

Synthesis, Characterization and Studies of Chemically Modified Poly(Acrylonitrile-Butadiene-Styrene) through Nitrile Functionalization

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Available online 01 January 2023

Abstract

Design and synthesis of novel functionalized polymers have received significant attention among scientific and industrial communities. This is mainly due to the wider prospects in enhancing the properties and thereby extending the scope and applications of the existing polymer. New polymeric materials are usually obtained by adopting several synthetic methods. The classical one is the homopolymerization reaction of single monomer or otherwise is the use of a mixture of monomers as starting materials leading to various kinds of copolymers depending on the reaction conditions. In this context, the possibilities of nitrile group functionalizations in polymers such as PAN, SAN and NBR have been explored recently. For example, reports are available on the modification of nitrile group in Polyacrylo nitrile (PAN) to tetrazole, oxazoline, amidoxime etc. Most of these modified systems shown to have improved properties and applications. For example a novel polyvinyl tetrazole grafted resin has been introduced for the selective adsorption of heavy metals such as Pb(II), Cu(II), and Cr(III) from waste water. Similar kinds of nitrile group functionalizations in NBR and SAN are also demonstrated. However, reactions of nitrile group in Poly (acrylonitrile-co-butadiene-co-styrene), ABS is studied not much and the available report describes the conversion of CN group into oxazoline and its derivatives in melt.

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Keywords: nitrile group, polymeric materials, Polyacrylo nitrile (PAN).

1. Introduction

Design and synthesis of novel functionalized polymers have received significant attention among scientific and industrial communities. This is mainly due to the wider prospects in enhancing the properties and thereby extending the scope and applications of the existing polymer.¹ New polymeric materials are usually obtained by adopting several synthetic methods. The classical one is the homopolymerization reaction of single monomer or otherwise is the use of a mixture of monomers as starting materials leading to various kinds of copolymers depending on the reaction conditions. The synthetic modification of functional groups in an already existing polymer is an another alternative. This approach is otherwise known as post polymer functionalization leading to modified polymer material with significantly different properties than the precursor.² These modifications introduce new functional and reactive groups on parent polymer and thereby suitable for a wide range of application such as internal compatibilizer in blending,³ chelating agent for metal ion uptake,⁴ polymer electrolyte membrane(PEMs) etc.¹

In this context, the possibilities of nitrile group functionalizations in polymers such as PAN, SAN and NBR have been explored recently. For example, reports are available on the modification of nitrile group in Polyacrylo nitrile (PAN) to tetrazole,⁵ oxazoline,⁶ amidoxime⁷ etc. Most of these modified systems shown to have improved properties and applications. For example a novel polyvinyl tetrazole grafted resin has been introduced for the selective adsorption of heavy metals such as Pb(II), Cu(II), and Cr(III) from waste water.⁸ Similar kinds of nitrile group functionalizations in NBR⁹ and SAN¹⁰ are also demonstrated. However, reactions of nitrile group in

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Poly (acrylonitrile-co-butadiene-co-styrene), ABS is studied not much and the available report describes the conversion of CN group into oxazoline and its derivatives in melt.^{3a,11}

Acrylonitrile Butadiene Styrene is a terpolymer of acrylonitrile, butadiene and styrene in which the proportions of these components can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. Depending on the variations in the proportions, different grades of ABS with wide range of features and applications are resulted. The different properties may also be selectively enhanced for specific applications by modification of the components. In this context, the present paper deals with the solution phase chemical modification of CN group in ABS into oxazoline functionality and its preliminary studies. The presence of oxazoline group has shown to have several properties and applications in diverse fields of polymer science. For example this functionality is used for grafting,¹² and oxazoline bearing polymers are used for the synthesis of hyperbranched polymers,¹³ for metal complexation¹⁴ and as reactive compatibilizers.¹⁵ In addition, the oxazoline group is susceptible for further functionalization and thereby makes it suitable for tuning structure-property correlation most effectively. To the best of our knowledge, this is the first report on the solution phase synthetic modification of nitrile group in Acrylonitrile Butadiene Styrene (ABS) into oxazoline and its morphological and thermal studies in comparison with the neat ABS.

2. Experimental details

2.1 Materials

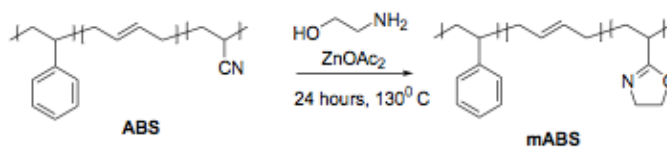
Poly(acrylonitrile-butadiene-styrene) (ABS) terpolymer with 25 wt% acrylonitrile content was purchased from Chi Mei Co.(Taiwan) and used as such. This ABS sample exhibits a weight-average molecular weight of 125200, a number-average molecular weight of 51300 and a polydispersity of 2.4. Other reagents ethanolamine (Merck, 99%), zinc acetate (Nice Chemicals, 98.5%) and chlorobenzene (Spectrochem, 99%) were used without further purification.

2.2 Methods

Shimadzu IR prestige-21 spectrometer was used for Fourier Transform Infrared Spectroscopy (FTIR) studies. Scanning Electron Microscopy (SEM) analysis was carried out on Digital Scanning Electron Microscope JEOL JSM-6390. The heat capacity as a function of temperature was determined by Perkin Elmer Diamond Differential Scanning Calorimeter. Thermo gravimetric analyses were performed using TA-Q50 TGA instrument.

2.3 Procedure

About 1 g of ABS and 0.025 g of $Zn(OAc)_2$ were dissolved in 10 mL chlorobenzene in a 50 mL round bottom flask equipped with a thermometer and a magnetic stirrer. To this reaction mixture 1.2 mL ethanolamine was added drop wise and refluxed at 130 °C under constant stirring. After 24 hours, the reaction mixture was mixed with 10 mL acetone and the resulting modified ABS (mABS) was isolated through precipitation from methanol and collected as light brownish solid after drying at 50 °C (Scheme 1)



Scheme 1: Synthetic modification of nitrile group in ABS into oxazoline

2. Results and discussions

3.1 Characterization by FTIR

The conversion of nitrile group into oxazoline was qualitatively determined using infrared spectroscopy. The IR spectra of both neat and modified ABS samples (Figure1) gave peaks at 1602 cm^{-1} corresponding to the C=C stretching frequency of the aromatic ring of styrene. The intensity of the peak due to the absorption of CN

group in neat ABS at 2236 cm^{-1} was found to be decreased in the mABS, revealing the targeted modification. The appearance of an additional peak at 1661 cm^{-1} was in support of the formation of the expected oxazoline functionality. The peak due to C=C from the polybutadiene part resonated around 1637 cm^{-1} remains intact during the course of the reaction. All the other peaks observed were in agreement with the literature report on the proposed modification.¹¹

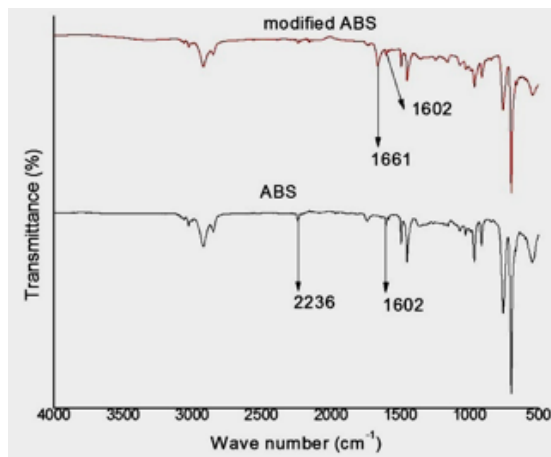


Figure 1. IR spectra of ABS and m ABS

3.2 Scanning Electron Microscopy (SEM)

SEM analysis was performed to understand the morphological changes occurred during nitrile group modification in the sample. The specimen surfaces were coated with a thin gold layer about 50 \AA thick. Differences in surface morphologies of the neat and mABS samples were clearly observed in the SEM images (Figure 2), and which provided additional evidence for the structural modification. In ABS the polybutadiene phase is can be considered as the rubber toughed polymer part which is dispersed in continuous poly(styrene-co acrylonitrile)(SAN) glassy phase. On modification significant change in the morphology in terms of disappearance of the surface disorders were observed.

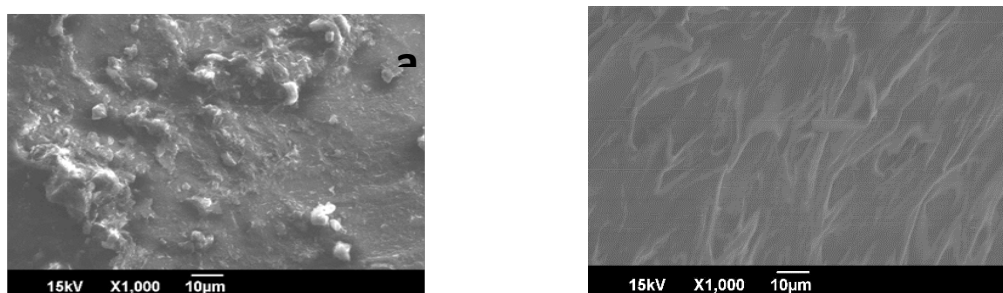


Figure 2. SEM images of (a) ABS (b) mABS

3.3 Differential Scanning Calorimetry (DSC)

| samples | Properties | | | |
|---------|---------------------|-------------------------|-----------------------|-------------------------------|
| | T _g (°C) | T _{onset} (°C) | T _{end} (°C) | Delta C _p (j/g °C) |
| ABS | 102.58 | 101.03 | 117.14 | 0.398 |
| mABS | 70.50 | 65.36 | 76.67 | 0.122 |

Table 1. DSC analysis data for ABS and mABS

The samples mABS and ABS were heated at a programmed rate of heating (10 °C/min) and the heat capacity of the samples were measured as a function of differential heat flow rate with temperature. Dry nitrogen was used as purge gas and samples of 20-30 mg were analyzed. The results are presented in Table 1. The glass Transition temperature (T_g) of the modified ABS sample was found to be less than that of ABS (102.58 °C). Oxazoline modified ABS showed T_g at 70.50 °C and a heat capacity of 0.122 j/g °C. The decrease in glass transition temperature of mABS is attributed to increase in free volume change in the sample. This could be referenced to the decrease in entanglement of polymer chains in the matrix resulting from the nitrile functionalization.

3.4 Thermo Gravimetric Analysis (TGA)

The thermal decomposition behaviour of a polymer sample depends on the macromolecular characteristics of polymers and the arrangement of polymer matrix. The TGA of the samples were performed at a heating rate of 10 °C min⁻¹ in N₂ atmosphere. The results of TGA analysis of neat and modified ABS samples (Figure 3) revealed major changes in the thermal behaviour of the ABS after oxazoline modification. ABS sample showed single stage decomposition whereas modified ABS sample showed three stage decomposition pattern.

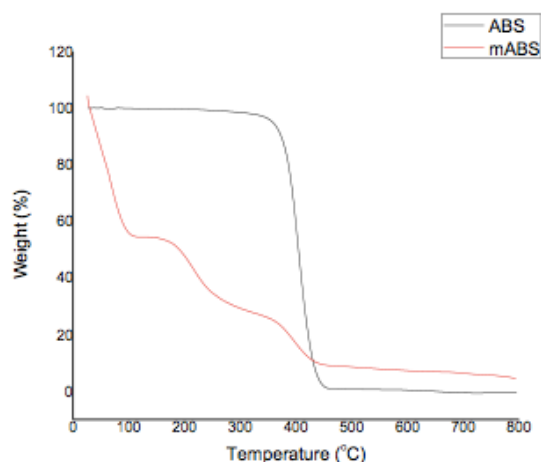


Figure 3. TGA curves of ABS and mABS

TGA results of neat ABS were found to be matching with the literature¹⁶ and showed the initial thermal degradation near 340 °C with a residue of 96% and continued rapidly until about 480 °C. The thermal decomposition behavior of ABS is known and which states that the degradation starts with the formation of butadiene monomer. At around 350 °C the aromatic styrene starts to evolve while elimination of acrylonitrile commences at 400 °C. Above 500 °C degradation ceased completely and weight percentage reaches to negative val

Table 2. TGA data for ABS and mABS

| Temperature (°C) | Reduced mass (Wt.%) of samples | |
|------------------|--------------------------------|-------|
| | ABS | mABS |
| 100 | 100 | 55.56 |
| 150 | 99.48 | 53.95 |
| 200 | 99.15 | 47.47 |
| 250 | 98.86 | 32.52 |
| 300 | 98.53 | 29.08 |
| 350 | 96.26 | 25.20 |
| 400 | 63.31 | 15.51 |
| 450 | 2.93 | 9.37 |
| 500 | 0.01 | 8.09 |
| 550 | 0.01 | 7.76 |
| 600 | -0.31 | 7.14 |
| 650 | -0.94 | 6.48 |
| 700 | -1.59 | 5.82 |
| 750 | -1.26 | 5.20 |
| 800 | -2.54 | 3.26 |

The thermo gravimetric data of mABS indicated that the modification of ABS lead to the decrease in early thermal stability of the polymer. In the case of mABS, the degradation commenced at a lower temperature near 60 °C and almost 50% got degraded at 150 °C. The weight loss due to degradation predominates until 400 °C. However, interestingly even at 700 °C a residue of 5 % of mABS was observed indicating the slightly enhanced thermal stability of the residual mABS at higher temperature.

4. Conclusions

The solution phase synthetic modification of nitrile group in ABS into oxazoline on reaction with ethanolamine is reported. The introduction of the new functionality is characterized by FTIR spectroscopy and the resulting morphological changes are visualized through SEM analysis. In order to understand and compare the thermal properties of polymer DSC and TGA analyses were carried out on neat and modified ABS samples. These studies hinted out that glass transition temperature (T_g) and initial degradation temperature of mABS is very low compared to the neat ABS. Detailed studies to understand the thermal behavior of modified polymer is in progress.

Acknowledgements

Authors thank NIIST (CSIR), Thiruvananthapuram for spectral and thermal analyses. The authors EG and JJ gratefully acknowledge UGC and PRS acknowledge CSIR for junior research fellowships. Thanks are due to Prof. Sabu Thomas for fruitful discussions.

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