GRAFTING OF ACRYLAMIDE TO LOW DENSITY POLYETHYLENE DURING MELT PROCESSING

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ABSTRACT: *Acrylamide was grafted in low density polyethylene during melt processing in the presence of a free radical initiator using a torque rheometer in a closed system. Effects of processing time, acrylamide and benzoyl peroxide concentrations were studied. FTIR studies revealed that the degree of grafting increased by an increase in acrylamide concentration. Maximum grafting was obtained at 7 minutes processing time and 1% (wt/wt) peroxide. Increase in acrylamide concentration led to reduction in melt flow index and increase in apparent melt viscosity.*

KEY WORDS: *Low density polyethylene (LDPE), Acrylamide, Melt processing, Macroalkyl radical, Reactive site, Grafting.*

INTRODUCTION

Ceresa and *Watson* for the first time showed that most polymers undergo a rapid reduction in molecular weight on shearing [1,2]. Formation of macroalkyl radicals by application of shear to polymers even in the melt state was subsequently reported [3-5]. These macroradicals react with oxygen and consequently leads to reduction in molecular weight [6]. When the oxygen concentration is limited, for example in a closed mixer, (or in an extruder), alkyl radicals participates in the termination reaction. In polyethylene this reaction leads to molecular enlargement [7]. Therefore, a competing chain scission and crosslinking reactions occur which are clearly dependent on the oxygen concentration in the mixer [7,8].

For many polymers, reactive processing is considered as an effective and economical way of achieving the modification using free radical chemistry [9,10]. Grafting of chemical containing polymerizable groups to polymers in the presence of free radical generators is a typical example [11]. By using this method, it is possible to functionalize polyolefines (e.g., LDPE) for the purpose of modifying certain characteristics of the polymer such as adhesions, permeability and biocompatibility [12,13].

The aim of present work was to investigate grafting of acrylamide (AAm) to low density polyethylene

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(LDPE) by using the above method.

EXPERIMENTAL
Materials

Commercial low density polyethylene granule (LFO45) containing no additives was supplied by Iranian National Petrochemical Company (Bandar Imam Petrochemical Co. Ltd.). The density and MFI of used LDPE were 0.92 g/cm^3 and 5.3 g/10 min respectively.

Acrylamide (m.p. 83-85 °C) and benzoyl peroxide were purchased from *Merck* Chemical Co. Ltd.

Processing of polymers

Different concentrations of AAm and benzoyl peroxide were tumble-mixed with polymer and the compounded polymers were processed in the Haake (HBI system 90) torque rheometer at 150 °C for 3,5,7 and 10 minutes in a closed mixer. The rotor speed was 60 r.p.m. On completion of mixing, the samples were rapidly removed and quenched in cold water to prevent further thermal oxidation. Films (0.15 mm) were compression moulded at 160 °C for 2 minutes using a special grade of cellophane as mould release agent. Films were extracted with hot water and acetone for 48 hours under nitrogen to remove unreacted monomer (AAm) and homopolymer (PAAm) by a soxhelet.

Spectrophotometric analysis

IR spectra were recorded on a Bruker FTIR (IFS 45) spectrophotometer. The change in the peak height at 3359 cm^{-1} (due to -NH- of amide group) was measured. The constant peak height at 1895

cm^{-1} was selected as the reference peak.

Rheological behaviour

Rheological behaviour of the samples studied by a melt flow index (MFI) apparatus (at 190 °C, 2.16 kg) and a rheoscope 1000 (at 150 °C, L/D=40/1) manufactured by CEAST Co. Italy.

The power law equation, $\tau = k(\dot{\gamma})^n$, was used to obtain apparent viscosity data. The two flowability parameters, k and n, are related to the molecular weight and its distribution respectively [14].

RESULTS AND DISCUSSION

Fig. 1 shows the effect of benzoylperoxide concentration on changes in AAm grafting in LDPE. An increase in the degree of grafting is observed from 0.5% to 1% (wt/wt) peroxide followed by a decrease (up to 1.5% peroxide). AAm grafting to LDPE is evident by a typical FTIR spectra of extracted films (Fig. 2). Variation in the peak height at 3359 cm^{-1}
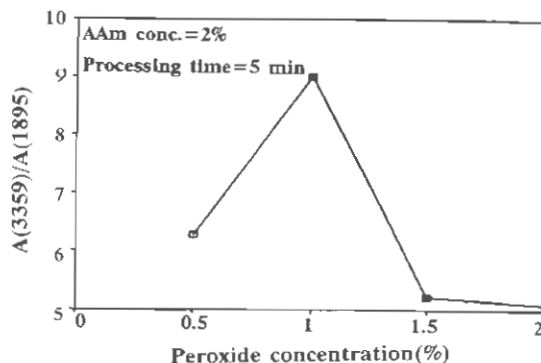

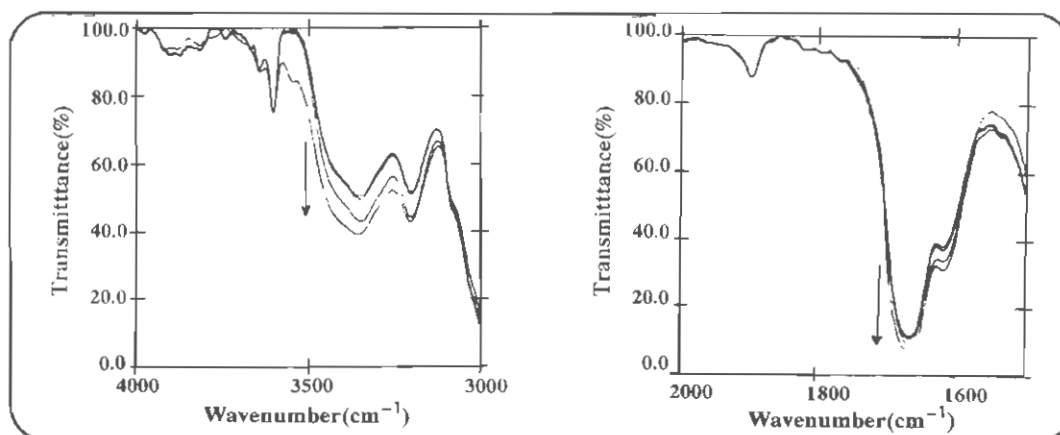*Fig. 1: The effect of benzoyl peroxide concentration on AAm grafting*

Fig. 2: A typical FTIR spectra of extracted films The direction of arrow shows different concentrations of peroxide: 2%, 1.5%, 0.5% and 1% (wt/wt) respectively.

indicates the effect of peroxide concentration on AAm grafting. Increase in AAm concentration from 1% to 4% (wt/wt) leads to an increase in AAm grafting (Fig. 3). Variation of torque/time/temperature of LDPE samples containing different concentration of AAm is depicted in Fig. 4. This figure shows a higher level of torque with increase in AAm concentration. Variation of temperature during processing is also observed in Fig. 4. Temperature in the mixer reaches 150 °C at 3.5 minutes and increases to 154 °C at 5 minutes.
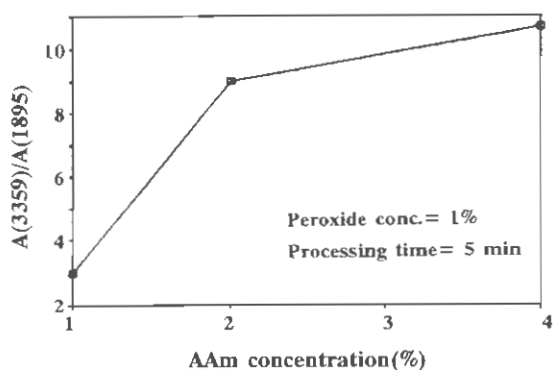
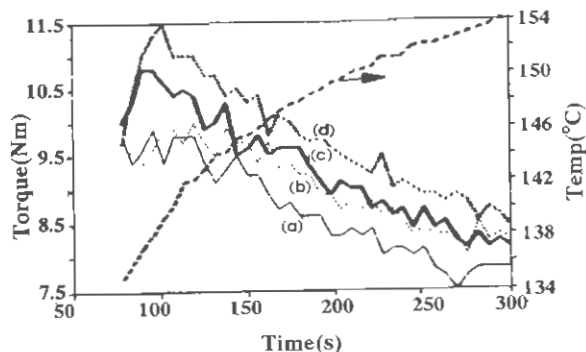*Fig. 3: The effect of AAm concentration on AAm grafting*

Fig. 4: Variation of torque/time/temperature of LDPE samples containing different concentrations of AAm: (a) 0% ; (b) 1% ; (c) 3% ; (d) 4%

The effect of processing time on the amount of AAm grafting is shown in Fig. 5. An increase in AAm grafting is seen up to 7 minutes followed by a decrease.

Fig. 6 illustrates the changes in MFI with AAm concentration. MFI decreases with increase in AAm concentration. A typical graph of apparent viscosity vs. Shear rate is shown in Fig. 7. As can be seen, at constant shear rate, the apparent viscosity of sample
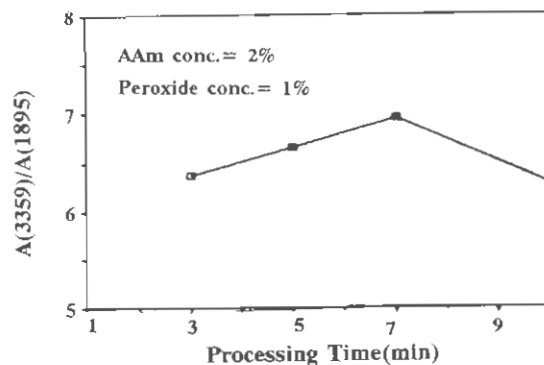

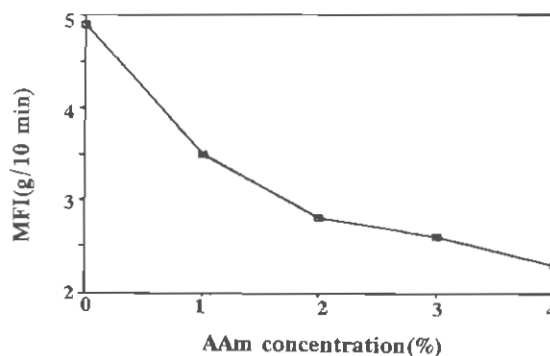*Fig. 5: The effect of processing time on AAm grafting*

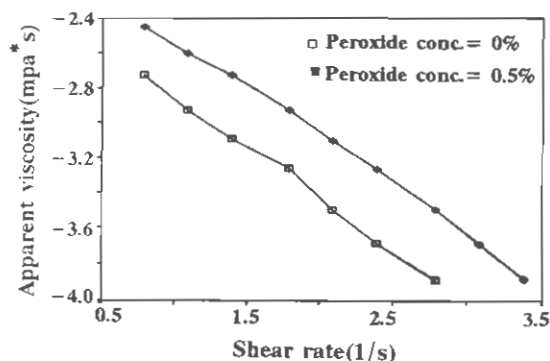*Fig. 6: The changes in MFI with AAm concentration*

Fig. 7: A typical graph of apparent viscosity vs. shear rate

containing 0.5% peroxide is higher than the control sample.

Reactive sites are formed on the polymer backbone due to hydrogen abstraction by peroxide radicals. AAm monomer is also polymerized by these radicals. As a consequence, AAm molecular chains (or AAm segments) are attached to the polymer molecular chains [see Eq.(1)].

Maximum grafting is obtained at 1% peroxide (Fig. 1). Decrease in AAm binding with increase in

(1)
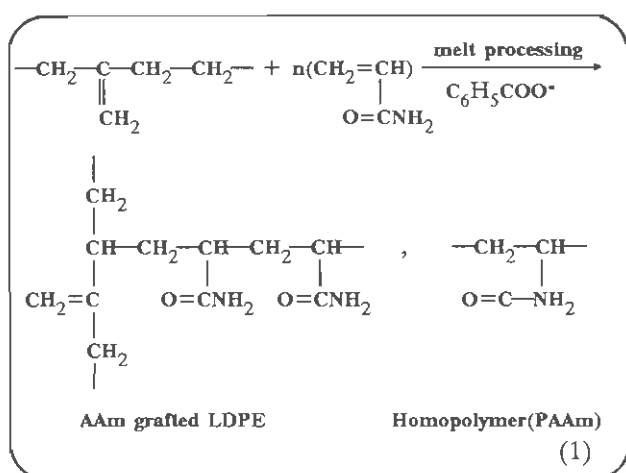
peroxide concentration ($>1\%$) may be explained by degradative action of peroxide radicals on attached AAm segments. Termination of macroalkyl radicals formed especially in the initial stages of processing, with benzoyl peroxide radicals may prevent molecular enlargement of the polymer.

Amide carbonyl groups in AAm segments act as photosensitizer during solar radiation [15]. Existence of these groups in addition to chemical impurities ($-OOH$, $-\overset{\parallel}{\underset{O}{C}}-$, ...) in the polymer may lead to a photodegradable material.

CONCLUSIONS

The following conclusions can be drawn:

1. Grafting of acrylamide monomer to LDPE takes place in the presence of a free radical generator during melt processing.
2. Maximum grafting was obtained at 1% peroxide and 7 minutes processing.
3. Increase in grafting level achieved by increasing AAm concentrations.
4. Combination of peroxide radicals with macroalkyl radicals in the initial stages of processing may prevent grafting.

ACKNOWLEDGMENTS

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