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### **Synthesis of (E)-N-(2-aminoethyl) docos-13-enamide: A dual functional additive**

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#### **ABSTRACT**

*With ever increasing demand for faster production speeds to remain global competitiveness, the packaging industry relies on incorporating slip additive to polyolefin. Though reduced coefficient of friction fastens the production, the quality of film obtained is doubtful. The property enhancement of film can be achieved by incorporation of nanofiller into polymer matrix such as organoclay. So a dual functional additive has been synthesized which induces slip into film as well as modify the clay and acts as an intercalating agent. The synthesis was confirmed by FTIR, NMR, MS and CHN analysis and COF was determined to ascertain slip properties. The characterization of organoclay obtained by incorporation of this additive by XRD and TGA shows its intercalating abilities. The characterization of organoclay obtained by incorporation of this additive by XRD and TGA shows its intercalating abilities.*

**Keywords:** coefficient of friction, slip additive, organoclay

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#### **INTRODUCTION**

Polymer additives are important areas of innovation for packaging materials. An additive is a material that is added to a polymer melt to enhance processability, performance, or appearance [1]. Polymeric materials are used in packaging products such as films, molded containers, and cushioning. Packaging materials benefit greatly from inclusion of additives to polymers to enhance processability and performance [2]. The packaging industry, for which polyolefin is one of the key materials, demands faster production speeds to remain global competitiveness. With these increased line speeds the polyolefin films are faced with more demanding performance requirements where controlling the friction between the equipment and travelling to film surface is critical to the successful packaging application [3]. The easy and fast processability can be achieved by incorporating a slip agent into the polymer matrix, which migrates to the film surface resulting in reduction of the coefficient of friction (COF) [4]. Although many substances can lower COF in polyolefin films, commonly used commercial slips are usually unsaturated, long-chain amides. The common chemistries are oleamide and erucamide, called primary amides, which are popular because they migrate rapidly, create low COF at modest addition rates, and are relatively inexpensive [5,6]. However, polyolefin find limited uses in their virgin form because of their low level of many desirable properties for end applications. One of the most promising ways of enhancing the properties of polymers has been realized through the production of polymer nanocomposites wherein nanosize inorganic particles such as clay are dispersed in an organic polymer matrix in order to improve the performance properties of the polymer. The relatively weak forces between the interlayers of clay facilitate intercalation of various molecules including polymers between the layers of the clay particles. But the existence of ionic bonds and the ability to form hydrogen bonds with water molecules make clay highly hydrophilic and thus become incompatible with the organic polymers. Hence, to disperse the silicates, it is necessary to modify it with intercalating agent [7,8].

While additives account for only a small percentage of the total weight or volume of polymer processing, they contribute significantly to the performance. Often, manufacturers rely on numerous different additives to achieve the desired functions but with different physical and chemical properties involved, interactions and possible conflicts between different additives are a concern, as are unwanted secondary effects. The development of multifunctional additives that address two or more performance issues at the same time is one approach that many suppliers have taken to overcome some of these challenges. Accordingly numerous attempts have been made to add functionality to the slip additive but most of them are restricted to issues related to moisture penetration (Ampacet 101499), extending product shelf life (Ampacet 101499), gloss improvement (Ampacet 102286), taste and odour improvement (Croda's Incroslip), colour and clarity improvement (Ampacet 102286) and scratch resistance (Evonik's Tegomer Antiscratch 100), etc. However, a slip additive also functioning as an intercalating agent is not reported till date and this justifies the scope of the present research. This slip additive synthesized with intercalating abilities can be then used to produce polyolefin nanocomposite.

## MATERIALS AND METHODS

Though Erucamide and Oleamide are the most commercially important slip additives, Erucamide has to great extent replaced Oleamide because of its lower volatility, superior colour and heat stability, improved organoleptic properties, better blocking performance and a lower final co-efficient of friction [9]. In this study, we have synthesized dual functional erucamide slip additive from its hydroxyl fatty acid which can also function as an intercalating agent. Our aim was to understand and optimize the reaction parameters for subsequent production and characterization.

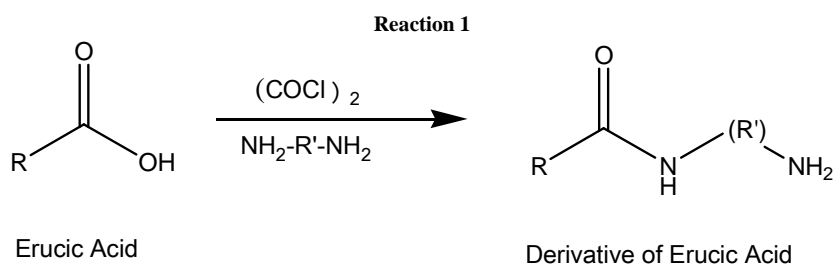
### 2.1 Materials

All the chemicals used for synthesis and analysis; oxalyl chloride, 1,2 ethylenediamine, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), hydrochloric acid were of analytical grade and purchased from S.D.Fine Chemicals Ltd., Mumbai, India. Erucic Acid is provided as a free sample from VVF Pvt. Ltd., Mumbai, India. The untreated bentonite clay having a cation exchange capacity (CEC) of 104 mequiv/100gms was given by Crystal Nanoclay Pvt. Ltd., Pune, India.

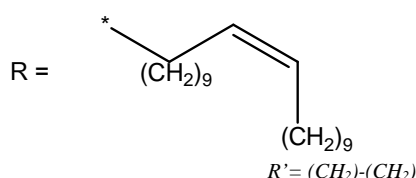
### 2.2 Reaction procedure

Under a nitrogen atmosphere, the solution of erucic acid (5 gm, 1mol) in  $\text{CH}_2\text{Cl}_2$  (34 mL) was cooled to  $0^\circ\text{C}$ , and oxalyl chloride (64 mL, 4 mmol) was added. The reaction mixture was stirred at room temperature for 8 hours and concentrated using Rotavapour to give the residue. Under a nitrogen atmosphere the solution of 1, 2 ethylenediamine (8.5gm, 8 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was cooled to  $0^\circ\text{C}$  and the residue (erucic chloride) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was slowly added over a period of 2 hours. The reaction mixture was stirred at room temperature for 5 hours and poured into distilled water. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine till neutral pH, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuum. Purification of the residue was done by column chromatography [10,11].

The scheme for the synthesis of amino functionalized amides is given below:



where



### 2.3 Preparation of Organoclay

Organophilic clay was prepared from hydrophilic clay by means of an ion exchange reaction between organic cations such as alkyl ammonium ions and inorganic cations. (reference) 30 gm Na-MMT clay (CEC of 104 meq/100 gm) was dispersed into 3000 ml of hot water at 80°C by using a homogenizer. In another beaker, stoichiometric equivalence (as per CEC of clay) of additive and hydrochloric acid were added to 1000 ml demineralised water and heated to 80°C. This additive dispersion was then added slowly to the hot clay water solution under vigorous stirring for 1 hour to yield precipitates. The precipitate was collected and washed with hot water till no chloride traces were detected by addition of silver nitrate. The resulting organoclay was dried at 60 °C in an air circulating oven at for 24 hours and grinded into the powder to obtain organically modified clay. The organoclay was passed through a sieve of 200 mesh.

### 2.4 Preparation of film sample

The additive (500ppm) and LLDPE were melt-blended using co-rotating twin screw extruder (Model MP 19 PC, APV BAKER, U.K.) having L/D ratio of 25:1. The screw speed was maintained at 60 rpm and the temperature profile for compounding was 130, 140, 150 and 160°C for four zones and 160°C for the die zone. The extrudate from the screw compounder was quenched in water and pelletized. The extruded pellets were dried and blown into films using a fabricated small scale blown film extruder at Duco Organics Pvt. Ltd., Taloja, India. The temperature profile was same as that for extrusion whereas the nip roll speed was 6m/min.

### 2.4 Analytical Methods

The raw material erucic acid was analysed for its respective physical and chemical characteristics and accordingly reported in the **Table 1**.

**Table 1. Analysis of Erucic acid**

Sr. no.	Property	Value
1.	Appearance at 35 °C	Pale yellow liquid
2.	Acid value, mg KOH/gms	166.1
3.	Saponification value, mg KOH/gms	167.2
4.	Ester value	1.1
5.	Color in 51/4'' cell	Y=2.0, R=0.2
6.	Iodine value, mg I <sub>2</sub> /gms	76.1
7.	Unsat matter, %	0.75
8.	Purity, %	90

The amino functionalized erucamide was prepared and optimized by taking different molar ratios of acid and amine. The effect of varying molar ratios is shown in **Table 2**.

**Table 2. Optimization of mole ratio**

Acid : Amine	Acid Value	Amine Value	Appearance	Yield %
1 : 1	0	87	Orange sticky solid	60
1 : 1.5	0	105	Yellow sticky solid	84
1 : 2	0	123	Yellow sticky solid	68
1 : 2.5	0	110	Pale yellow sticky solid	62
1:4	0	137	Yellow solid flakes	80
1:8	0	168	Yellow solid flakes	86

Acid Value and Amine Value was done as per AOCs method (Cd-3a 63) [12]. The structure of additive was confirmed by FTIR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS and CHN analyzer. The FTIR spectrum of the sample in KBr pellets was recorded using (company name) ATR PRO 450 S spectrometer. The NMR characteristics were done using Bruker 300 Ultrashield NMR spectrometer which was calibrated using tetramethylsilane as internal standard and CDCl<sub>3</sub> as solvent at 300MHz. The CHN analysis was carried out using Thermo Finningan CHNS analyzer. The Thermo Finnigan LCQ Advantage Max instrument was used to get the mass of the product. To ascertain the slip properties of the product, the coefficient of friction was measured as per ASTM D1894.

However, the organoclay was characterized by XRD and TGA. XRD patterns were obtained with a D8 Advanced Bruker X ray diffractogram from 2 ° to 30 ° at a scan speed of 0.2 sec/step. The thermal stability of organoclay was

studied by SHIMADZU DTG-60H simultaneous thermogravimetric apparatus. The samples were heated under nitrogen atmosphere at a heating rate of 20°C/min from 0 °C to 600°C.

## RESULTS AND DISCUSSION

### 3.1 Characterization of Additive

To get the desired compound amino functionalized erucamide, different molar ratios of acid to amine were tried as depicted in **Table 1**. The molecular and structural characterization was confirmed by FTIR spectra (**Figure 1**), <sup>1</sup>HNMR spectra (**Figure 2**), <sup>13</sup>CNMR spectra (**Figure 3**), LCMS (**Figure 4**), and CHN analysis (**Figure 5**).

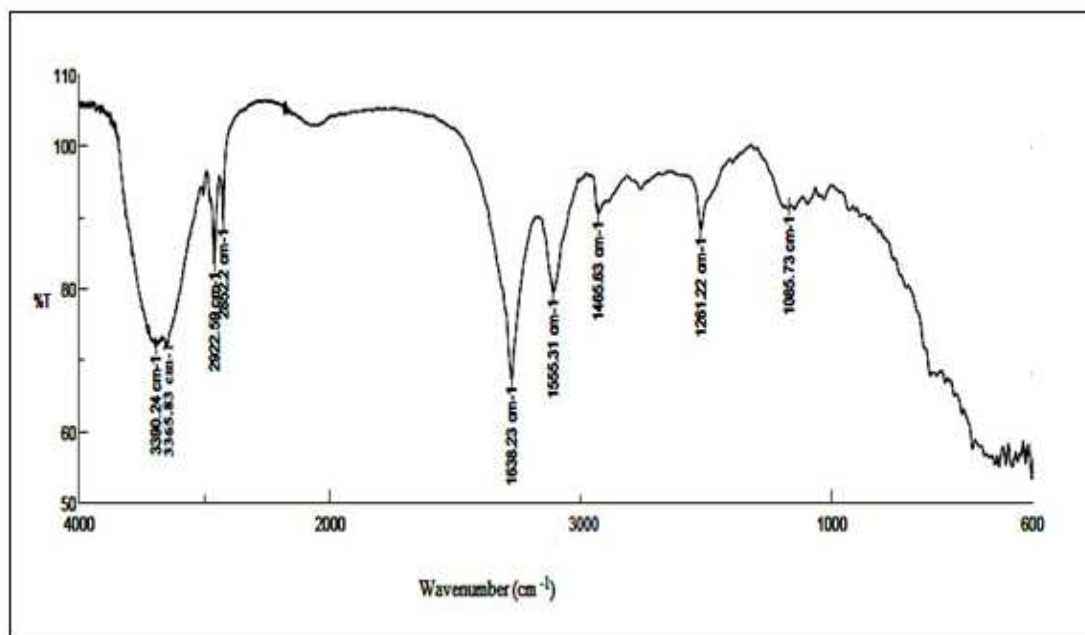


Figure 1. FTIR spectra of amino functionalized erucamide

IR spectra:- 3390, 3305 $\text{cm}^{-1}$ ( $\text{NH}_2$ ) ; 1638  $\text{cm}^{-1}$ (amide CO); 1261  $\text{cm}^{-1}$ (C-N stretching); 2922  $\text{cm}^{-1}$ (aliphatic CH).

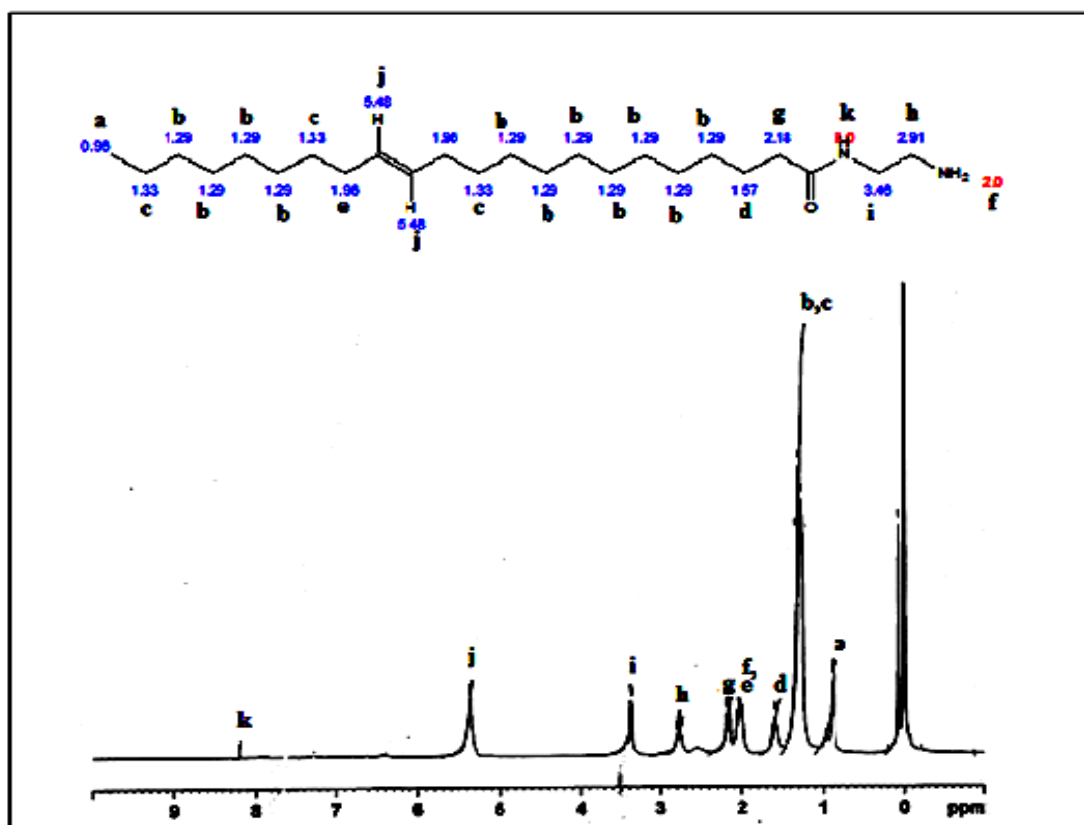


Figure 2.  $^1\text{H}$  NMR spectra of amino functionalized erucamide

$^1\text{H}$  NMR spectra:-  $\delta$  ppm: 0.96 (3H, t);  $\delta$ : 1.29-1.33 (28H, m);  $\delta$ : 1.57 (2H, t);  $\delta$ : 1.96 ( $\text{NH}_2$ , s);  $\delta$ : 1.96 (2H, m);  $\delta$ : 2.18 (2H, t);  $\delta$ : 2.91 (2H, t);  $\delta$ : 3.46 (2H, t);  $\delta$ : 5.48 (2H, m);  $\delta$ : 8.0 (NH, s).

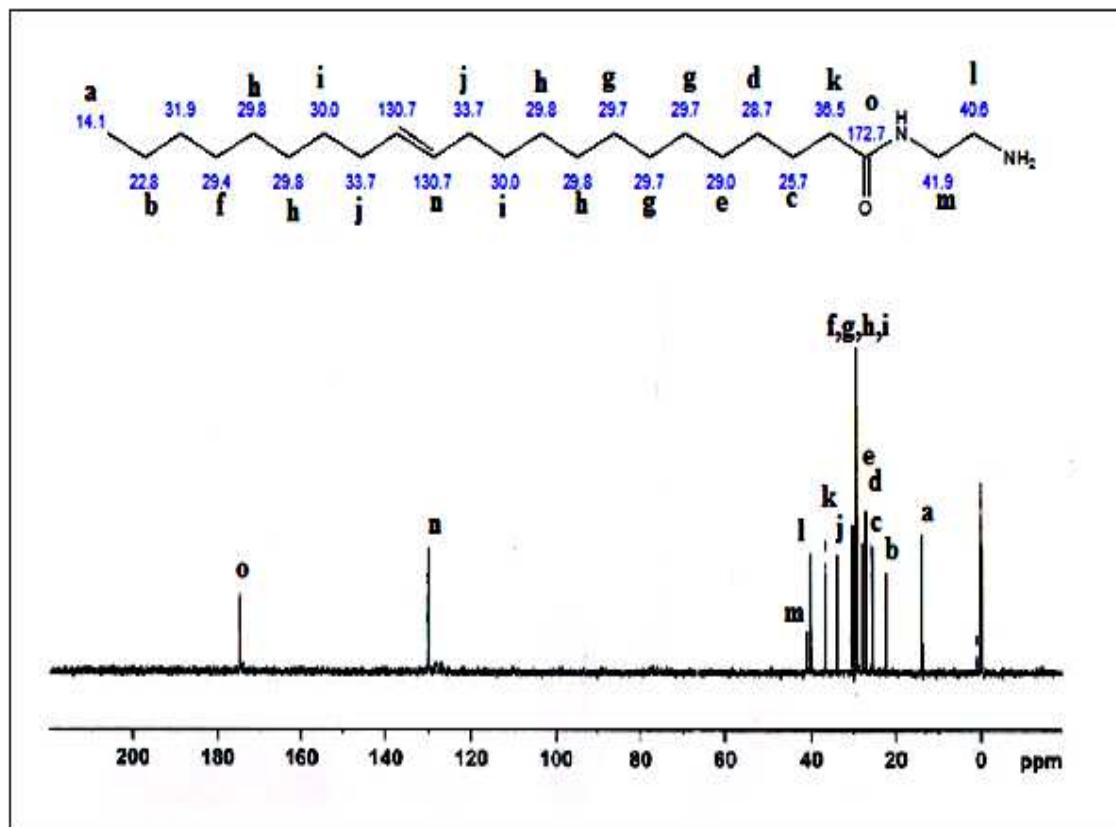


Figure 3.  $^{13}\text{C}$  NMR spectra of amino functionalized erucamide

$^{13}\text{C}$  NMR spectra: -  $\delta$  ppm: 14.1, 22.8, 25.7, 28.7, 31.9, 36.5, 40.6, 41.9 (1C); 33.7, 130.7 (2C); 29.8-30.0 (9C); 172.7 (1C-CO).

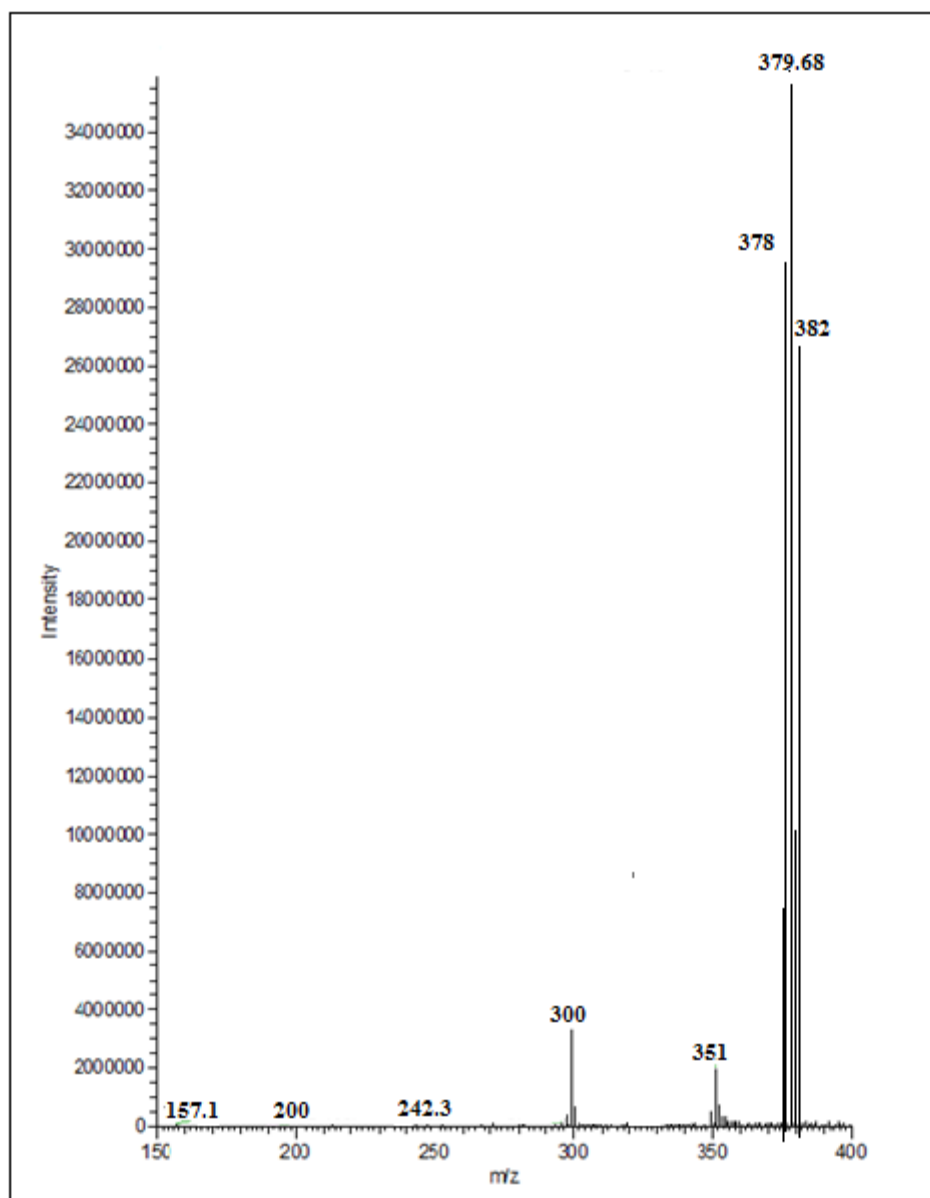


Figure 4. LCMS of amino functionalized erucamide

LCMS:- Molecular ion peak M+1 is 381 and M-1 is 379 which indicates that the molecular weight of the  $C_{24}H_{48}N_2O$  is 380.

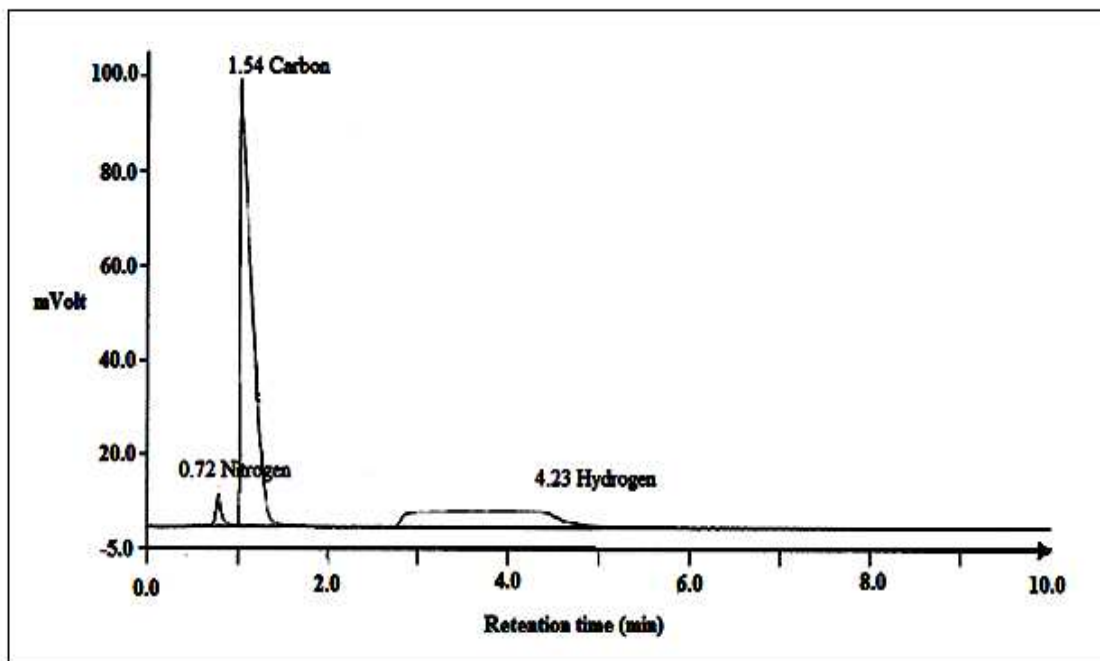


Figure 5. CHN analysis of amino functionalized erucamide

CHN analysis:- (% cal, % found) : (79.1, 79.0); H : ( 13.1., 12.89); N : (7.8, 8.11)

### 3.2 Measurement of COF

The COF was measured as per ASTM D1894. Prior to COF measurement, all film samples were allowed to age for 7 days at room temperature after extrusion to achieve equilibrium surface concentration. The static COF was found out to be 0.24 whereas the kinetic COF was 0.2 (**Figure 6**) which is better than that reported by Adam Maltby where the value for kinetic COF for LLDPE blown film containing 1000ppm additive was quoted as around 0.3 [13].

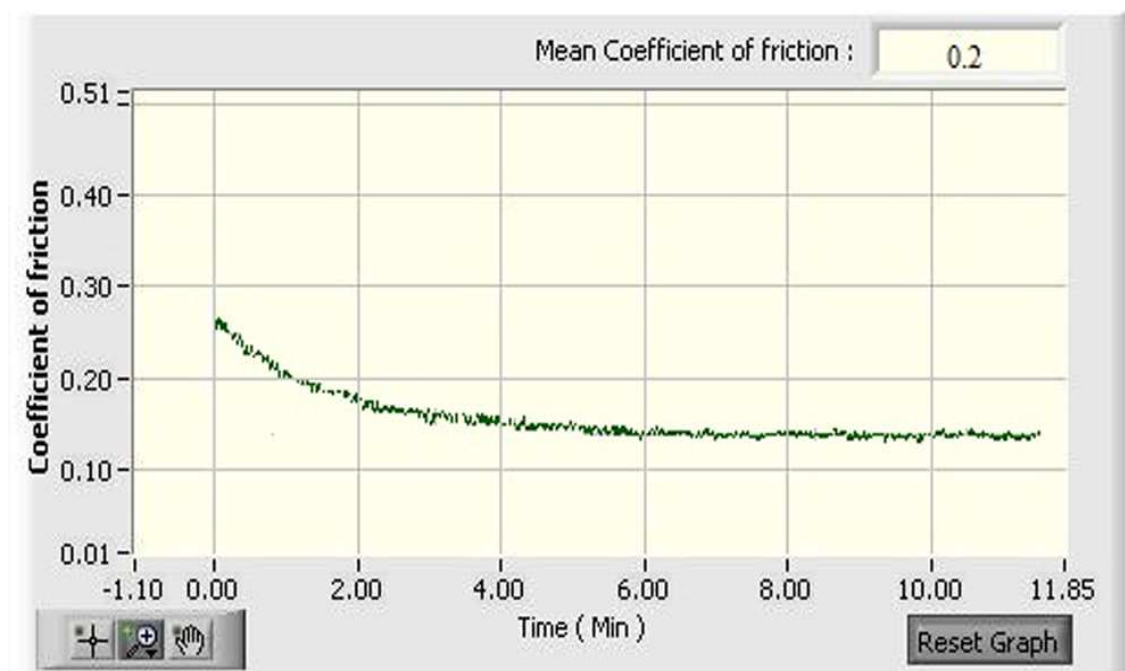


Figure 6. COF of amino functionalized erucamide



### 3.2 Characterization of Organoclay

The key parameter to assess the successful intercalation and exfoliation due to organic modification of clay is basal spacing. After modification of clay, the basal spacing increases and an increase of the interlayer distance leads to a shift of the diffraction peak toward lower angles [14]. This can be confirmed from the XRD diffractograms for untreated and treated clay as depicted in **Figure 7**. The untreated MMT showed a peak at  $5.98^\circ$ , corresponding to the interlayer spacing of  $14.57 \text{ \AA}$ , which was then increased to  $27.87 \text{ \AA}$  showing a peak at  $4.86^\circ$  for organically modified clay. This enhanced *d*-spacing may be attributed to presence of large hydrophobic groups on the surfactant and the decrease in surface energy of MMT. Also the disappearance of two original peaks of unmodified clay at  $8.86^\circ$  and  $11.6^\circ$  indicates better exfoliation of organoclay.

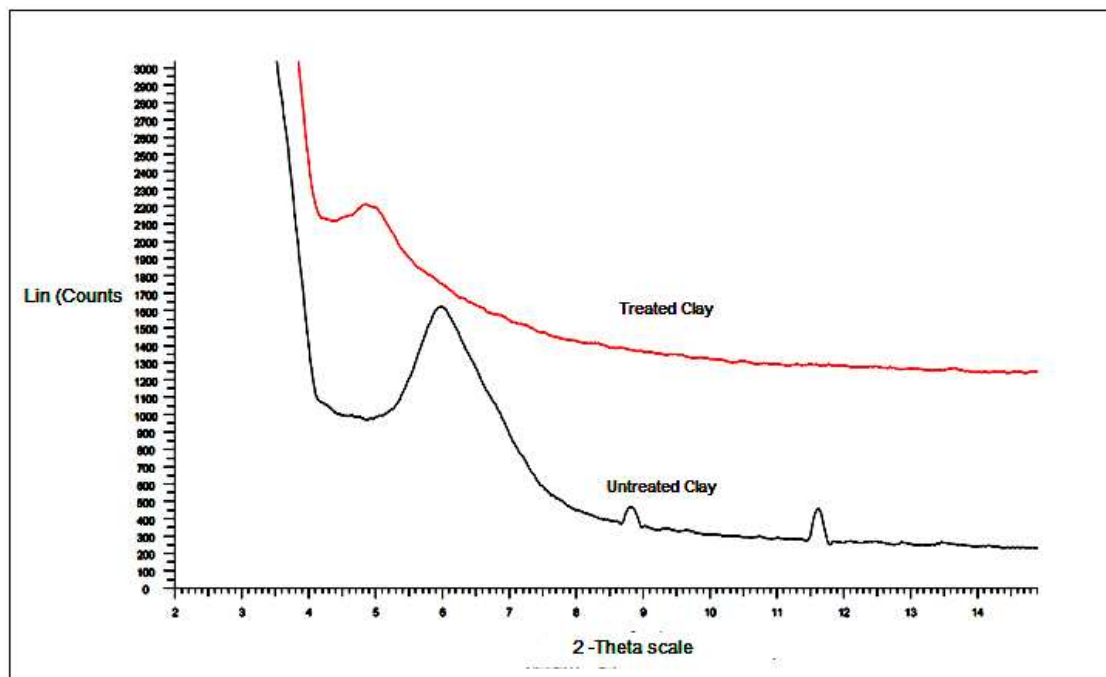


Figure 7. X ray analysis of untreated and treated clay

The low thermal stability of ammonium surfactants presents a problem for melt compounding and processing of polymer nanocomposites. Thermal degradation during processing could initiate/catalyze polymer degradation, in addition to causing a variety of undesirable effects during processing and in the final product. TGA gives us information about the thermal stability of the organoclay. The TGA curves for unmodified and organically modified clays are shown in **Figure 8**.

It is noted that the TGA of the unmodified montmorillonite has three mass loss steps: Between ambient and  $100^\circ\text{C}$ , at  $135^\circ\text{C}$  and at  $450^\circ\text{C}$ . These mass loss steps are attributed to desorption of water from the clay, dehydration of the hydrated cation in the interlayer and the dehydroxylation of the montmorillonite respectively. The first and second decomposition steps are important for utility of such organically modified montmorillonites in polymer-based composite materials prepared via melt state processing, as most polymers are processed within this temperature range. Hence, these new organically modified MMT can be used for preparing organic-inorganic hybrids by melt processing with thermoplastic polymers such as polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA) and others which are relatively polar [15].

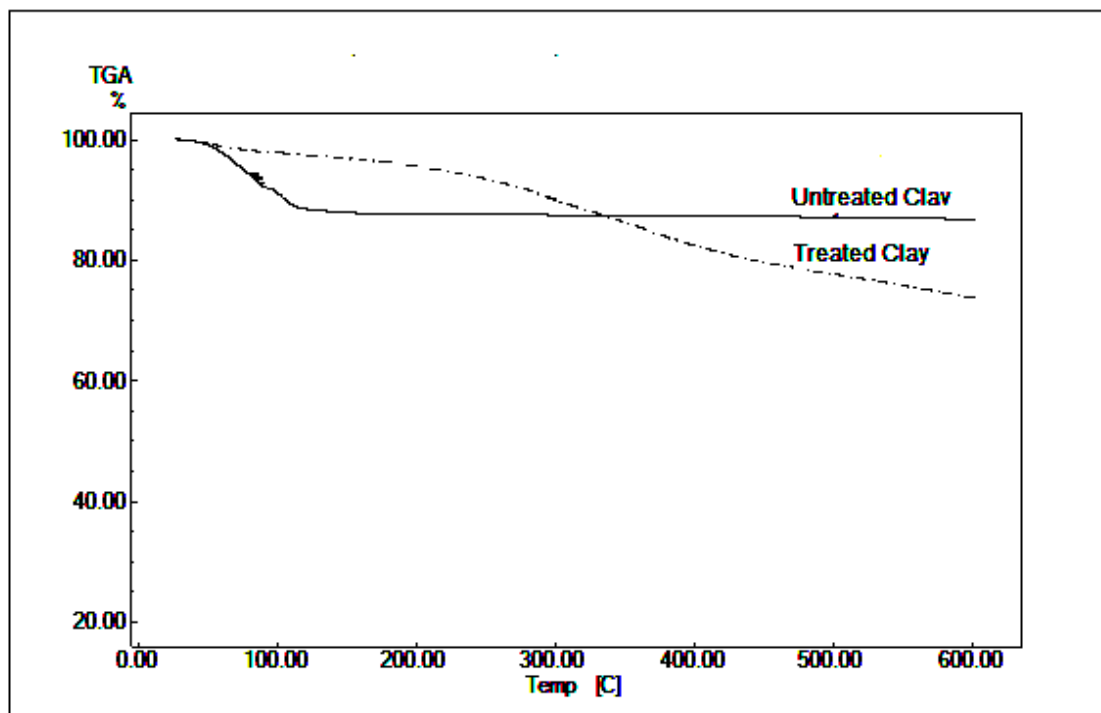


Figure 7. TGA analysis of untreated and treated clay

### CONCLUSION

To meet the requirement of increased speed and excellent film quality, the dual functional additive was synthesized and characterized. The erucic acid was converted into amino functionalized erucamide by reacting it with oxalyl chloride and 1,2 ethylenediamine. The FTIR spectra show presence of free amines at 3390, 3305  $\text{cm}^{-1}$  and amide linkage at 1638  $\text{cm}^{-1}$ . The molecular structure was further confirmed by  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR. The MS data clearly indicates the molecular weight as 380 which is equivalent to the theoretical one. The number of carbon, hydrogen and nitrogen obtained from CHN analyzer also matches with the theoretically calculated. The XRD diffractograms for untreated and treated clay shows increased interlayer spacing which is indicative of intercalation ability. Also the TGA graphs points to the fact that the modified MMT can perform well in the processing temperature range without the risk of degradation.

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