Polymer Bulletin 34, 301–308 (1995)

Polymer Bulletin

Thermal polymerization and reactive blending of 2-(4-hydroxyphenyl)-1,3-oxazoline

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Received: 6 October 1994/Accepted: 28 November 1994

Summary

Upon heating above its melting temperature at 195°C, 2-(4-hydroxyphenyl)-1,3-oxazoline (**HPO**) was polymerized thermally in melt phase within a few minutes to produce a polymer with etheramide and N-4-hydroxybenzoyl-ethyleneimine repeat units. Polymerization in solution afforded only oligomers with 93% etheramide structure after several hours. Reactive blending, combining 2-phenyl-1,3-oxazoline (**PO**) grafting with in-situ **HPO** thermal polymerization in poly(ethene-co-methacrylic acid), was the key to novel self-reinforced multiphase ethene copolymer blends containing spherical dispersed poly(**HPO**) microphases. Poly(**HPO**) microstructures, blend morphologies, thermal and mechanical properties were investigated.

Introduction

Activated dual-functional derivatives of 4-amino- and 4-hydroxy-benzoic acid are monomers useful in reactive processing technology for production of microcomposites. Such microcomposite comprise isotropic or preferably anisotropic microphases of rigid polymers which are dispersed in a more flexible polymer matrix. As a function of their morphology, aspect ratio, stiffness, and interfacial adhesion, such dispersed microphases reinforce the continuous polymer matrix. Anisotropic dispersion polymerization of dual-functional rigid rod polymer precursors in polymer melts represents an attractive route to particle-, whisker- and short-fiber-reinforced thermoplastics. For instance, when the dual-functional N-(4-aminobenzoyl)-caprolactam monomer was injected into polyamide-6 melts, anisotropic whisker-like poly(p-benzamide) was obtained with excellent interfacial adhesion resulting from covalent coupling of the amino end groups of the polyamide with N-acyl-caprolactam groups at the poly(p-benzamide) particle surface (1,2). Also matrix reinforcement was achieved when anisotropic polymer-polyol dispersions, containing in-situ formed poly(p-benzamide) whiskers, were applied as components of polyurethanes (3). One of the prime requirements in reactive processing application is high reactivity of the dual functional monomers. At temperatures typical for thermoplastic polymer process-

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ing, polymerization must take place within a few minutes hold-up time during processing of the thermoplastic matrix polymer component.

Here we report thermal solution and bulk polymerization of 2-(4-hydroxyphenyl)-1,3-oxazoline (**HPO**) as well as **HPO** melt polymerization in the presence of poly(ethene-co-methacrylic acid), grafted with 2-phenyl-1,3-oxazoline (**PO**). Objective of this research has been to evaluate the potential of in-situ **HPO** dispersion polymerization in reactive blending technology and in-situ microcomposite formation useful in matrix reinforcement of ethene copolymers.

Experimental

Materials

N-Methylcaprolactam was distilled under nitrogen after drying over CaH_2. 2-Phenyl-1,3-oxazoline (**PO**) was prepared similar to Seeligers (4) procedure. Poly(ethen-co-methacrylic acid) (**EMA**), containing 4,25 mol-% (12 wt-%) methacrylic acid, (Nucrel® 1207, melting temperature T_m = 100°C, melt flow index MFI 7,0 dg/min) was purchased from E.I.Du Pont de Nemours & Co, Geneva, and carefully dried in vacuo at 85°C prior use.

Instruments

GPC analysis was performed using solutions in distilled N,N-dimethylacetamid with 3% LiCl at 80°C (column PL-Gel, 10^3, 10^4, 10^5, 10^6 Å, calibrated with PEG, flow rate: 1 ml/min). Titration was carried out using a Mettler DL 25. NMR-measurements were recorded on a Bruker ARX 300. For tensile testing, tensile bars (according to DIN 53455) were cut and machined. Tensile tests to determine Young's modulus and tensile strength at break, were performed at 10 mm/min crosshead speed on an Instron 4204 at 23°C. Scanning electron micrographs of polymer blends were taken on a Zeiss Model DSM 960 microscope. Samples were prepared by fracturing the blend in liquid nitrogen and sputtering with gold, to obtain a surface of 2-3 mm^2. Micrographs were taken in the magnification range 1000-10000. Glass transition temperatures were measured by dynamic mechanical analysis on a Rheometrics solids analyzer at 1 Hz and a heating rate of 5 K/min, and differential scanning calorimetry on a Perkin Elmer DSC 7 with a heating rate of 20 K/min. Reactive blending was performed in a Haake Rheomix 90, equipped with a 60 ml double-screw blender which was preheated at 225°C and operated at 100 r.p.m.

Synthesis of 2-(4-hydroxyphenyl)-1,3-oxazoline

2-(4-Hydroxyphenyl)-1,3-oxazoline (**HPO**) was prepared according to the method reported by Saegusa et al. (5). After the recrystallization the product was sublimated in vacuo at 160°C; m.p. 194-195°C. $C_9H_9NO_2$ (163,18) Calc. (Found): C 66,25 (66,03) H 5,56 (5,61) N 8,58 (8,47). ^{1}H-NMR (DMSO-d_6): δ = 10,05 (s, 1H, OH); 7,67 (d, 2H, C_6H_4); 6,78(d, 2H, C_6H_4); 4,28 (t, 2H, CH_2O); 3,87 ppm (t, 2H, CH_2N). ^{13}C-NMR (DMSO-d_6): δ = 163,0 (C=N); 160,3 (COH); 129,7; 118,4; 115,3 (C_{arom}); 67,1 (CH_2O); 54,3 ppm (CH_2N). IR (KBr): 1635 cm^{-1} (C=N). According to titration (0,1 N $HClO_4$ (AcOH) in DMF/AcOH = 9:1) purity was > 99%.

Bulk polymerization of 2-(4-hydroxyphenyl)-1,3-oxazoline

8,00 g (49,0 mmol) of **HPO** were placed in a flask under nitrogen and heated at 220 °C. The monomer melted completely within 2 min. A highly viscous light yellow polymer was obtained after 10 min. The brittle and transparent polymer was soluble in DMF, DMSO, DMAc and formic acid. $[C_9H_9NO_2]_x$ Calc. (Found): C 66,25 (66,34) H 5,56 (5,44) N 8,58 (8,51). ^{1}H-NMR (DMSO-d_6, 80°C): 9,62 (s, OH); 8,21 (m, NH); 7,73; 7,22; 6,95; 6,75 (m, aromatic H); 4,16 (s, CH_2O); 3,63 (s, CH_2NH); 3,80-3,36 ppm (m, CH_2NCH_2) (see Fig.1). ^{13}C-NMR (DMSO-d_6, 80°C): 171,9 ($CONR_2$); 166,9 (CONH); 161,6; 160,8; 159,8 ($C_{arom}O$); 129,6; 129,1 (*C*HCCO); 127,6 (*C*CONH); 125,9 (*C*$CONR_2$); 115,5; 114,8 (*C*HCO); 67,2; 66,2 (CH_2O); 47,4 (CH_2NCH_2); 39,5; 38,4 ppm (CH_2NH) (see Fig.1). IR (KBr): 1633 (C=O), 1548 cm^{-1} (N-H). Titration (0,1 N KOH (MeOH) in DMF): 21% phenolic groups. According to titration (0,1 N $HClO_4$ (AcOH) in DMF/AcOH = 9:1) the residual oxazoline content was < 1%.

Solution polymerization of 2-(4-hydroxyphenyl)-1,3-oxazoline.

A solution of 6,13 g (37,6 mmol) **HPO** and 0,72 g (16,9 mmol) LiCl in 25 ml N-methylcaprolactam was stirred 24 h under nitrogen at 220°C. The product was purified by precipitation in methanol and the isolated white powder was dried in vacuo (86 % yield). The polymer is soluble in hot DMAc/3% LiCl, DMSO and DMF. After cooling to room temperature the polymer precipitated after several days when DMF or DMSO were used as solvents. $[C_9H_9NO_2]_x$ Calc. (Found): C 66,25 (65,92) H 5,56 (5,78) N 8,58 (8,69). ^{1}H-NMR (DMSO-d_6, 80°C): 9,64 (s, OH); 8,20 (m, NH); 7,74; 7,68; 7,23; 6,95; 6,75 (m, aromatic H); 4,33 ($CH_2OC{=}N$); 4,13 (m, CH_2O); 3,89 ($CH_2N{=}C$); 3,57 (m, CH_2NH); 3,76-3,31 ppm (m, CH_2NCH_2) (see Fig.1). ^{13}C-NMR (DMSO-d_6, 80°C): 166,2 (CONH); 160,7; 160,1 ($C_{arom}O$); 129,0 (*C*HCCO); 126,4 (*C*CONH); 114,7; 113,9 (*C*HCO); 66,1 (CH_2O); 38,5 ppm (CH_2NH) (see Fig.1). IR (KBr): 1632 (C=O), 1548 cm^{-1} (N-H). Titration (0,1 N KOH (MeOH) in DMAc/3% LiCl): 9% phenolic groups. According to titration (0,1 N $HClO_4$ (AcOH) in DMAc (3% LiCl)/AcOH = 9:1) the residual oxazoline content was 6%.

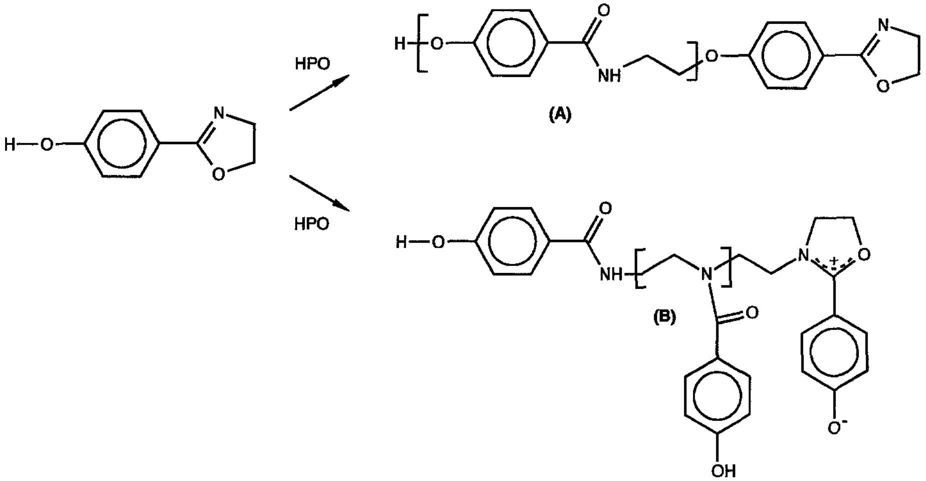
Reactive blending

IB-HPO15 was prepared as follows. 31,9 g (containing 44,5 mmol methacrylic acid unit) poly(ethene-co-methacrylic acid) (**EMA**) , containing 30 mg stabilizer (Irganox 1010), was melted in the blender at 225°C and 6,54 g (44,5 mmol) **PO** was injected. Ten minutes of initial mixing were needed for the formation of the matrix **EMA-g-PO** by melt-grafting reaction (6). Then, 6,75 g (41,4 mmol) **HPO** was added and thermally polymerized. After an additional time of sixteen minutes, no further increase of torque signalized complete reaction. The obtained material was removed and compression molded under vacuum at 200°C to give sheets of 2 mm thickness, using a Schwabenthan Polystat 100 press.

IB-HPO25 was performed accordingly. 27,8 g (containing 38,7 mmol methacrylic acid unit) **EMA** was reacted with 5,70 g (38,7 mmol) **PO**. Then, 11,25 g (68,9 mmol) **HPO** was polymerized. No residual **PO** or **HPO** could be detected by extraction with acetone and analyses by NMR measurements of both blends.

Results and discussion

In 2-position substituted 1,3-oxazolines are readily available derivatives of nitriles or carboxylates and have found a wide spectrum of applications ranging from coatings to reactive blending (7). In reactive processing, 1,3-oxazolines are being used as chain extenders and stabilizers for polyesters (8) and for selectively attaching side chains onto poly(ethene) backbone during melt-processing of ethene copolymers (6). Phenolic hardeners such as novolacs, were used to cure di-and polyfunctional 1,3-oxazolines in order to produce thermally stable, high-T_g polymer networks (9). Similar to procedures reported in the literature (5), reaction of ethyl(4-hydroxybenzoate) with 2-aminoethanol followed by dehydration in the presence of thionylchloride gave 2-(4-hydroxyphenyl)-1,3-oxazoline (**HPO**) in high yields. As depicted in Scheme 1, **HPO** polymerization can involve two different reaction pathways: in pathway A, nucleophilic attack of the phenolic group at the carbon atom in 5 position causes ring-opening and step-growth formation of linear poly(oxy-p-phenylene-carbonyl-iminoethylene) (**A**); in pathway B, strong acids or alkylating agents give oxazolinium salts which are efficient initiators for cationic **HPO** ring-opening polymerization involving nucleophilic attack of 1,3-oxazoline-nitrogen at the carbon atom in 5-position of the terminal oxazolinium group. As a result of cationic **HPO** ring-opening polymerization phenolic poly(N-4-hydroxybenzoyl-ethylenimine), referred to as (**B**), is obtained. In a model reaction using 2-phenyl-1,3-oxazoline and p-hydroxyphenyl methyl benzoate the only product which could be detected by ^{1}H- and ^{13}C-NMR involved structure **A**.



Scheme 1. Building of etheramide (**A**) and phenolic amide (**B**) structure units by **HPO** polymerization.

Upon thermal **HPO** polymerization in bulk, complete **HPO** conversion was found at 220°C within 10 minutes. As was apparent from DSC analysis of the polymerization reaction, highly exothermic polymerization started immediately after **HPO** was melted at 195°C. The resulting polymer exhibited glass temperature of 152°C and inherent viscosity in DMF of $\eta_{inh} = 0.25$ dl/g (30°C). No residual monomer could be detected by GPC and

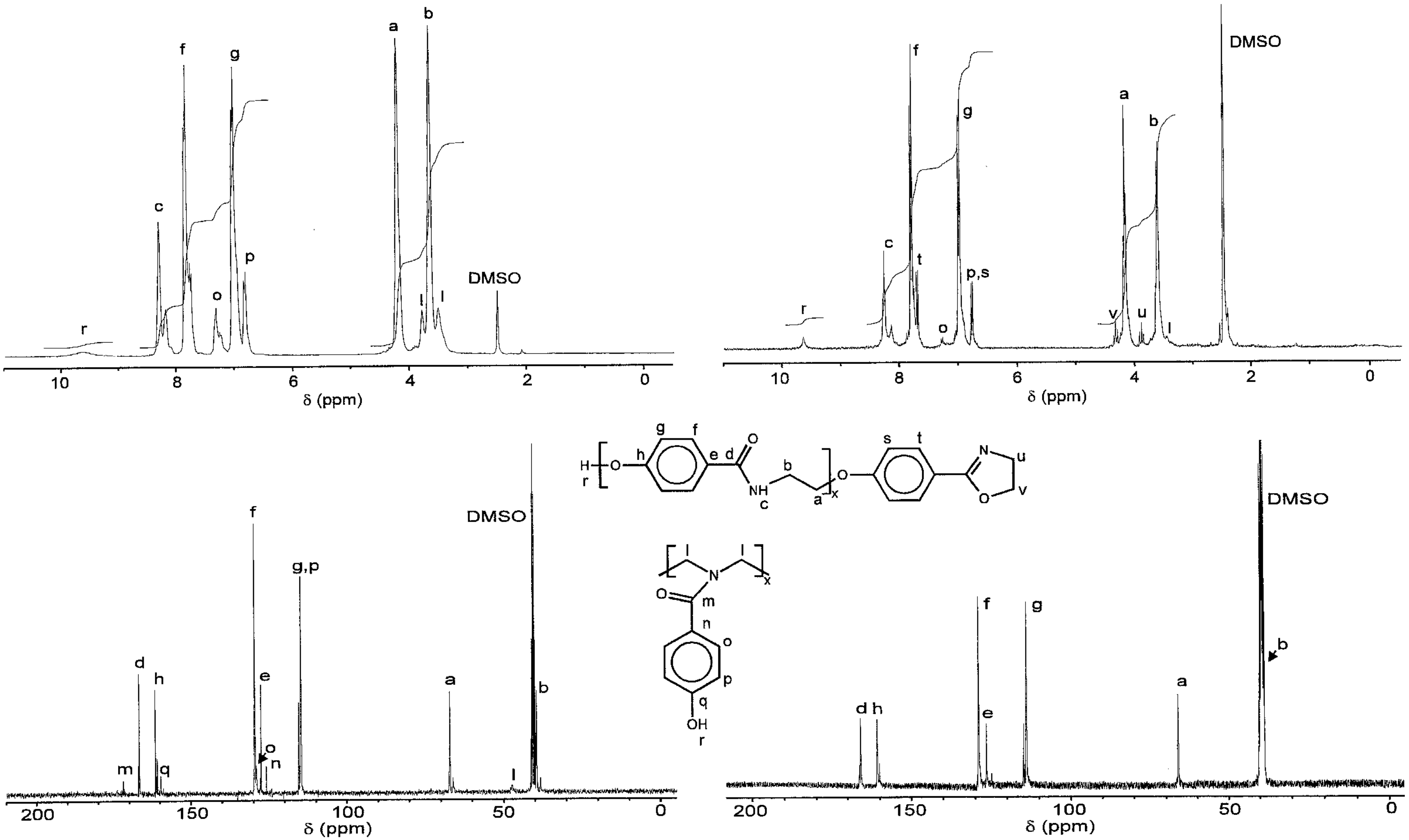
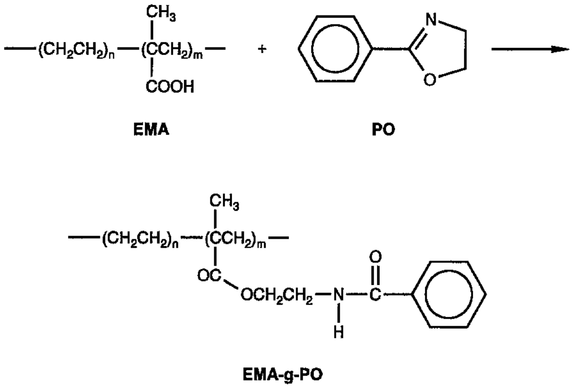


Fig.1. ^{1}H- (300 MHz) and ^{13}C-NMR (75MHz) spectra of poly(**HPO**) prepared in bulk (left side) and in solution (right side).

the molecular weight of the polymer was M_n = 18850 g/mol (M_w/M_n = 2,09; unimodal). For comparison, solution **HPO** polymerization in N-methylcaprolactam containing 3 wt-% LiCl after 24 hours still contained few residual **HPO** and gave polymers of T_g=147°C, η_{inh} = 0.18 dl/g (DMF, 30°C) and M_n = 3280 g/mol (M_w/M_n = 1,75). Both polymers contain segments of linear polyetheramide (**A**) and phenolic polyamide (**B**). Using ^{1}H- NMR spectroscopy, as depicted in Fig.1, it was possible to determine the ratio of (**A**) and (**B**). The signals a, b, c, f and g were assigned to structure (**A**) and l, o and p to structure (**B**). Also the ^{13}C-NMR spectrums in Fig. 1 confirms the two different structures. While solution polymerization gave 93% polyetheramide (**A**), thermal bulk polymerization produced a polymer with 80% etheramide (**A**)/ 20% amide (**B**) units. The much lower content of phenolic amide structures (**B**) in the case of solution polymerization was attributed to the presence of N-methylcaprolactam as Lewis base as scavenger for the acidic proton of the phenolic group. Therefore, the content of phenolic anions increased and nucleophilic attack of phenolate is more favoured. In the absence of Lewis base, the rather acidic hydroxy group of **HPO** and polyamide (**B**) could initiate cationic ring-opening polymerization. So nitrogen attack of the oxazoline group at the oxazolinium ion, resulting from protonation of the oxazoline, took place.



Scheme 2. Melt grafting of **PO** onto EMA.

When **HPO** was injected into the melt of poly(ethene-co-methacrylic acid) containing 4,25 mol-% (12 wt-%) methacrylic acid, referred to as **EMA**, drastic melt viscosity build caused severe processing problems. Therefore a modified process was introduced. Similar to procedures reported previously for reactive processing of 2-phenyl-1,3-oxazoline (**PO**), stoichiometric amounts of **PO** were injected into the **EMA** melt. During 10 minutes, as shown in Scheme 2, the carboxylic acid groups were converted quantitatively into graft copolymers containing esteramide side chains (**EMA-g-PO**) (6). Then 15 wt-% (sample **IB-HPO15**) or 25 wt-% **HPO** (sample **IB-HPO25**) respectively was injected and polymerized within 5 minutes at 225°C. The torque versus time plot shows torque decrease when **PO** after 1 min, and **HPO** after 10 min are injected, also melt viscosity increase, caused by melt grafting of **PO** and polymerization of **HPO**. ^{1}H- and ^{13}C-NMR analysis as well as extraction studies using acetone confirmed the absence of both residual **PO** and residual **HPO**. Moreover, poly(**HPO**) composition was identical to that of poly(**HPO**) formed in bulk polymerization, showing the identical molecular weight in GPC. DSC studies revealed that a second polymer phase, equivalent to poly(**HPO**), with glass temperature at 148°C was incorporated in the blend. According to scanning electron microscopic imaging of blend fracture surfaces, prepared by cryogenic fracture in liquid nitrogen and displayed in Fig.2, average diameters of the dispersed microphases varied between 0,2 and 3 μm. Since the poly(**HPO**) consisted of a segmented polymer with

Table 1. Properties of matrix and blends.

Sample	content PO in wt-%	content HPO in wt-%	domain size in μm	T_g a) in °C	T_g b) in °C	T_m c) in °C	Young's modulus d) in MPa	tensile strength at break d) in MPa	elongation at break e) in %
EMA	0	-	-	27	26	100	67	23	680
EMA-g-PO	16,9	-	-	13	15	98	30	15	719
IB-HPO15	14,5	15	0,2-3	20/148	18	99	57	13	544
IB-HPO25	12,7	25	0,3-3	18/148	18	100	84	11	339

a) Glass transition temperature, determined by means of differential scanning calorimetry.
b) Glass transition temperature, determined by means of dynamic mechanical analysis.
c) Melting point, determined by means of differential scanning calorimetry.
d) Mean value of a number of eight samples, divergence < 4 %.
e) Mean value of a number of eight samples, divergence < 10 %.

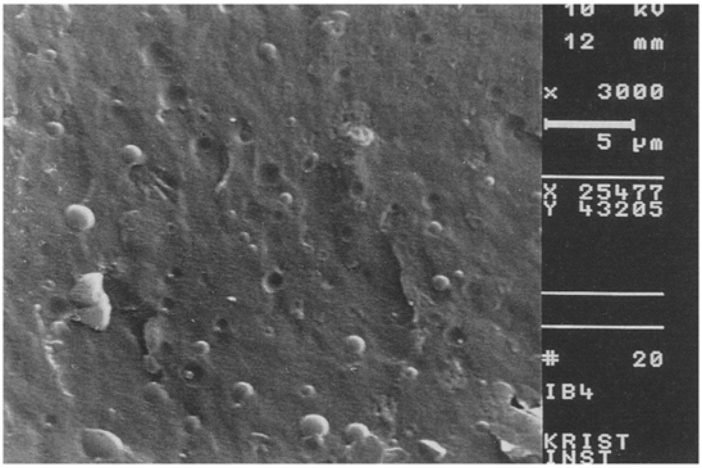


Fig.2. SEM image of **IB-HPO15** fracture surface.

flexible polyetheramide **A** segment, it was not surprising that spherical particles were formed and no whisker- or slab-like microphases could be detected. During cryogenic fracture, some of the poly(**HPO**) microphases were pulled out of the matrix typical for adhesive failure at the particle/matrix interface. Inadequate interfacial adhesion to matrix **EMA-g-PO** may account for rather low tensile strengths of blend samples. However, incorporation of the poly(**HPO**) microparticles gave substantially larger Young's moduli of the blend with respect to **EMA-g-PO**.

Conclusion

The rapid thermal polymerization of **HPO** at temperatures above the **HPO** melting temperature of 195°C can be applied to incorporate poly(**HPO**) microphases, consisting of a polymer with etheramide and phenolic amide repeat units, into various thermoplastics. In order to achieve property synergisms and matrix reinforcement, interfacial adhesion must be improved in the case of ethene copolymers containing less than 5 mol-% comonomer. Combination of in-situ grafting reaction and in-situ melt-phase polymerization can be applied to improve interfacial adhesion and expand the scope of this reactive processing technology.

Acknowledgement

The authors would like to thank the Deutsche Forschungsgemeinschaft for supporting this research as part of the "Sonderforschunsgbereich" SFB60.

References

1. Mülhaupt R, Rösch J (1994) Polym. Adv. Techn. 5:282
2. Mülhaupt R, Rösch J, Dehmharter S (Nov 1993) J. Phys. IV Suppl., 3:1519
3. Demharter S, Rösch J, Mülhaupt R (1993) Polym. Bull. 31:421
4. Witte H, Seeliger W (1974) Liebigs Ann. Chem. 6:996
5. Kobayashi S, Mizutani T, Saegusa T (1984) Makromol. Chem. 185:441
6. Müller P, Wörner C, Mülhaupt R (1994) Macromol. Chem. Phys., submitted
7. Frump J A (1971) Chem. Rev. 71: 483
   Kobayashi S (1990) Prog. Polym. Sci. 15:751
8. Inata H, Matsumura S (1985) J. Appl. Polym. Sci. 30:3325, (1986) ibid. 32:5193, (1987) ibid. 33:3069
9. Culbertson B M (1993) Polym. Materials Sci. Eng. 68:20