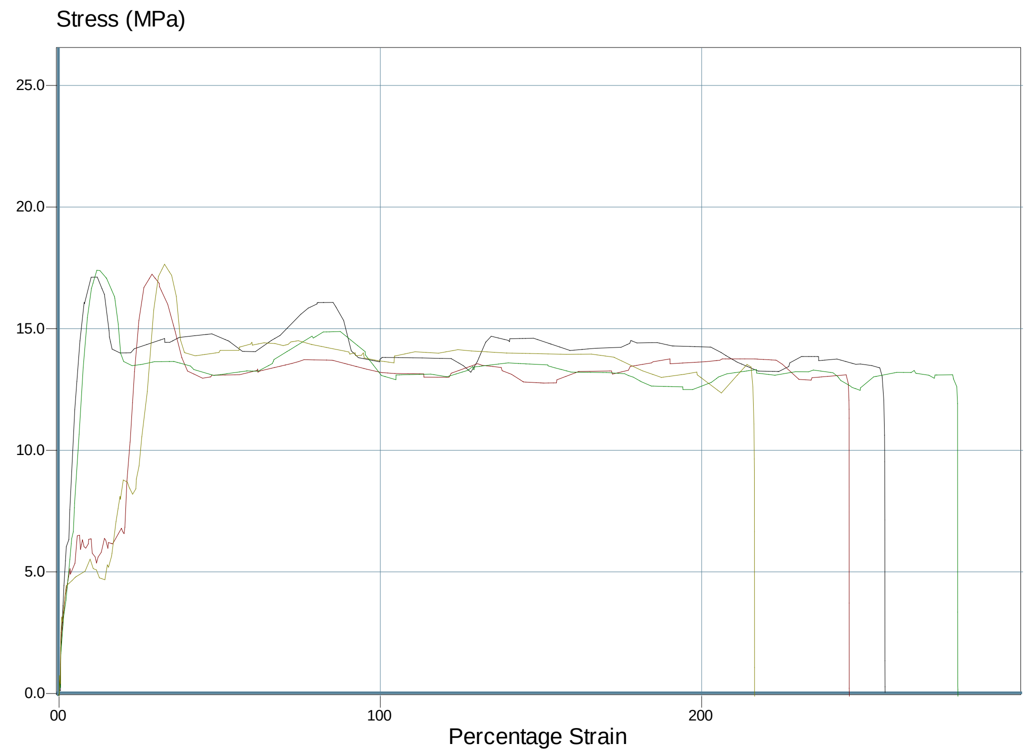


Figure A. 3: Stress-Strain Graph of HDPE 1.0% (w/w) DCP

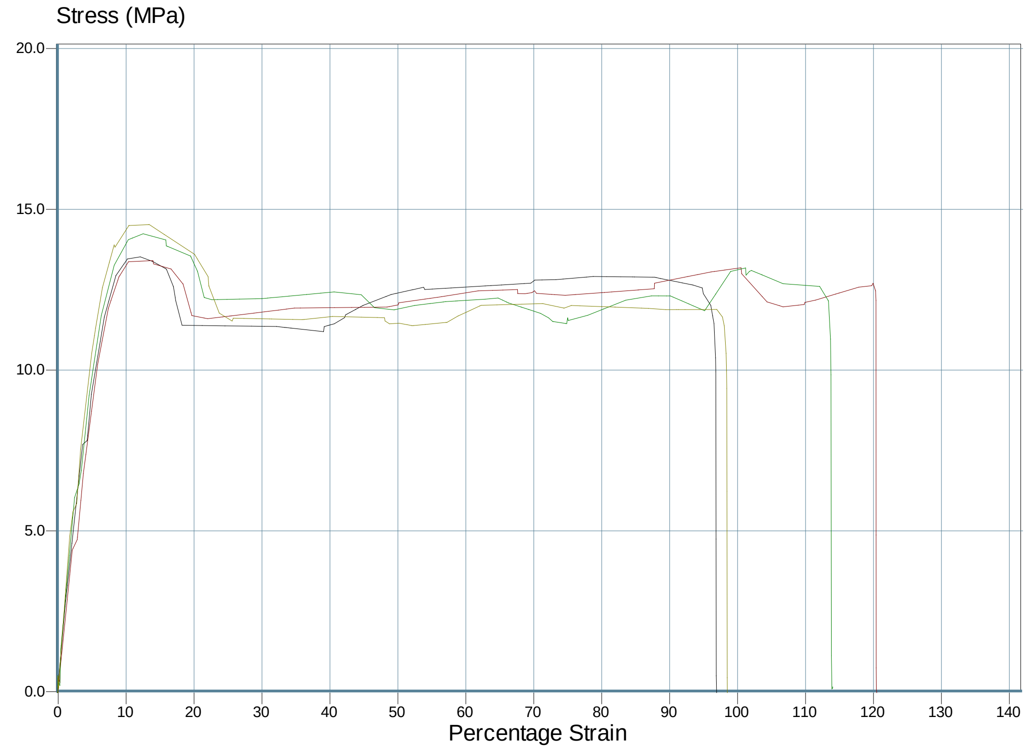


Figure A. 4: Stress-Strain Graph of HDPE 2.0% (w/w) DCP

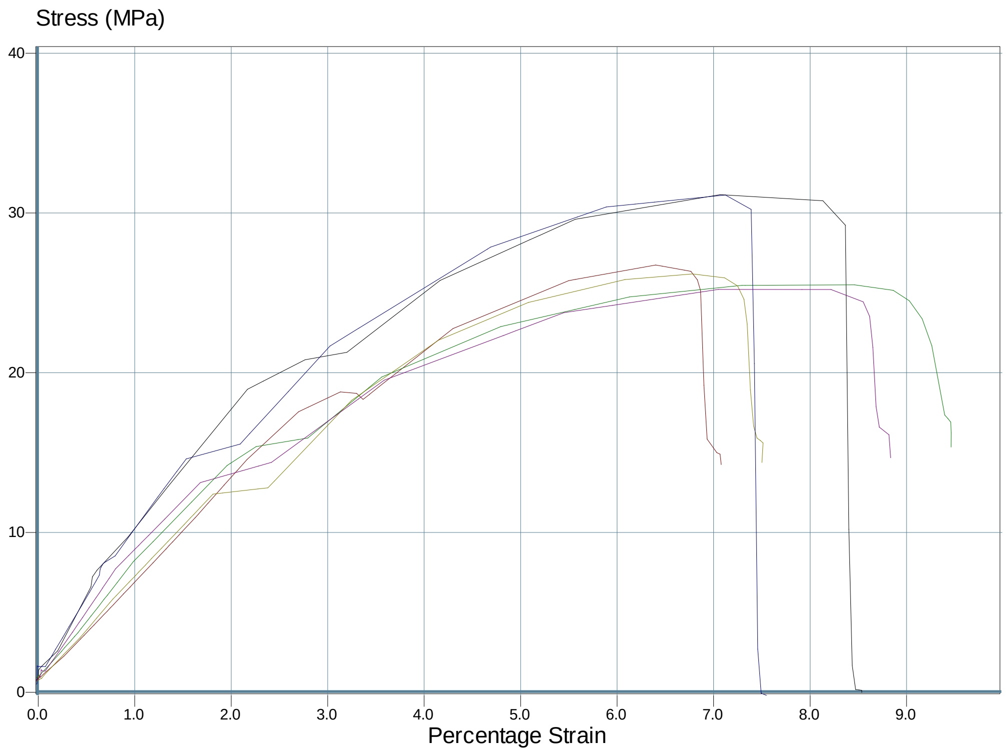


Figure A. 5: Stress-Strain Graph of Pristine PP

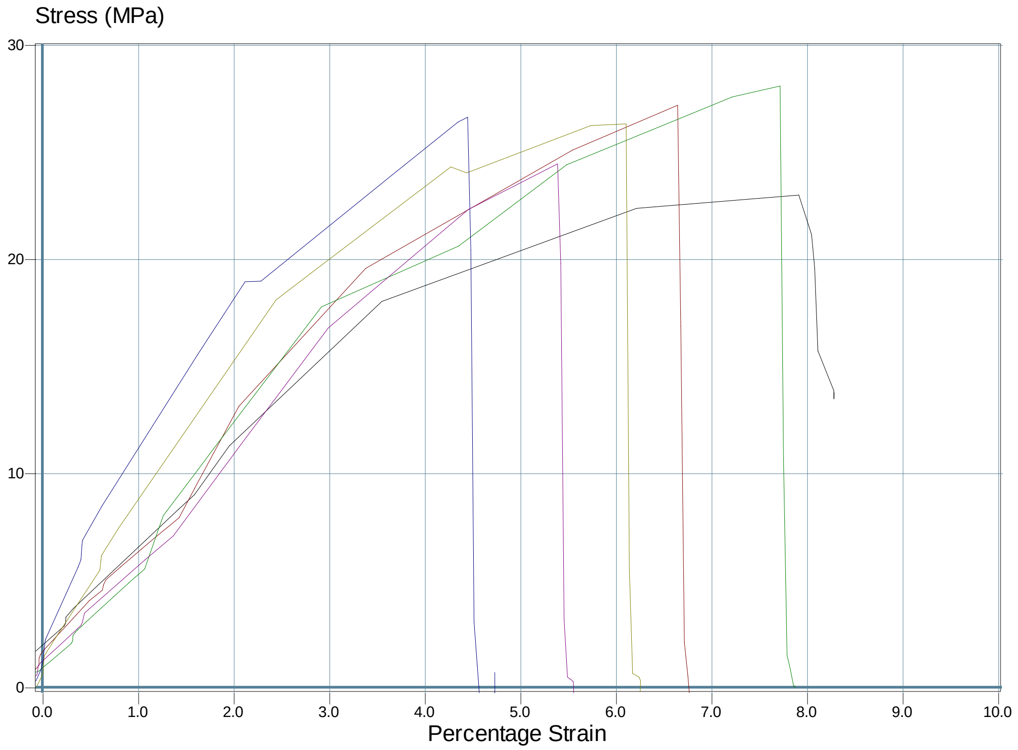


Figure A. 6: Stress-Strain Graph of PP 0.5% (w/w) DCP

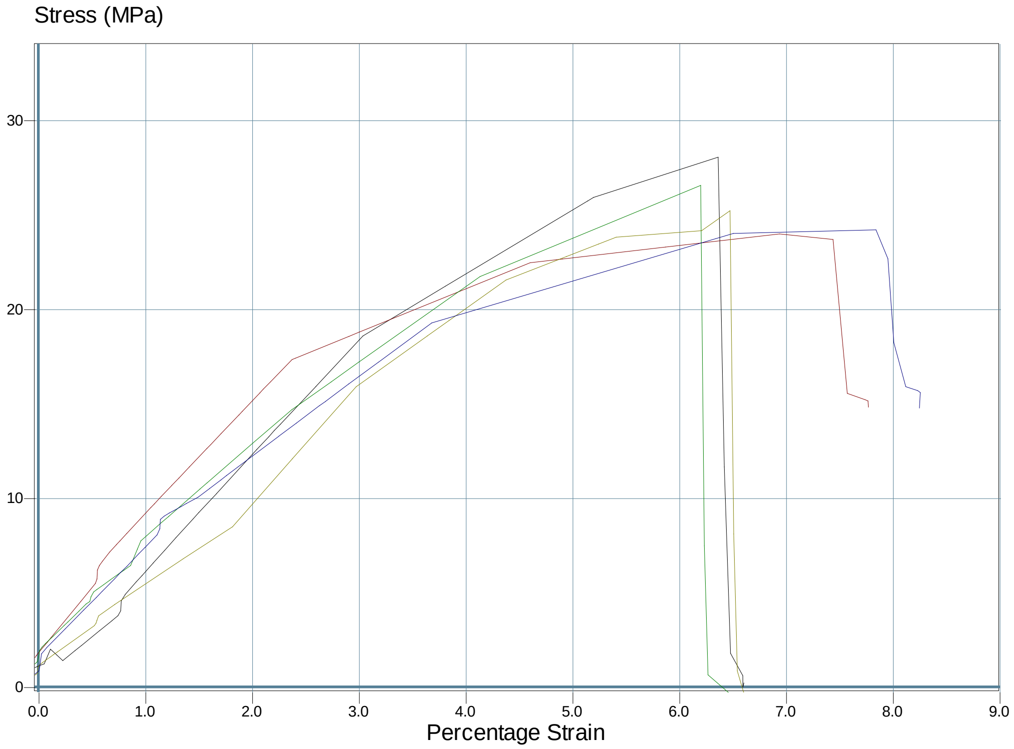


Figure A. 7: Stress-Strain Graph of PP 1.0% (w/w) DCP

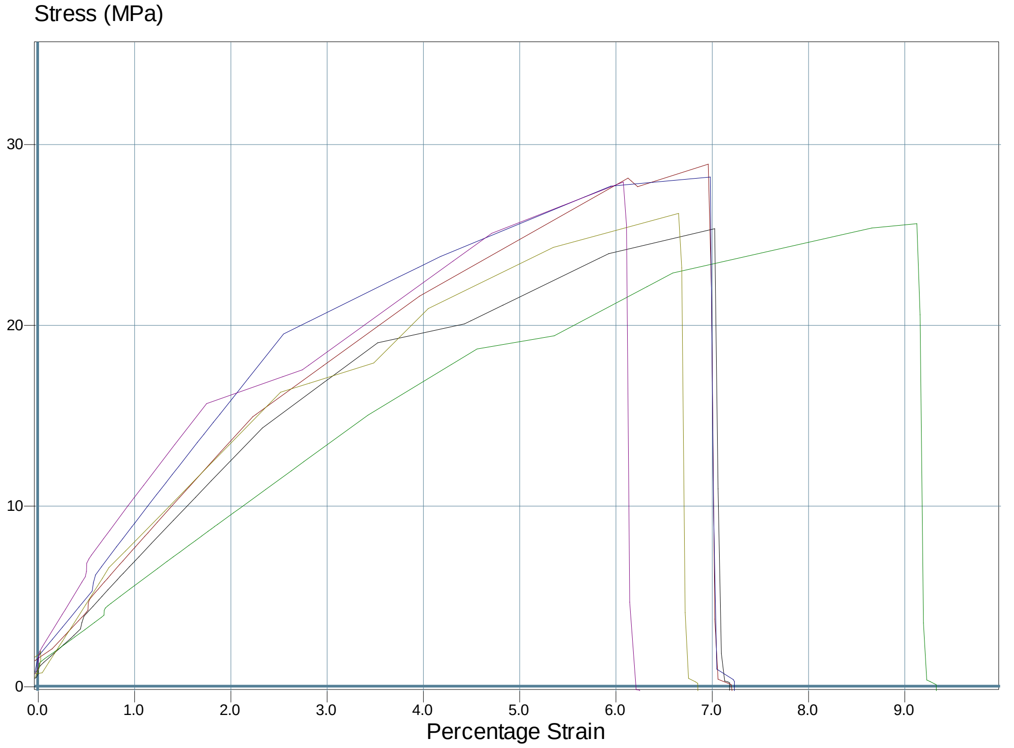


Figure A. 8: Stress-Strain Graph of Pristine 30HDPE70PP

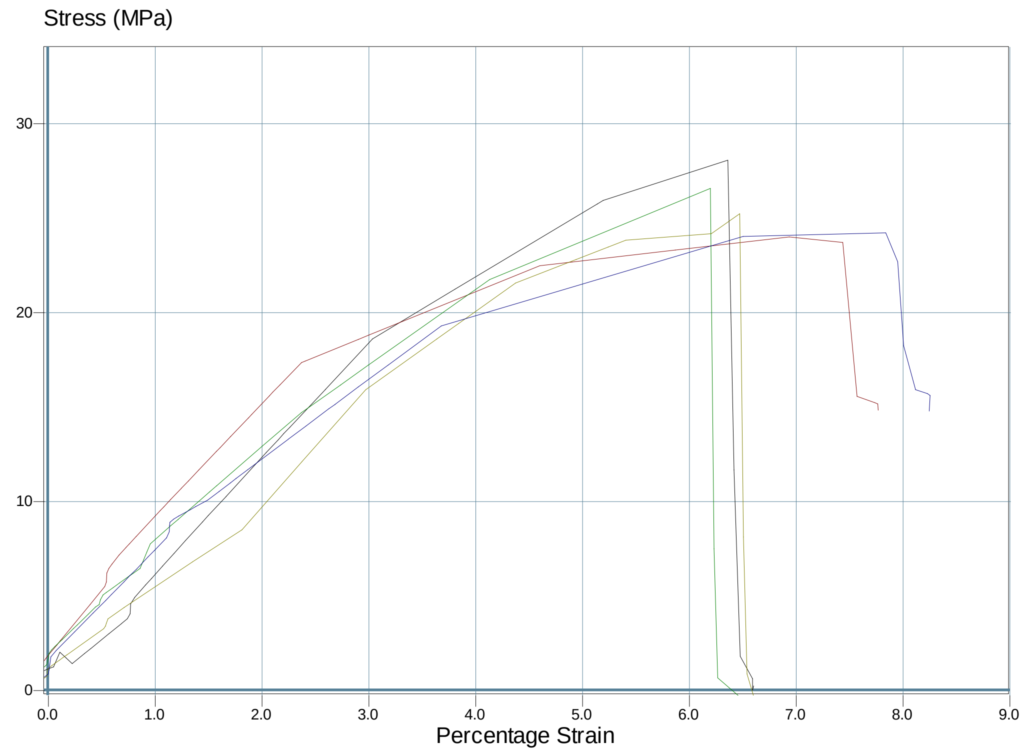


Figure A. 9: Stress-Strain Graph of 30HDPE70PP 0.5% (w/w) DCP

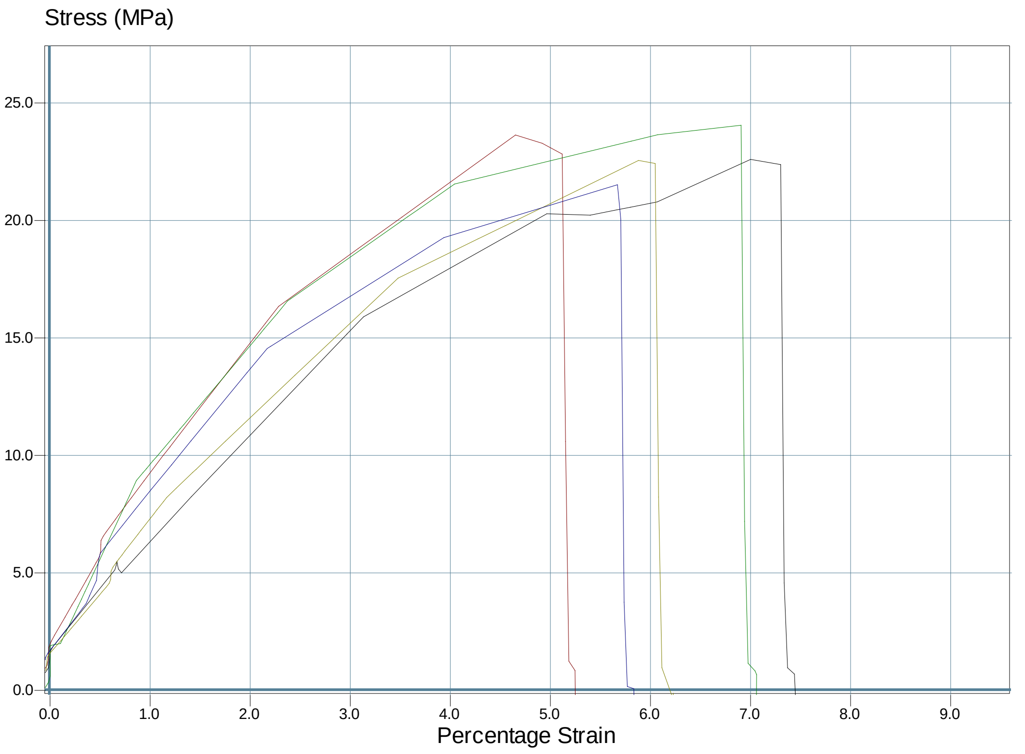


Figure A. 10: Stress-Strain Graph of 30HDPE70PP 1.0% (w/w) DCP

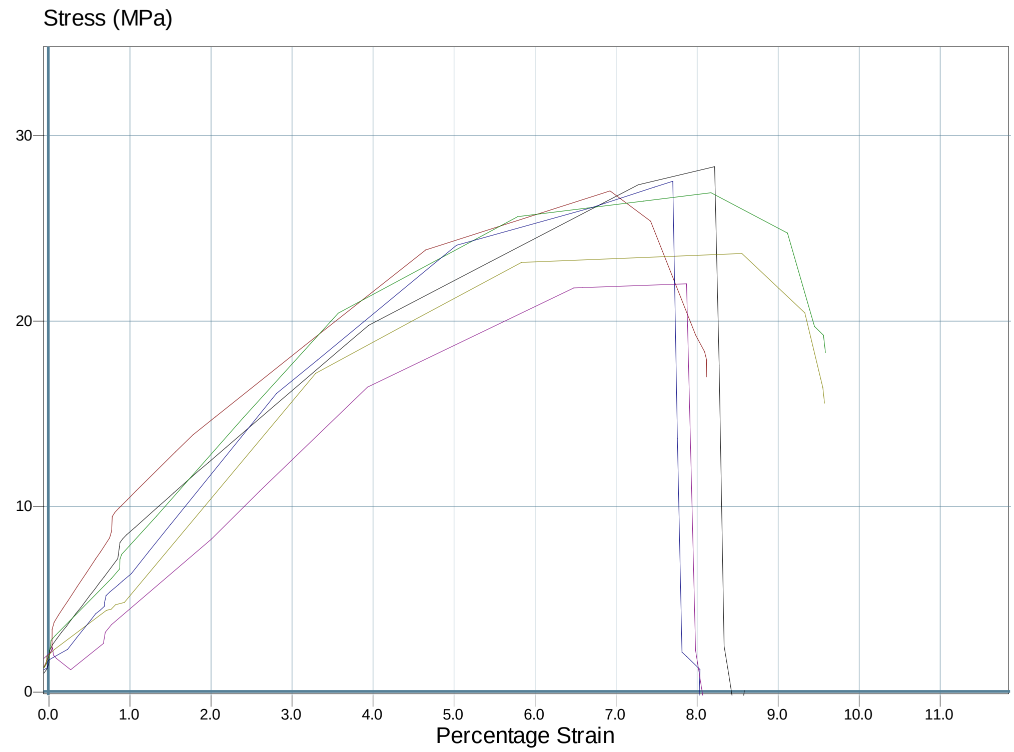


Figure A. 11: Stress-Strain Graph of 30HDPE70PP 2.0% (w/w) DCP

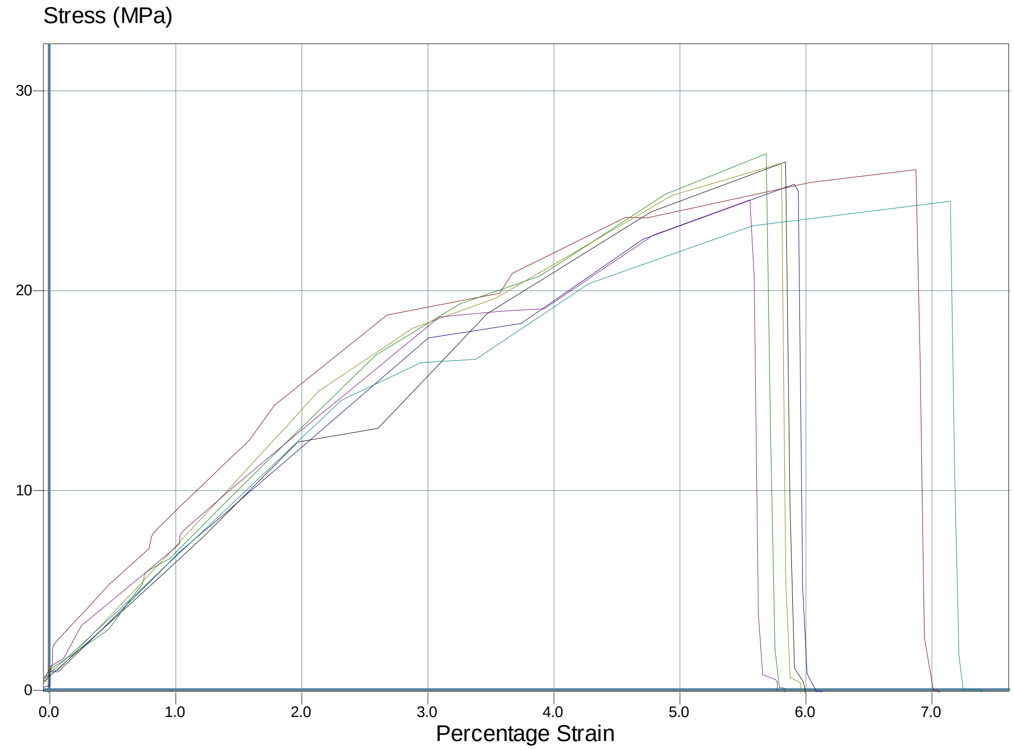


Figure A. 12: Stress-Strain Graph of Pristine 50HDPE50PP

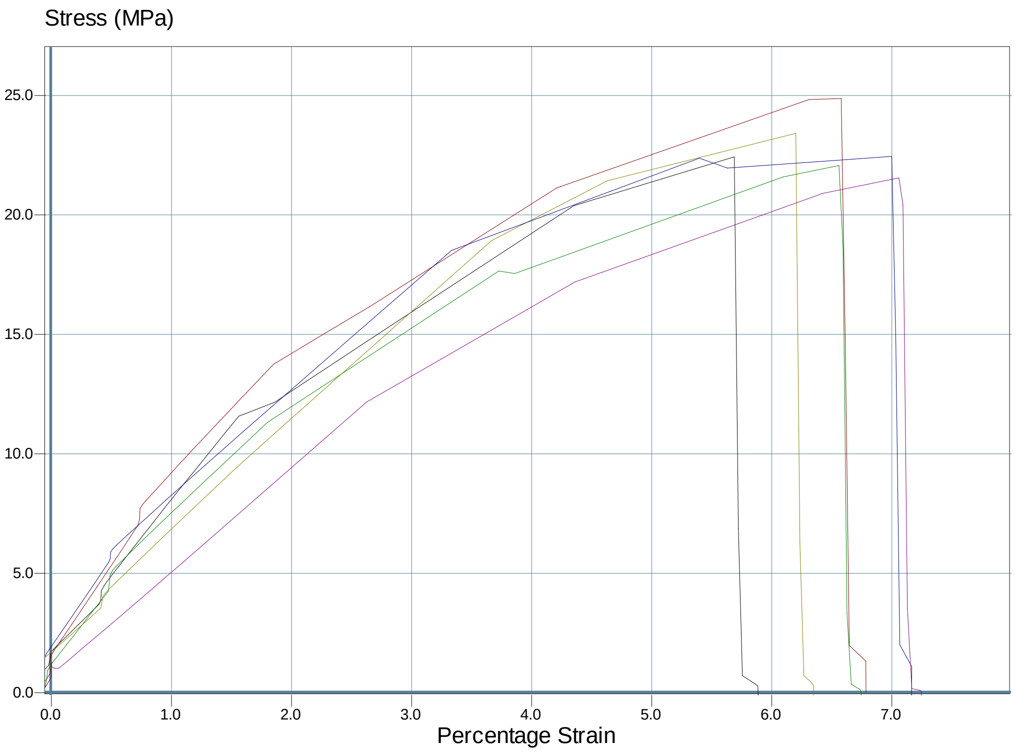


Figure A. 13: Stress-Strain Graph of 50HDPE50PP 0.5% (w/w) DCP

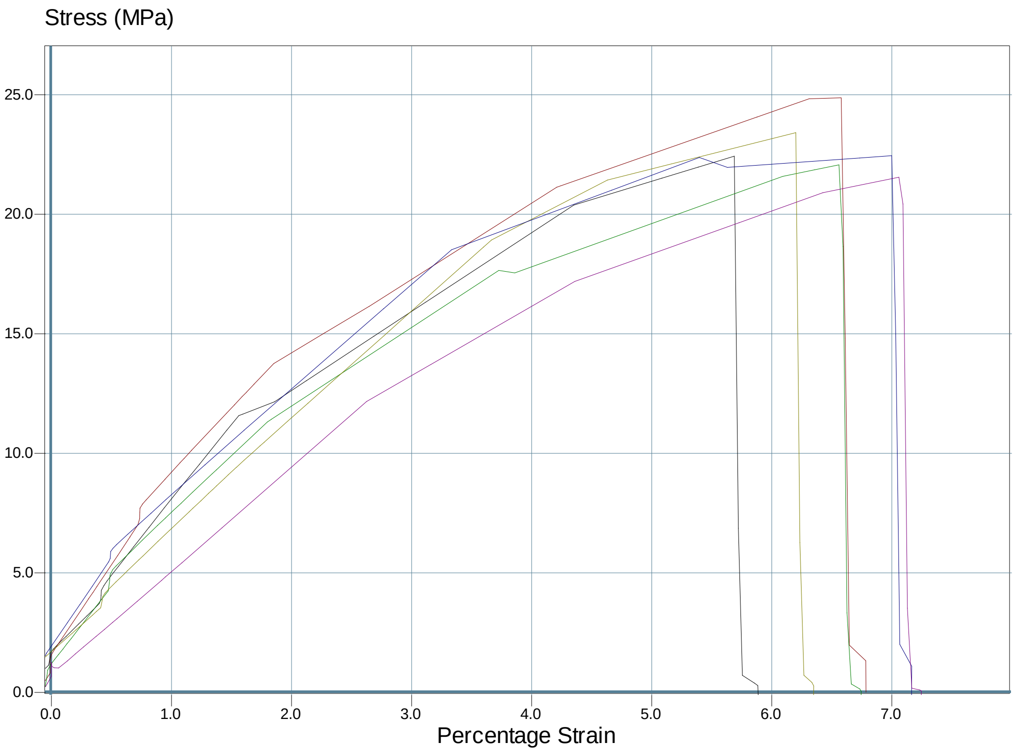


Figure A. 14: Stress-Strain Graph of 50HDPE50PP 1.0% (w/w) DCP

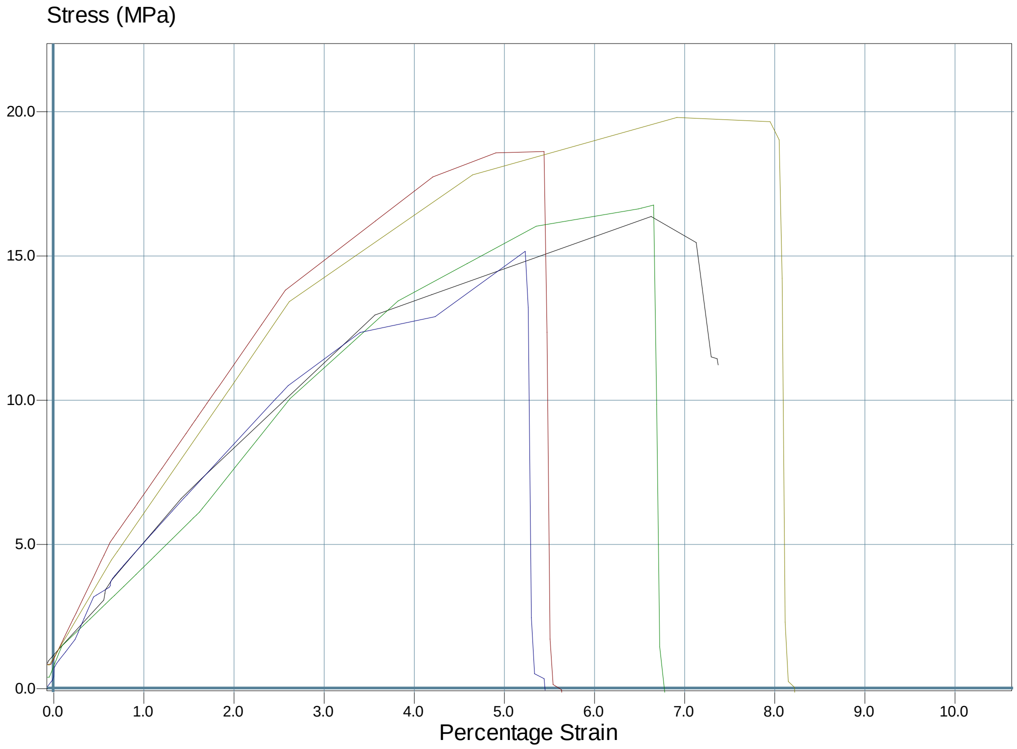


Figure A. 15: Stress-Strain Graph of 50HDPE50PP 2.0% (w/w) DCP

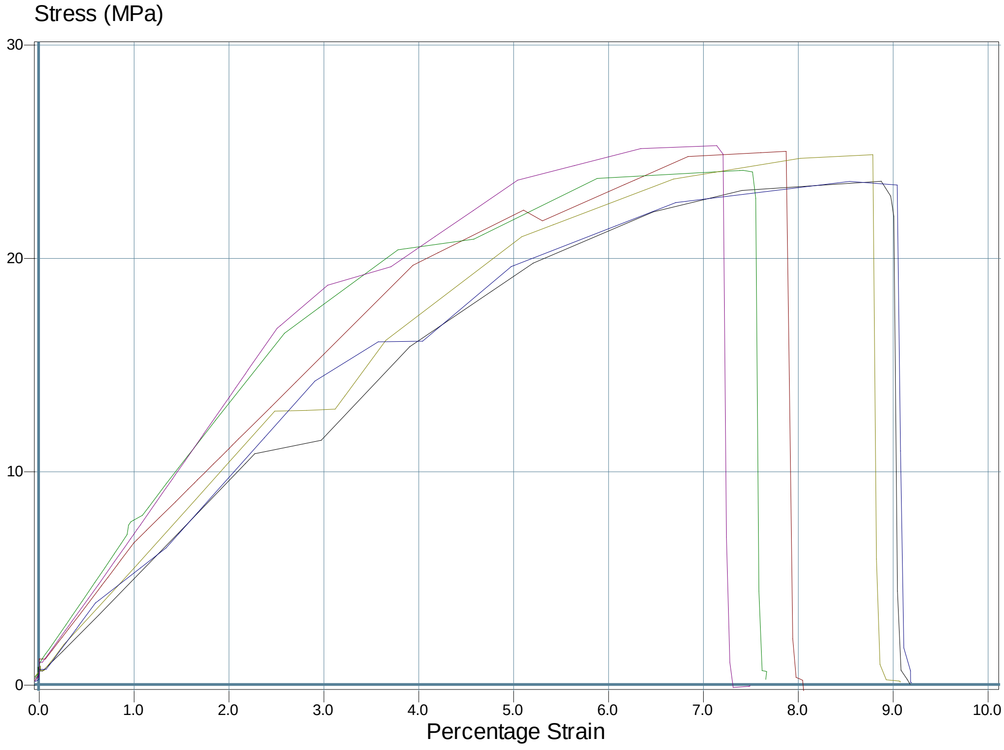


Figure A. 16: Stress-Strain Graph of Pristine 70HDPE30PP

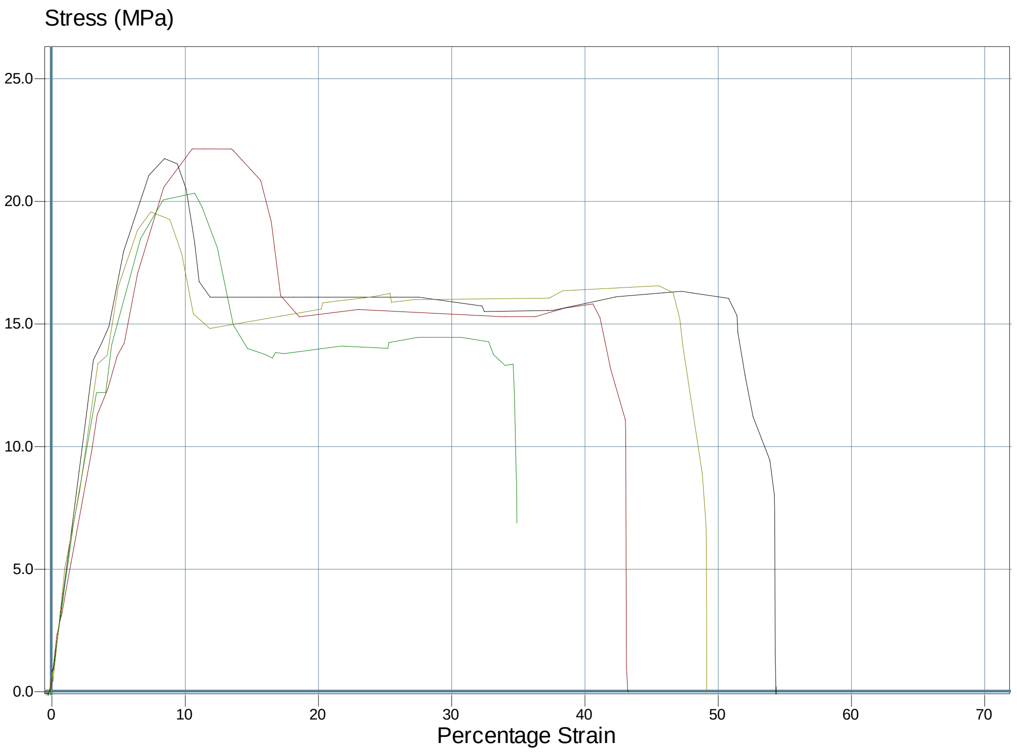


Figure A. 17: Stress-Strain Graph of 70HDPE30PP 0.5% (w/w) DCP

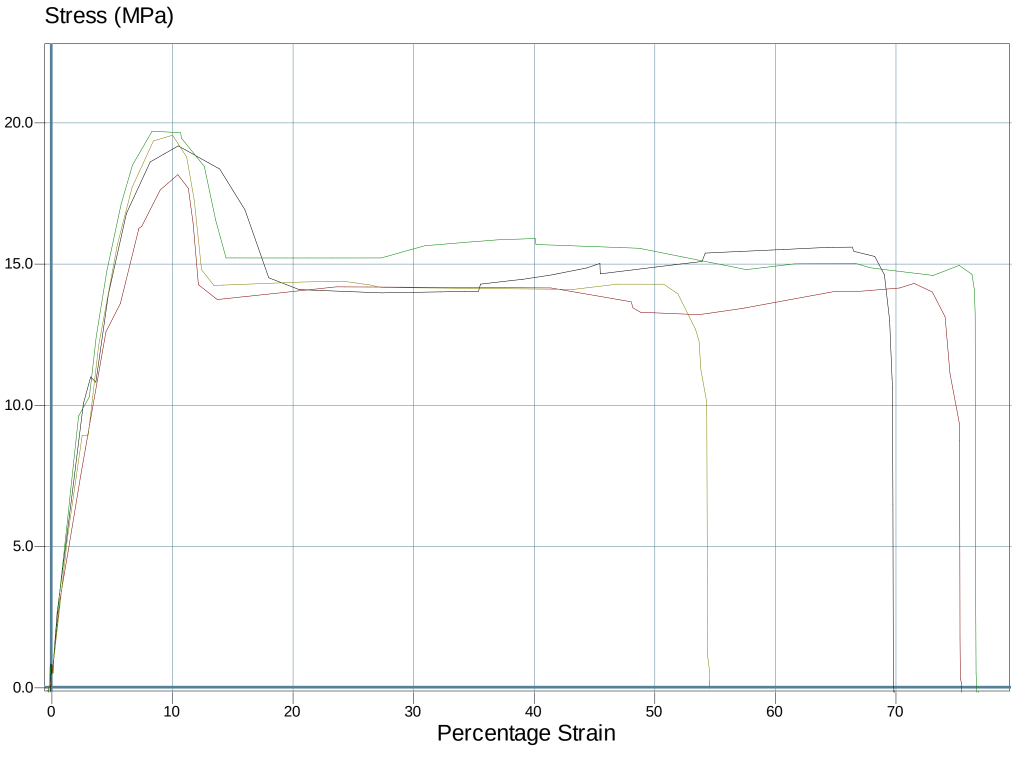


Figure A. 18: Stress-Strain Graph of 70HDPE30PP 1.0% (w/w) DCP

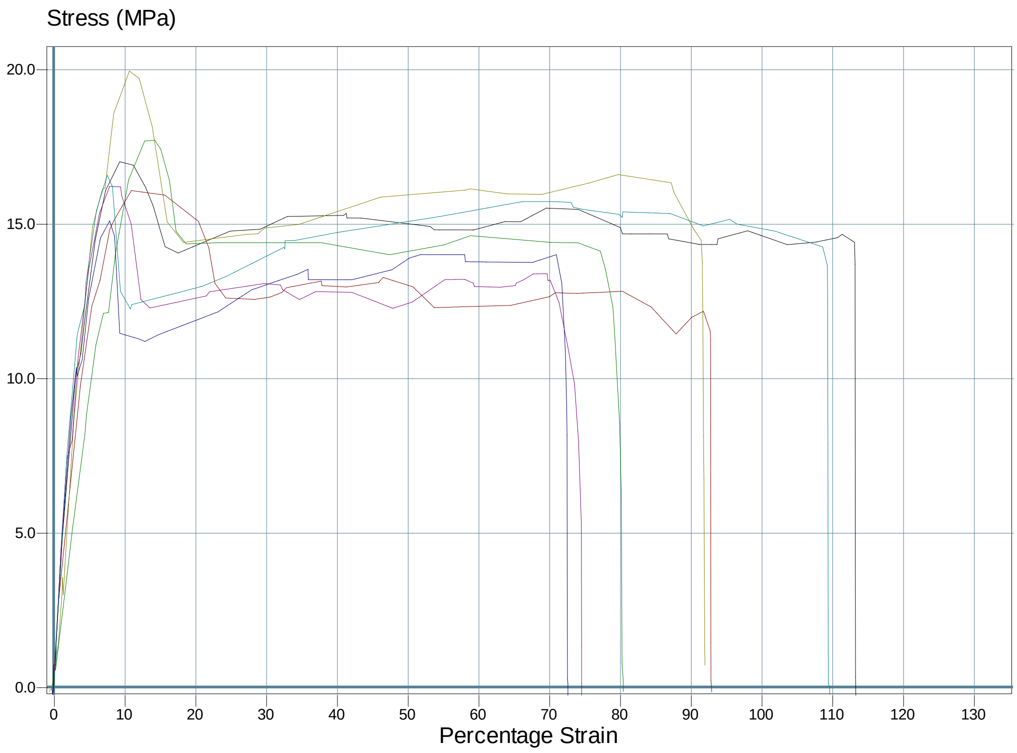
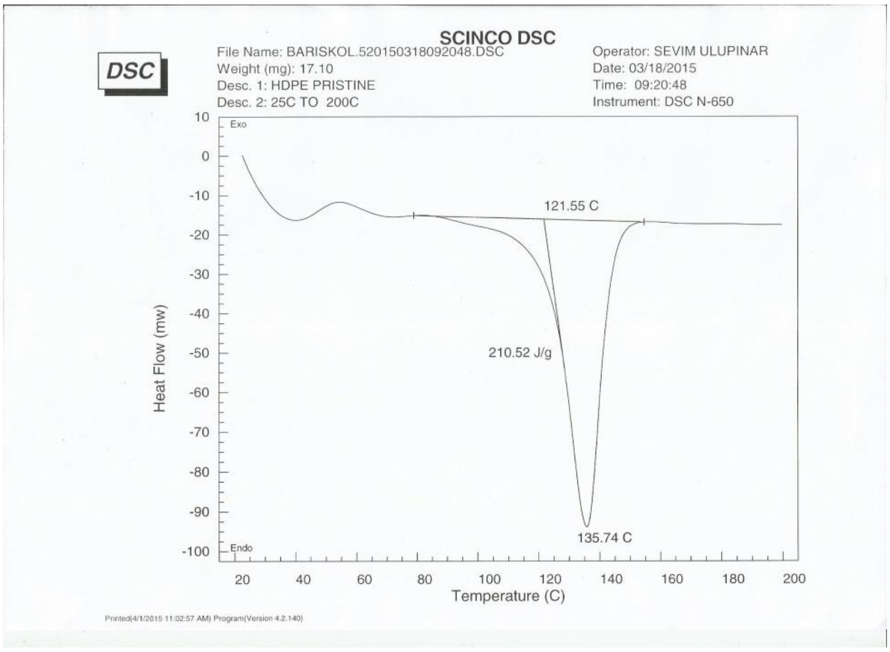


Figure A. 19: Stress-Strain Graph of 70HDPE30PP 2.0% (w/w) DCP

APPENDIX B

CALORIMETRIC ANALYSIS DATA



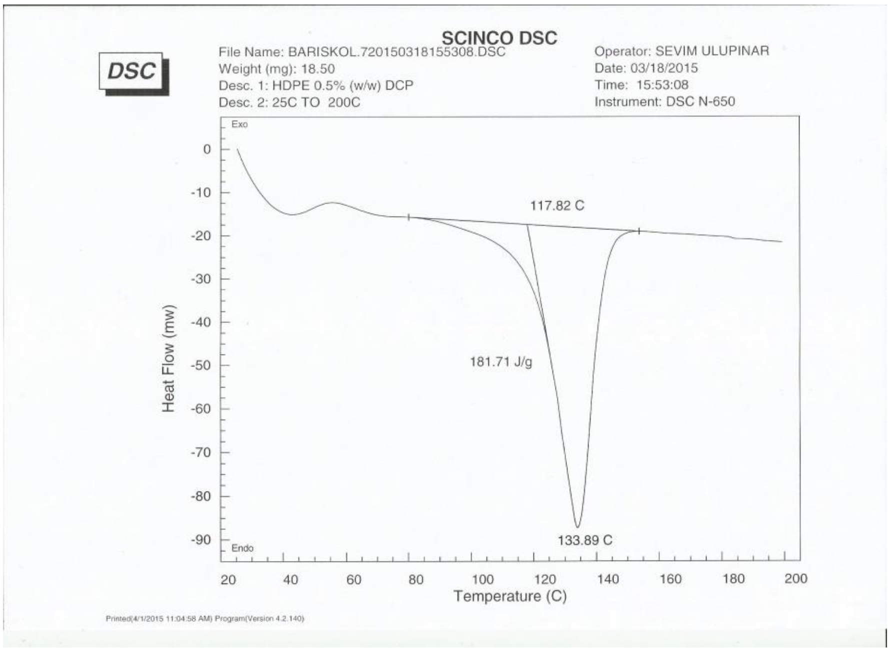
SCINCO DSC

File Name: BARISKOL.520150318092048.DSC
Weight (mg): 17.10
Desc. 1: HDPE PRISTINE
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/18/2015
Time: 09:20:48
Instrument: DSC N-650

Printed(4/1/2015 11:02:57 AM) Program(Version 4.2.140)

Figure B. 1: Thermogram of Pristine HDPE



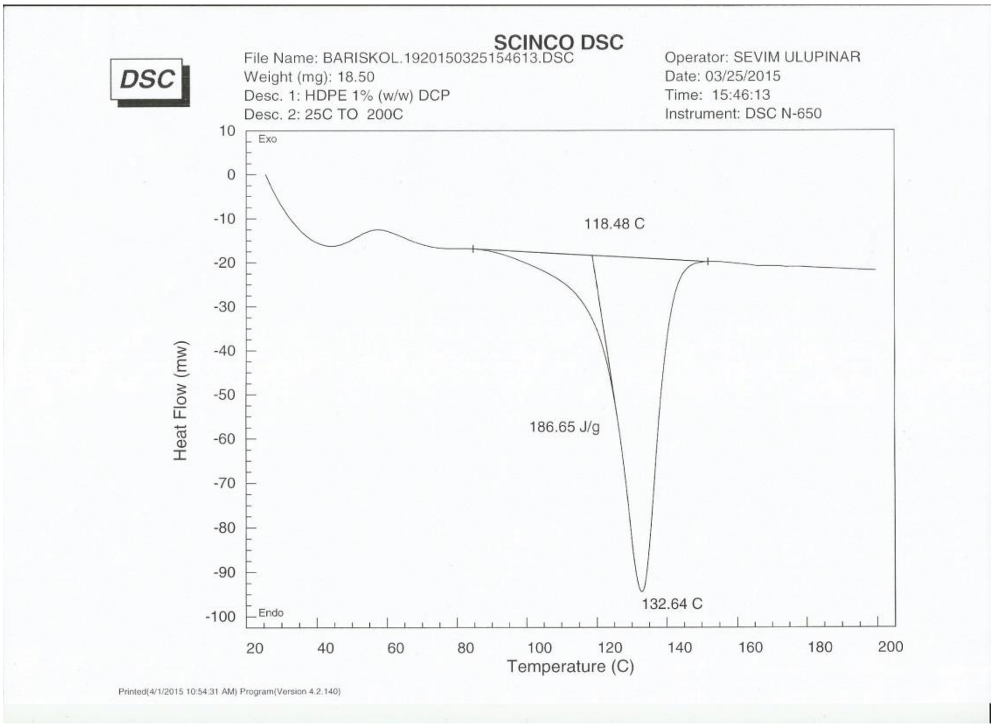
SCINCO DSC

File Name: BARISKOL.720150318155308.DSC
Weight (mg): 18.50
Desc. 1: HDPE 0.5% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/18/2015
Time: 15:53:08
Instrument: DSC N-650

Printed(4/1/2015 11:04:58 AM) Program(Version 4.2.140)

Figure B. 2: Thermogram of HDPE 0.5% (w/w) DCP

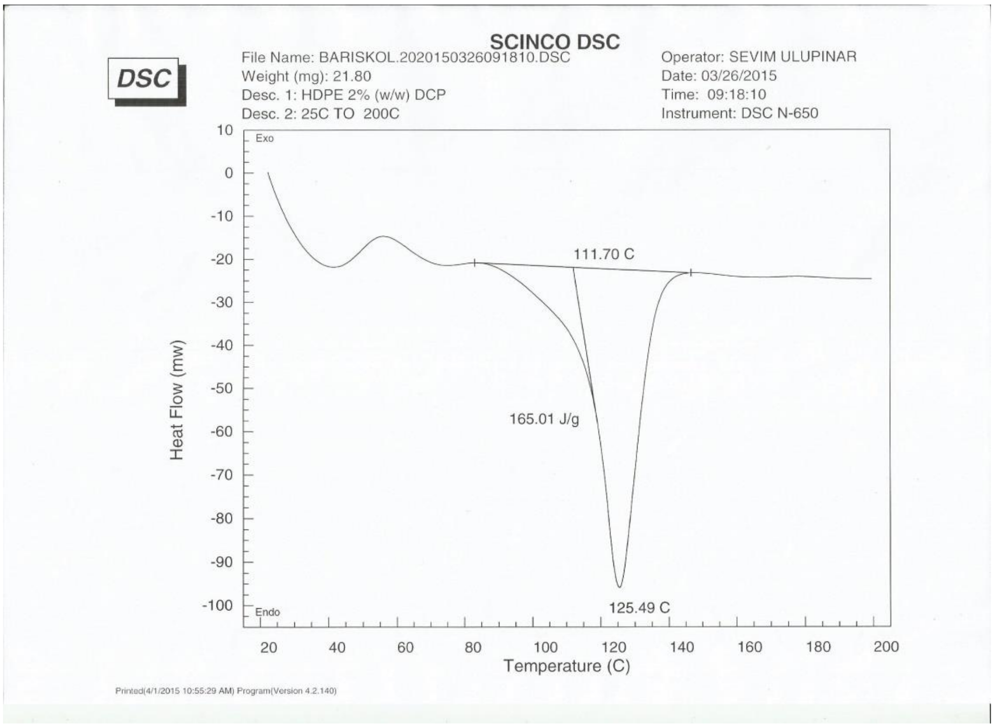

SCINCO DSC

File Name: BARISKOL.1920150325154613.DSC
Weight (mg): 18.50
Desc. 1: HDPE 1% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/25/2015
Time: 15:46:13
Instrument: DSC N-650

Printed(4/1/2015 10:54:31 AM) Program(Version 4.2.140)

Figure B. 3: Thermogram of HDPE 1.0% (w/w) DCP

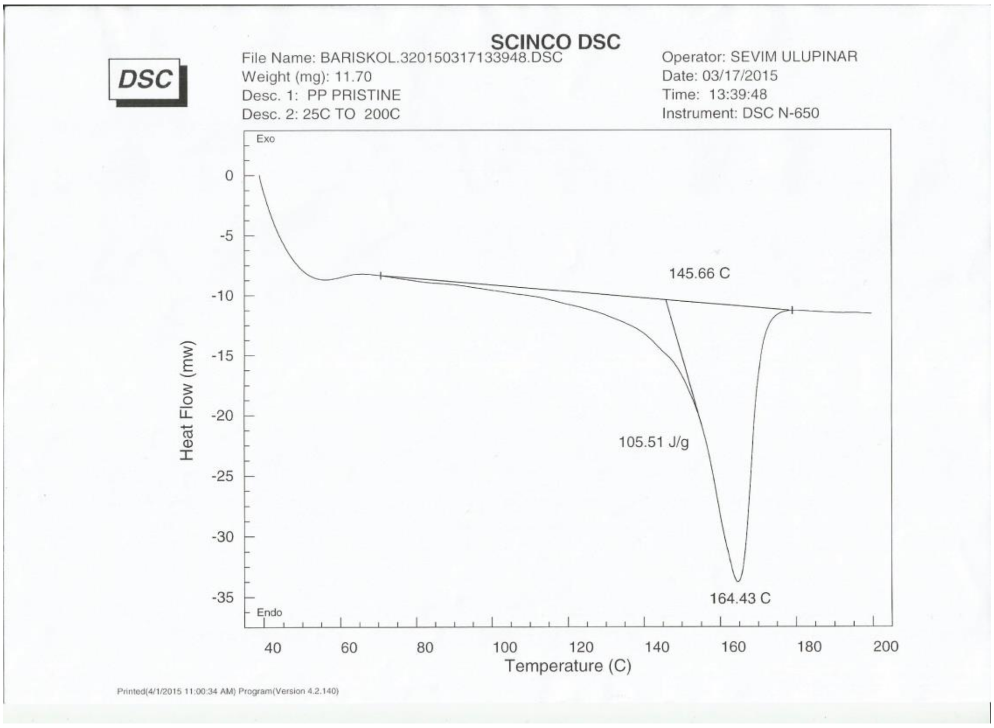

SCINCO DSC

File Name: BARISKOL.2020150326091810.DSC
Weight (mg): 21.80
Desc. 1: HDPE 2% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/26/2015
Time: 09:18:10
Instrument: DSC N-650

Printed(4/1/2015 10:55:29 AM) Program(Version 4.2.140)

Figure B. 4: Thermogram of HDPE 2.0% (w/w) DCP



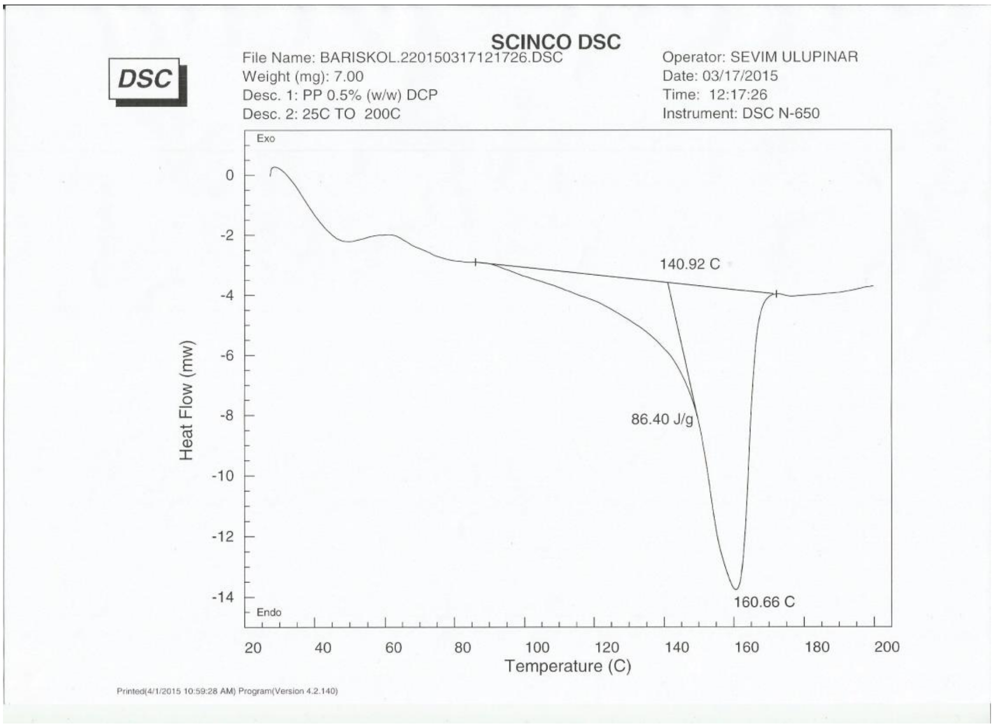
SCINCO DSC

File Name: BARISKOL.320150317133948.DSC
Weight (mg): 11.70
Desc. 1: PP PRISTINE
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/17/2015
Time: 13:39:48
Instrument: DSC N-650

Printed(4/1/2015 11:00:34 AM) Program(Version 4.2.140)

Figure B. 5: Thermogram of Pristine PP



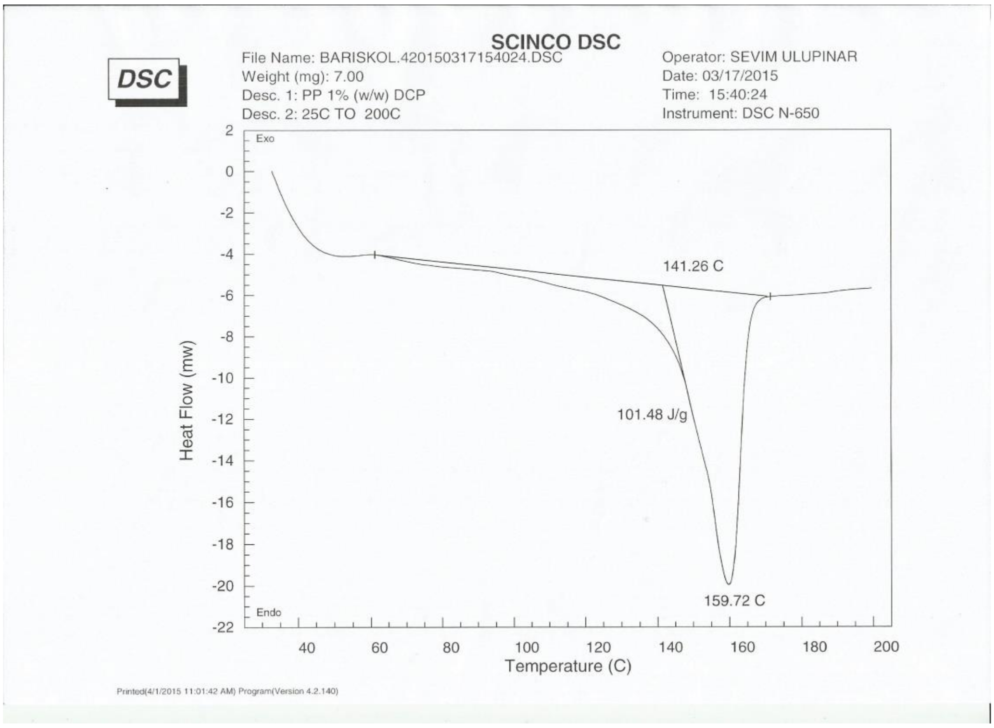
SCINCO DSC

File Name: BARISKOL.220150317121726.DSC
Weight (mg): 7.00
Desc. 1: PP 0.5% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/17/2015
Time: 12:17:26
Instrument: DSC N-650

Printed(4/1/2015 10:59:28 AM) Program(Version 4.2.140)

Figure B. 6: Thermogram of PP 0.5% (w/w) DCP



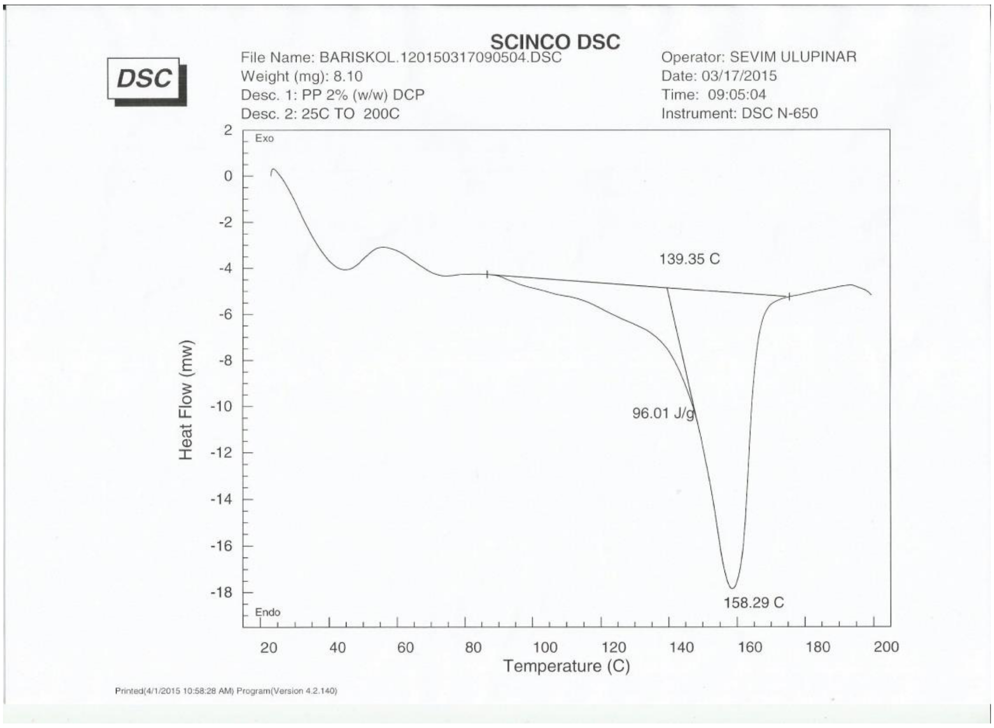
SCINCO DSC

File Name: BARISKOL.420150317154024.DSC
Weight (mg): 7.00
Desc. 1: PP 1% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/17/2015
Time: 15:40:24
Instrument: DSC N-650

Printed(4/1/2015 11:01:42 AM) Program(Version 4.2.140)

Figure B. 7: Thermogram of PP 1.0% (w/w) DCP



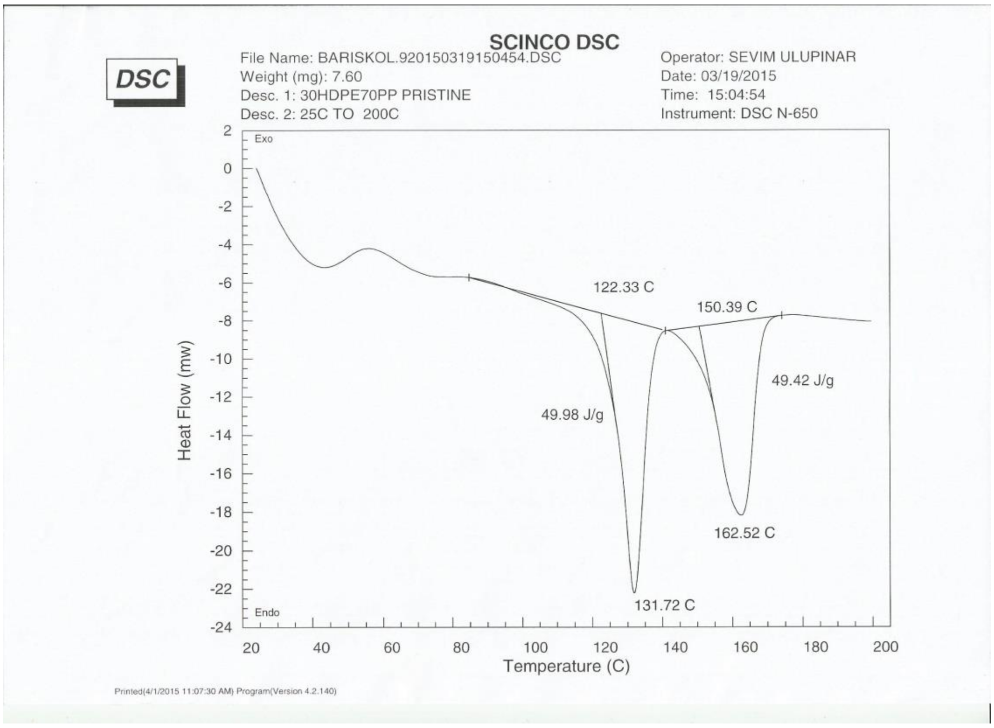
SCINCO DSC

File Name: BARISKOL.120150317090504.DSC
Weight (mg): 8.10
Desc. 1: PP 2% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/17/2015
Time: 09:05:04
Instrument: DSC N-650

Printed(4/1/2015 10:58:28 AM) Program(Version 4.2.140)

Figure B. 8: Thermogram of PP 2.0% (w/w) DCP



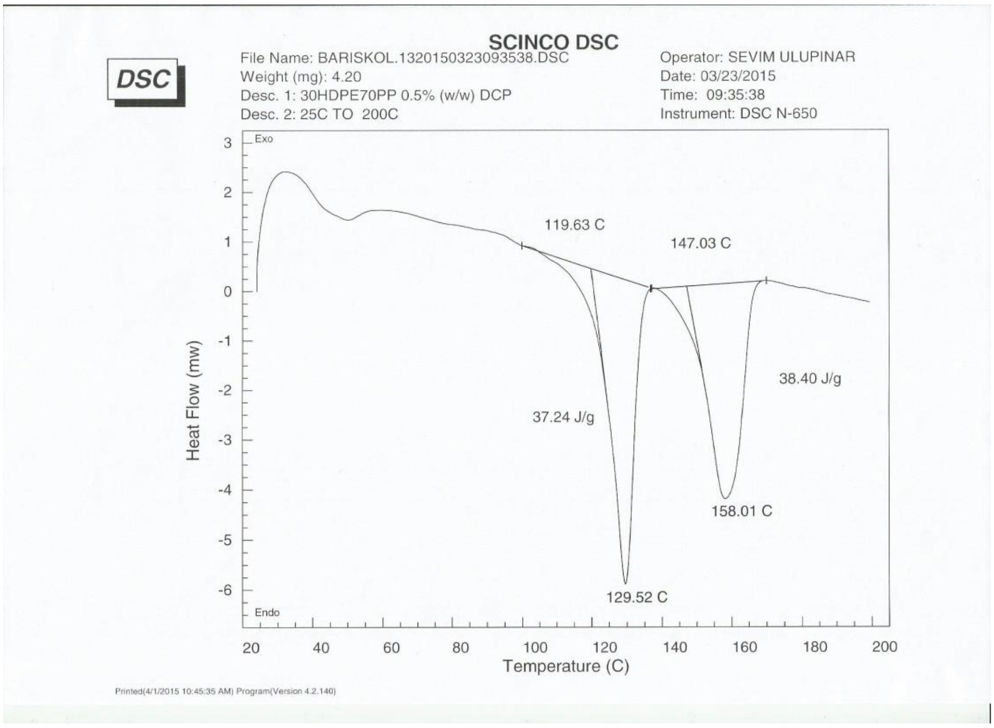
SCINCO DSC

File Name: BARISKOL.920150319150454.DSC
Weight (mg): 7.60
Desc. 1: 30HDPE70PP PRISTINE
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/19/2015
Time: 15:04:54
Instrument: DSC N-650

Printed(4/1/2015 11:07:30 AM) Program(Version 4.2.140)

Figure B. 9: Thermogram of Pristine 30HDPE70PP Set



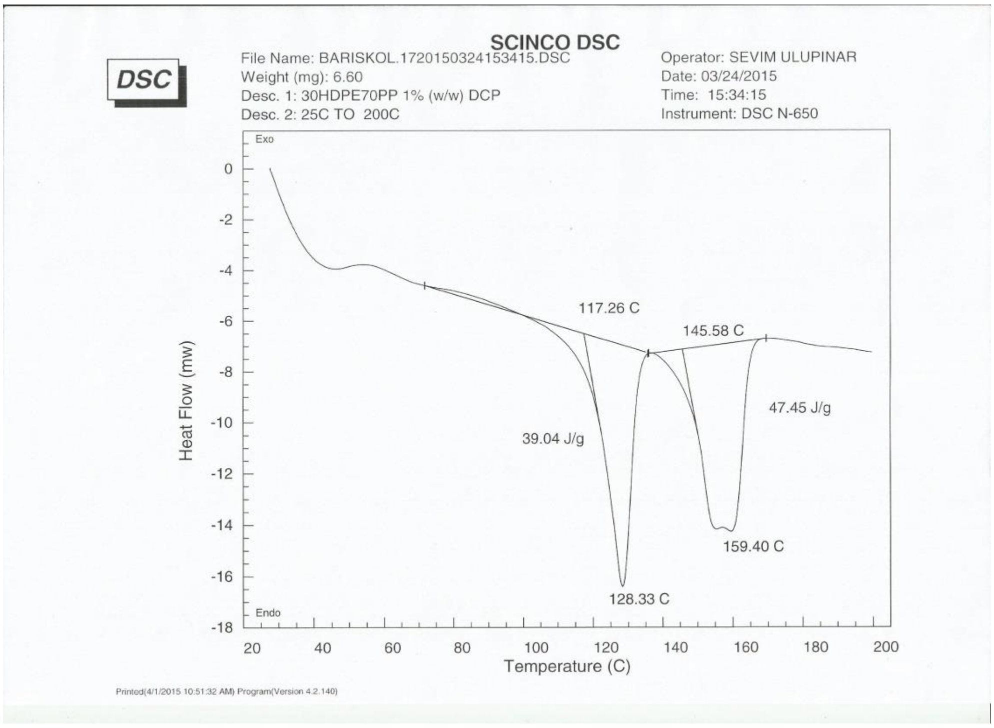
SCINCO DSC

File Name: BARISKOL.1320150323093538.DSC
Weight (mg): 4.20
Desc. 1: 30HDPE70PP 0.5% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/23/2015
Time: 09:35:38
Instrument: DSC N-650

Printed(4/1/2015 10:45:35 AM) Program(Version 4.2.140)

Figure B. 10: Thermogram of 30HDPE70PP 0.5% (w/w) DCP



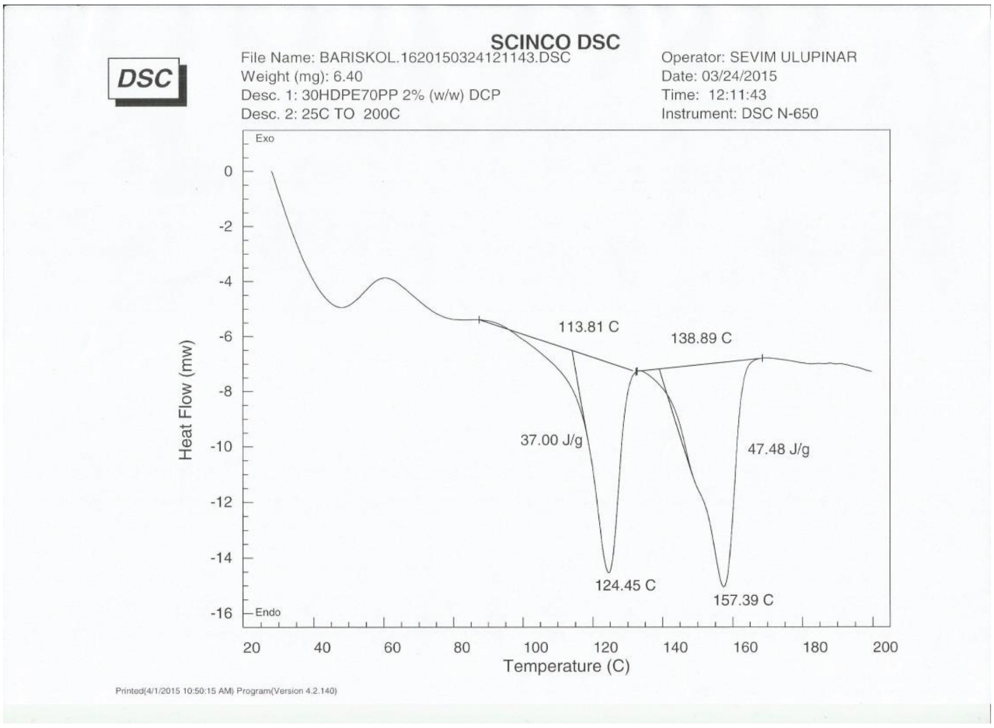
SCINCO DSC

File Name: BARISKOL.1720150324153415.DSC
Weight (mg): 6.60
Desc. 1: 30HDPE70PP 1% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/24/2015
Time: 15:34:15
Instrument: DSC N-650

Printed(4/1/2015 10:51:32 AM) Program(Version 4.2.140)

Figure B. 11: Thermogram of 30HDPE70PP 1.0% (w/w) DCP



SCINCO DSC

File Name: BARISKOL.1620150324121143.DSC
Weight (mg): 6.40
Desc. 1: 30HDPE70PP 2% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/24/2015
Time: 12:11:43
Instrument: DSC N-650

Printed(4/1/2015 10:50:15 AM) Program(Version 4.2.140)

Figure B. 12: Thermogram of 30HDPE70PP 2.0% (w/w) DCP

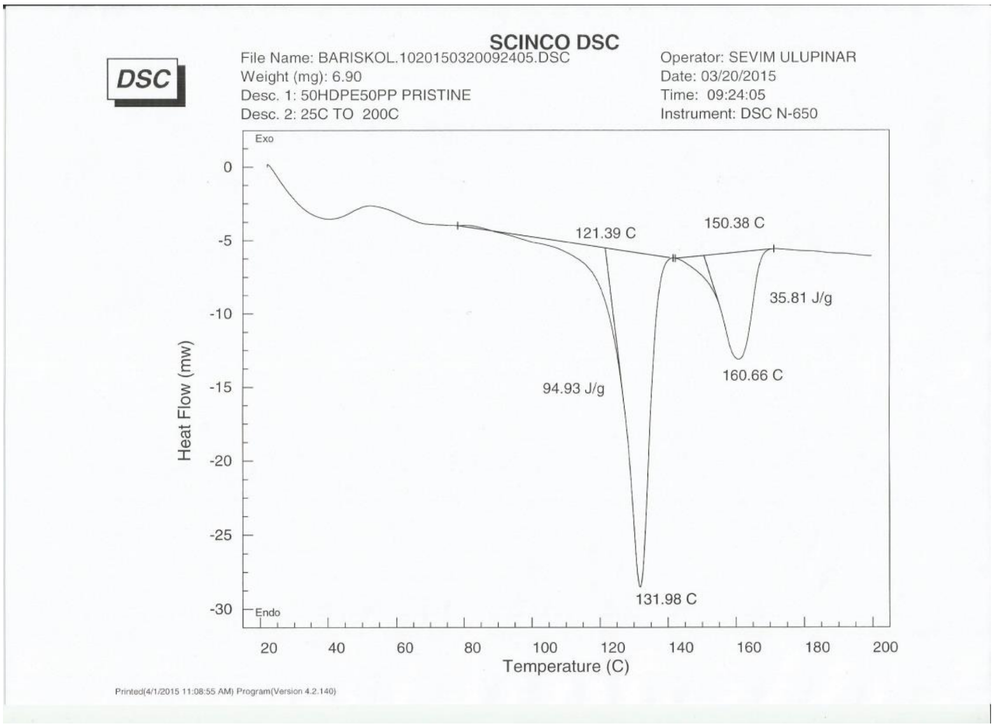


Figure B. 13: Thermogram of Pristine 50HDPE50PP Set

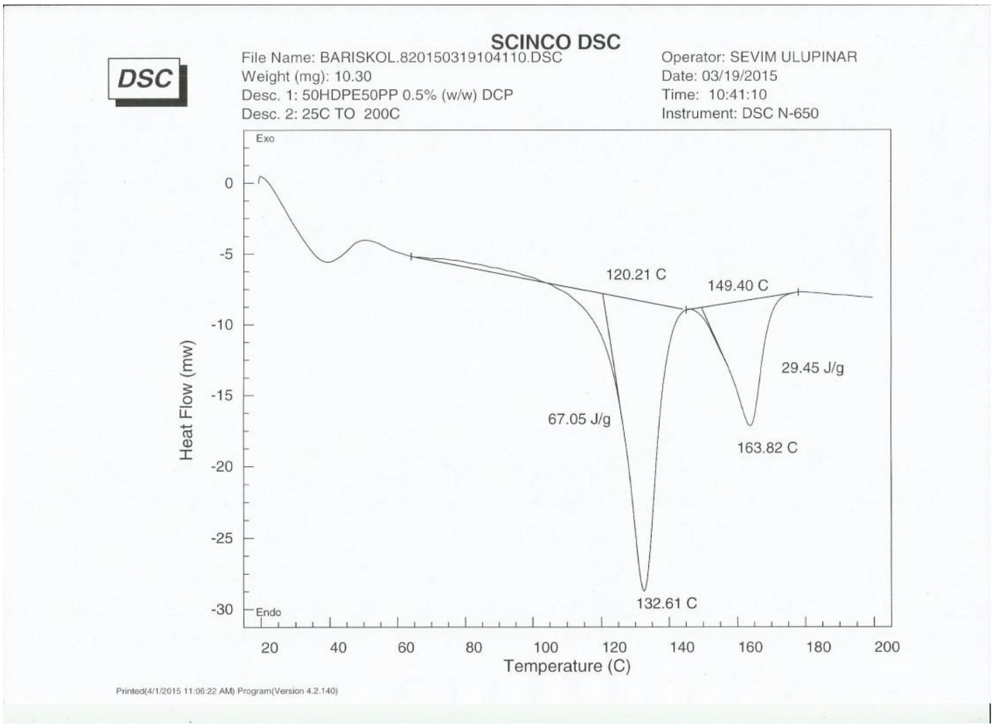


Figure B. 14: Thermogram of 50HDPE50PP 0.5% (w/w) DCP

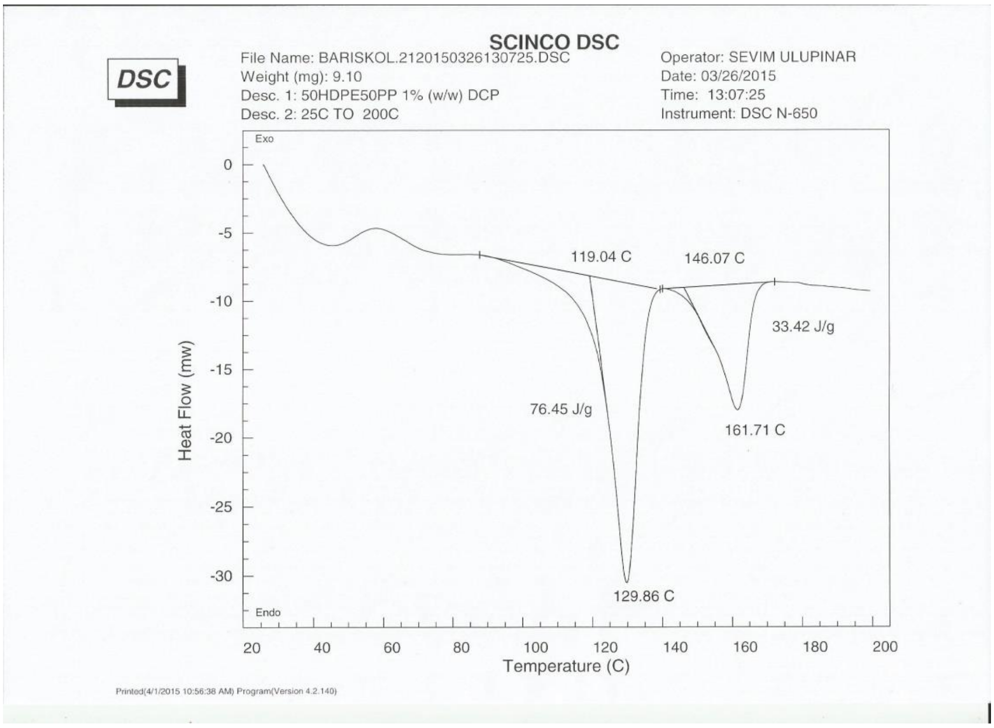


Figure B. 15: Thermogram of 50HDPE50PP 1.0% (w/w) DCP

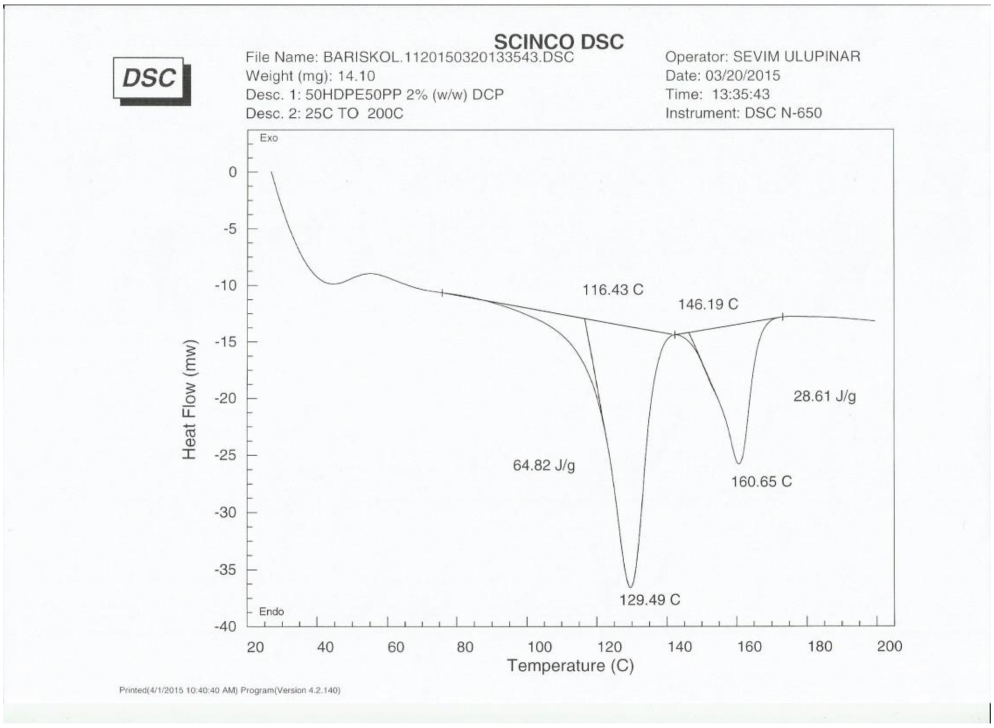
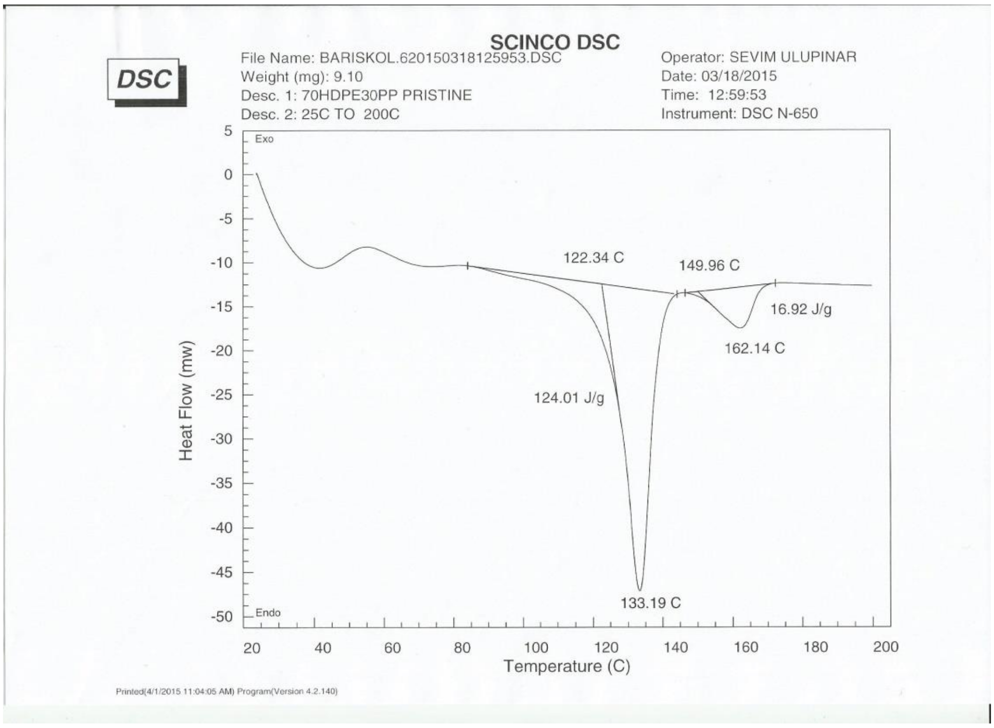


Figure B. 16: Thermogram of 50HDPE50PP 2.0% (w/w) DCP



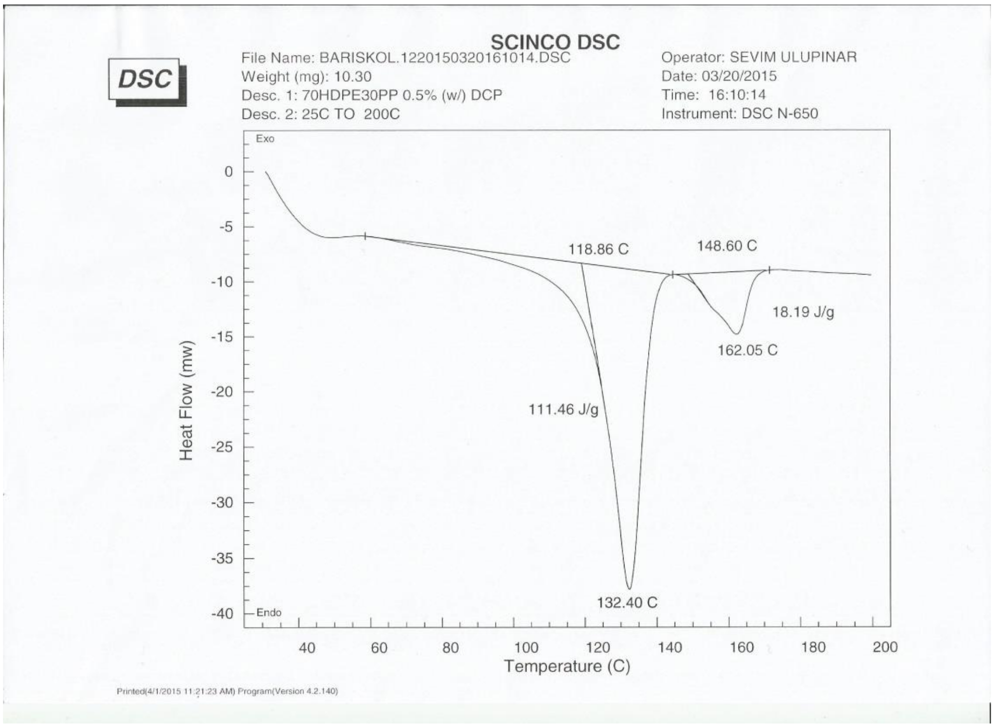
SCINCO DSC

File Name: BARISKOL.620150318125953.DSC
Weight (mg): 9.10
Desc. 1: 70HDPE30PP PRISTINE
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/18/2015
Time: 12:59:53
Instrument: DSC N-650

Printed(4/1/2015 11:04:05 AM) Program(Version 4.2.140)

Figure B. 17: Thermogram of Pristine 70HDPE30PP Set



SCINCO DSC

File Name: BARISKOL.1220150320161014.DSC
Weight (mg): 10.30
Desc. 1: 70HDPE30PP 0.5% (w/) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/20/2015
Time: 16:10:14
Instrument: DSC N-650

Printed(4/1/2015 11:21:23 AM) Program(Version 4.2.140)

Figure B. 18: Thermogram of 70HDPE30PP 0.5% (w/w) DCP

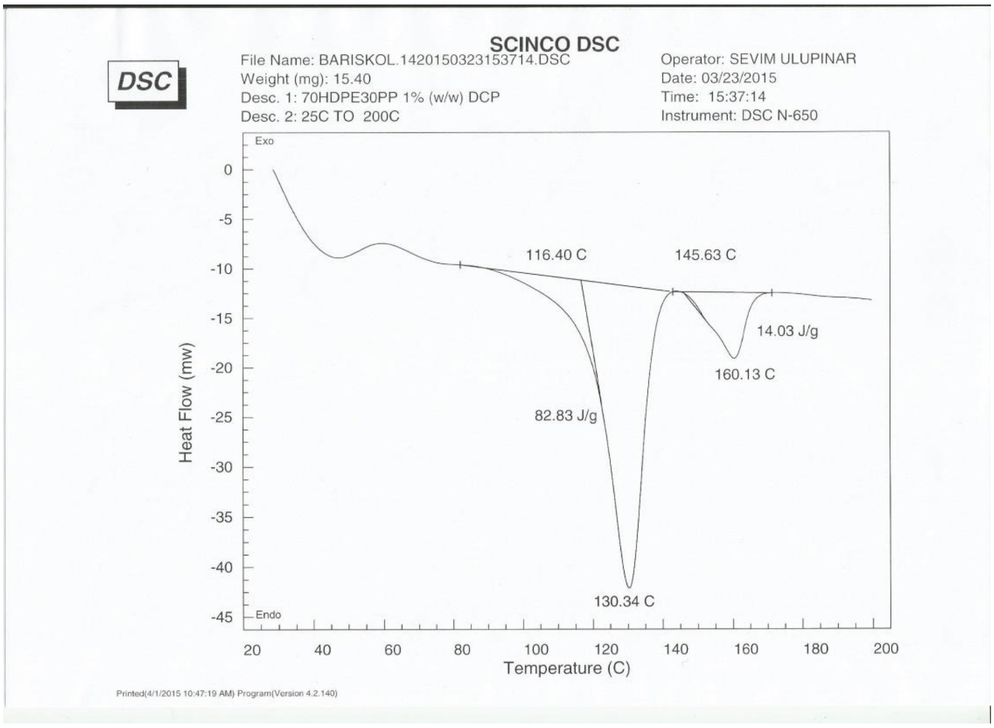


Figure B. 19: Thermogram of 70HDPE30PP 1.0% (w/w) DCP

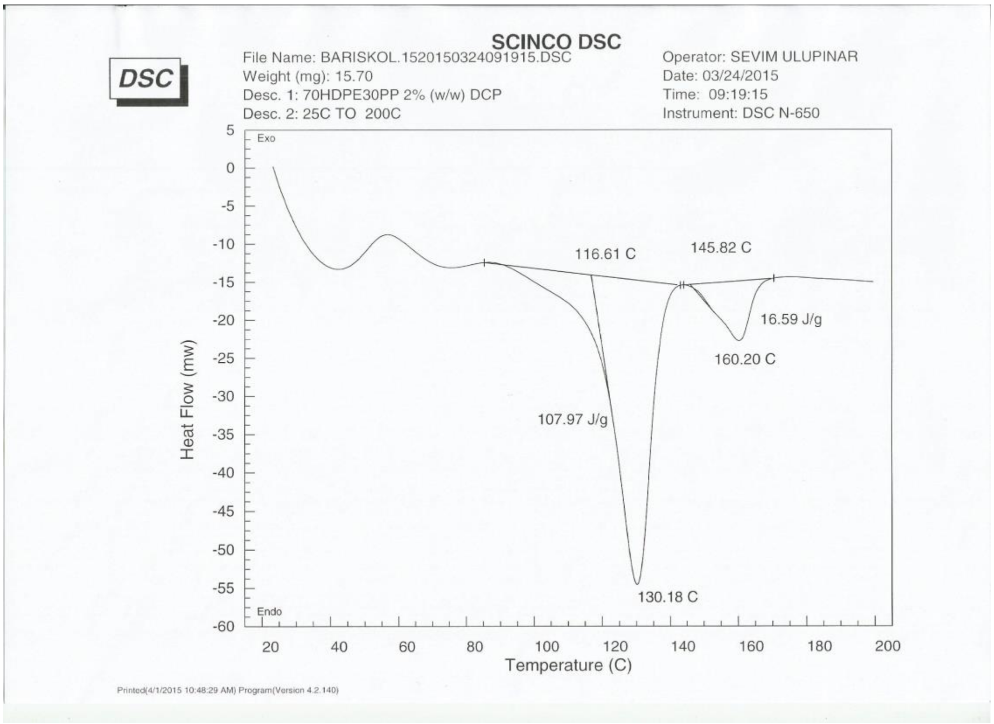
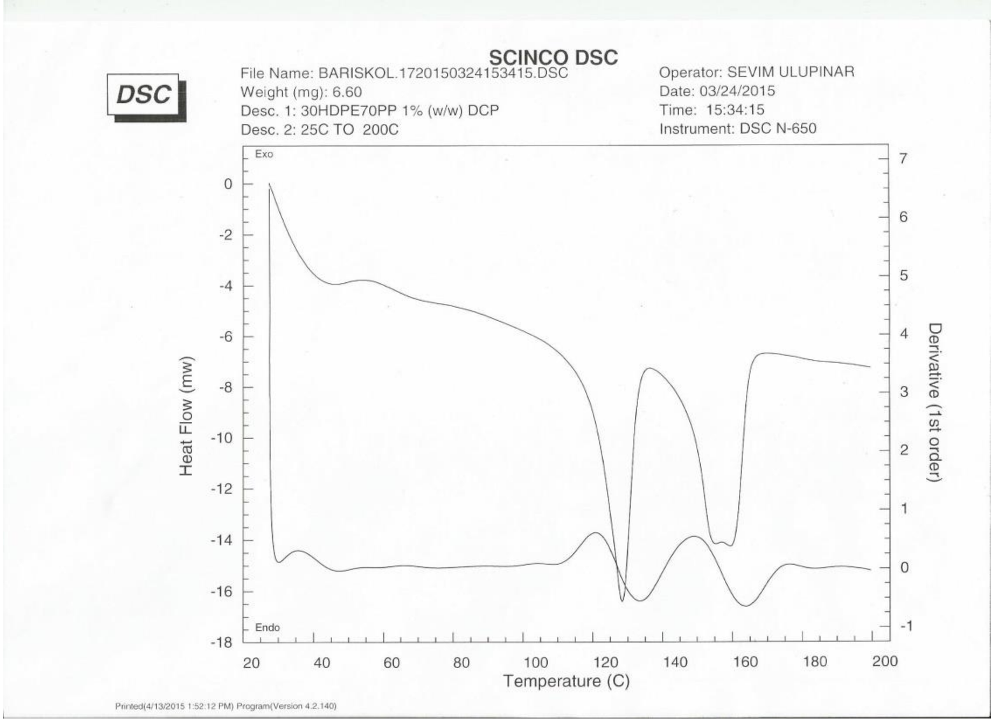


Figure B. 20: Thermogram of 70HDPE30PP 2.0% (w/w) DCP



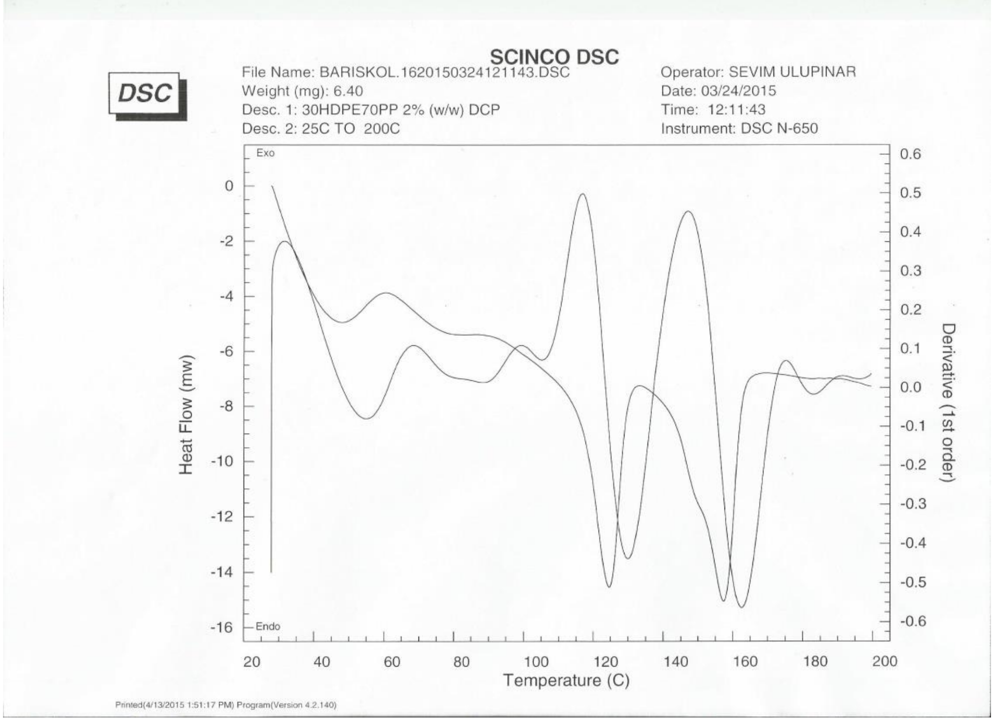
SCINCO DSC

File Name: BARISKOL.1720150324153415.DSC
Weight (mg): 6.60
Desc. 1: 30HDPE70PP 1% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/24/2015
Time: 15:34:15
Instrument: DSC N-650

Printed(4/13/2015 1:52:12 PM) Program(Version 4.2.140)

Figure B. 21: Derivative Thermogram of 30HDPE70PP 1.0% (w/w) DCP



SCINCO DSC

File Name: BARISKOL.1620150324121143.DSC
Weight (mg): 6.40
Desc. 1: 30HDPE70PP 2% (w/w) DCP
Desc. 2: 25C TO 200C

Operator: SEVIM ULUPINAR
Date: 03/24/2015
Time: 12:11:43
Instrument: DSC N-650

Printed(4/13/2015 1:51:17 PM) Program(Version 4.2.140)

Figure B. 22: Derivative Thermogram of 30HDPE70PP 2.0% (w/w) DCP

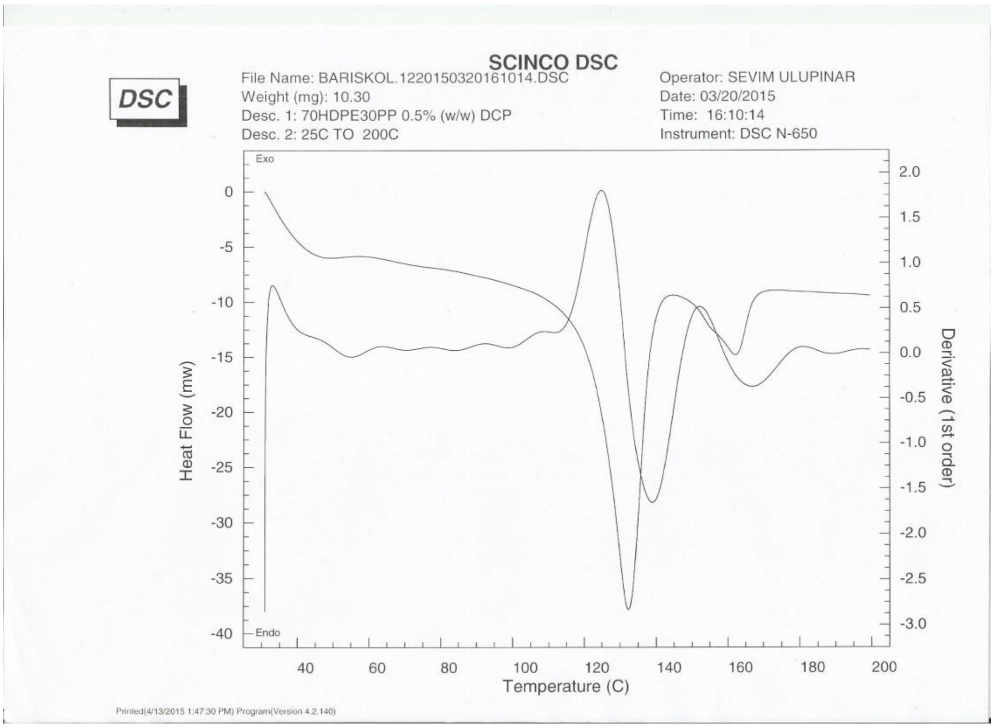


Figure B. 23: Derivative Thermogram of 70HDPE30PP 0.5% (w/w) DCP

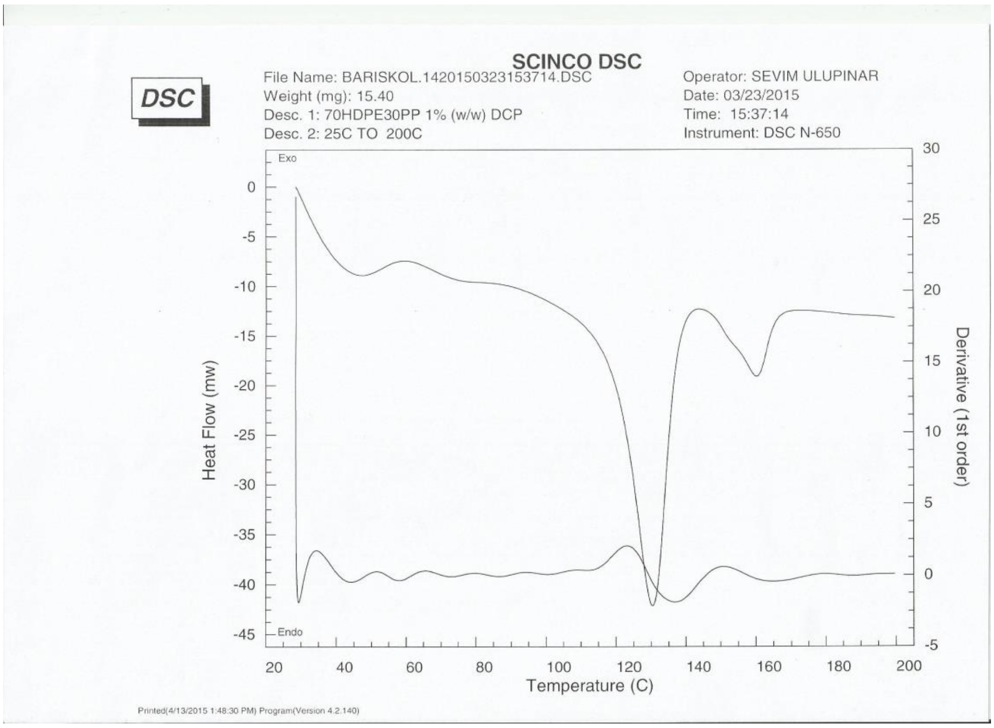


Figure B. 24: Derivative Thermogram of 70HDPE30PP 1.0% (w/w) DCP

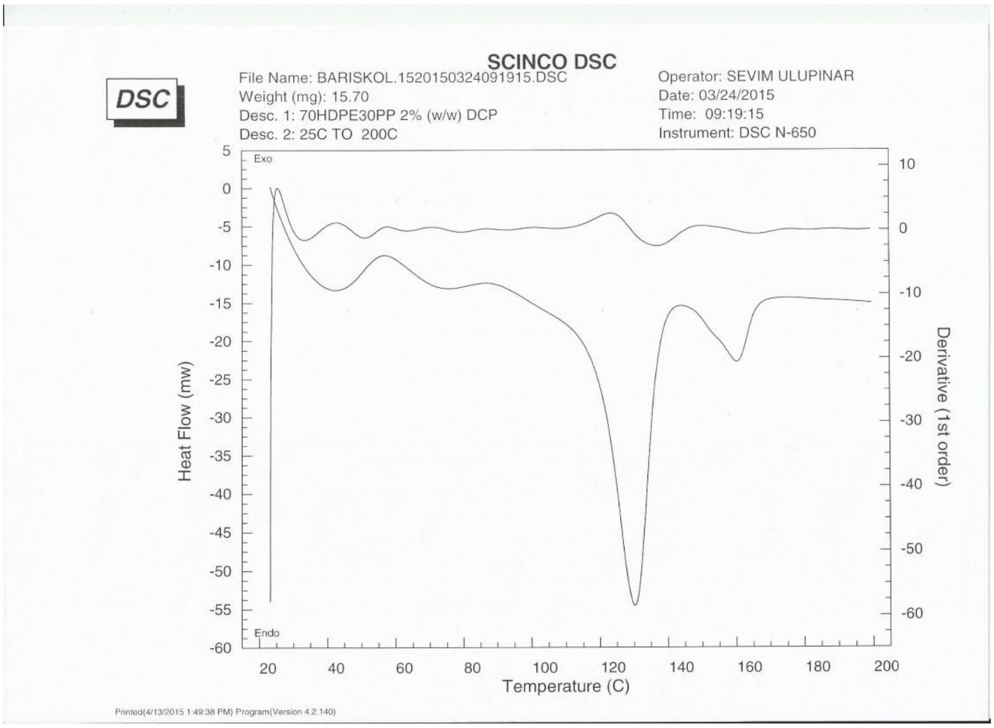


Figure B. 25: Derivative Thermogram of 70HDPE30PP 2.0% (w/w) DCP