Free Radical Grafting of Methyl Methacrylate onto Ethylene-Propylene Amorphous Copolymer

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Abstract. This study investigated the free radical graft copolymerization of methyl methacrylate (MMA) onto amorphous poly(ethylene-*co*-propylene) (EPC) in toluene solution, when using benzoyl peroxide (BPO) and 2,2´-azobisizobutyronitrile (AIBN) initiators over a wide composition and temperature range. Graft copolymer formation was verified by selective solvent extraction, infrared spectroscopy, and the turbidimetric titration method. Besides graft copolymerization, the homopolymerization reaction of vinyl monomer takes place as well. It was found that grafting is more efficiently induced by BPO, as compared to AIBN. The grafting efficiency (GE) decreased with increasing polymerization temperature and, more significantly, with the increasing MMA concentration. The GE steadily decreased from 90 % to about 30 % over a two hours reaction period at 90 ºC reaction temperature, in response to increasing MMA concentration from 0.2 to 1.8 mol dm^{-3} at a constant EPC concentration of 60 g dm^{-3}. A reaction temperature increase from 70 ºC to 95 ºC caused a decrease in GE from ~100 % to 75 %. The obtained graft copolymers were characterized for molecular weight distribution and viscometric behavior in dilute xylene solutions and compared with corresponding EPC / PMMA physical mixtures.

Keywords: graft copolymerization, poly(ethylene-*co*-propylene), methyl methacrylate, solution, viscosity

INTRODUCTION

In recent years, there has been significant practical interest in the grafting of vinyl monomers to polyolefin. These polymers, which contain a high concentration of functional (polar) groups with desirable polyolefin properties, are very effective interfacial agents that improve the compatibility of polyolefin with other materials. In general, the chemistry involved in the preparation of polyolefin graft copolymers is limited.[1–5] Numerous approaches, based on post polymerization processes, have been employed in forming polyolefin graft copolymers. Ionizing radiation in the presence of air, ozone, UV with accelerators, and free radical initiators has all been used to form polymeric peroxides. When heated in the presence of monomers, some polymeric peroxides initiate graft polymerization. As far as the grafting mechanism is concerned, it is generally accepted that the primary steps are decomposition of the initiator, hydrogen abstraction from the polymer backbone, and reaction of the macroradical with a monomer molecule to form a branched macroradical. This branched macroradical may continue to react with more monomer molecules forming longer grafts. It may also

undergo transfer with a hydrogen atom of the same or another polymer backbone forming a new macroradical and a graft consisting of a single monomer unit. However, these high-energy reactions that are heavily dependent on reaction conditions may lead to many undesirable side reactions, such as crosslinking and chain cleavage. In most cases, the structure and composition of copolymers are difficult to control given the considerable amounts of ungrafted homopolymers. Furthermore, the free radical grafting process of vinyl monomers is often complicated by the simultaneous occurrence of homopolymerization.[1–6]

In large part, grafting reaction has been performed with polypropylene (PP),[1–3,7] ethylene / propylene rubber (EPR)[1–3,8] and a copolymer of ethylene / propylene / diene monomer (EPDM)[1–3,9] as backbone polymers to introduce new or improve existing properties, particularly the miscibility or compatibility of the polymer blends. Most preparations of PP grafting are made with maleic anhydride,[10] however, other common monomers of the vinyl or vinylidene type have also been used.[1–3,7,11–15] The most examined grafting on EPR and EPDM were performed by the mixture of styrene and acryloni-

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trile[16,17] or methyl methacrylate.[18] The reactions were performed in the solid phase, in melt or in a solution at relatively high temperatures due to the low solubility of the hydrocarbon backbone. However, in such systems, the crosslinking reaction also occurs resulting in gelation. These studies revealed that initiation of the grafting reaction is strongly controlled by hydrogen abstraction reaction from the polyolefin backbone, specifically, the hydrogen atom on tertiary carbon of propylene moieties by the initiator primary radicals.[19]

In this study, graft copolymerization of methyl methacrylate onto amorphous poly(ethylene-*co*-propylene) (EPC) in toluene solution by the free radical initiation has been described. Aside from the effects of the two initiator types, reaction temperature, EPC and MMA concentration on graft formation were investigated; some structural and viscometric properties of obtained graft copolymers were also undertaken. Both, amorphous, more soluble EPC and poly(alkyl methacrylates) are well known as effective rheology modifiers of lubricating mineral oils[20] while their mixtures show some complementary effects, as discussed in our previous paper.[21] It is expected that graft copolymers of these polymers will overcome their inherent incompatibility.[22,23]

EXPERIMENTAL

Materials

The poly(ethylene-*co*-propylene) (EPC) (Lubrizol 7067, Lubrizol Chem. Co.) was purified by repeated precipitation in methanol from a toluene solution ($w = 5$ %). The molar fraction of ethylene units was found to be 60, as deduced by ^{1}H NMR spectroscopy, and the average molecular weights were $M_w = 109 \times 10^3$ and $M_n = 59 \times 10^3$, as deduced by the size exclusion chromatography. Methyl methacrylate monomer (MMA) (RohMax Chem.) was washed with diluted aqueous sodium hydroxide, dried over calcium chloride, and distilled under nitrogen atmosphere at reduced pressure. The initiator 2,2′-azobisisobutyronitrile (AIBN) (Akzo Chemie) was purified by crystallization from a methanol solution. Benzoyl peroxide was recrystallized twice from the methanol–chloroform mixture and dried in a desiccator. Xylene and toluene of high purity (*p.a.*) (Kemika) were used as received.

Methods

The ^{1}H NMR spectrum of EPC copolymer was recorded on the 90 MHz Varian EM-360 spectrometer at room temperature. The polymer elution volume and molecular weight distributions were determined by size exclusion chromatography (SEC) performed on the GPC-20 Po-

lymer Laboratories instrument fitted with a RI detector in tetrahydrofuran (THF) as a solvent. Molecular weights were calculated as polystyrene equivalents. Infrared spectra (IR) were recorded on a Perkin Elmer 2000 FT spectrophotometer on polymer films cast from chloroform solution. Turbidimetric titration was performed on a Zeiss-Pulfrich tindalometer using red spectral by turbidimetric titration of polymer solution in tetrahydrofurane ($w = 0.1$ %) by methanol. Viscometric measurements were conducted in xylene solutions at 30 ºC using the Cannon-Fenske 50 K capillary viscometer.

Graft Copolymer Preparation

Graft copolymerization experiments were performed in a thermostated double jacket glass reactor (volume 100 mL) fitted with a mechanical stirrer and thermometer under inert nitrogen atmosphere. The EPC solution in toluene, and an appropriate quantity of methyl methacrylate and the initiator were heated and maintained at the reaction temperature. After a given reaction time, the sample was withdrawn and precipitated in methanol and filtered off. The polymer was reprecipitated from toluene and dried under a vacuum at 60 ºC. The methyl methacrylate homopolymer (PMMA) was removed from the polymers mixture by exhaustive Soxhlet extraction with acetone for 24 hours. The total polymerized MMA was obtained as a difference between weight of the total polymer (PMMA, EPC and EPC-graft-PMMA) and weight of the starting EPC backbone polymer. Conversion of MMA monomer was obtained as the weight ratio of the MMA polymerized and MMA monomer charged. The *degree of grafting* (DG / %) was obtained as a weight ratio of grafted PMMA and EPC, whereas the *grafting efficiency* (GE / %) equaled the weight ratio of grafted PMMA and the total polymerized MMA.[15]

RESULTS AND DISCUSSION

The free radical polymerization of methyl methacrylate (MMA) in the presence of poly(ethylene-*co*-propylene) (EPC) was performed in toluene as an inert solvent using benzoyl peroxide as the initiator. For comparison, some experiments were performed using 2,2′-azobisizobutyronitrile as an initiator. Under these conditions, both grafting of MMA onto an EPC backbone and MMA homopolymerization occurred simultaneously. Grafting reaction was confirmed by selective solvent extraction using acetone as a good solvent for poly(methyl methacrylate) (PMMA) and a nonsolvent for EPC and their graft copolymers, and further by IR spectrophotometry and the turbidimetric titration method. The IR spectra of EPC-graft-PMMA (Figure 1) exhibited combined features of both constituent poly-
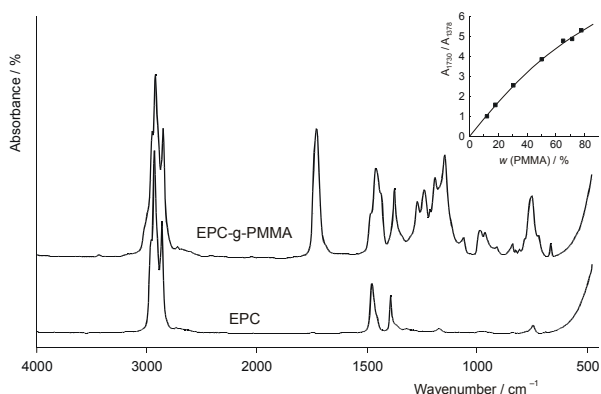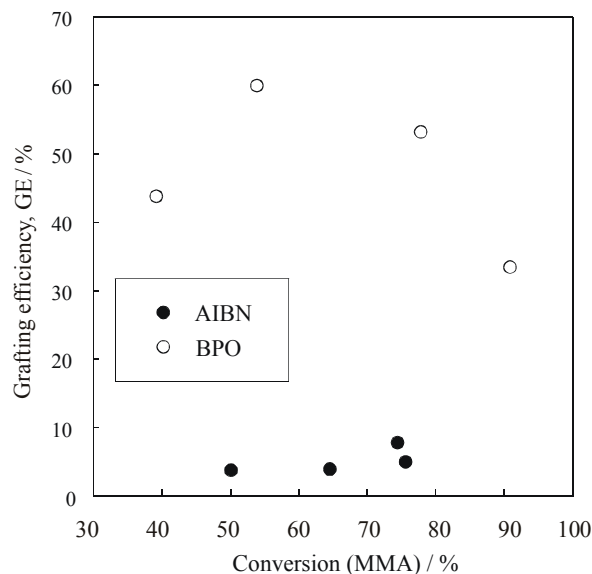
Figure 1. IR spectra of poly(ethylene-*co*-propylene) (EPC) and poly(ethylene-*co*-propylene)-graft-poly(methyl methacrylate) copolymer (EPC-g-PMMA). The inset: dependence of characteristic absorbance intensity ratio at 1730 and 1378 cm^{-1}, A_{1730} / A_{1378}, on weight percent of poly(methyl methacrylate) in mixture with poly(ethylene-*co*-propylene).
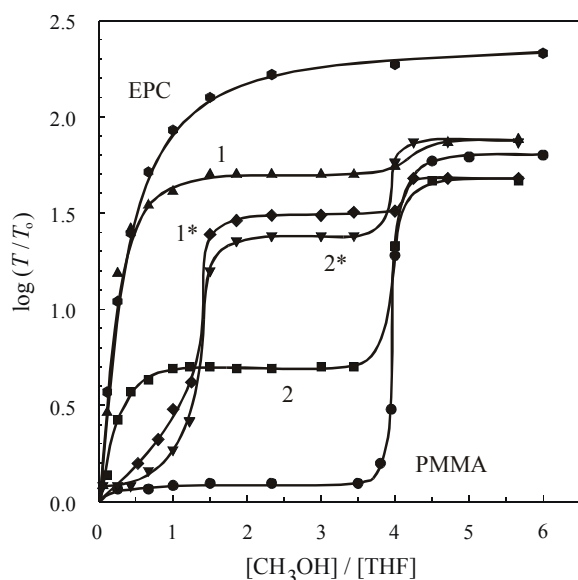
Figure 2. Turbidimetric curves of polymer in tetrahydrofurane (w = 0.1 %) (THF) solutions of poly(methyl methacrylate) (PMMA), poly(ethylene-*co*-propylene) (EPC), their mixtures with w (EPC) = 35 % (1) and 5 % (2) and graft copolymers of equal compositions (1* and 2*), titrated by methanol.

Figure 3. Influence of initiator type on grafting efficiency in graft copolymerization of methyl methacrylate / poly-(ethylene-*co*-propylene) in a toluene solution at 91 ºC with benzoyl peroxide (BPO) and at 82 ºC with 2,2´-azobis-izobutyronitrile (AIBN); [MMA] = 2 mol dm^{-3}, [EPC] = 50 g dm^{-3}, [I] = 1×10^{-2} mol dm^{-3}.
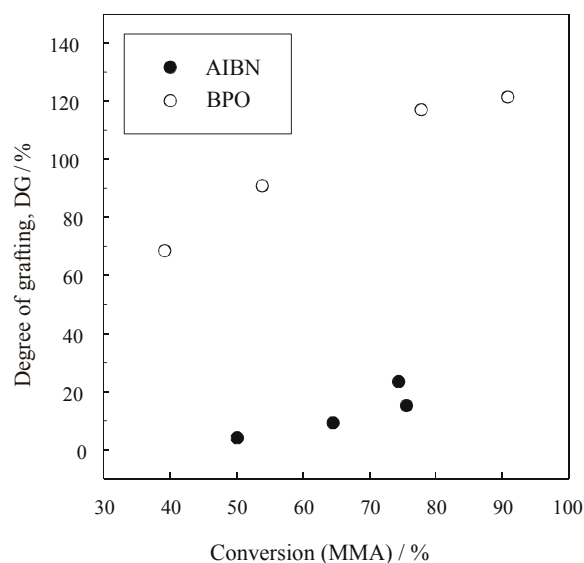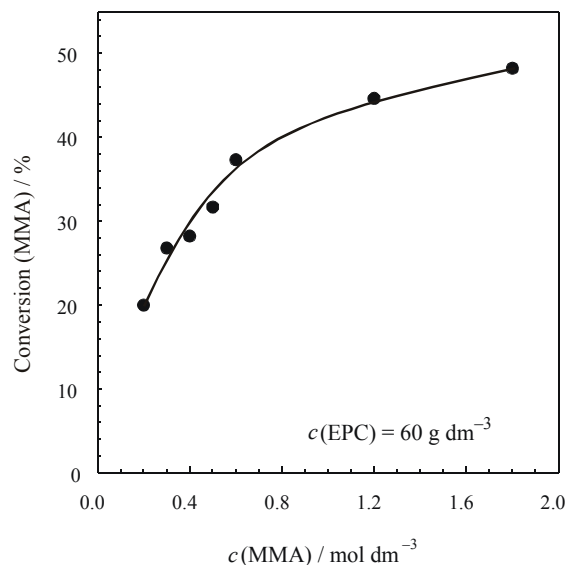
Figure 4. Influence of initiator type on degree of grafting in graft copolymerization of methyl methacrylate / poly-(ethylene-*co*-propylene) in toluene solution at 91 ºC with benzoyl peroxide (BPO) and at 82 ºC with 2,2´-azobis-izobutyronitrile (AIBN); [MMA] = 2 mol dm^{-3}, [EPC] = 50 g dm^{-3}, [I] = 0.01 mol dm^{-3}.

mers. Graft content was quantified by the characteristic absorbance ratio of the carbonyl absorption band at 1730 cm^{-1} belonging to methacrylate moieties and absorption band at 1378 cm^{-1} belonging to the methyl group in the EPC backbone and PMMA polymer,[2] applying the previously established calibration curve. The IR calibration curve (Figure 1, inset) was obtained by measuring physical polymer mixtures with different EPC / PMMA ratios, which were prepared by solution mixing.

Graft copolymer existence was also verified by turbidimetric measurements.[24,25] The polymer solutions in THF (w = 0.1 %) were titrated by methanol as non-

solvent. For comparison, the measurements were also performed using pure EPC and PMMA polymer constituents and EPC / PMMA mixtures of the same composition as the graft copolymer samples. The characteristic curves obtained are shown in Figure 2. It is evident from the sharp increase in log (T/T_o) value, where T_o is turbidity of polymer solution in THF and T is turbidity of polymer solution after methanol addition, that EPC precipitates immediately with the addition of small quantities of methanol in solution. PMMA precipitates at much higher methanol concentration, between $CH_3OH / THF = 3.5$ and $CH_3OH / THF = 4.5$, with a relative turbidity value increase from log $(T/T_o) = 0.1$ to more than 1.5. Turbidimetric titration curves of EPC / PMMA polymer mixtures and graft copolymers are settled between pure polymer component curves. From the shape of the curves, it is evident that the EPC / PMMA blend essentially consists of two parts with pronounced curve inflections at very low values of the CH_3OH / THF ratio, as a result of EPC precipitation and higher CH_3OH / THF ratio values resulting from PMMA component precipitation. The first inflection part of the EPC-graft-PMMA turbidimetric titration curves are shifted towards much higher CH_3OH / THF ratio values as a result of chemical bonding with PMMA chains. The initial increase in relative turbidity is smooth, likely due to a small part of less grafted EPC macromolecules.

Effect of Initiator

The effect of the initiator type, namely benzoyl peroxide (BPO) and 2,2′-azobisisobutyronitrile (AIBN), on graft efficiency and degree of grafting are presented in Figure 3 and Figure 4, respectively. The reaction temperature of 91 °C and 82 °C corresponded to one hour half-life of the initiator used,[26] therefore, a similar rate for their primary radical formation could be assumed. It is evident that copolymerization with BPO initiator results in greater appreciable grafting extent, as compared to the AIBN initiator. The grafting efficiency in copolymerization system with BPO is between 30 % and 60 % in the investigated conversion range. In the same conversion range, AIBN initiator grafting efficiency did not exceed 10 %. In both initiator systems, the degree of grafting increased with increases in monomeric conversion, but due to grafting efficiency, DG in the BPO case increased from 70 % to 120 %, while the maximum value of DG in the AIBN case was only about 20 %. This finding is in a good agreement with the grafting mechanism based on a relatively higher rate of hydrogen atom abstraction from the polyhydrocarbon backbone by BPO free radicals. Similar to other azonitriles, AIBN yielded cyanoalkyl radicals that were relatively unreactive in hydrogen abstraction reactions. Thus, they tended to initiate homopolymerization of the vinyl monomer rather than its grafting.[1–4,15]

Figure 5. Influence of methyl methacrylate (MMA) concentration on conversion in graft copolymerization of methyl methacrylate / poly(ethylene-*co*-propylene) in toluene solution over two hours at 90 °C: [EPC] = 60 g dm^{-3}, [BPO] = 0.01 mol dm^{-3}.
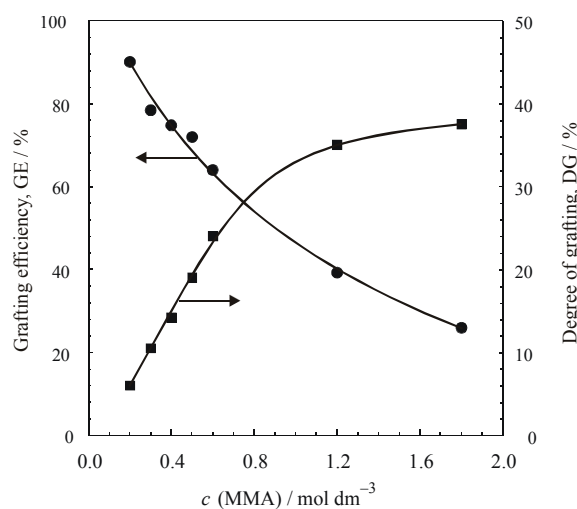
Figure 6. Influence of methyl methacrylate (MMA) concentration on grafting efficiency and degree of grafting in graft copolymerization of methyl methacrylate / poly(ethylene-*co*-propylene) system in toluene solution over two hours at 90 °C: [EPC] = 60 g dm^{-3}, [BPO] = 0.01 mol dm^{-3}.

Effect of Monomer Concentration

The effect of methyl methacrylate concentration on the conversion and graft copolymer yield is shown in Figures 5. and 6, respectively. The MMA concentration was increased from 0.2 mol dm^{-3} to 1.8 mol dm^{-3}, in toluene, under a constant concentration of 60 g dm^{-3} of EPC, using BPO as an initiator and during a reaction time period of 2 hours. The overall MMA conversion

Table 1. Influence of methyl methacrylate (MMA) concentration on methyl methacrylate/poly(ethylene-*co*-propylene) graft copolymerization reaction parameters in toluene solution over two hours at 90 °C: [EPC] = 60 g dm^{-3}, [BPO] = 0.01 mol dm^{-3}

| Sample	[MMA] / g dm^{-3}	X / %	M_n (PMMA)$_H$ / g mol^{-1}	GD [a]	GF [b]
1	40	28.2	41200	0.23	7622
2	60	37.0	39600	0.41	4276
3	120	44.8	38700	0.59	2971
4	180	48.3	39000	0.95	1845
5	240	58.6	28100	0.49	3577

[a] graft density, defined as the number of grafted PMMA chains per backbone chain
[b] graft frequency, defined as the number of backbone repeat units between graft sites

increased with increases in monomer concentration; however, dependence was influenced by both, the EPC and MMA concentrations. The degree of grafting slowly increased with an increase in the MMA concentration with a value of about 35 % at the maximal MMA concentration. As expected, the lower the MMA concentration, the less homopolymer was produced. Hence, at low monomer concentrations, the graft efficiency was as high as 90 %. This value steadily decreased as the MMA concentration increased to a plateau level of about 30 % at a MMA concentration of 1.5 mol dm^{-3}. The results showed that the free radical EPC/MMA-facilitated grafting could be favored by altering the reaction conditions. These parameters are in agreement with the general free radical grafting scheme in solution, where DG is directly dependent on the backbone polymer concentration.[1–3,15] The reaction conditions of a constant viscosity ([EPC] = 60 g dm^{-3}) and the phase separation absence make it likely that the molecular weight of the grafted and free PMMA chain was similar. This assumption is accepted for a free radical graft copolymerization reaction,[27] as it is believed that the propagation and termination reaction rates of grafted and free polymer radicals should be the same. Given this assumption, it is possible to compute graft frequency by knowing the total number of graft and backbone chains, both derived from the molecular weight analysis of each PMMA and EPC. Hence, the calculations were performed only in purpose of a qualitative inspection. It is evident that the average M_n of PMMA slightly differs for the constant EPC concentration ([EPC] = 60 g dm^{-3}), whereas, it is considerably smaller with diluted EPC solution ([EPC] = 20 g dm^{-3}), as is shown in Table 1. The details of the GF calculations were described by Sundberg and others.[27,28] Assuming that all backbone EPC chains have the same number of repeat units, 1753 per molecule (EPC, M_n = 59000 with an average hypothetic molecular weight of 33.66, will give 1753 repeat units), the *grafting density* (GD), the number of grafted PMMA chains per backbone chain and the *grafting frequency* (GF), the number of backbone repeat units between graft sites have been calculated. The value of GD under the described experimental condition varied
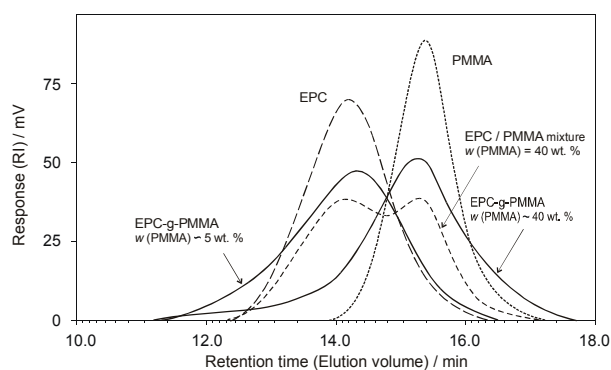
Figure 7. Size exclusion chromatograms of poly(ethylene-*co*-propylene) (EPC), poly(methyl methacrylate) (PMMA) and poly(ethylene-*co*-propylene)-*graft*-poly(methyl methacrylate) (EPC-g-PMMA) copolymers with *w* (PMMA) = 5 % and 40 %.
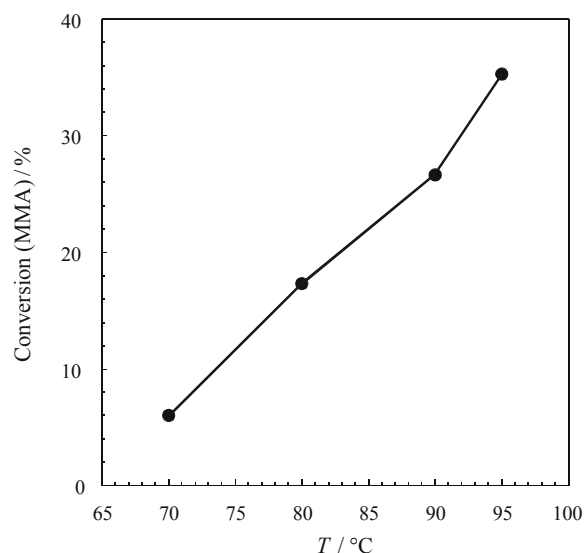
Figure 8. Influence of temperature on conversion in graft copolymerization of methyl methacrylate/poly(ethylene-*co*-propylene) system in toluene solution over two hours: [MMA] = 0.3 mol dm^{-3}, [EPC] = 60 g dm^{-3}, [BPO] = 0.01 mol dm^{-3}.
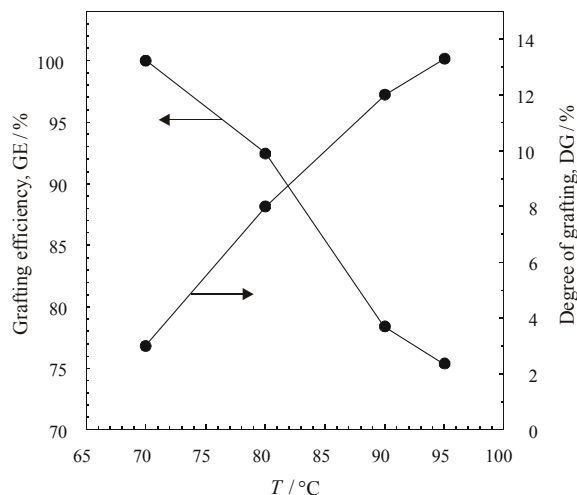
Figure 9. Influence of temperature on grafting efficiency and degree of grafting in graft copolymerization of methyl methacrylate/poly(ethylene-*co*-propylene) system in toluene solution over two hours: [MMA] = 0.3 mol dm^{-3}, [EPC] = 60 g dm^{-3}, [BPO] = 0.01 mol dm^{-3}.
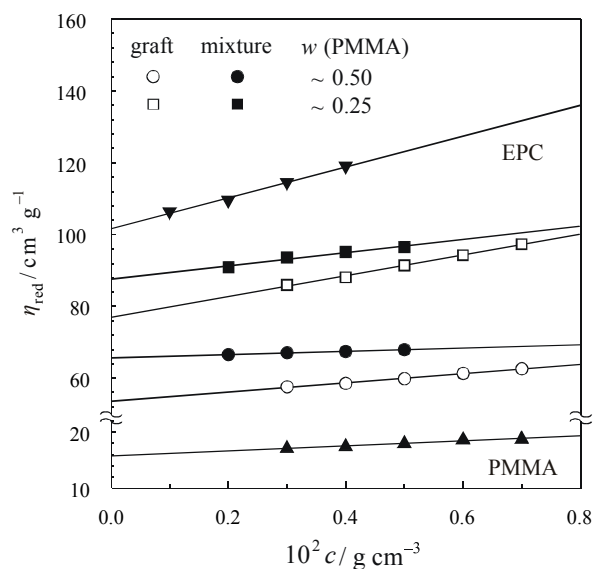
Figure 10. Reduced solution viscosity dependence on total polymer concentration and composition of poly(ethylene-*co*-propylene)/poly(methyl methacrylate) graft copolymers and corresponding mixtures, in xylene at 30 ºC.

from 0.23 to 0.95 PMMA molecules per EPC molecule chain. These results are in agreement with the findings that the propylene base saturated hydrocarbon polymers are not successful in producing high grafting with vinyl monomers.[1–4] However, the obtained results also showed a higher grafting efficiency relative to PP or EPR polymer backbone,[17,18] likely due to the completely amorphous nature of the ethylene/propylene copolymer used.
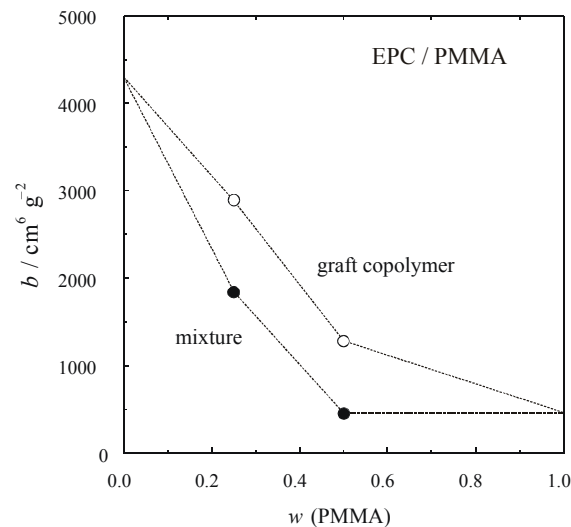
Figure 11. Viscometric polymer-polymer interaction parameter dependence on composition of poly(ethylene-*co*-propylene) and poly(methyl methacrylate) mixture and graft copolymer, in xylene at 30 ºC.

Size exclusion chromatograms of the graft copolymers were compared with EPC/PMMA polymer mixture of similar composition and molecular weight (Figure 7). As shown, there are considerable differences. While the graft copolymers show uniform curves and a wider distribution with a long tail, the polymer mixture shows two well-separated peaks from each of the components. The apparent molecular weights of graft EPC/PMMA copolymers decreases with increasing grafting density and PMMA content in the copolymer, as seen in Figure 7. However, the interpretation and behavior of the molecular weight distribution obtained by the SEC method of graft copolymer is rather complex. Outside the molecular architecture, molecular weights measured by SEC can be strongly affected by repulsive/attractive intermolecular-intramolecular interactions within the column and other solution effects such as molecule association.[29]

Effect of Reaction Temperature

The influence of reaction temperature of the EPC/MMA graft copolymerization on conversion, degree of grafting and grafting efficiency is shown on Figure 8. and Figure 9, respectively. The reaction was performed in the range from 70 ºC to 95 ºC, while all the other reaction variables were kept constant. The reaction was performed at a low concentration of MMA (0.3 mol dm^{-3}) to obtain the appropriate conversion at higher temperatures. When the reaction temperature is increased, monomer conversion is increased and the DG steadily increased from as little as 3 % at 70 ºC to 13.3 % at 95 ºC, whereas the GE slowly decreased from above 100 % to 75 %. At temperatures higher than 95 ºC, significant polymer gelation occurred, especially at higher conversions.[1–3]

Solution Viscosity Properties

The influence of concentration and composition of EPC / PMMA graft copolymers and corresponding polymer mixtures on reduced viscosity of their dilute solutions in xylene at 30 ºC are shown in Figure 11. The viscosities are between those of pure components, EPC and PAMA, and increase as the content of EPC increases. The experimental values follow the typical linear relationship of the Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c = [\eta] + bc$$

where η_{sp} is the solution specific viscosity, $[\eta]$ is the limiting viscosity number (intrinsic viscosity), c is the total mass concentration of the polymeric component(s) and b is the parameter attributed to the mutual interaction of macromolecules in solution. Interaction parameter b denotes the slope of Huggins' equation: $b = k_H [\eta]^2$ where k_H is the Huggins' constant characterized by the overall hydrodynamic and thermodynamic interactions between two kinds of polymer molecules. These preliminary results show that obtained b values were much higher for EPC / PMMA graft copolymers, as compared to the corresponding polymer mixtures (Figure 11). Since the slope of Huggins' equation is a measure of polymer-polymer interaction in solution, a higher slope value denotes a more pronounced attractive interaction.[30,31] As a result, it follows that repulsive interactions in solutions of EPC/PMMA mixtures can be prevailed by the addition of their graft copolymer. This is of particular practical value in the blending of polymeric additives and lubricating oils,[32,33] where the mixtures of poly(alkyl methacrylates) and olefin copolymers are widely used as rheology improvers.

CONCLUSION

Graft copolymerization of methyl methacrylate onto amorphous poly(ethylene-*co*-propylene) (EPC) was successful in the toluene solution using benzoyl peroxide initiator. The graft copolymer formation was verified by selective solvent extraction, infrared spectroscopy and turbidimetric titration method. The grafting yield varies considerably under different reaction parameters, such as monomer concentration, the ratio of backbone EPC to methyl methacrylate, temperature and overall conversion. Near 100 % grafting efficiency was achieved by increasing the EPC concentration, however, varying the reaction conditions in the same manner did not have a significant effect on the chain length of grafted PMMA. The preliminary results on solution behavior show that EPC / PMMA graft copolymers, relative to corresponding polymer mixtures, possess higher values of Huggins interaction parameter.

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SAŽETAK

Slobodno radikalska cijepljena kopolimerizacija metil-metakrilata na amorfni kopolimer etilena i propilena

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Istražena je slobodno radikalska cijepljena kopolimerizacija metil-metakrilata (MMA) na amorfni poli(etilen-*ko*-propilen) (EPC) u otopini toluena, uz benzoil peroksid (BPO) i 2,2´-azobisizobutironitril (AIBN) kao inicijatore, u širokom području sastava i temperature. Nastajanje cijepljenog kopolimera potvrđeno je ekstrakcijom selektivnim otapalom, infracrvenom spektroskopijom i metodom turbidimetrijske titracije. Za reakciju cijepljenja znatno je uč-inkovitiji BPO inicijator, u usporedbi s AIBN. Djelotvornost cijepljenja smanjuje se s povećanjem temperature po-limerizacije, i posebice, povećanjem koncentracije MMA monomera: pri temperaturi reakcije od 90 ºC i vremenu od dva sata djelotvornost cijepljenja se smanjuje od 90 % do 30 % s povećanjem koncentracije MMA od 0,2 na 1,8 mol dm^{-3}, uz stalnu koncentraciju EPC od 60 g dm^{-3}. Povećanjem reakcijske temperature od 70 ºC do 95 ºC smanjuje se djelotvornost cijepljenja s ~100 % na 75 %. Cijepljenim EPC/ PMMA kopolimerima određeni su ras-podjela molnih masa i viskoznost razrijeđenih otopina u ksilenu.