

Methacryloyl carbamate functionalized ethylene-propylene copolymer

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In order to introduce a masked isocyanate functional group into ethylene propylene copolymer (EPM), methacryloyl carbamate (MAC) was synthesized. Grafting of MAC onto EPM was performed by the solution process with the addition of dicumyl peroxide (DCP) as an initiator. The efficiency of grafting tends to decrease with increasing MAC or DCP content and increasing the polarity of solvent; the optimal condition for the present reaction system appeared to be at a low DCP level, a moderate MAC loading and nonpolar solvent. In dynamic rheological measurement, significant degradation and crosslinking of EPM do not arise during the grafting reaction. © 2001 Kluwer Academic Publishers

1. Introduction

The modification of polyolefins by means of graft reactions, where a peroxide initiator is used with various unsaturated polar monomers, has received much attention in the past several decades [1–3]. Modification of polyolefins has been successfully achieved using solution, melt, and solid state routes. The functionalized polyolefins have been extensively used for the improvement of their physical and chemical properties or compatibilization of immiscible polymer blends as well as interfacial adhesion in polymeric composites [4, 5].

For the organic peroxide-initiated functionalization of polyolefins, it is generally observed that crosslinking or chain scission may occur simultaneously with the graft reaction [6–8]. For polyethylene (PE), the dominant side reaction is crosslinking [6] while for polypropylene (PP), the dominant side reaction is chain scission [7]. Since saturated ethylene-propylene copolymer elastomers (EPM) contain ethylene and propylene units in the chain, both cross-linking and degradation should occur on reaction with polar monomer in the presence of peroxides [9–11]. Therefore, in addition to the graft reaction itself, effects of the side reactions on the chain structure and rheological properties are also of practical interest.

Many important applications for functionalized EPM are the productions of multipurpose lubricating oil additives [12], thermally reversible crosslinkers [13] and impact modifiers [14]. Until now, the most frequently employed monomers are unsaturated carboxylic derivatives, such as maleic and itaconic anhydrides [15, 16], and vinylic and acrylic substances containing epoxy, oxazoline and isocyanate functionality [17–19]. Especially, however, when isocyanate is introduced to polyolefins as a functional group, the humidity sensitivity still remains an undesirable factor.

In order to resolve this problem, we have attempted to synthesize methacryloyl carbamate (MAC) as a reactive monomer including the masked isocyanate functionality and grafted this monomer onto EPM. The grafting reactions were carried out under various experimental conditions; dependence of the functionalization degree on the concentration of the monomer, on the concentration of the peroxide initiator, and on the nature of the solvent was particularly investigated. In addition, effects of side reactions on the chain structure were studied by means of dynamic rheological measurements.

2. Experimental

2.1. Materials

EPM (Kumho Polychem, ethylene content = ca. 69 wt%, $M_w = 111,000$) was used as received. MAC was synthesized by reaction of methacrylamide (MAA, Aldrich Chemical) with ethyl chloroformate (ECF, Junsei Chemical). MAA and sodium hydroxide were dissolved in a dioxane, followed by dropwise addition of an excess of ECF, and then the reaction was maintained for 3 h at below 30°C. The reaction solution was extracted using chloroform and the extractant was evaporated in vacuum. The detailed condition of reaction of MAA with ECF for synthesizing MAC was described previously [20, 21]. The overall yield was ~75%. Dicumyl peroxide (DCP, Aldrich Chemical) was used as a radical initiator.

2.2. Functionalization

The functionalization of the EPM was carried out in a four neck round-bottom flask equipped with overhead stirrer, condenser, thermometer, and a nitrogen gas inlet. The EPM was dissolved in xylene at 100°C under

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nitrogen gas stream. DCP and MAC were added to this homogenized solution and the reaction was continued for 2 h. The reaction mixture was then poured into the acetone under vigorous stirring. The precipitated graft copolymer was isolated and washed several times with acetone to eliminate unreacted monomer, initiator and homopolymers of MAC that could possibly be formed during the grafting reaction. Finally, the products were dried in a vacuum oven at 50°C for 24 h.

2.3. Measurements

The synthesized MAC was characterized using proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$, Varian, model Unity Inova NMR 300). The evidence of grafting and the extent of grafting were determined from $^1\text{H-NMR}$ spectroscopy and Fourier-transform infra-red spectroscopy (FT-IR, Nicolet model Magna IR-550). Dynamic rheological properties including storage modulus (G') and loss modulus (G'') of the reaction products were measured using the rotational rheometer (Rheometric Scientific, ARES), with a 10% strain at 150°C under dry nitrogen. Parallel plates, 25 mm in diameter and a gap of 1 mm, were used for the frequency sweep.

3. Results and discussion

$^1\text{H-NMR}$ spectra of the synthesized MAC through the reaction of MAA with ECF are represented in Fig. 1. The doublet at 6.53 and 6.07 ppm assigned to NH_2 of MAA changed to 8.04 ppm assigned to NH in the carbamate group of MAC after the reaction of NH_2 of MAA with Cl of ECF, which was clear evidence for the formation of carbamate bond.

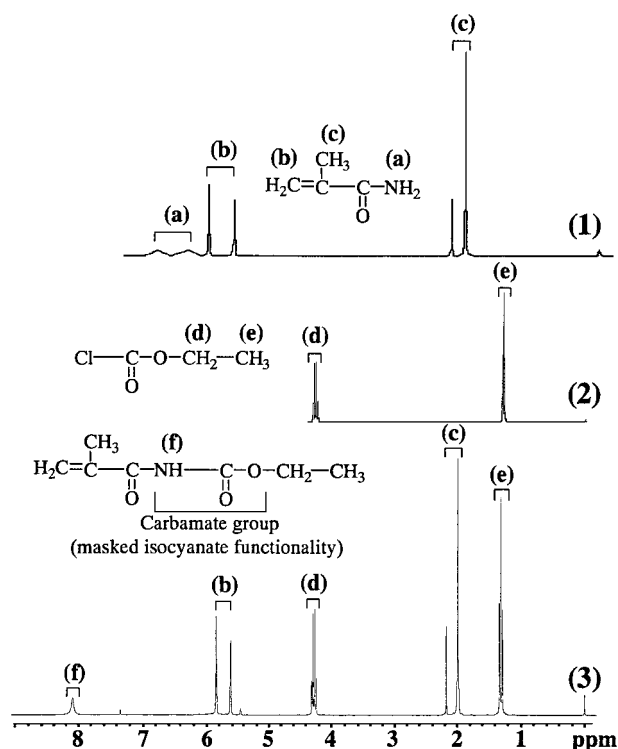


Figure 1 $^1\text{H-NMR}$ spectrum for (1) MAA, (2) ECF, and (3) MAC.

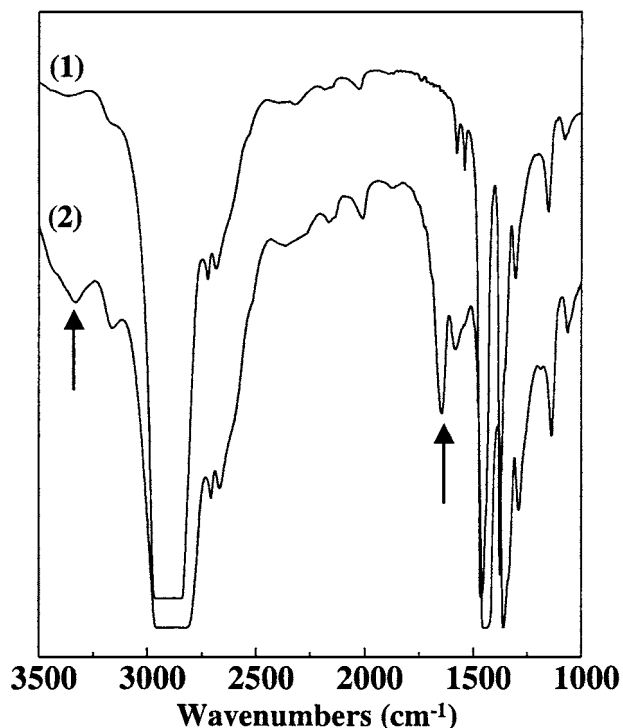


Figure 2 FT-IR spectrum of (1) EPM and (2) 0.32 wt% of MAC grafted onto EPM.

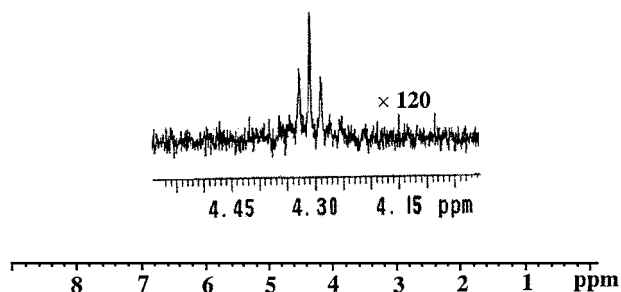


Figure 3 $^1\text{H-NMR}$ spectrum of MAC grafted EPM.

The presence of grafted MAC in EPM was confirmed by FT-IR spectroscopy. Fig. 2 shows the FT-IR spectra for MAC incorporated in the EPM chain. It is possible to observe the $\text{C}=\text{O}$ absorption band and N-H stretching band of the carbamate group of MAC around 1680 cm^{-1} and 3300 cm^{-1} , respectively.

$^1\text{H-NMR}$ spectroscopy (Fig. 3) of the purified product in deuterated benzene solution was used to determine the extent of grafting. The extent of grafting was calculated from the ratio of the integral of peaks for the hydrogen atoms on the MAC to the integral of peaks for the hydrogen atoms of the EPM. The amount of MAC in EPM-g-MAC was 0.32 wt%. Quantitative analysis of the extent of grafting was performed on the other samples by calibrating the ratio of the height of peak of the $\text{C}=\text{O}$ peak at 1680 cm^{-1} and that of C-H peak at 1368 cm^{-1} in the FT-IR spectra.

The effect of monomer concentration on the extent of grafting is shown in Table I. The extent of grafting increases initially with an increase in monomer concentration up to low values (10 phr) and then keeps nearly constant. This result may be due to the homopolymerization tendency of MAC, opposite to the case of maleic

TABLE I Variation of MAC grafted onto EPM for different monomer concentration^a

Monomer concentration (phr) ^b	Initiator concentration (phr) ^b	Grafting extent (wt%)
5	1.0	0.28
10		0.32
15		0.34
20		0.35

^aGrafting reactions were carried out at 100°C for 2 h in xylene.

^bphr: Parts per hundred parts of resin.

TABLE II Variation of MAC grafted onto EPM for different initiator concentration^a

Initiator concentration (phr) ^b	Monomer concentration (phr) ^b	Grafting extent (wt%)
0.5	5	0.13
1.0		0.28
2.0		0.17
0.5	10	0.19
1.0		0.32
2.0		0.28

^aGrafting reactions were carried out at 100°C for 2 h in xylene.

^bphr: Parts per hundred parts of resin.

anhydride. It is also possible that the number of active radical sites available on the EPM backbone is limited by the initial concentration of the initiator used in the grafting reaction.

Table II shows the effect of initiator concentration on the extent of grafting with respect to different initial monomer concentrations. The observed trend is typical for the graft copolymerization reaction occurring via chain transfer. For both monomer concentrations used, the extent of grafting shows the same tendency. The initial increase in the extent of grafting is caused by an increase in concentration of radicals formed through the decomposition of initiator. Furthermore an increase in initiator concentration decreases the incorporation of the monomer. This effect is due to the higher homopolymerization tendency of MAC when the concentration of the initiator increases. These two opposing tendencies result in the appearance of a maximum.

Sun *et al.* reported that the limited solubility of monomers in grafting reactions is also an important factor that controls the overall grafting [14]. The effect of the medium on the extent of grafting was studied by preparing the graft copolymers in *o*-dichlorobenzene, *o*-xylene, toluene, and decaline. The results obtained are given in Table III. Table III shows that the maximum extent of grafting was achieved in nonpolar solvents, whereas as the polarity of solvent increased the extent of grafting continued to decrease. With increasing solvent polarity, the solvency of MAC increased, and thus the homopolymerization tendency of MAC increased, resulting in lower extent of grafting. This result implies that the number of monomers diffusing through the reaction medium and reaching the active radical sites on the EPM backbone governs the grafting extent.

The rheological properties of grafted EPM were also important for the understanding of the grafting reaction. Fig. 4 shows the dependencies of G' and G'' for

TABLE III Variation of MAC grafted onto EPM for different reaction medium at constant concentration of monomer (10 phr^b) and initiator (1 phr^b)^a

Solvent	Dipole moment	Grafting extent (wt%)
decalin	0.00	0.87
Toluene	0.42	0.87
<i>o</i> -dichlorobenzene	2.26	0.37
<i>o</i> -xylene	2.57	0.32

^aGrafting reactions were carried out at 100°C for 2 h.

^bphr: Parts per hundred parts of resin.

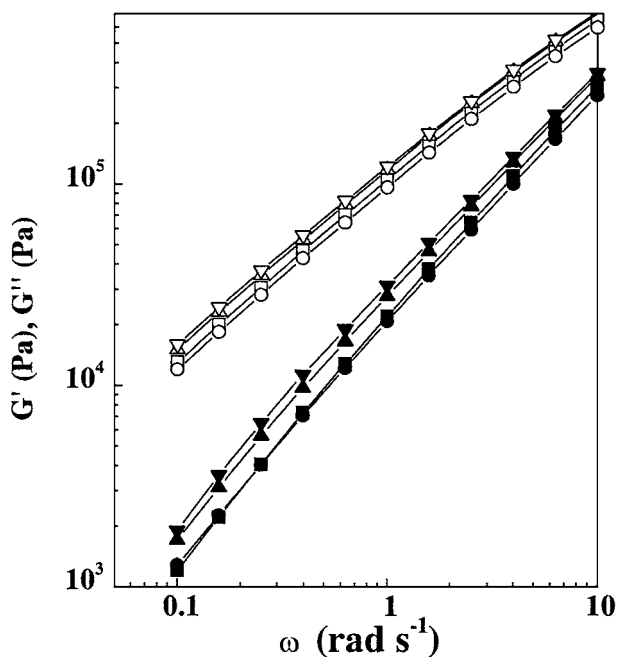


Figure 4 Storage (G' , solid symbol) and loss modulus (G'' , open symbol) versus angular frequency (ω) for EPM-g-MAC samples with increasing the extent of grafting. (●) EPM, (■) 0.13 wt% EPM-g-MAC, (▲) 0.28 wt% EPM-g-MAC, and (▼) 0.35 wt% EPM-g-MAC.

unmodified EPM and modified EPM with different extent of grafting on the frequency. The G' values of the EPM increased with increase of grafting extent, indicating that there was no significant chain degradation. Also, the modified EPM did not exhibit any transition in which G' and G'' crossed over at the low frequencies tested, as in the case of unmodified EPM. At low frequencies, deformation is generally more viscous than elastic for most thermoplastics, hence G'' is greater than G' , whereas the reverse is true for crosslinked materials [22]. In the observation of rheological values, lower G' than G'' over the frequency range tested indicated that the modified EPM is not crosslinked. From the above results, it is not considered that significant chain degradation and crosslinking of the EPM arise during the grafting process.

4. Conclusions

In order to introduce a masked isocyanate functional group into EPM, MAC was synthesized. Functionalized PP, prepared by solution process with various amounts of MAC and DCP, has been analyzed by means of ¹H-NMR, FT-IR and dynamic rheological analysis.

From the ¹H-NMR and FT-IR spectra of the grafted EPM, it was found that MAC was introduced into EPM. The efficiency of grafting tends to decrease with increasing MAC or DCP content and increasing polarity of solvent; the optimal condition for the present reaction system appeared to be at a low DCP level, a moderate MAC loading and nonpolar solvent. From the dynamic rheological measurements it was concluded that significant degradation and crosslinking of EPM do not arise during the grafting reaction. So, our future aim is to apply this type of functionalized EPM to a compatibilizer in reactive blends.

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