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Exploring the simultaneous effect of organoclay and controlled peroxide curing on thermal stability of LLDPE/EMA blend

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ABSTRACT

The effects of organoclay, Cloisite®20A on the thermal degradation behavior of LLDPE/EMA blends were investigated using thermogravimetric analysis in nitrogen atmosphere. Organoclay, Cloisite®20A was melt blended with LLDPE/EMA system at different loadings by varying the sequence of addition. The kinetics of thermal degradation of the nanocomposites had also been studied. Experiments were carried out at heating rates of 5, 10, 15 °C/min in nitrogen atmosphere. Kissinger–Akahira–Sunose method has been used to determine the activation energies of degradation. The loading of Cloisite®20A and their sequence of addition has significant effect on the thermal stability of LLDPE/EMA blends. The results showed that Cloisite®20A slightly decreases the initial decomposition temperature (T_{onset}) of LLDPE/EMA blend but significantly enhances the maximum decomposition temperature (T_{max}). Addition of dicumyl peroxide (DCP) to the LLDPE/EMA/Cloisite®20A further increases the thermal stability of the nanocomposites. Overall, the thermal stability of the LLDPE/EMA/Cloisite®20A nanocomposites is the function of the extent and sequence of clay addition as well as extent of DCP loading.

1. Introduction

The study of thermal degradation and stabilization of polymer blends and composites are very important to predict their suitability in the specific field of application. It is also important for designing and fabrication process because the threshold temperature for decomposition determines the upper limit of the fabrication temperature. The thermal stability and mode of decomposition of polymer blends and composites are largely dependent on the chemical structure of the repeating units of the polymers as well as the nature of interactions between polymers and reinforcing materials [1]. Thermogravimetry is the most widely used and accepted methods for studying the thermal properties of polymer. It measures the weight loss or gain of a material as a function of temperature. The integral (TGA) and derivative (DTG) thermogravimetric curves provide information about the degradation pattern, number of stages of thermal break down, weight loss of the material in each stage, threshold temperature, stability and extent of degradation of the polymeric materials.

The thermal degradation of polymers, polymer blends and nancomposites have been extensively studied by various researchers [2–9]. From literature survey it was found that the thermal decomposition of LLDPE involves random chain scission, leads to the formation of cross-linking and branched chain that compete with the backbone cleavage reactions [10]. Basuli et al. reported that thermal decomposition of ethylene methyl acrylate (EMA) copolymer initiates by the hemolytic scission of methoxycarbonyl side groups followed by β scission rather than by main chain scission [11]. The presence of methoxycarbonyl side group makes the β C–C scission easier due to its electronic and steric effects [12]. Thus the loss of methoxycarbonyl side group is the initial degradation step. Scission in ethylene chain is the major degradation step. Recently Borah and Chaki studied the effect of blend ratio and compatibilization on the thermal stability of LLDPE/EMA blends [13]. It was reported that phase morphology has a significant role on the thermal stability of the both uncompatibilized and compatibilized blends. It was also reported that compatibilized blends are thermally more stable than the uncompatibilized one. Jana and Nando also made similar kind of observations for LDPE/PDMS blend [1]. The thermal stability of polymer layered silicate nanocomposites was reviewed by Leszczynska et al. [14]. Basuli et al. reported that in MWNT-EMA nanocomposites, MWNT has stabilizing effect on EMA and increases the onset of degradation [11]. The effect of nanoclay on the morphology and thermal stability of LLDPE/clay nanocomposites was studied by Qiu et al. where it was reported that nanoclay significantly enhances the thermal stability of virgin LLDPE [15]. Hui et al. explored the effect of nano silica and electron beam radiation on the thermal and thermo-oxidative degradation

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Table 1
Sample designations.

Sample code	LLDPE (wt%)	EMA (wt%)	LLDPE-g-MA (wt%)	Cloisite®20A (wt%)	DCP (wt%)	Sequence of clay addition
LLDPE	100	–	–	–		–
EMA	–	100	–	–		–
20AL	100	–	3	5		–
20AE	–	100	–	5		–
3CE40	60	40	3	–	–	–
20AM1/5	60	40	3	5	–	M1
20AM2/5	60	40	3	5	–	M2
20AM2/1	60	40	3	1	–	M2
20AM2/3	60	40	3	3	–	M2
20AM2/7	60	40	3	7	–	M2
3E40/0.3	60	40	3	–	0.3	–
3E40/0.5	60	40	3	–	0.5	–
20AM1/5/0.3	60	40	3	5	0.3	M1
20AM1/5/0.5	60	40	3	5	0.5	M1
20AM2/5/0.3	60	40	3	5	0.3	M2
20AM2/5/0.5	60	40	3	5	0.5	M2

of LDPE/EVA blends [16]. Chuang et al. studied the thermal stability and flammability of LLDPE/EVA/MMT nanocomposites [17].

However, to our knowledge, no investigation has been made to understand the degradation behavior of organoclay filled LLDPE/EMA TPE system. The effect of organoclay on the properties of LLDPE/EMA system, their selective dispersion and distribution has been reported in our earlier communication [18]. In this paper we have studied the thermal degradation behavior of LLDPE/EMA/clay nanocomposites. Detailed kinetic analyses (both isothermal and non isothermal) have been performed to analyze their degradation behavior at different heating rates under nitrogen atmosphere. Finally an attempt has also been made to understand the influence of peroxide curing (DCP at low level) on the thermal stability of LLDPE/EMA/clay nanocomposites.

2. Experimental

2.1. Materials

LLDPE (LLT12) having a density of 0.926 g/cm^3 and MFI (melt flow index) 3.7 g/10 min, was obtained from Haldia Petrochemicals Ltd., India. Commercial grade of EMA, Elvaloy 1330 with 30 wt% of methyl acrylate and a melt flow index (MFI) of 3.0 g/10 min of DuPont, USA was supplied by NICCO Corporation Ltd., India. Dicumyl peroxide (DCP) (Perkadox-BC-40B-PD) having an active peroxide content of 40% was purchased from Akzo Nobel Chemical Company, The Netherlands.

The compatibilizer used for this study is maleicanhydride grafted linear low density polyethylene (LLDPE-g-MA). LLDPE-g-MA was prepared by melt blending LLDPE (100 g) with maleic anhydride (5 g) and dicumyl peroxide (DCP – 40% activity; 0.5 g). The melt mixing was carried out in an internal mixer at 180 °C and 60 rpm for 8 min.

The organoclay Cloisite®20A was purchased from Southern Clay Products Inc. Cloisite®20A is also a natural montmorillonite that has been ion exchanged with dimethyl, dehydrogenated tallow, quaternary ammonium chloride to form an organoclay. The weight loss on ignition of Cloisite®20A was 38 wt%.

2.2. Preparation of nanocomposites and their vulcanizates

Prior to mixing, LLDPE, EMA and clay were dried at 80 °C, 50 °C and 70 °C, respectively, for 12 h in a vacuum oven. The melt blending was carried out in a HAKKE Rheomix OS (Germany) at 140 °C and a rotor speed of 60 rpm by the variation of two different mixing sequences.

In sequence M1, LLDPE and LLDPE-g-MA was first allowed to melt for 2 min; it was followed by EMA (4 min) and nanoclay (4 min). The total mixing time was 10 min. In sequence M2, first LLDPE and LLDPE-g-MA was allowed to melt for 2 min, and it was followed by nano clay for 4 min. Then EMA was added to this mixture and mixed for another 4 min. For dicumyl peroxide (DCP) treated sample, DCP was added to the prepared nanocomposites and mixed for further 3 min. The mixes so obtained were sheeted out in a two roll mill set at 2 mm nip gap.

The sheeted material was then cured in an electrically heated hydraulic press (Moore Presses, George E. Moore & Sons Birmingham Ltd., UK) at 170 °C for 12 min under a pressure of 5 MPa. The mold was allowed to cool under pressure till ambient temperature is attained before removing the rectangular sheet from the mold. The details of the sample and their appropriate designations are given in Table 1.

2.3. Thermogravimetric analysis

Thermogravimetric analyses (TGA) of the nanocomposites were carried out on a TA Instrument's (USA), model Q 50 at various heating rates. The samples (5.5 ± 0.5 mg) were placed in alumina crucibles and heated from room temperature to 600 °C under steady flow of nitrogen (60 ml/min). An empty alumina crucible was used as reference. To study the kinetics of thermal degradation, experiments were carried out at three different heating rates, e.g. 5, 10 and 15 °C/min, respectively. For each sample, three tests were carried out under the same heating rate and the temperatures were reproducible to ±1.0 °C. In this experiment, the temperature corresponding to the 5 wt% loss was taken as the initial degradation temperature (T_{onset}) and the temperature corresponding to the maximum value (peak) in derivative thermogram (DTG) was considered as temperature for maximum degradation (T_{max}). Percentage error in thermal measurements was found to be ±3%. The average values of T_{onset} and T_{max} along with their standard deviations are reported here.

2.4. Kinetic methods

2.4.1. Kissinger–Akahira–Sunose method (KAS method)

This is an isoconversional integral method based on the following equation [19]

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT}$$

where $g(\alpha)$ is the algebraic expression for integral methods.