Development of Nickel Based Multifunctional Additive & Performance Evaluation of Photo Biodegradation with Polypropylene

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Abstract - Nickel Based Multifunctional additive (Ni-MFA) was successfully synthesized and their performance on the photo biodegradability of PP film was evaluated by observing the disparity in the structural characteristic, surface morphology, mechanical, and thermal properties upon degradation. PP films blended with different compositions (1, 2 & 3 wt %) of Ni -MFA by melt blending. The structural characteristics of all the films was studied using Fourier transformed Infrared spectroscopy (FTIR), surface morphology by Scanning Electron Microscopy (SEM), mechanical properties by Universal Testing Machine (UTM) and thermal properties by Differential Scanning Calorimetry (DSC). After initiated the photolysis examine films were incubated in the presence of the microbes such as asspergillus Niger and pencillium funculosum isolated from a dump. Both living organism were capable of degrading polypropylene. It was concluded that polypropylene modified with 1%, 2% and 3% was biodegraded within 45 days, the result revealed that 3% Ni- MFA modified polypropylene was biodegraded 20%.

Keywords: Photo degradation; Ni based Multi functional additive (Ni-MFA); biodegradation; polypropylene

1. INTRODUCTION

The solution of plastic ecological problem lies in the development of photodegradable and biodegradable polymer with controlled lifetime. The purpose of this research work is to synthesize a new class of biodegradable additives comprising transition metal salts of alkenoicacid. These metal salts are named as multi functional additives (MFA) as they may exhibit required characteristics because of structural features viz. carbonyl group, pendent group, long alkenoic chain, unsaturation in the chain and metal ion containing structure. The previous research [1-25] shows that the additives containing carbonyl group are susceptible to UV radiation and unsaturation leads to self lubricating or plasticizing effect and metal salt will not cause thermal degradation during processing and give combined effect of photo activators which will facilitate to break-down the polymer chain in presence of UV radiation. These high performance Nickel based Multi functional Additives (Ni-MFA) enhance the biodegradation characteristics without affecting the processing parameters at a very low level of incorporation and better dispersion in the polymer. Hence these MFA systems will provide photo-degradation the and subsequent biodegradation of polymeric material and as well as enhanced end use properties for packaging applications.

A new class of biodegradable additive is visualized with following generic structure as shown in Fig. 1.



Fig.1. Generic structure of Ni based Multi Functional Additive (Ni-MFA)

2. EXPERIMENTAL

2.1. Material

Polypropylene was purchased from Reliance petro chemicals and used without further purification, Ammonium Nickel (II) sulfate hexahydrate crystal Pure Merck product, Ethanol china product, demineralised water Merck product, Ricinoleicacid(12-hydroxy-(cis)-octadecenoic acid) is known as castor oil, hydrochloric acid qualigens product in fisher Scientific.

2.2. Blending and film preparation of PP

The MFA was melt blended with PP at three different formulations 1, 2 & 3% respectively in Torque Rheometer. Blending was carried out at temperature range of 210,200, 190,180 and 150° C (from die to hopper) & a screw speed of 100 rpm. Subsequently, the pellets are dried in a dehumidifier at 70° C for two hours to remove moisture. The pellets produced were subsequently dried & subjected to film cast process to produce films of 50 microns thickness.

The above mentioned film was used in ASTM D 5338-98 test method determine the degree and rate of aerobic biodegradation of plastic materials on

exposure to a controlled- composting environment under laboratory conditions. This test method is designed to yield reproducible and repeatable test results under controlled conditions that resemble composting conditions. The test substances are exposed to inoculums that are derived from compost from municipal solid waste. The aerobic composting takes place in an environment where temperature, aeration and humidity are closely monitored and controlled.

2.3. Photo degradation

All the blended samples were subjected to photodegradation studies as per ASTM D 5208 using ATLAS UV Weather-o-meter. Films of 25 mm width were used to evaluate the degradation phenomenon. Samples were exposed to two different test cycles of UV irradiation & condensation (condensation means water sprinkler phase as per ASTM D 5208 to simulate the actual condition of day & night.) & subsequently tested & characterized at 1, 2, 4 & 6 days interval time. The cycle time is given in the Table 1

Table 1 UV cycle for photo degradation studies

S. No	Cycle	Irradiation W/m ²	Temperature °C	Time Hrs
1.	UV Irradiation	0.63	60^{0} C	8
2.	Condensation	-	50^{0} C	4

In a test for 24 hours, first eight hours is UV cycle and the next four hours is condensation cycle. For the remaining time the cycle was repeated in the same order.

2.4. Mechanical Properties

Tensile properties of virgin PP with Ni-MFA melt blended samples (PP) before and after UV exposure, with dimensions 150 x 0.060mm were subjected to tensile tests as per ASTM D 882, using Universal Testing Machine (UTM), Lloyd Instrument Ltd, UK which has a cross head speed of 500mm/min and gauge length of 50mm in both machine and transverse directions.

2.5. Optical Properties

Optical properties such as luminous transmittance and haze were studied for the Ni MFA blended

2.7. Thermal Properties

2.7.1. Differential Scanning Calorimeter (DSC) Analysis

samples (PP) before UV exposure and after UV exposure to find the effect of additive on the optical characteristics of the film. For measuring haze and luminous transmittance, The BYK Gardner Spectrophotometer was employed (ASTM D 1003).

2.6. Fourier Transforms Infrared Spectroscopy (FTIR)

A Fourier Transforms Infrared Spectrophotometer (FTIR) can generate an infrared spectral scan of samples that absorb infrared light. If the material does not absorb infrared light a spectral scan cannot be obtained. FTIR is also used for quality control of materials and for contamination analysis/ the rate of photo oxidation of the UV degraded films. The FTIR measurements used was a Perkin Elmer system 2000 infrared spectrum analyzer with the wave number range of 400-4000 cm^{-1.}

Melting behavior of MFA blended samples (PP) is being studied by employing Perkin Elmer (USA). Differential Scanning Calorimeter. Sample of 5 mg weight was scanned from 45 to 200°C at the heating rate of 10°C/min to detect the melting characteristics of the sample before and after exposure to UV radiation

2.7.2. Thermo gravimetric analysis

Thermal degradation of PP Fe-MFA blended sample of before and after UV Exposure were analyzed by Perkin Elmer (USA), at the heating rate of 10°C/min from 50 to 700°C.

2.8. Scanning Electron Microscopy (SEM)

The scanning electron microscopic analysis of fractured surface of PP-Ni MFA film was carried out using CARL ZESIS Model; EVO MA 15 scanning electron microscope. The surface of the samples was coated with conductive heavy metal such as gold / palladium.

3. RESULT AND DISCUSSION

3.1. Mechanical properties evaluation

The tensile strength data of PP film with Nickel (Ni) multi functional additives (MFA) before and after UV exposure are presented in the Table 2.

The tensile strength of PP virgin sample decreases with the incorporation of Ni-MFA in the concentration of 1%, 2% and 3%. There was a considerable decrease in the tensile strength and elongation at break on exposure of the films with additive to UV radiation. The Nickel based additives show considerable decrease in the tensile strength and elongation at break. The deterioration

2.9. Biodegradation Test

Nickel 12 hydroxyl oleate with blended PP film was subjected to biodegradation test as per ASTM D 5338-98. This test method determines the degree and rate of biodegradation of plastic materials on exposure to controlled composting environment under controlled laboratory conditions. The samples were exposed to inoculums that are derived from compost from municipal solid waste [26]. The aerobic composting takes place in an environment where temperature, aeration and humidity are loosely monitored and controlled. The percentage of biodegradability is obtained by determining the percentage of carbon in the test sample that is converted into CO₂ during the duration of the test.

in mechanical properties of films was observed in both the machine direction and transverse direction, but the rate of deterioration was high in transverse direction. Also, increasing the concentration of additive from 1% to 3% increases the degradation. PP films with Ni-MFA additive show decrease in tensile strength and elongation and ultimately become brittle when exposed to UV radiation for 72 hrs (Third day). This could be due to the fact that in the photolysis process of Ni -MFA, the Ni²⁺ ions oxidizes to Ni³⁺ (high radiation) readily and these ions causes photo degradation of the polymer chains to form carbonyl groups following the Norrish type 1 reactions

Table 2: Effect of UV exposure on mechanical properties of Ni- MFA blended PP films

S.No.	Sample ID	Tensile strength (MPa)	Elongation at break (%)
1	PP Virgin-MD	50.17	20.07
2	PP Virgin TD	48.25	139.67
3	PP-MFA 1% D0 MD	48.46	18.97
4	PP- MFA 1% D0 TD	35.80	97.56
5	PP- MFA 1% D1 MD	28.17	10.76
6	PP- MFA 1% D1 TD	18.96	47.98
7	PP- MFA 1% D2MD	Brittle	Brittle
8	PP- MFA 1% D2 TD	Brittle	Brittle
9	PP- MFA 2% D0MD	36.87	14.98
10	PP- MFA 2% D0 TD	33.13	80.67
11	PP- MFA 2% D1MD	21.98	9.78
12	PP- MFA 2% D1 TD	13.87	67.45
13	PP- MFA 2% D2 MD	Brittle	Brittle
14	PP- MFA 2% D2 TD	Brittle	Brittle
15	PP- MFA 3% D0 MD	20.54	8.10

16	PP- MFA 3% D0 TD	6.43	80.76
17	PP- MFA 3% D1 MD	Brittle	Brittle
18	PP- MFA 3% D1 TD	Brittle	Brittle
19	PP- MFA 3% D2 TD	Brittle	Brittle
20	PP- MFA 3% D2 TD	Brittle	Brittle

3.2. Thermal properties

3.2.1. Differential scanning Calorimetric analysis

The differential scanning calorimetric data pertaining to the melting point and degree of crystallinity of Ni- MFA blended PP film before and after exposure to accelerated UV is presented in Table 3

The virgin PP shows its melting point at 165.30°C. On the incorporation of Ni- MFA, the melting point is found to change slightly due to the presence of additive in PP matrix. In case of the PP- Ni MFA samples exposed to UV for three days a marginal decrease in the melting point from 164.87 to 154.94°C was observed. This could be due to the faster photo degradation of PP films in the presence of Ni -MFA additive. Corresponding Δ H peak get broadening indicates the formation of low molecular weight species due to photo degradation. The Percentage of Crystalline decreases by increasing the additive concentration. It was observed that the degree of crystallinity of PP films with 3 % Ni -MFA decreases from 100 to 64 when the samples were exposed to UV for 5 days. These results are in agreement with the mechanical properties data thus revealing higher degradation rate at higher additive percentage.

Table 3: Effect of UV exposure on melting point of Ni-MFA blended PP films

S.No.	Sample ID	Melting	Degree of
		Temperature °C	crystallinity
1.	PP Virgin	165.30	100
2.	PP-Ni MFA-1 D0	164.87	97
3.	PP- Ni MFA-1 D1	163.16	93
4.	PP- Ni MFA-1 D2	162.46	89
5.	PP- Ni MFA-1 D3	160.74	86
б.	PP- Ni MFA-2%D0	165.57	95
7.	PP- Ni MFA-2% D1	162.98	90
8	PP- Ni MFA-2 %D2	161.98	86
9	PP Ni -MFA-2% D3	160.54	81
10	PP- Ni MFA-3% D0	165.27	86
11	PP- Ni MFA-3% D1	158.67	79
12	PP- Ni MFA-3% D2	156.78	70
13	PP- Ni MFA-3% D3	154.94	64

3.2.2. Thermo Gravimetric Analysis (TGA)

The thermo gravimetric analysis of PP with Ni -MFA additive is summarized in Table 4. The results show that the initial decomposition temperature of PP after blending with Ni-MFA decreases significantly. The increase in percentage of additive further decreases the initial decomposition temperature. In fact about 48°C decrease in initial decomposition temperature was observed with 3% additive concentration. This is because of the initiation of degradation due to the presence of metal ions. The degradation due to UV exposure involves the chain scission and formation of carbonyl groups following the of Norrish type 1 reaction. However, there is a significant increase in ultimate decomposition temperature with increasing the concentration of Ni -MFA in PP films. It was observed that about 50°C increase in ultimate decomposition temperature for PP films with 3% additive. This could be due to the formation more stable metal complexes on addition of Ni -MFA.

S.No.	Sample ID	Initial Decomposition Temperature(°C)	Ultimate Decomposition Temperature (°C)
1.	PP Virgin	449.25	498.5
2.	PP-1%Ni MFA- D0	439.15	503.3
3.	PP-1% Ni MFA-D1	421.65	509.6
4.	PP-1% Ni MFA-D2	412.45	515.6
5.	PP-2% Ni MFA-D0	434.8	524.4
6.	PP-2% Ni MFA-D1	430.5	532.2
7.	PP-2% Ni MFA- D2	425.7	539.5
8.	PP-3% Ni MFA-D0	430.3	542.9
9.	PP-3 % Ni MFA-D1	429.0	546.9
10.	PP-3% Ni MFA-D2	401.5	547.9

Table 4: Effect of UV Exposure on Thermal degradation of Ni- MFA blended PP films

3.3. Optical property

The results of optical properties of Ni-MFA blended PP before and after exposure to UV radiation are given in Table 5.

It is evident that with the increase in additive concentration there was a decrease in transmittance level, which is due to the carbonyl formation in the process of photo oxidative degradation of PP film. In case of the films containing 3% additive possess low transmittance and high haze. As the UV exposure time increases the % haze and luminous transmittance decreases which could be due to the faster rate of degradation

Table 5: Optical properties of PP	- Ni MFA samples before a	nd after exposure
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S. No	Sample Identification	Luminous Transmittance %	Haze%
1	PP Virgin	94.1	20.4
2	PP-MFA-1%D0	92.65	23.32
3	PP-MFA-1%D1	90.32	28.56
4	PP-MFA-1%D2	87.70	34.76
5	PP-MFA2%D0	90.76	29.54
6	PP-MFA-2%D1	86.95	35.56
7	PP-MFA-2%D2	Become Brittle	Become Brittle
8	PP-MFA-3%D0	85.34	43.90
9	PP-MFA-3%D1	Become Brittle	Become Brittle
10	PP-MFA-3%D2	Become Brittle	Become brittle

3.4. Fourier Transforms Infrared Spectroscopy (FTIR)

The characteristic peak absorptions of virgin PP film and multi functional additive (MFA) are given in Table 6 and 7 respectively. The FTIR spectra of MFA, PP are shown in Fig.7 and 8. PP with different percentage of additive is given in Fig. 9-11.

As shown in Fig. 7 and 8 a peak at around 1712 cm^{-1} corresponding to carbonyl group of MFA was observed for PP films with 1%, 2% and 3% additive. It can be seen from the figure that the absorption intensity increases with increasing the concentration of the additive from 1% to 3%. On exposure of the films to the accelerated UV radiation further increases the intensity which is

due to the formation of new carbonyl groups on photo degradation involving the chain scission following the Norrish type 1 reaction.

	Absorption bands (cm ⁻¹) and their peak assignments	
S.No.	PP (Polypropylene)	
1.	973	-CH ₂ Rocking Vibration
2.	997	-CH ₃ Rocking Vibration
3.	1167	-CH ₃ symmetric deformation
4.	1454	-CH ₂ symmetric deformation
5.	1167	-CH ₃ symmetric deformation
6.	2929	-CH ₂ anti symmetric deformation

Table 6: Characteristic peak values in FTIR spectra for virgin PP

Table 7: Characteristic peak values in FTIR spectra for MFA

Absorption bands (cm ⁻¹) and their peak assignments Multifunctional Additive		
2723	-C-H out of plane bend	
2922	C-H stretching	
1432	-C=C stretching	
1377	-CH ₃ symmetric deformation	



Fig.7 FTIR spectra of MFA (Nickel 12- hydroxyl oleate)



Fig.8 FTIR spectra of virgin PP



Fig.9 Comparison FTIR spectra of PP- Ni MFA in presence of one day UV Exposure



Fig.10 Comparison FTIR spectra of PP- Ni MFA in presence of two day UV Exposure



Fig.11 Comparison FTIR spectra of PP- Ni MFA in presence of three day UV Exposure

3.5. Scanning Electron Microscopy

The scanning electron microscopic analysis of fractured surface of PP, PP- Ni MFA film is presented in the Fig. 12 and Fig.13. The SEM micrographs of PP- Ni MFA blended films with 1, 2 and 3% of additives show the uniform dispersion of additive in the polymer matrix.

The scanning electron micrographs of fractured surface of films after UV exposure given in Fig. 14-16 show the brittle mode of fracture. It can be seen that the surface agglomerates were formed which could be due to the photo



Fig.12 virgin PP

degradation involving chain scission and deterioration of molecular chains. More surface agglomerations could be seen in the case of PP- Ni -MFA indicating the faster rates of photo degradation. Also, the brittleness of the surface increases with increasing the exposure time and percentage of additive concentration.



Fig.13 PP -1% Ni-MFA without UV Exposure



Fig.14. PP-1% Ni MFA D3



Fig.15. PP-2% Ni MFA D3



Fig.16. PP-3% Ni MFA D3

3.7. Subsequent bio-degradation of the photodegradable film

Biodegradation testing in the laboratory-scale compost was conducted according ASTM 5338-98. A series of twelve composting vessel (three test specimen, blank, negative and positive control) were repeatedly tested twice time. Mixture of testing organic fraction solid compost (600 g dry basis) and test specimen (10g on dry basis) were introduced and incubated at $58\pm2^{\circ}$ C The air flow rate controlled between 15 ml/min .The CO₂ evolved was absorbed by 0.012 M Ba (OH) ₂ and the amount of CO₂ was determined by titrated the solution with 0 .05 M HCl (frequency every or the first 2 to 3 weak and after every 1 to3 weak).

The sample of PP film blended with Ni-MFA was oxidized by oven ageing, and the fragments incubated with cultures of a bacterium aspergillums niger and pencillium funculosum.

Calculation:

1. The total carbon content (Ci) in the test material was determined by elemental analysis.

2. Observation

(1) Conditions of reaction mixtures

2. Cumulative CO_2 produced in grams (Cg test) from the test sample, was calculated.

3. Cumulative CO_2 produced in grams (Cg blank) from the blank (compost) sample was calculated.

4. Percentage of biodegradation was determined by dividing the net average gaseous carbon produced in the test compound by the original average amount of carbon in the test compound and multiplying it by 100.

$$\frac{Mean C_g(test) - Mean C_g(blank)}{C_i} \times 100$$

Where, $C_g =$ amount of gaseous carbon produced, gm,

 C_i = amount of carbon in test compound added, gm

3.7.1. Observation for biodegradability test as per ASTM D-5338

1. Sample detail: Light Yellow Color photodegraded Film

Origin of compost : Live stock excrement, municipal and vegetable waste

Reaction Temperature	$:58^{0}C(\pm 2^{0}C)$
Dry Solid (%)	: 52

Volatile Solid (%)	: 19
Air flow rate	: 100 ml/min
Test duration (day)	: 50 days
Reference material	: Cellulose
Volume of reaction vessel	: 3000 ml
Moisture percentage in compost	: 27 %

3. Results: The curve of biodegradation is shown in Fig. 17 and Percentage biodegradation relative to positive reference.



Fig.17. Bio-degradation curve for the photodegradable product of PP-Ni MFA

The PP- 3% Ni MFA was initially subjected to photo degradation and subsequent biodegradation using compost method was showing quit sufficient amount of biodegradation i.e. ~20%(percentage of biodegradation) within 45 days. The correlation can be done from the above studies that an increase in the number of days could increase in the percentage biodegradation. This of shows that the photodegradable product will lead to the biodegradation and this can be increased if the photo degradation will be higher at the initial stage. The reason for the biodegradation could be the formed low molecular weight product will lead to fragment easily by enzymatic action during biodegradation.

4. CONCLUSION

The new class of biodegradable additives was successfully synthesized and their performance of photo degradability was evaluated based on mechanical, thermal properties and structural analysis by FT-IR spectroscopy. The mechanical properties like Tensile strength and elongation at break marginally affected by the addition of Nickel- MFA, but the UV exposure shows the drastic change in elongation compare to tensile strength in both machine and transverse direction. The elongation at break is lower in the case of machine when compared to transverse direction. The polymer gets brittleness irrespective of Ni MFA concentration, i.e., all three compositions PP-Ni MFA 1%, 2% and 3% shows brittleness on eight day. The rate of degradation is higher in case of 3%Ni MFA blended PP compared to 2% and 1%. The DSC result shows the low molecular weight product formation during the UV exposure. The luminance transmittance decreases upon UV exposure due to photo degradation. FT-IR shows the clear indication of photo degradation by the formation of carbonyl group during irradiation. The effect of additive fractured morphology in SEM Ultimately Analysis. the new type of multifunctional additive shows а good compatibility with the polymer, inducing the photo degradation and leads to low molecular weight product, i.e., reduction in the length of the polymer chain. The low molecular weight products favor the increase of rate of bio degradation.

It can be concluded that addition of small amount Nickel 12 -Hydroxyl Oleate effectively influences the photo processes in PP. It has been found that photo-oxidative degradation of PP more efficient in the presence of transition metal contains Ni- MFA additives is nor more strong and more weak, especially in sample with its very low content. In UV-irradiated PP cross linking and carbonyl group formation are increased in the presence of the initiators. The present study indicates that all the transition metal 12-Hydroxyloleate, promote photodegradation of PP. The photo reaction affected PP

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Nickel- MFA within six days. It can be concluded that besides metal content, the chain length of carboxylate also plays a vital role in PP for photodegradation.

It was concluded that polypropylene modified with 1% 2% and 3% was biodegraded within 45 days; the result revealed that 3% Ni- MFA modified polypropylene was biodegraded 20%.

Result obtained suggest, that effectivity of photoinitiator depends on its chemical structure, concentration life-time of its excited states and stability of radicals formed during their photolysis.

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