

Electron Spin Resonance Study and Reactive Extrusion of Polyacrylamide and Polydiallyldimethylammonium Chloride

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ABSTRACT: In this article we report results from an experimental investigation on reactive extrusion of water-soluble polymers. A polymer system containing homopolymers of diallyldimethylammonium chloride (PolyDADMAC) and acrylamide (PAM) was chosen for this study. Reactive extrusion was performed in a counter-rotating, tangential twin screw extruder using glycerol as a plasticizer and 2,5-dimethyl-2,5-di-(*t*-butylperoxy) hexene-3 (Lupersol 130) as an initiator. The effects of three processing parameters (polyDADMAC/PAM weight ratio, extrusion temperature, and residence time) on grafting efficiency and degree of grafting of polyDADMAC on PAM were examined. We found the grafting efficiency of polyDADMAC onto PAM decreased with increasing extrusion temperature, polyDADMAC/PAM weight ratio, and residence time. The degree of grafting of polyDADMAC increased with increasing polyDADMAC/PAM weight ratio, but decreased with increasing extrusion temperature and residence time. The insoluble gel fraction in the extruded copolymer increased with increasing extrusion temperature and residence time, but decreased with increasing polyDADMAC/PAM weight ratio. The chemistry and free radical mechanism of PAM-peroxide and polyDADMAC-peroxide systems were studied for three different peroxides using an electron spin resonance technique. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1154–1164, 2000

Key words: reactive extrusion; polydiallyldimethylammonium chloride; polyacrylamide; electron spin resonance

INTRODUCTION

Water-soluble polymers (polyelectrolytes) play an important role as flocculants in wastewater treatment, sludge dewatering, papermaking, and mineral processing.^{1–7} Commercial synthetic polyelectrolyte flocculants used in industrial and municipal wastewater treatment as well as in the pulp and papermaking industry are ionic polymers manufactured by modifying polyacrylamide

(PAM) or copolymerizing acrylamide (AM) with comonomers having ionic charge groups.^{1,8–11}

Current commercial acrylamide copolymer flocculants are manufactured via a free radical polymerization mechanism or by post-reaction modification of PAM by Mannich- and Hoffman-type reactions to give cationic polymers with relatively high molecular weight.^{1,12–15} The charge units or cationic centers in these polymers are randomly distributed along the backbone of the polymer chain. According to charge neutralization and chain bridging mechanism of flocculation,¹⁶ such a random copolymer may not be an efficient flocculant. To be more effective, it has been hypothesized that the charge units should be concentrated on several sections along the

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backbone of the polymer chain to form charge clusters. This can be achieved by grafting charged monomers from the backbone of PAM or grafting preformed charged polymer chains onto the backbone of PAM.

Such grafting has been successfully accomplished in dilute aqueous solution using γ -radiation as a free radical initiator for a polydiallyldimethylammonium chloride (polyDADMAC) and PAM system.¹⁷⁻²⁰ The grafted copolymers showed remarkable improvement in some flocculation and sludge dewatering performance over the homopolymers and their blends as well as commercial linear random copolymers. The graft copolymerizations to date¹⁷⁻²⁰ were done in dilute aqueous solution (<1% wt of polymer), which lacks commercial viability. Other techniques such as reactive extrusion have potential to provide a more efficient grafting process.

Reactive extrusion, or reactive compounding, refers to chemical reaction during extrusion processing of polymers. The extruder, which can be considered another form of a chemical reactor,²¹ provides extensive and intensive mixing, good temperature control, and a controlled residence time distribution. There are two common types of extruders, namely, single screw extruder and twin screw extruder. The twin screw extruder provides more screw and operating options for different types of reaction, and hence is commonly used for reactive extrusion. A comprehensive list of reactive extrusion processes ranging from bulk polymerization, controlled degradation, functionalization, and grafting to formation of interchain polymers has been summarized by Ganzeveld and Jansen.²²

In this study, the chemistry of free macroradicals was examined by the electron spin resonance (ESR) technique. It is the only technique with the potential to detect radical types and their concentration. The advent of ESR has provided a powerful tool to study the modification of polypropylene via a free radical mechanism,²³ peroxide modification of high-density polyethylene,²⁴ peroxide-induced crosslinking and degradation of polyvinyl chloride,²⁵ and peroxide crosslinking of isotactic and syndiotactic polypropylene.²⁶ We used ESR to study the chemistry and free radical mechanism of PAM-peroxide and polyDADMAC-peroxide systems at high temperatures for three different peroxides.

Also, we investigated the graft copolymerization of polyDADMAC onto PAM by reactive extrusion in a counter-rotating, tangential twin screw

extruder using glycerol as a plasticizer and 2,5-dimethyl-2,5-*di*-(*t*-butylperoxy) hexene-3 (Lupersol 130) as a free radical initiator. The effects of three processing parameters (polyDADMAC/PAM weight ratio, extrusion temperature, and residence time) on the grafting efficiency (GE) of polyDADMAC and the degree of grafting (DOG) of polyDADMAC onto PAM are presented.

EXPERIMENTAL

Materials

For ESR experiments, PAM (mol wt = 5×10^6 g/mol) containing 1.5% by weight of polyacrylic acid was supplied in granular form by Sigma Aldrich Chemical Company and used without further purification. PolyDADMAC (mol wt = 3×10^5 g/mol) was supplied by Sigma Aldrich Chemical Company in the form of an aqueous solution containing 20% by weight of DADMAC. It was vacuum-dried to solid polymer at room temperature and then ground into fine powder before mixing with peroxide. For this study, we used three different peroxides, namely, dicumyl peroxide (DCP) (Sigma Aldrich Chemical Co.), 2,5-dimethyl-2,5-*di*-(*t*-butylperoxy) hexene-3 (Lupersol 130) (Akzo Chemicals Inc.) and cumene hydroperoxide (CHP) (Sigma Aldrich Chemical Co.). They were used without further purification. Before mixing peroxide with PAM and polyDADMAC, the peroxide was dissolved in acetone and the acetone was evaporated with continuous stirring. The polymer-peroxide mixtures were then vacuum-dried at room temperature, and the dried PAM-peroxide and polyDADMAC-peroxide samples were placed in ampoules of 3-mm inner diameter.

For reactive extrusion experiments, PAM (mol wt = 10×10^6 g/mol) and polyDADMAC were supplied in granular form by Nalco Chemical Company, and used without further purification. Glycerol, used as a plasticizer for extrusion, was supplied by Fisher Scientific Ltd. Lupersol 130 (L-130), an organic peroxide, was supplied by Elf Atochem Inc. Samples for reactive extrusion were prepared by mixing glycerol, Lupersol 130, PAM, and polyDADMAC at room temperature. The resulting mixture was stored in sealed plastic containers overnight before feeding into the extruder.

Experimental Design

ESR measurements were conducted in a Bruker EPR Spectrometer (EP 072). The spectrometer

Table I Weight Fraction of Peroxide in PolyDADMAC- and PAM-Peroxide Systems for ESR Studies

Peroxide	Molecular Weight	Weight Fraction Based on Polymer (%)		
		0.01 g mol/kg	0.02 g mol/kg	0.03 g mol/kg
CHP	152.2	0.152	0.304	0.456
Lupersol 130	286.4	0.286	0.572	0.858
DCP	270.4	0.271	0.542	0.813

was operated at a microwave power of 2.007 mW (20 dB) and modulation frequency of 100 kHz. The saturation behavior of the radical spectra was studied, and no power saturation was found at the level of 2.007 mW. Peroxide concentration levels of 0.01, 0.02, and 0.03 g mol/kg polymer were used and their corresponding weight fractions are listed in Table I. The temperature was set at 170, 180, and 190°C for PAM-DCP, PAM-L130, polyDADMAC-DCP and polyDADMAC-L130 systems, and 180, 190, and 200°C for PAM-CHP and polyDADMAC-CHP systems. At these temperatures, ESR spectra having good signal-to-noise ratios were observed for samples with peroxide concentration levels of 0.01–0.03 g mol/kg polymer. The glass ampoule was inserted into the cavity of the spectrometer, and the generation of radicals and their termination were determined by the intensity of the ESR signal. The absolute concentration of radicals were obtained by numerical integration of ESR spectra and calibrated with 2,2-diphenyl-1-picryl-hydrazyl hydrate (obtained from Sigma Aldrich Chemical Co.) dissolved in benzene at room temperature.

The graft copolymerization of polyDADMAC on PAM by reactive extrusion was performed in a nonintermeshing, counter-rotating, tangential twin-screw extruder (Welding Engineers 30 mm, L/D = 36 : 1 with a 6 : 1 single screw section). The concentration of plasticizer (glycerol) and initiator (Lupersol 130) was fixed at 20% and 1% by weight, respectively, based on the total weight of PAM and polyDADMAC. The weight ratio of polyDADMAC/PAM was set at 0.25, 0.5, and 1.0, and the reaction (or extrusion) temperature was set at 120, 140, 160, and 180°C. To study the effect of residence time on copolymerization, screw speeds of 20 and 40 rpm were chosen. Higher screw speeds lead to

shorter average residence (reaction) time. Extruded copolymers of polyDADMAC and PAM were collected in large glass containers, cooled to room temperature, and then stored in sealed plastic bags for further analysis.

GE and DOG

The GE and DOG for the copolymerization of polyDADMAC onto PAM are defined as follows:

$$GE = \text{polyDADMAC}_{gr} / \text{polyDADMAC}_0$$

$$DOG = \text{polyDADMAC}_{gr} / \text{PAM}_0$$

where polyDADMAC_{gr} is the amount of polyDADMAC grafted onto PAM, polyDADMAC_0 is the initial amount of polyDADMAC, and PAM_0 is the initial amount of PAM. The grafted amount of polyDADMAC is determined after copolymer separation of the extruded product.

Copolymer Separation

Extruded copolymers were purified to evaluate the GE and DOG. A 2% by weight solution of each of the extruded copolymers was prepared by dissolving 1 g of the extruded product in 50 mL of deionized water at room temperature. Acetone was used as a solvent to dissolve the ungrafted polyDADMAC from the extruded copolymer solution. This requires one to determine the critical nonsolvent (acetone) to solvent (water) ratio for precipitation, i.e., the volume of acetone at which point the solution starts to become turbid. When the ratio of volume of acetone over the polymer solution is higher than the critical ratio, polyDADMAC precipitates. Ma and Zhu¹⁸ have listed the critical ratios for polyDADMAC solutions of seven different concentrations. They found that at higher concentrations of polyDADMAC solution, less acetone was needed for precipitation. Because the molecular weight of PAM in this study is approximately 50–100 times that of polyDADMAC, PAM solutions of the same concentration as polyDADMAC require less acetone to precipitate polymer. Therefore, by carefully selecting a volume ratio of nonsolvent to solvent, the graft copolymers and PAM can be precipitated while ungrafted polyDADMAC will remain in solution. This facilitates the separation of ungrafted polyDADMAC from the extruded product. For this study, we chose a nonsolvent to solvent volume ratio of four to separate ungrafted polyDADMAC

from dilute polymer mixture solutions of polyDADMAC and PAM. At this volume ratio, >94% by weight of PAM precipitates out, whereas polyDADMAC remains in solution even when the volume ratio is above 15.

Acetone was added to each of the 2% (by weight) solution of extruded copolymers, and centrifuged in a Beckman GS-15R Centrifuge at 3000 r.p.m. and room temperature for 15 min. The precipitate (containing PAM, and graft copolymer of PAM and polyDADMAC) was separated from the liquid (containing acetone, water, glycerol, and ungrafted polyDADMAC), placed in a glass dish, and vacuum-dried at room temperature to remove traces of acetone and water. The amount of grafted polyDADMAC was obtained by weighing the vacuum-dried sample, and both GE and DOG were calculated.

Gel Fraction

The grafting of polyDADMAC onto PAM using a free radical initiator is done by extracting hydrogen atoms from the backbone of polyDADMAC and PAM. These backbone radicals are then terminated by combination. It has been inferred from viscosity measurements that a polyDADMAC radical does not easily combine with another polyDADMAC radical, i.e., crosslinking between cationic chains is limited.¹⁷ However, a PAM radical is prone to termination with either another PAM radical or a polyDADMAC radical. Because of the high activity of PAM radicals, macrogel formation is an important feature of the grafting process and must be controlled. Significant levels of gelation (crosslinking) tend to occur at high initiator and polymer concentrations, leading to the formation of water-insoluble copolymers. In this study, the gel fractions of extruded graft copolymers were measured using a Soxhlet extractor. Samples of 0.5 g of the extruded graft copolymer were cut into small pieces and placed on a 150-mm diameter circular filter paper (Whatman, Qualitative No. 1). The filter paper was then folded and placed in the Soxhlet extractor. The graft copolymers in the extractor were washed with refluxing deionized water for 2 days and vacuum-dried at room temperature for 3 days to remove water. The amount of water-insoluble gel in the extruded graft copolymer was obtained by weighing the vacuum-dried sample, and the gel fraction was calculated.

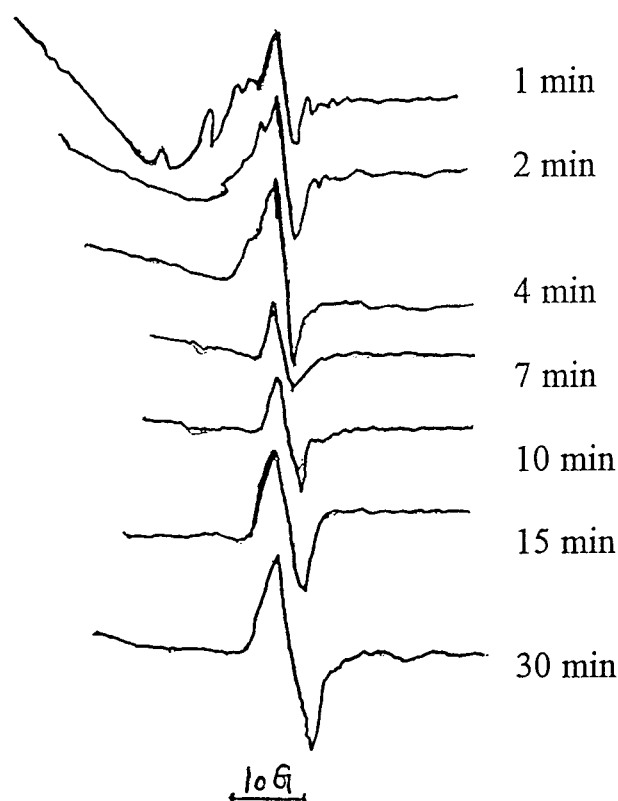


Figure 1 An ESR spectrum of a PAM-L130 system at 180°C, concentration of L130 = 0.03 mol/kg PAM.

RESULTS AND DISCUSSION

ESR Measurements

Figure 1 shows a typical ESR spectra recorded on-line during the course of PAM modification. Upon exposure to high temperature, the peroxide molecules decompose and generate primary radicals. These primary radicals, in turn, abstract hydrogen from PAM chains and produce polymer radicals. The polymer radicals are immediately detected by the ESR spectrometer as a singlet line spectrum. The shape and position of the peak is very similar to an ESR signal obtained from a γ -radiated PAM sample at room temperature.²⁷ In the study by Reddy et al.²⁷ the authors obtained a three-line ESR signal at liquid nitrogen low temperature conditions, and the signal quickly changed to singlet line at room temperature. This change was due to the change in the structure of a PAM radical as shown in Figure 2. It has been reported that the hydrogen atom bound to the tertiary carbon atom can be easily rejected as compared with those bound to the primary and secondary carbon atoms.²⁸ The

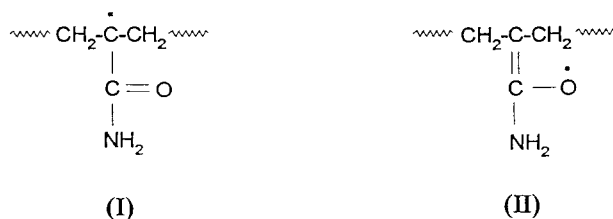


Figure 2 Structures of a PAM radical.

three-line ESR signal corresponds to structure (A) that is caused by the loss of a tertiary hydrogen on the backbone of PAM due to the high-energy γ -radiation. As the temperature increases, the structure (A) quickly changes to a more stable structure (B) that is similar to a polyene radical structure, and shows only a singlet line. In PAM-peroxide systems, the primary radicals, generated by the decomposition of peroxide in PAM, abstract the tertiary hydrogen on backbone of PAM and form a PAM radical with structure (A). These radicals are very active and short-lived at high temperatures. Some of these radicals may combine with each other immediately to form intermolecular crosslinking between PAM chains but most of them would quickly convert to structure (B) that is more stable at high temperatures. Structure (B) accounts for the singlet line we obtained in our PAM-peroxide systems.

Figure 3(a–c) shows the concentration of PAM radicals as a function of reaction time for the PAM-DCP system at temperatures of 170, 180, and 190°C. For the system without any peroxide (i.e., PAM only), there is an increase in free radical concentration with time after an initial delay of approximately 2 min and almost plateaus after 30–40 min. In contrast, the presence of dicumyl peroxide leads to a rapid increase in the free radical concentration of PAM within the first 4 min followed by a decrease in the concentration of free radicals up to approximately 10 min. Then there is a small but steady increase in the free radical concentration with time.

The peroxide-induced generation of free radicals at high temperature involves two stages that originate from peroxide initiation and thermal initiation. In the first stage, there is a sharp increase in the free radical concentration due to peroxide-induced generation of PAM radicals. During this short period of time, the peroxide decomposes and abstracts hydrogen from the backbone of PAM. Then some PAM radicals terminate with each other through combination to form a crosslinked structure, and the concentra-

tion of free radicals decreases when the termination reaction dominates over the generation of radicals via peroxide decomposition. In the second stage, the peroxide is depleted and thermal initiation becomes significant. A possible explanation is that structural defects created along the backbone of PAM during the first stage now provide favorable sites for thermal initiation of free radicals at high temperature. This causes the concentration of PAM radicals to increase slightly in the second stage. The greater the amount of peroxide consumed in the first stage, the larger the structural defects created and hence, an increased free radical concentration generated in the second stage. In general, higher peroxide levels and temperatures produce higher free radical concentrations. However, the nature and the type of the structural defects cannot be elucidated with the ESR spectra, as shown in Figure 1. Another possible explanation is that higher peroxide levels generated more radicals in the first stage and yielded a higher level of crosslinking in the PAM network. Radicals trapped in more highly crosslinked network experienced greater difficulty in termination and thus resulted in higher radical concentrations at the second stage. Figure 4(a–c) and Figure 5(a–c) show the concentration of PAM radicals as a function of reaction time for the PAM-L130 system at temperatures of 170, 180, and 190°C, and for the PAM-CHP system at temperatures of 180, 190, and 200°C, respectively. They exhibit similar trends like the PAM-DCP system.

Figure 6(a–c) shows the concentration of polyDADMAC radicals as a function of reaction time for the CHP/polyDADMAC system at temperatures of 180, 190, and 200°C. With and without the peroxide initiator (CHP), the polyDADMAC structure is more stable compared with PAM at high temperatures. At 180°C, we could not obtain an ESR signal for the polyDADMAC system without any peroxide, which means that polyDADMAC is stable at this temperature. At 190°C, we detected a weak ESR signal for the system without peroxide after approximately 15 min. At 200°C, we detected a thermal-initiated ESR signal within 5 min. With CHP in the system, the concentration of polyDADMAC radicals versus reaction time exhibited trends similar to that of PAM-CHP, although the increase in concentration of polyDADMAC radicals in the second stage due to thermal initiation is much smaller compared with the PAM-CHP system. This indicates that the polyDADMAC struc-

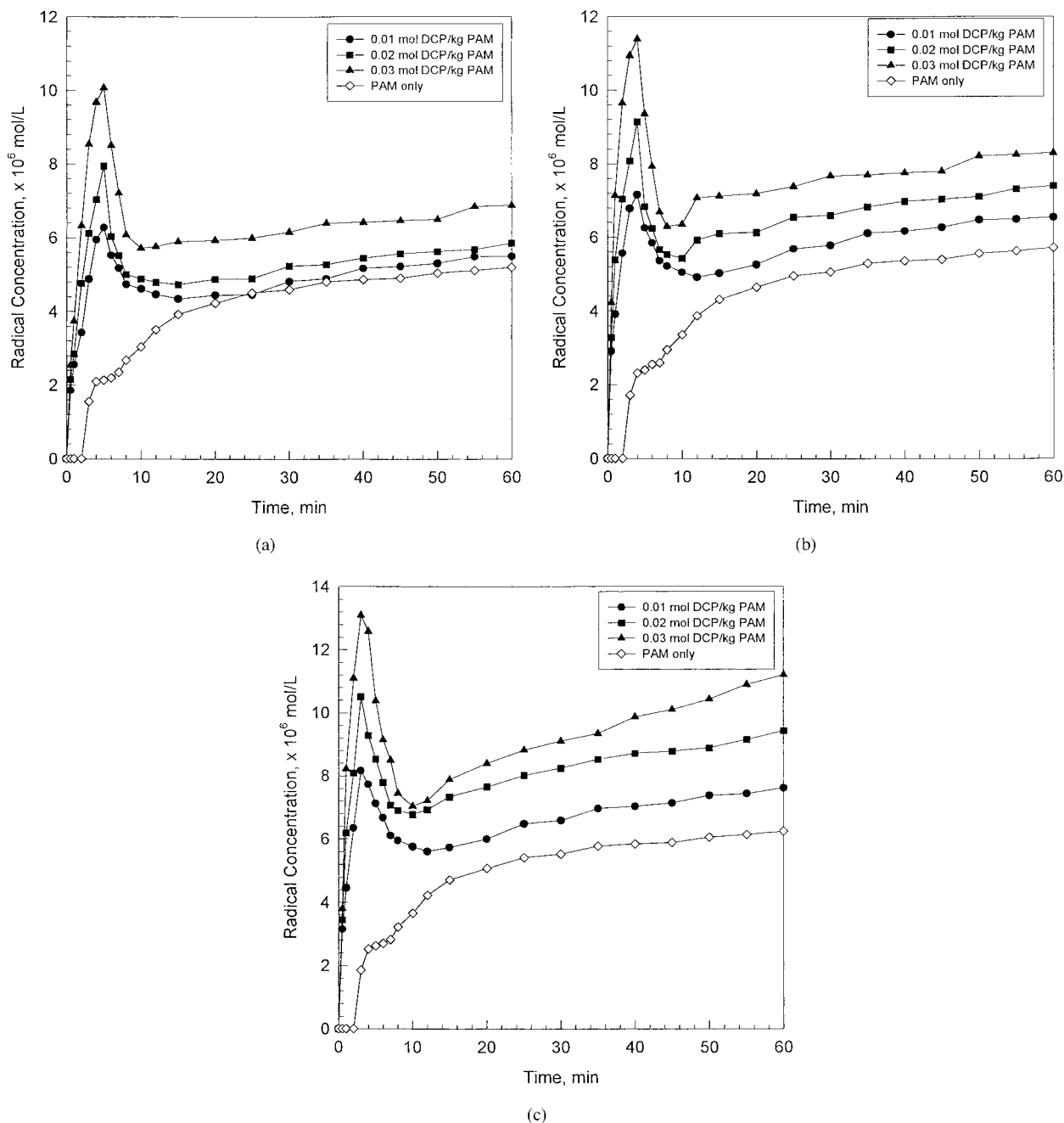


Figure 3 Radical concentration versus reaction time profiles of PAM-DCP system: (a) $T = 170^{\circ}\text{C}$, (b) $T = 180^{\circ}\text{C}$, and (c) $T = 190^{\circ}\text{C}$.

ture is more stable than PAM under the peroxide-induced thermal degradation process. Measurements were also made for the polyDADMAC-L130 and polyDADMAC-DCP systems at temperatures of 170, 180, and 190°C . Like the PAM-peroxide systems, the polyDADMAC-peroxide systems also produced higher concentration of free radicals at higher peroxide levels and temperatures.

GE and DOG

Figures 7 and 8 show the GE and DOG of polyDADMAC onto PAM as a function of extrusion temperature for different polyDADMAC/PAM ratios and screw speeds. Nearly 50% of polyDADMAC was grafted onto PAM at a temperature of 120°C and a screw speed of 40 rpm. We found that both GE and

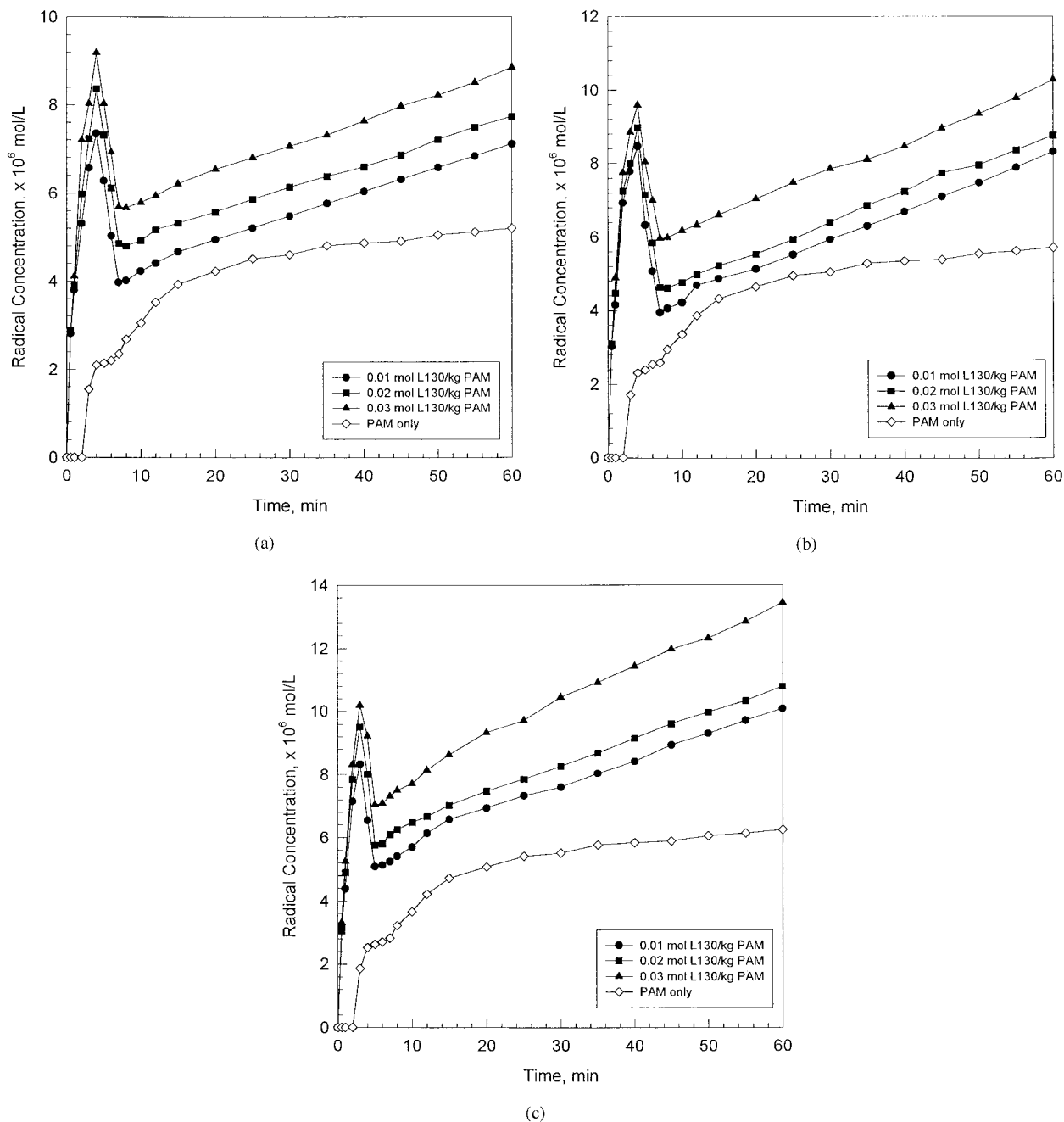


Figure 4 Radical concentration versus reaction time profiles of PAM-L130 system: (a) $T = 170^{\circ}\text{C}$, (b) $T = 180^{\circ}\text{C}$, and (c) $T = 190^{\circ}\text{C}$.

DOG were a strong function of extrusion temperature, and they decreased with increasing temperature. For a given temperature, a higher ratio of polyDADMAC/PAM resulted in a higher DOG but a lower GE. This was because even though a higher amount of polyDADMAC was grafted onto PAM with increasing polyDADMAC/PAM ratio, the percentage of grafted polyDADMAC over the initial

polyDADMAC decreased. As more polyDADMAC molecules were grafted onto PAM, the grafting reaction became progressively less favorable. The grafted polyDADMAC may have prevented other polyDADMAC molecules from approaching PAM, thereby reducing the possibility of further grafting.

For a given temperature and polyDADMAC/PAM weight ratio, decreasing the screw speed (de-

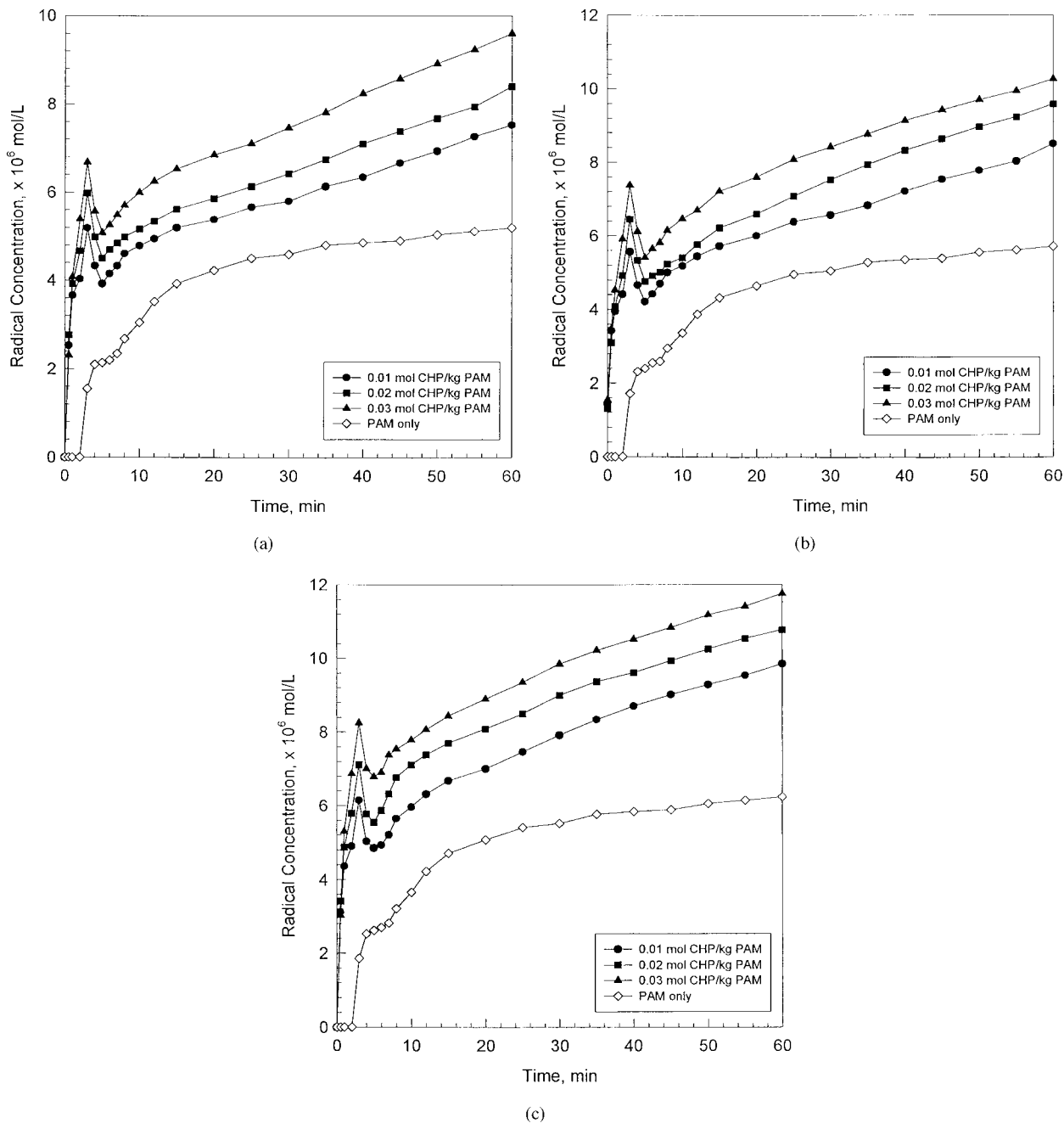


Figure 5 Radical concentration versus reaction time profiles of PAM-CHP system: (a) $T = 180^{\circ}\text{C}$, (b) $T = 190^{\circ}\text{C}$, and (c) $T = 200^{\circ}\text{C}$.

creasing the shear rate experienced by the polymers and/or increasing residence time of the polymers in the extruder) decreased the GE and DOG. Decreasing the shear rate experienced by polymer particles in the extruder leads to an increase in the probability of termination of PAM radicals with each other, leading to crosslinking. However, this does not mean one can significantly reduce the crosslinking or en-

hance grafting by extruding the polymers at an extremely high speed (near-zero residence time). The polymers have to spend a minimum time in the extruder for the grafting reaction to take place. It should be noted that we were unable to extrude any copolymers at a temperature of 180°C and a screw speed of 20 rpm because of severe crosslinking of PAM in the twin screw extruder at these conditions.

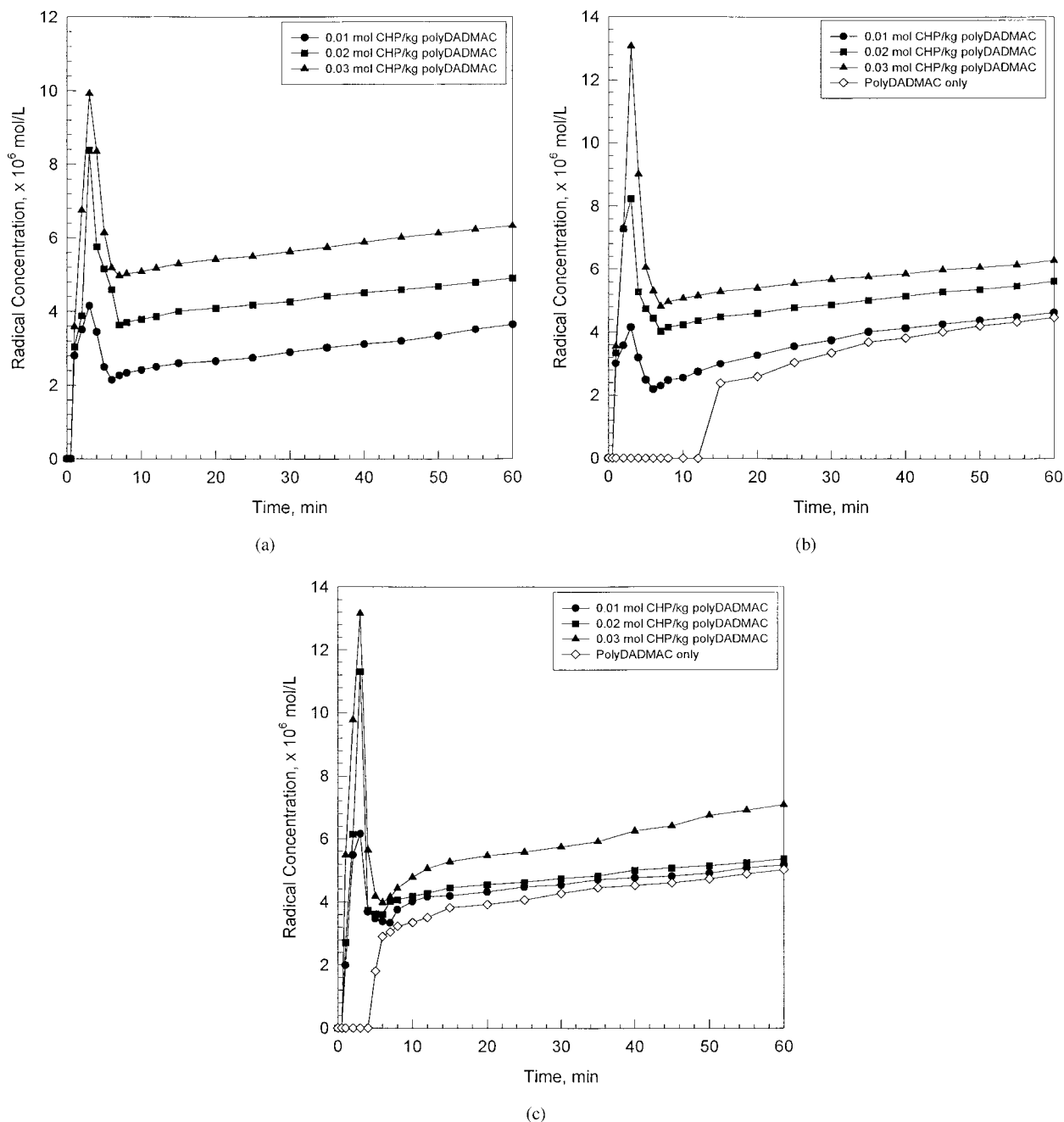


Figure 6 Radical concentration versus reaction time profiles of PolyDADMAC-CHP system: (a) $T = 180^{\circ}\text{C}$, (b) $T = 190^{\circ}\text{C}$, and (c) $T = 200^{\circ}\text{C}$.

To study the effect of thermal initiation on the grafting of polyDADMAC onto PAM, we extruded a polymer mixture with a polyDADMAC/PAM ratio of 1.0 at a temperature of 180°C and a screw speed of 40 rpm without any peroxide initiator. The GE and DOG for this copolymer was found to be 0.26% (Figs. 7 and 8). This is not surprising because

it is very difficult to thermally abstract the hydrogen from tertiary carbon of polyDADMAC and generate radicals for grafting.

Insoluble Gel Fraction

The fraction of water-insoluble gel fraction in some of the extruded copolymers at a screw speed

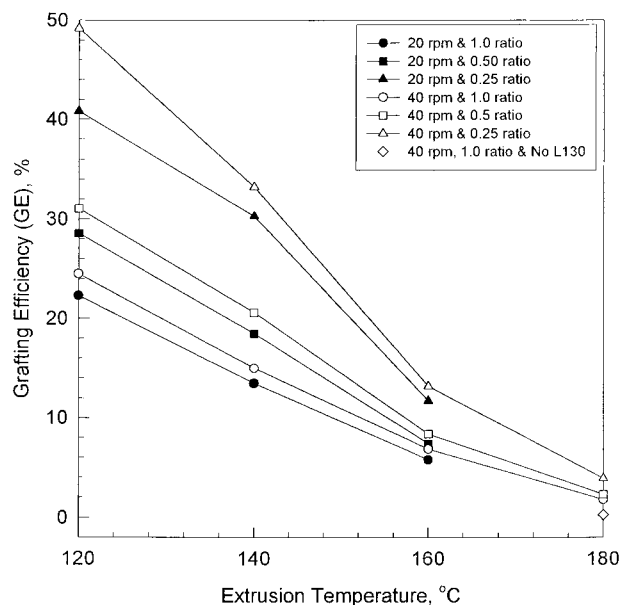


Figure 7 GE versus extrusion temperature profiles of PAM-polyDADMAC system.

of 40 rpm are listed in Table II. The sample with a polyDADMAC/PAM ratio of 0.25 extruded at a temperature of 160°C contained nearly 50% of insoluble gel by weight. The gel fraction increased with increasing temperature, but decreased with increasing polyDADMAC/PAM ratio. This was due to high activity of PAM radicals at higher temperature and higher PAM concentration (or lower polyDADMAC/PAM ratio). A sample with a polyDADMAC/PAM weight ratio of 1, and no peroxide initiator, was also extruded at a temperature of 180°C and a screw speed of 40 rpm to study the effect of thermal initiation on the gel fraction. It was found to contain nearly 30% of insoluble gel fraction by weight. The insoluble gels in the extruded copolymer, obtained using a peroxide initiator may contain some of the grafted polyDADMAC onto PAM, thereby trapping polyDADMAC in the crosslinked network structure.

CONCLUSIONS

The results of an experimental investigation using ESR studies and graft copolymerization of polyDADMAC onto the backbone of PAM by reactive extrusion are reported. The chemistry of free macroradicals was elucidated by monitoring changes in the intensity of ESR spectra. Single line ESR spectra were observed during the course

of polymer-peroxide reactions. The concentration of polymer radicals proved to be highly dependent on the type of peroxide and its concentration, reaction time, and temperature. A sharp increase in the concentration of peroxide-induced generation of polymer radicals takes place within the first few minutes followed by a reduction due to termination of some of the macroradicals, and then a gradual increase in the radical concentration over time due to thermal initiation. Analysis of the extruded copolymers showed the following:

1. The GE of polyDADMAC onto the backbone of PAM decreased with increasing extrusion temperature, polyDADMAC/PAM weight ratio, and residence time.
2. The DOG of polyDADMAC decreased with increasing extrusion temperature and residence time, but increased with increasing polyDADMAC/PAM weight ratio.
3. The amount of insoluble gel in the extruded product increased with increasing extrusion temperature and residence time, but decreased with increasing polyDADMAC/PAM weight ratio.

The trend in the DOG, GE, and gel fraction obtained from reactive extrusion concur with the behavior of PAM-peroxide and polyDADMAC-peroxide systems from ESR measurements. In-

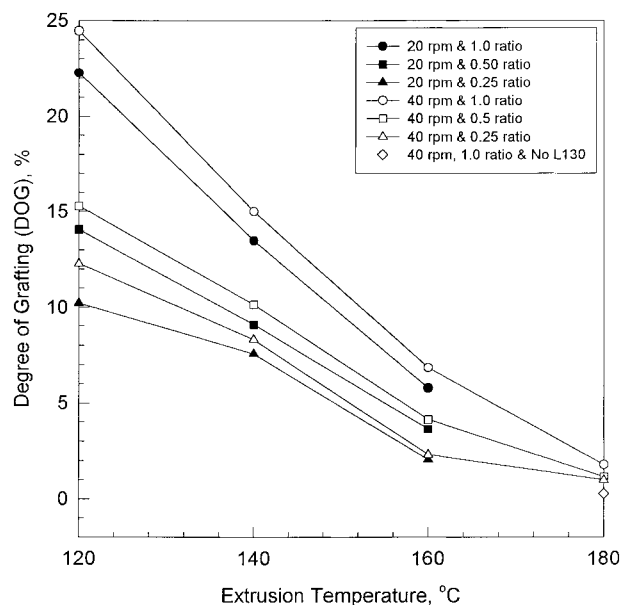


Figure 8 DOG versus extrusion temperature profiles of PAM-polyDADMAC system.

Table II Insoluble Gel Fraction in Extruded Copolymers of PolyDADMAC and PAM at a Screw Speed of 40 rpm

PolyDADMAC/PAM Weight Ratio	Insoluble Gel Fraction (%)			
	$T = 120^{\circ}\text{C}$	$T = 140^{\circ}\text{C}$	$T = 160^{\circ}\text{C}$	$T = 180^{\circ}\text{C}$
0.25	27.40	38.96	48.97	—
1.0	22.60	—	36.65	—
1.0 (No L130)	—	—	—	29.23

creasing temperature and residence time (or reaction time) favors termination of PAM radicals with each other, and leads to crosslinking (i.e., higher gel fraction). For the polyDADMAC-PAM system, it is recommended to perform reactive extrusion at lower temperatures, shorter residence times, and higher polyDADMAC/PAM weight ratios to minimize the fraction of insoluble gels and increase the DOG.

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