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Synthesis and characterization of maleimide functionalized polystyrene/ethylene-propylene-dieneterpolymernetwork material

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Abstract: The newintercross linked system comprising maleimide functionalized polystyrene/ethylene-propylene-dieneterpolymer(EPDM) have been synthesized using maleimide functionalized polystyrene and EPDM in presence of dicumylperoxide radical initiator. The methodology adopted here is the functionalization of polystyrene with maleimide moiety to form PS-g-Maleimide which, then cross linked with EPDM to get PS-g-maleimide/EPDM network. The formation of maleimide functionalised polystyrene (Scheme-I) and formation of intercross-linked network between maleimide functionalized polystyrene and EPDM (Scheme-II) reactions were confirmed by FTIR and NMR spectral studies. Differential scanning calorimetry (DSC) and thermogravimetric (TGA) analysis of polystyrene, meleimide functionalized polystyrene and the intercross-linked network system of maleimide functionalized polystyrene and EPDM were performed to determine their glass transition temperature (Tg) and thermal stability. Izod impact strength was studied to determine the toughness of the pristine polystyrene and maleimide functionalized polystyrene/EPDM network. Morphological behavior was also studied by scanning electron microscopy(SEM). Thermal, mechanical and morphological studies reveal that the introduction of EPDM onto maleimide functionalized polystyrene which, improves the toughness, glass transition temperature and thermal degradation temperature of polystyrene

Key words: EPDM, maleimide functionalized polystyrene/EPDM network, glass transition temperature, thermal stability and toughness

Introduction

The need for the development of high performance material with high thermal stability, good fracture toughness, high impact strength and improved mechanical properties becomes essential in order to utilize them in the place of conventional structural material for high performance commodity as well as engineering applications. Polymer network material is one of the most rapidly growing areas for the development of high performance materials for specific applications using available commodity and engineered plastics[1-3]. These materials are obtained by mixing of structurally different polymers bonded together by secondary forces. The most remarkable advantage of these materials is the development of impact resistant plastics for high performance applications[4]. The introduction of moderate concentration of the rubbery phase into the matrix of glassy polymers imparts enhanced impact strength without any major loss in stress-strain and thermal properties. However, the exploitation of these effects on properties depends on the extent of compatibility of the constitution polymers involved in the formation of network material[5-8].

Polystyrene is one of the most widely used commodity plastics and exhibits glassy and brittle behavior at room temperature. The brittleness of polystyrene can be reduced by incorporation of rubber in to polystyrene matrix. Few investigations are made and reported on the development of high impact polystyrene by making polystyrene with polybutadiene rubber or its graft network co-polymer material, but the resulting products exhibits poor weathering resistance because of photo oxidation on the unsaturation part of the rubber and it greatly limits the outdoor applications. However, it is reported that the toughened polystyrene polymeric materials consisting of ethylene-propylene-dieneterpolymer possess better weather ability and ozone resistance[9-13].

Many experimental methods have been used to investigate polymer-polymer compatibility, determination of glass transition temperature (Tg), thermal stability, morphology and dynamic mechanical properties. EPDM is incompatible with polystyrene[14-17]. The ability of rubber to improve the impact strength of brittle and glassy polymers depend on the size of the rubber particle, degree of cross-linking and mechanical compatibility of the rubber phase with the plastic matrix, This is usually achieved by grafting the plastic matrix onto the rubber backbone.

A new methodology has beendeviced in the present work for the modification of polystyrene using maleimide and incorporation of ethylene-propylene-dieneterpolymer in the form of intercross-linked system has been synthesized by curing with decumylperoxide as radical initiator. The EPDM /maleimide functionalized polystyrene polymericmaterial have been characterized by physiochemical, thermal, mechanical and morphological studies in order to compare the same with unmodified polystyrene and to utilize them for high performance applications. In order to ascertain the optimum percentage incorporation of EPDM in this new material, the varying weight percentage of EPDM in the blend of maleimide modified polystyrene. The varying percentages of EPDM i.e. 1%, 3%, 5%, 7% and 9% have been used in this polymeric material and studied their impact behavior. From the result, it is ascertained that about 5% incorporation of EPDM in the polystyrene yields better impact properties.

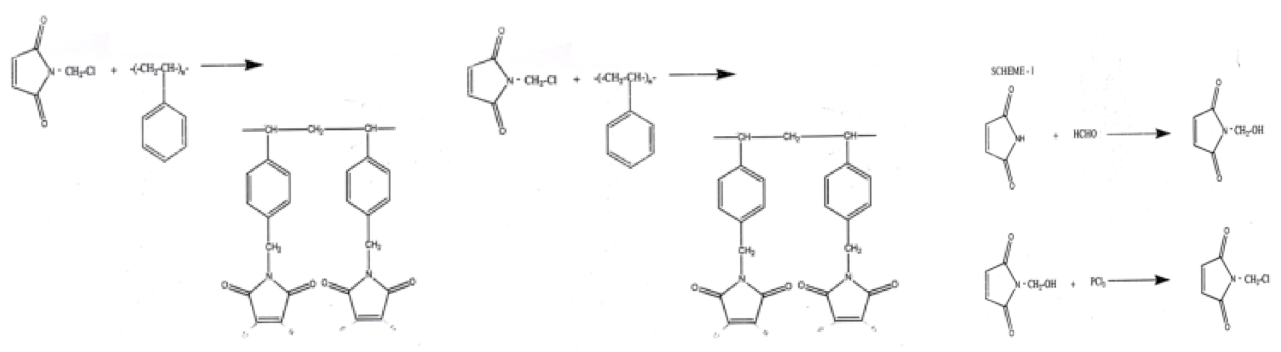
Experimental

Materials

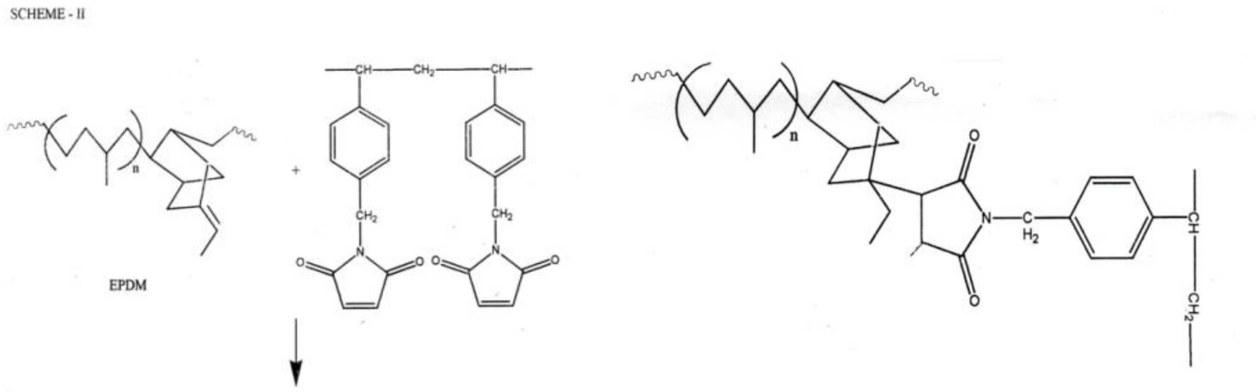
Maleimide procured from Lancaster, UK, Phosphorous trichloride, tin tetra chloride obtained from Aldrich chemical company, USA, ethylene-propylene-dieneterpolymer (EPDM) procured from Dupond Dow elastomers, USA and polystyrene obtained from Supreme petrochemicals Ltd., India were used as received.

Synthesis of Functionalized Polystyrene

Maleimide functionalized polystyrene was synthesized through the reaction between the maleimide and 30% formalin solution in 500ml RB flask, at room temperature for about four hour with 1% solution of sodium hydroxide. The resulting product is reprecipitated from methanol solution and it is in the form of hydroxyl group functionalized maleimide. The hydroxyl group functionalized maleimide is converted into chloride-functionalized maleimide by reacting the hydroxyl functionalized maleimide with phosphorous trichloride in nitrogen atmosphere at 70˚C for about 5 hrs. The chloride functionalized maleimide was allowed to react with polystyrene polymer at 80˚C for five hour in nitrogen atmosphere and its formation was confirmed by FTIR and NMR spectral studies. The sequence of reactions involved during the synthesis of maleimide-functionalised polystyrene is presented in Scheme-I.



Scheme I : Synthesis of Functionalized Polystyrene



Scheme II Synthesis of Polystyre-g-maleimide/EPDM

Development of Maleimde Functionalized Polystyrene/Epdm Network Materials

The maleimide functionalized polystyrene and EPDM intercross-linked network was synthesized by reacting the solution of maleimidefunctionalized polystyrene and EPDM, which is dissolved in toluene and heated at 80°C by using dicumylperoxide initiator with tin tetrachloride catalyst. The formation of polystyrene-g-maleimide/EPDM network is presented in scheme-II

Extraction

The degree of maleimide functionalized polystyrene polymer grafted to the EPDM rubber was determined via Soxhlet extraction procedure. The n-hexane was selected as extraction solvent because it is a solvent for ungrafted EPDM. A sample of the graft polymer was placed in a Soxhlet extraction device for a minimum of 3 days. The n-hexane soluble component was recovered by precipitate into methanol. The percentage grafting of maleimide functionalized polystyrene on to EPDM rubber was determined from the following equation.

$$A = \frac{\text{Total weight of polystyrene-g-maleimnide/EPDM}}{\text{Total weight of polymer formed}} \times 100$$

Spectral Analysis

The functionalisation of hydroxyl and chloro group on to maleimide, functionalisation of maleimide on to polystyrene and grafting of functionalized polystyrene on to EPDM were confirmed by FTIR and NMR spectral analysis.

Thermogravimetric analysis

Thermal stability of polystyrene, maleimide functionalized polystyrene and polystyrene-g-maleimide/ EPDM were carried out in a thermogravimetricanalyszer in nitrogen atmosphere over a temperature range between 20°C and 800°C at a heating rate of 20 minute.

Diffferential Scanning calorimetry

Thermal behavior of polystyrene, maleimide functionalized polystyrene and polystyrene-g-maleimide /EPDM were studied by using a DSC mettler thermal analyser. The samples were inserted into the apparatus and heated to 200˚C at a rate of 40˚C per minute and kept for 1 minute at this temperature in order to remove the volatile impurities. The samples were quenched and heated from -100˚C to 250˚C at a heating rate of 5˚C per minute in nitrogen atmosphere.

Izod Impact strength

The notched Izod impact strength of the sample was tested as per ASTM D 256-88. All samples were notched and tested. So, they would be more sensitive to the transition between ductility and brittleness. Specimen having thickness 2-3mm with 10mm cross section and 64 mm length were clamped in the base of the pendulum testing machine. So, that they cantilevered upward. The pendulum was released and the force consumed in breaking the sample calculated from the height of the pendulum reached on the followed through.

SEM analysis

The morphological texture of the network material was observed by scanning electron microscopy (SEM). SEM micrographs were taken from cryogenically fractured and surface sputtered with gold before viewing.

Results and Discussion

FTIR Spectra

FTIR Spectra of EPDM, hydroxly group functionalized maleimide, choloro group functionalized maleimide, maleimide functionalised polystyrene and polystyrene-g-maleimide/EPDM and unmodified polystyrene are presented in Figure1a, b,c,d,e,and f respectively. Figure 1a, shows the frequency C-H band at 3055cm^{-1} CH_2 band at 2935cm^{-1}, -OH band at 3565cm^{-1}, C=O band at 1690cm^{-1} and C=C band at 1592 cm^{-1}. In Figure 1b shows that the C-H band at 3097cm^{-1}, –CH_2 band at 2900cm^{-1}, -Cl band at 694 cm^{-1}, C=O band at 1680 cm^{-1} and C=C band at 1595cm^{-1} and it indicates that C-H band at 3565 cm^{-1} disappears and Cl band at 694cm^{-1} was appeared and conformed that the incorporation Cl group on to maleimide moiety. In Figure 1c, shows that C-H band at 2988 cm^{-1}, CH_2 band at 2913 cm^{-1}, =CH band at 3098 cm^{-1} C=O band at 1720 cm^{-1} and C=C band at 1600 cm^{-1} and it indicates that the formation of maleimide functionalized polystyrene because of the absence of Cl band at 694 cm^{-1}. In figure1d, show that the formation and functionalisation of meleimide functionalized polystyrene on to EPDM was conformed due to the absence of peak at 1592 cm^{-1} and formation of C=O band at 1723 cm^{-1}. In Figure 1e is the FTIR spectrum of polystyrene. It shows that the CH band (aliphatic) at 2922 cm^{-1}, CH_2band at 1493 cm^{-1} CH band (aromatic) at 3081 cm^{-1}, C=C band due to phenyl group at 1601 cm^{-1} and CH_2-CH band at 757 cm^{-1} due to presence of polyethylene backbone. Figure 1f is the FTIR spectrum of EPDM. It shows that the CH band (aliphatic) at 2906 cm^{-1} CH_2 band at 1461 cm^{-1} CH_3 band at 1375 cm^{-1} due to the presence of propylene group CH_2 wagging band at 750 cm^{-1} due to presence of polyethylene chain C-C stretching band at 2854 cm^{-1} and the unsaturation band >C=CH- at 820 cm^{-1} due to the presence of ENB content and in figure 1 d, the band at 820 cm^{-1} disappears due to formation of inter-cross-linked network between maleimide functionalized polystyrene and EPDM.

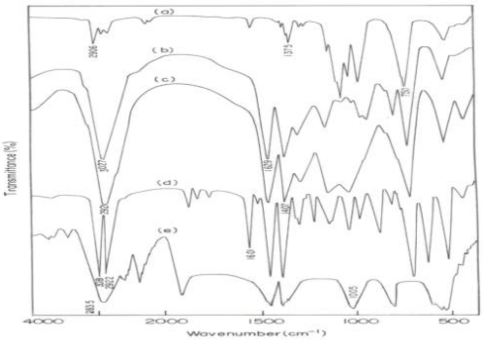


Figure 1

Figure 1.FTIR Spectra of EPDM, hydroxly group functionalisedmaleimide, choloro group functionalisedmaleimide, maleimidefunctionalised polystyrene and polystyrene-g-maleimide/EPDM and unmodified polystyrene are presented in Figure1a, b,c,d,e,and f respectively.

NMR Spectra

The NMR data obtained for different modifier and blends are presented below.

NMR data of OH maleimide: ^{1}H-NMR 300Hz, $CdCl_3$): δ=6.7,5.2 and 2.0 ppm and ^{13}C-NMR: δ=170 ppm and 61.1 ppm
NMR data of Clmaleimide: ^{1}H-NMR 300Hz, $CdCl_3$): δ=6.84, and 5.49 ppm and ^{13}C-NMR: δ=168.18 ppm, 135.27 ppm and 44.25 ppm
NMR data ofmaleimidefunctionalized polystyrene: ^{1}H-NMR 300Hz, $CdCl_3$): δ= 6.4-7.3 (broad), 4.9-5.2 (broad), 1.87 ppm 1.6-2.0 ppm and 5.49 ppm and ^{13}C-NMR: δ=168.18 ppm, 135.27 ppm and 44.25 ppm
NMR data of maleimide functionalized polystyrene and EPDM network: ^{1}H-NMR 300Hz, $CdCl_3$): δ= 6.4-7.3 (broad), 4.9-5.2 (broad), 1.87 ppm 1.6-2.0 ppm and 5.49 ppm and ^{13}C-NMR: δ=168.18 ppm, 135.27 ppm and 44.25 ppm

Thermal properties

Thermogravimetricanalysis (TGA)

From the TGA analysis, the degradation temperature of polystyrene, maleimide functionalized polystyrene and polystyrene-g-maleimide/EPDM intercross-linked network are presented in Table 1. From the results, it is observed that the degradation temperature network is increases due to grafting of maleimide functionalized polystyrene on to EPDM, which results, in the formation of IPN linkage between maleimide functionalized polystyrene and EPDM.. The formation of cross-linking is the cause for improving the degradation temperature of modified polystyrene.

Table 1: The TGA data on thermal stability of polystyrene Polystyre-g-maleimideansPolystyre-g-maleimide/EPDM

Samples	Initial Degradation Temperature. (◦C)	Mid Point Degradation Temperature(◦C)	Final Degradation Temperature. (◦C)
polystyrene	300	340	390
Polystyre-g-maleimide	355	400	430
Polystyre-g-maleimide/EPDM	390	440	497

Differential Scanning Calorimetry (DSC)

From the DSC analysis, Glass transition temperature of the sample was determined The DSC thermogramsgives the Tg values of polystyrene, maleimide functionalized polystyrene and polystyrene-g-maleimide/EPDM intercrosslinkednetwork are presented in Table 2. From the results, it is observed that the Tgof polystyreneis increases, it is due to the introduction of maleimide moiety on to polystyrene and it is also grafted with EPDM. Further grafting of EPDM, which enhance the intercross-linking density of the polystyrene-g-maleimide/EPDM network and hence the Tg values are increased.

Table 2: The glass transition temperature of polystyrene, Polystyre-g-maleimide and Polystyre-g-maleimide/EPDM

Samples	Tg(◦C)
Polystyrene	91.3
Polystyrene-g-Maleimide	94.0
Polystyre-g-Maleimide/EPDM	95.3

Mechanical Properties

The values of impact strength of polystyrene and polystyrene-g-maleimide/EPDM intercross linked network are presented in Table 3. When compared with the value obtained for unmodified polystyrene, the impact strength of polystyrene-g-maleimide/EPDM is increased due to grafting of EPDM into maleimide functionalized polystyrene, which in turn influences the uniform dispersion of EPDM particle in the polystyrene matrix. The improvement of compatibility is observed from SEM micrographs of intercross-linked network (Fig 4b) and the formation of cross link (grafting) between EPDM and maleimide functionalized polystyrene and consequent enhancement in the value of impact strength of EPDM modified polystyrene. The enhancement of impact strength is about 6.5 times higher for polystyrene-g-maleimide/EPDM network when compared with that of unmodified polystyrene[18-24].

Table 3: The impact strength of Polystyrene and Polystyrene-g-Maleimide/EPDM

Samples	**Notched Impact Strength (J/M)**
Polystyrene	20.0
Polystyre-g-Maleimide/EPDM	133.0

SEM analysis

The scanning electron micrographs of the fractured surface of thepolystyrene-g-maleimide/EPDM and unmodified EPDM are presented in Figure 2a and 2b.The finemorphology due to uniform dispersion of rubber atmicroscopic level in the matrix (Figure 2a), which results an improvement in the compatibility between rubbery phase and plastic matrix phase and consequent enhancement in the values of impact strength. Figure 2b shows the existence of coarse morphology due to the large particles size of EPDM

Figure 2a. SEM micrographs of Polystyrene-g-Maleimide/EPDM Figure 2b. SEM micrographs of EPDM

Conclusion

The new intercross linked system comprising maleimide functionalized polystyrene/ethylene-propylene-dieneterpolymer (EPDM) have been synthesized using maleimide functionalized polystyrene and EPDM in presence of dicumylperoxide radical initiator.The formation of intercross-linked maleimide functionalized/ EPDM structure was ascertained from FT-IR spectroscopy. Thermal properties like degradation temperature and glass transition temperaturewere determined sung TGA and DSC analysis. From the results, it was observed that the degradation temperature and Tg of network material were increased due to grafting which results in the formation network. From the results obtained from impact strength, the impact valueof polystyrene-g-maleimide/EPDM network was increased to about 6.5 times than pristine polystyrene, it is due to improvement in the compatibility between modified polystyrene and EPDM. The SEM micrographs of intercross-linked network material indicated that the homogeneity at microscopic level and confirm uniform dispersion of rubber in the network material,, which in turn enhance the intimate compatibility of components involved with consequent improvement of thermal and mechanical properties.

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