

Recycling of Polymers in the Presence of Nanocatalysts: A Green Approach towards Sustainable Environment

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Abstract—This work involves the degradation of plastic waste in the presence of three different nanocatalysts. A thin film of LLDPE was formed with all three nanocatalysts separately in the solvent. Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetric (DSC) analysis of polymers suggest that the presence of these catalysts lowers the degradation temperature and the change mechanism of degradation. Gas chromatographic analysis was carried out for two films. In gas chromatography (GC) analysis, it was found that degradation of pure polymer produces only 32% C3/C4 hydrocarbons and 67.6% C5/C9 hydrocarbons. In the presence of these catalysts, more than 80% of polymer by weight was converted into either liquid or gaseous hydrocarbons. Change in the mechanism of degradation of polymer was observed therefore more C3/C4 hydrocarbons along with valuable feedstock are produced. Adjustment of dose of nanocatalyst, use of nano-admixtures and recycling of catalyst can make this catalytic feedstock recycling method a good tool to get sustainable environment. The obtained products can be utilized as fuel or can be transformed into other useful products. In accordance with the principles of sustainable development, chemical recycling i.e. tertiary recycling of polymers along with the reuse (zero order recycling) of plastics can be the most appropriate and promising method in this direction. The tertiary recycling is attracting much attention from the viewpoint of the energy resource.

Keywords—Degradation, differential scanning calorimetry, feedstock recycling, gas chromatography, thermogravimetric analysis. DSC.

I. INTRODUCTION

THE dramatic increase in production and lack of biodegradability of commercial polymers, particularly commodity plastics used in packaging (e.g. fast food), industry and agriculture, focused public attention on a potentially huge environmental accumulation and pollution problem that could persist for centuries [1]. Several communities are now more sensitive to the impact of discarded plastic on the environment, including deleterious effects on wildlife and on the aesthetic qualities of cities and forests because improperly disposed plastic materials persist in our environment and harm life. On the other side, the burning of polymers and plastics produce persistent organic pollutants (POPs) known as furans and dioxins [2].

There are four mechanisms by which plastics degrade in the environment: photo-degradation, thermo-oxidative degradation, hydrolytic degradation and biodegradation by

microorganisms [3]. It is understood that natural degradation of plastic begins with photo-degradation because ultraviolet light from the sun provides the activation energy required to initiate the incorporation of oxygen atoms into the polymer, which leads to thermo-oxidative degradation [3], [4]. This causes the plastic to become brittle and to break into smaller and smaller pieces, until the polymer chains reach sufficiently low molecular weight to be metabolised by microorganisms [3]. These microbes either convert the carbon of the polymer chains to carbon dioxide or incorporate it into bio-molecules [3], [5]. However, this entire process is very slow, and it can take 50 or more years to fully degrade plastics [6].

Polyolefins (polyethylene, polypropylene, polystyrene) are plastic materials used extensively in containers and packing. Polyethylene (PE) is the worldwide most produced polymer with about 60 million tons per year and the main component of plastic waste [7]-[10]. Other than PE polypropylene (PP), polyvinyl chloride (PVC) and polystyrene are the main components of solid waste [11]-[13]. They present approximate 60% of the total solid plastic waste generated in urban solid waste [8].

The current strategies to deal with the solid plastic waste (around 62% of total available solid waste is collectable) are still based on land filling, incineration without energy recovery [14] and recycling. Because of this huge plastic solid waste, many municipalities are facing disposal problems such as emission of toxic substances (dioxins and furanes) on incineration and shortage of landfill sites [14]. Although polymers are actually high-yielding energy sources, incineration method has been widely accused as ecologically unacceptable owing to the health risk from air born toxic substances e.g. dioxins (in the case of chlorine containing polymers). In the last decade, many environmental regulations have been implemented for a more sustainable recycling oriented society [15]. The objective of a plastic management policy, in accordance with the principles of sustainable development, should be not only the reuse of polymeric materials but also the production of raw materials (monomers), from which they could be reproduced, or other secondary valuable products [16].

Plastic material has almost the same composition to petroleum and they are high yielding energy sources. For example, one liter of heating oil has a net calorific value of 10200 kcal, whereas 1 kg of plastic releases 11000 kcal worth of energy. 1 kg briquettes (blocks of pressed coal dust) have a net calorific value of 4800 kcal only. So it can be recycled into

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petroleum products safely with suitable technique without producing any harmful gases [7], [17]-[20]. At one side it will provide sustainable alternative of energy recovery and material recovery and other side society will get rid from the disposal problem of plastic waste.

Polyethylene (PE) and polypropylene (PP) as typical commodity plastics are better known as randomly degrading polymers rather than depolymerizing polymers [7], [21]. This is not surprising because the heat of polymerization, an important parameter for estimating the depolymerizability of polymers, has larger negative values for ethylene and propylene, than for styrene (St) and methyl methacrylate, indicating the difficulty in depolymerising PE and PP [22]. However, cases in which the zip length is controlled by chain-transfer reactions and in which the activation energy value for a depolymerisation reaction, such as β -scission, is higher than that of the chain-transfer reactions, the monomer yield can be increased with increase in temperature.

Many methods have been investigated by different researchers for feedstock recycling. These are broadly divided into two categories as mechanical recycling and chemical recycling methods. A promising method for the reprocessing of waste plastic is feedstock recycling, or clean incineration of municipal solid waste which allows the conversion of plastic residues into raw chemicals, monomers of plastics and hydrocarbon feedstock. It is a sustainable way for the recovery of the organic content from polymeric waste and also to preserve petroleum resources in addition to protecting environment [7], [21]-[23].

In spite of many R&D projects over the three decades, it is reported that recycling of waste plastic in oil production process covers negligible amount in the total amount of waste plastic generated all over the world. Moreover, these methods are economically not good due to technical problems such as low treatment ability of techniques and high energy consumptions and low quality of products obtained. The produced oils have limited uses and applications only in industrial boilers, burners and power generators. And the fuel gas generated by plastic recycling is two or three times more expensive than fuel oil [7], [24].

So, it is the correct time to develop more economic, safe, eco-friendly and sustainable method for feedstock recycling of waste polymer.

In this study, attempts are taken to obtain useful products and virgin monomer by degradation of polymers in the presence of different nanocatalysts without generation of any further hazardous/poisonous chemicals at low temperature.

II. MATERIALS AND METHOD

A. Linear Low Density Polyethylene (LLDPE)

It was purchased from B.R. Scientific and Chemicals Company, Faridabad, Haryana. It was washed, and dried in open air for one day. After that it was used for practical purposes. It was soaked in solvent for three days then warmed to get in liquid state.

B. Toluene, Transition Metal Oxide and Nonmetal Oxide

These entire chemicals are also purchased from B. R. Scientific and Chemicals Company, Faridabad, Haryana. These all were used without further purification.

C. Preparation of Films of Polymers Samples

Films of polymer samples are prepared by dissolving polymer into solvent in the presence of weighed amount of desired catalyst and dried in oven at 330 K.

D. TGA and DSC Analysis

TGA and DSC analysis of pure polymer and in the presence of nano-catalyst was carried out at Saurashtra University, Maharashtra. All these analyses were carried out on Shimadzu DSC- 60 & Shimadzu TGA- 60 WS.

E. GC Analysis

The GC studies were carried out in a special GC-MS instrument equipped with gas sample injector. This facility was kindly provided by Mahatma Gandhi University, Kottayam.

III. RESULT AND DISCUSSION

The objective of the study was to obtain useful products and virgin monomer by degradation of polymers in the presence of different nano-catalysts at low temperature. It is observed that certain catalysts decrease the degradation temperature of polymers. In the presence of these catalysts, polymer degrades in more than one step, whereas in absence of these catalysts, they show decomposition in one step at little higher temperature thus decrease the reaction temperature. The quality of degradation products is improved as well as percentage of dioxins and aromatic compounds are decreased. These harmful products and aromatics are generally produced at high temperature (above 600 °C).

Preliminary TGA data presented in Figs. 1-3 show that there is considerable increase in the thermal decomposition of polymer sample when cracked in the presence of catalyst A in comparison to catalyst B and C. From the graph, it can be seen that in the former case the weight loss is 36%, whereas in the latter case it is only 20%. The amount of catalyst required for this change is only 10% of the total polymer mass. However, the onset of decomposition temperature remains the same in both cases. Nevertheless, the interesting point is that the substantial drop in the decomposition temperature to ~ 220 °C, in the presence of catalyst (Figs. 1-3). The possibility of decreasing the catalyst amount and its reusability for this cracking experiment was also tested. The DSC results showed a marked effect on the ability of catalyst to effect the endothermic decomposition process. This can be clearly distinguished from the sluggish and sharp changes in DSC profiles at the decomposition temperature in absence and presence of catalyst (Figs. 4-7).

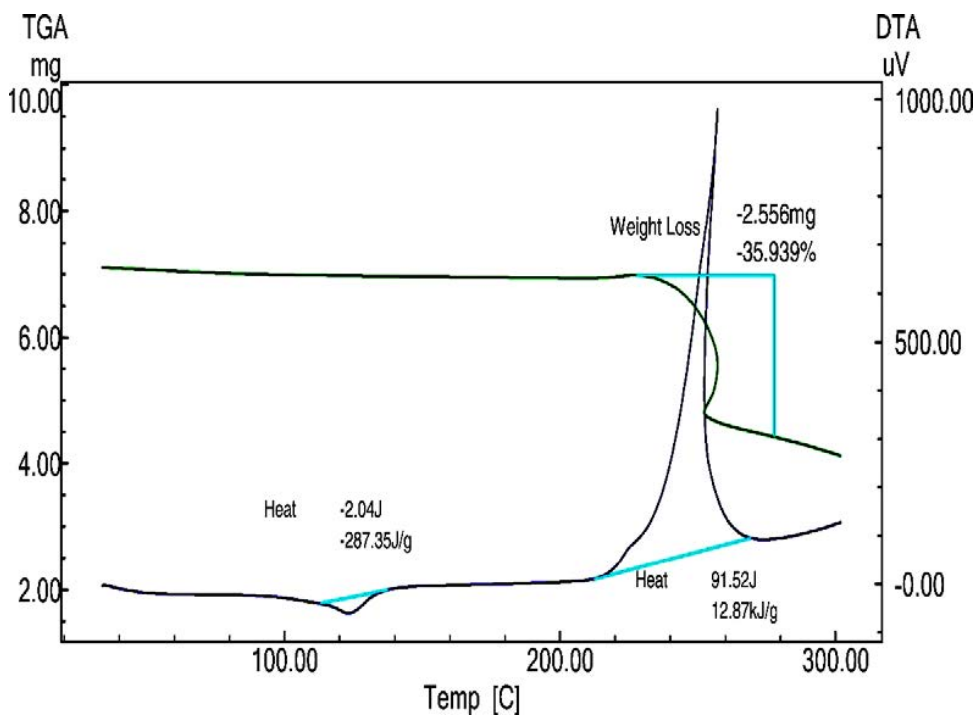


Fig. 1 TGA of polymer in the presence of catalyst A

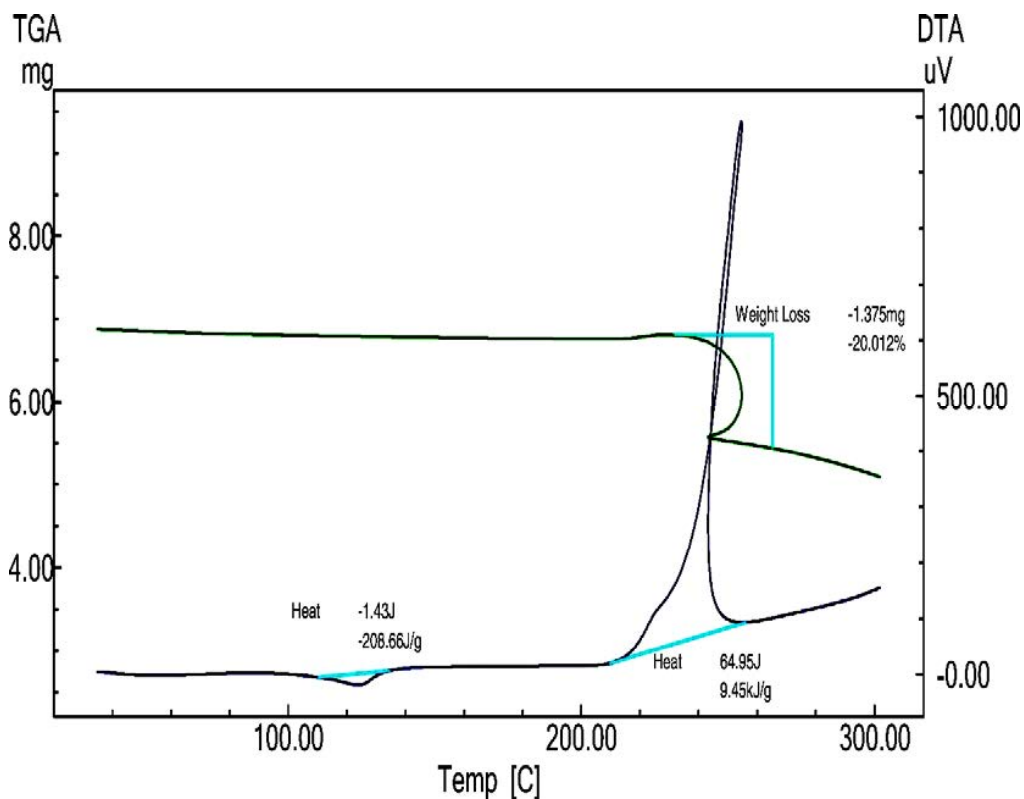


Fig. 2 TGA of polymer in the presence of catalyst B

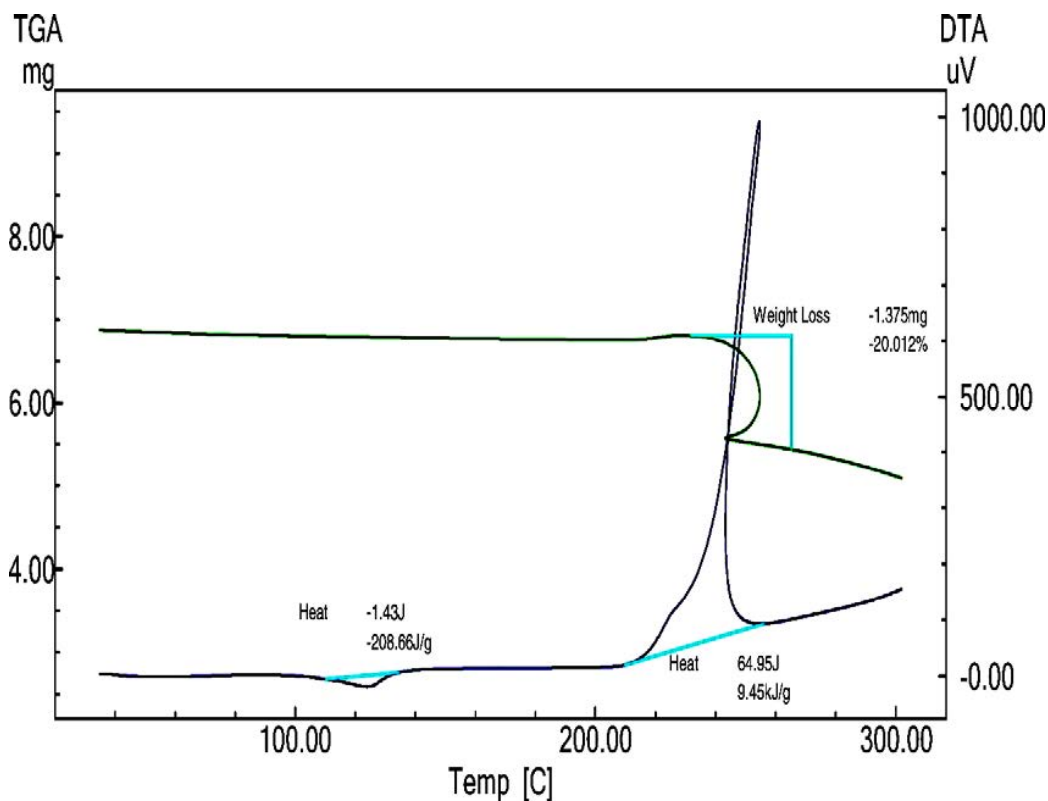


Fig. 3 TGA of polymer in the presence of catalyst C

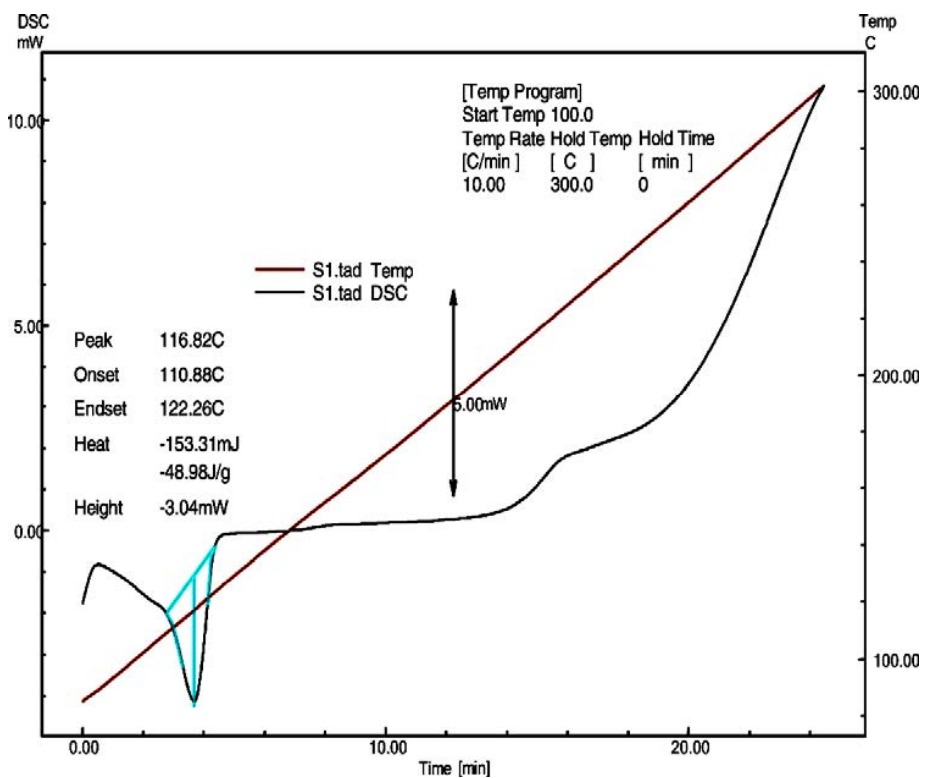


Fig. 4 DSC of polymer in absence Catalyst

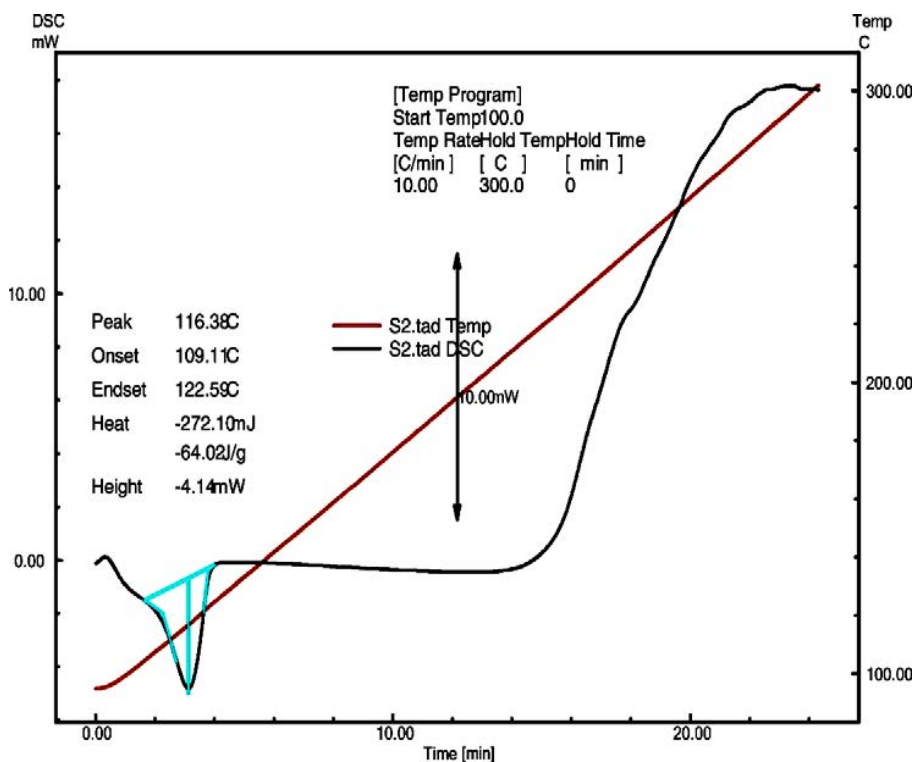


Fig. 5 DSC of polymer in the presence Catalyst A

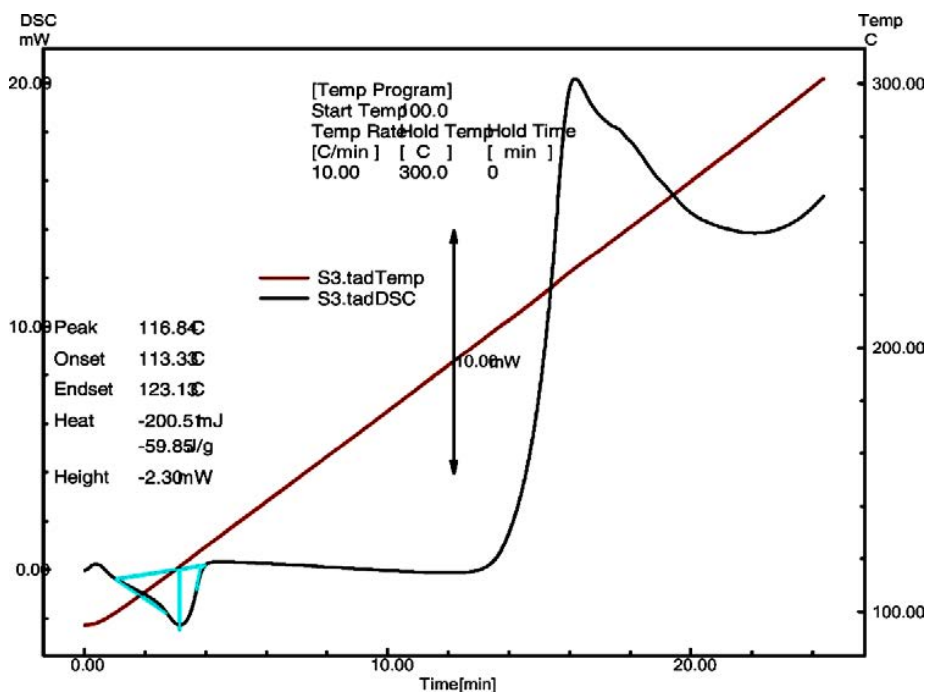


Fig. 6 DSC of polymer in the presence Catalyst B

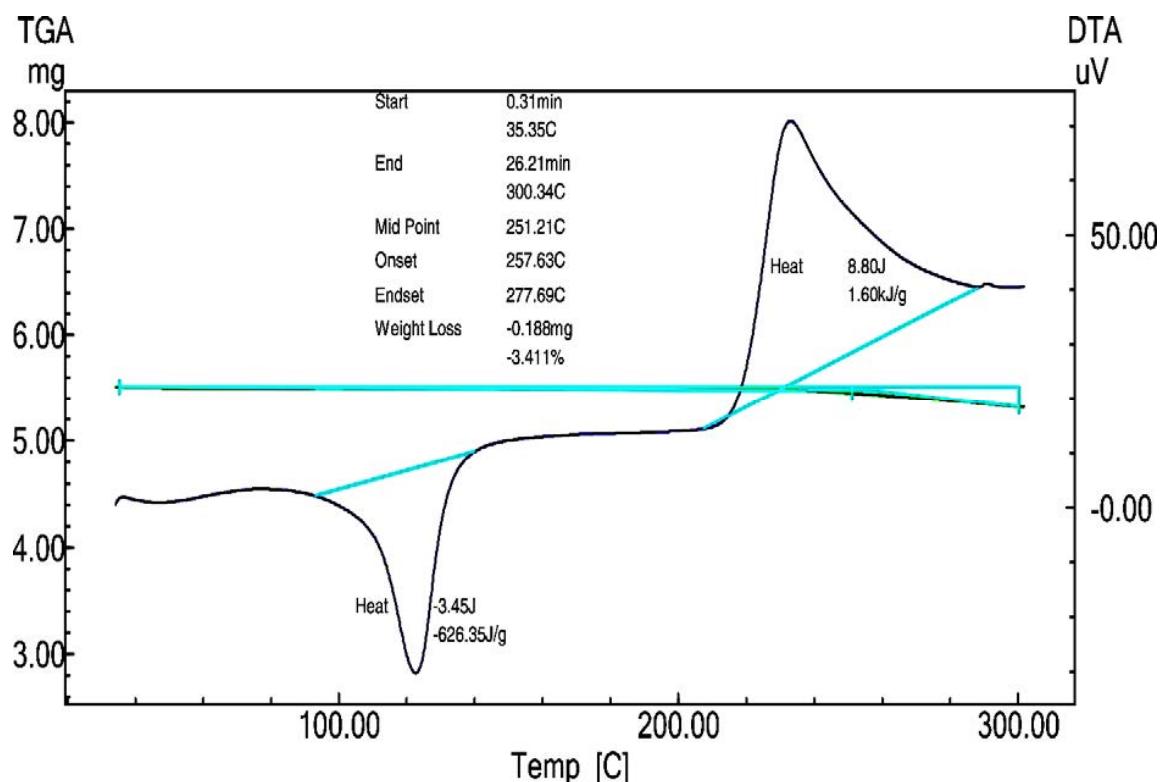


Fig. 7 DSC of polymer in the presence of catalyst C

TGA and DSC were carried out each time prior to GC analysis. This gave information about the number of steps involved in each reaction and the optimum and starting temperature for each step of reaction.

To test the obtained degradation products, GC analysis of effluent gases was carried out in absence and presence of catalysts. The obtained results are given in Table I. The GC studies were carried out in a special GC-MS instrument equipped with gas sample injector.

GC results of degraded products show that in the presence of catalyst A, B, and in the presence of catalyst C, percentage of C3- C4 hydrocarbons is very high while percentage of higher hydrocarbons (above C10) is almost negligible.

TABLE I
FRAGMENTS OBTAINED DURING CATALYTIC CRACKING OF LLDPE
(GC ANALYSIS)

Fragments %wt	Sample +A	Sample +B	Sample +C	Pure Sample
C3/C4	72	82	72	32
C5/C9	17	18	25	67
>C10	11	0	3	1

It was found that on degradation of pure polymer results only 32% C3-C4 hydrocarbons while, in the presence of catalysts A, B, and C percentage of C3-C4 hydrocarbon was 72 and 82 and 72 respectively and low percentage of higher hydrocarbons.

To get good quality of products by varying dose of catalysts, admixtures, temperature and rate of heating is still required. Attempts will be made to use the mixture of nano

particles of catalyst to check catalytic activity in future. Possibility of recyclization of catalysts will also be tested by some methods. Attempts will be made to get maximum fraction of monomer and gaseous fraction.

All the above studies encouraged us and created a lot of interest to pursue further the degradation of polymer in the presence of catalysts.

IV.CONCLUSION

From the experimental findings of the present work, the following conclusion can be drawn:

1. Pure polymer degrades at much higher temperature and it involves single step in the association of production of green house and toxic gases like dioxin.
2. In the presence of nano-catalysts A, B and C, degradation temperature lowers and degradation reaction involves more than one steps.
3. Degradation of pure polymer produces only 32% C3/C4 hydrocarbons while in the presence of catalysts A, B, and C degradation of polymer produces 72%, 82% and 72% C3/C4 hydrocarbons respectively.
4. There is need to search new catalyst along with adjustment of dose of catalyst to get valuable hydrocarbons which can be used as fuel or to get other valuable products.
5. This can help to get sustainable source of petroleum products.

ACKNOWLEDGMENT

The author sincerely thanks to Dr. Jignesh, Assistant Professor in Chemistry, Saurashtra University, Maharashtra, giving facility of TGA and DSC analyzers to carry out this study successfully

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