Polymer-Additive Extraction via Pressurized Fluids and Organic Solvents of Variously Cross-Linked Poly(methylmethacrylates)

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Abstract

Variously cross-linked poly(methylmethacrylates) (PMMAs) are synthesized with three additives incorporated at theoretically 1000 µg of the additive per gram of prepared polymer. The additives are Irganox 1010, Irganox 1076, and Irgafos 168. The "in-house" synthesized polyacrylates are then subjected to supercritical fluid extraction (SFE) to determine if additive recovery is a function of percent cross-linking. Although considerable work in this regard has been performed with non-cross-linked polyolefins, the literature is lacking regarding polyacrylates. Some additive degradation apparently occurs during the synthesis, as judged by the increased complexity of the extract high-performance liquid chromatographic trace and the low percent recoveries observed especially for the Irganoxes. For low polymer cross-linking (1%), it appears that both PMMA synthetic reproducibility and readily observed polymer swelling during SFE are serious issues that adversely affect additive percent recovery and precision of results. Higher percent cross-linking yields more consistent analytical data than low percent cross-linking, even though the amount of additive extracted in all PMMA samples (regardless of cross-linking percentage) is essentially the same whether the extraction is via SFE or liquid–solid extraction with methylene chloride. Results for comparably cross-linked poly(ethylmethacrylate) and poly(butylmethacrylate) are similar to PMMA.

Introduction

Polymeric materials are formidable matrices for achieving the quantitative extraction of polymer additives. Generally, extractions should be performed above the glass transition temperature and below the melting temperature. Alternatively, a solvent that swells the polymer may be desirable for extraction at lower temperatures. Several complicating features add to the difficulty of additive extraction. For example, low-molecular-weight oligomeric components are readily coextracted along with the additive. Second, the polymer must be ground in order to afford greater surface area because the extraction will be most likely diffusion-limited. Finally, the additive is subject to chemical change resulting from reaction with various oxygenated species.

Depending on the polymer and its intended application, the number of additives in a single polymer sample can be surprisingly high. Additives may be incorporated to assist polymer processing, modify polymer bulk mechanical properties, alter surface and optical properties, and inhibit oxidation and aging. A recent review on the analysis of additives in polymers suggests that there is much activity in this area (1). Because of the complexity of polymer formulations, extraction of the additive mixture from the polymer matrix is usually required (often followed by chromatographic separation and purification) for quantitation. Two conventional extraction techniques have been used in the past to isolate the additive from the polymer matrix (i.e., dissolution of the polymer in a solvent followed by selective precipitation of only the polymer and direct liquid–solid extraction (LSE) of additives from the polymeric matrix). It is clear that any chosen analytical sample preparation technique must be sensitive, selective, and maintain the integrity of the mixture composition (2).

Supercritical fluid extraction (SFE) with solvent-modified carbon dioxide affords an efficient, mild, noninvasive, environmentally friendly alternative to the conventional methods. Over 90% of all reported polymer-additive investigations have concerned themselves with polyolefins and polyesters. In this regard our laboratory has widely published on the SFE of various additives from low- to high-density polyethylene (3–5), polypropylene (6), nylon (7), polystyrene (8), polyurethane (9), polyester (10), and aramid (7). Both online SFE coupled directly with chromatography–spectroscopy for small samples and trace analysis and offline SFE configurations that can accommodate much larger sample sizes have been successfully employed. In 1997 Vandenbury et al. (1) reviewed the field concerning the analytical extraction of additives from polymers with most of the emphasis on SFE. Approximately fifty published studies were noted concerning SFE alone. Janssen et al. (11) have noted that in many cases rapid and quantitative extraction have been achieved using ground samples or thin films.

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Effects such as polymer functionality, molecular weight, and cross-linking on the extraction and analysis of polymer additives is of current interest to us. A variety of variously cross-linked polyacrylates have been studied in conjunction with several primary and secondary antioxidants (e.g., Irganox 1010, Irganox 1076, and Irgafos 168). We report in this study on the polymer synthesis and additive incorporation and then the extraction of these three polymer additives from poly(methylmethacrylates) (PMMA) prepared with 1%, 5%, 10%, and 20% cross-linking and 0.1% (w/w) additive doping. Cross-linking was accomplished with triethyleneglycol dimethacrylate (TEGDMA). A search of the literature suggests that this may be the first study that deals with the SFE of additives in polyacrylates.

Experimental

TEGDMA and methylmethacrylate (MMA) were obtained from Aldrich Chemical Company (Milwaukee, WI). Both compounds were colorless liquids. Also, the initiator, benzoyl peroxide (BPO), was obtained from Aldrich Chemical Company as a white solid. Air Products and Chemicals, Inc. (Allentown, PA) provided SFE- and supercritical fluid chromatographic (SFC)-grade CO_2. The additives Irganox 1010, Irganox 1076, and Irgafos 168 were obtained from Ciba Specialty Chemicals Company (Tarrytown, NY) and were used as received. All three additives were white powders.

Preparation of 1.0% TEGDMA cross-linked PMMA

In order to make 15 g of 1.0% cross-linked polymer, 14.85 g of MMA and 0.15 g of TEGDMA were needed. The amount of initiator (BPO) used was 0.36 g (e.g., 1 mole polymer per 0.01 mole of initiator). In order to dope the cross-linked polymer with 0.1% of the selected additives, 0.015 g of each additive (Irganox 1010, Irganox 1076, and Irgafos 168) was used. Prior to the synthesis, all of these materials were weighed and placed in a test tube. After shaking the test tube for a few seconds, it seemed that all the solids (initiator and additives) dissolved. Then, the test tube was placed in a mixture of dry ice–acetone and a vacuum was applied for approximately 5-6 min to remove any dissolved gases. Tap water was used to warm the frozen solution to ambient and make it liquid. This process was repeated three times to make sure all gases were removed from the test tube. Then, while the test tube was under vacuum and in the mixture of dry ice–acetone, it was sealed. Again, tap water was used to change the temperature of the frozen solution to ambient and make it liquid. Next, the test tube was placed in an oven at 85°C for 3 h. The polymer was formed during this time. The tube was then mechanically broken and the solid polymer was isolated and stored in a bottle.

Preparation of higher percent TEGDMA cross-linked PMMA

In order to make 15 g of higher percent cross-linked polymer (PMMA), 0.75 g TEGDMA and 14.25 g MMA for 5% cross-linked product, 1.5 g TEGDMA and 13.5 g for 10% cross-linking, and 3.0 g TEGDMA and 12.0 g MMA for 20% cross-linking were needed. The amount of initiator that was needed was 0.35 g for 5%, 0.34 g for 10%, and 0.33 g for 20% in each case. In order to dope the cross-linked polymer with 0.1% of the selected additives, 0.015 g

of each additive (Irganox 1010, Irganox 1076, and Irgafos 168) was used. The synthetic procedure was the same as described previously. The synthesis procedure for 20% TEGDMA cross-linked poly(ethylmethacrylate) (PEMA) and 20% TEGDMA cross-linked poly(butylmethacrylate) (PBMA) was exactly as described for PMMA.

Extraction of additives from PMMA, PEMA, and PBMA as a function of percent cross-linking

All extractions were performed on an Isco-Suprex (Lincoln, NE) AP-44 extractor using a 5-mL stainless steel extraction vessel. In all cases, exactly 1 g of previously ground, synthesized polymer and approximately 4 g of sand were mixed together and introduced into the vessel. The temperature, CO_2 pressure, and flow rate in all of the experiments were kept constant: the temperature remained at 100°C, the CO_2 pressure at 450 atm, and the liquid CO_2 flow rate at 2 mL/min.

Several other variable parameters were investigated in order to optimize the extraction efficiency such as trapping material, trap rinse solvent, extraction time, and extraction fluid.

All reversed-phase high-performance liquid chromatographic (HPLC) analyses of the extracted additives were performed with a 1100 Series Hewlett Packard (Little Falls, DE) system. The following conditions were used for each analysis: the column used was a Nova Pack C_{18} (5-μm particle size), the injection volume was 50 μL, the mobile phase was initially 80% CH_3CN–20% H_2O then changed to 100% CH_3CN in 5 min, the concentration of standard was 40 ng/μL additive, and the UV detection was at 254 nm.

Results and Discussion

Optimization of SFE using 1% cross-linked PMMA

Initially, the three polymer-additive standards were analyzed as received via reversed-phase HPLC (Figure 1). The additives (Irganox 1010, Irganox 1076, and Irgafos 168) were dissolved and
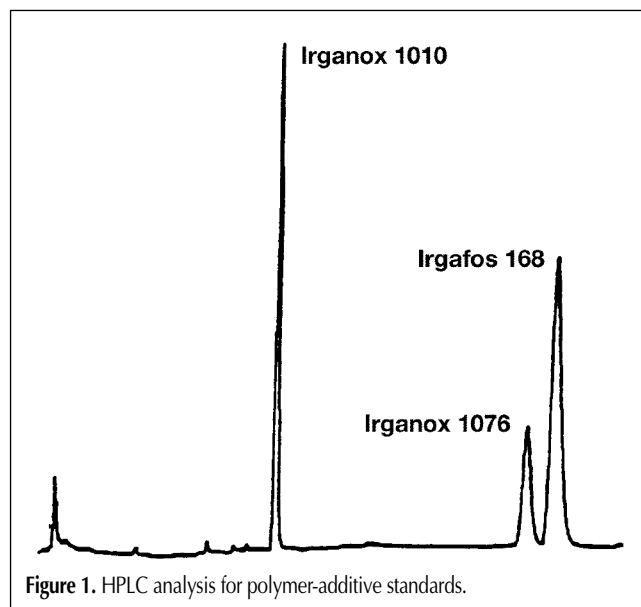

Figure 1. HPLC analysis for polymer-additive standards.

injected in methanol and were observed at the retention times of 8.2, 16.5, and 17.8 min, respectively. Minimal impurities were noted in the chromatographic trace.

Next, optimization of the SFE procedure was carried out on 1% cross-linked polymer. In order to determine a suitable solid-phase material for trapping the extracted additives, the following parameters were used: the extraction temperature was 100°C, the CO_2 pressure 450 atm, the dynamic extraction time 60 min, the liquid flow rate 2 mL/min, the modifier 10% CH_3OH (v/v), and the extraction trap temperature 40°C.

Octadecylsiloxane (C_{18}) was initially used as a solid-phase packing material for the trap; however, extensive washing of the trap to remove extracted analytes was required (i.e., 90% CH_3CN–10% CH_2Cl_2 (v/v)). Next, 30% C_{18}–70% stainless steel balls (w/w) were used with essentially the same results. However, with 10% C_{18}–90% stainless steel balls (w/w), only 5 mL of 90% CH_3CN–10% CH_2Cl_2 (v/v) was necessary to wash all analytes off the trap. Consequently, this trapping material was used for the remaining parts of the study.

Next, in order to study the influence of extraction time and fluid composition, two sets of experiments were performed. Initially, two samples of 1% cross-linked PMMA were extracted at a fixed pressure, temperature, and flow rate using 10% CH_3OH-modified CO_2 (e.g., 450 atm, 100°C, and 2 mL/min), and the extraction time was varied from 30 to 60 min. There was an increase (e.g., ~30%) in Irganox 1010's recovery when the extraction time increased from 30 to 60 min. However, no changes in recovery were observed for Irganox 1076 and Irgafos 168 when increasing the extraction time from 30 to 60 min. Nevertheless, 60 min was chosen as the extraction time to be employed in our study. The chromatographic trace arising from the 30-min extraction is
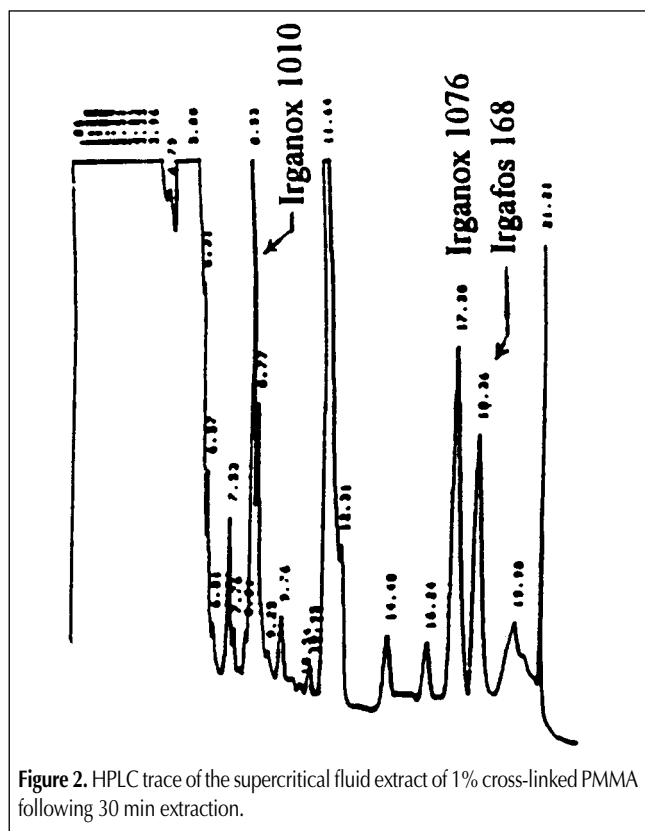
shown in Figure 2. Considerably more peaks were observed in this trace than the standard additive solution HPLC trace (Figure 1), thus suggesting that the extraction of other components had been achieved. These analytes may have been low-molecular-weight oligomers of PMMA, but more likely they were degradation products of the polymer additives that were generated during the polymer synthesis because the UV detection wavelength for the chromatography was 254 nm. Negligible polymer-additive degradation would be expected under anaerobic SFE conditions.

In a second study, two samples were sequentially extracted using both pure CO_2 and 10% methanol-modified CO_2 as an extraction fluid while pressure, temperature, flow rate, and time were kept constant (e.g., 450 atm, 100°C, 2 mL/min, and 60 min, respectively) in an effort to determine the more efficient fluid for additive extraction. Using pure CO_2 as an extraction fluid, the HPLC peak area for Irganox 1010 in the extract solution was approximately 50% less than the peak area using 10% methanol-modified CO_2. For Irganox 1076 and Irgafos 168, the HPLC peak areas (e.g., injection of extract solution) using pure CO_2 were approximately 20% and 45% less than the peak area using 10% methanol-modified CO_2, respectively. Therefore, it was concluded that 10% methanol-modified CO_2 was more efficient than pure CO_2 as an extraction fluid for PMMA and these additives.

SFE of additives in synthesized PMMA at various degrees of cross-linking

After optimizing the extraction conditions in terms of extraction fluid and time, we were next interested in determining the concentration of additives in each synthesized, cross-linked polymer. A calibration curve with four different concentrations of each additive standard (e.g., 0.01, 0.02, 0.04, and 0.08 µg/µL) was prepared. In order to prevent overloading of the column, 20 µL of solution was injected, which meant that 200, 400, 800, and 1600 ng of each analyte were injected. By plotting the area count versus mass injected, an equation relating the response and mass for each additive was obtained. The equations were then used to determine the concentration of extracted additives in the synthesized polymers (e.g., 1%, 5%, 10%, and 20% cross-linked). It is important to note for the following discussion that the theoretical mass for each additive in each one of the synthesized polymers was 0.015 g additive per 15 g polymer or 1000 µg/g polymer.

Figure 2. HPLC trace of the supercritical fluid extract of 1% cross-linked PMMA following 30 min extraction.

Table I. Mass of Additives Extracted from Three Replicates of One Sample of Synthesized 1% Cross-Linked PMMA via SFE

	Additive	Mass of additive (µg/g)
Sample 619A	Irganox 1010	110
	Irganox 1076	362
	Irgafos 168	890
Sample 619B	Irganox 1010	76
	Irganox 1076	359
	Irgafos 168	867
Sample 619D	Irganox 1010	55
	Irganox 1076	274
	Irgafos 168	515

The 1% cross-linked sample was extracted first using the optimized SFE conditions. The extract volume (i.e., solid-phase trap wash) was adjusted to 5 mL and analyzed immediately via HPLC. In order to have a better understanding of how the values were obtained, the following sample calculation for one of the additives (e.g., Irganox 1010) is given. Assuming that an area-count value of 78343 was read from the chromatogram for Irganox 1010 in the sample, by substituting this value (y) into the equation for Irganox 1010, a mass (x) of 427 ng is yielded. Because the injection volume was 50 µL, the concentration of additive in 1 g of extracted polymer (e.g., 5 mL solution) would be: (427 ng / 50 µL) × 5000 µL / 1000 ng/µg = 43 µg/g. Table I gives the mass of each additive extracted per gram of polymer for sample 619A. One is struck immediately by the fact that the measured values are much lower than the theoretical values (e.g., polymers were synthesized to contain additives at 1000 µg/g), especially for Irganox 1010 (~110 µg/g) and Irganox 1076 (~362 µg/g). Replicates of sample 619A (e.g., 619B and 619D) were next extracted under identical conditions. Although some variability was observed in the data, the general trend of lower than expected recoveries for each additive for all three replicates was the same. A second and third independent 1% cross-linked polymer synthesis (e.g., sample 620 and 621) was performed. Extraction of these samples in duplicate with similar methanol-modified CO_2 yielded somewhat scattered data (Table II) but with the same conclusions (i.e., much lower values for both Irganoxes relative to Irgafos 168).

In order to determine if the extraction of additives from the 1% cross-linked polymer via SFE was exhaustive, the raffeinate in the extraction vessel was re-extracted with CH_2Cl_2 at room temperature using a standard liquid–solid procedure. After dissolution of the polymer in CH_2Cl_2, the polymer was precipitated from solution via the addition of methanol. After complete precipitation of the polymer, the solution was filtered, and the filtrate was analyzed for additional extracted additives. Obviously, SFE did not remove all of the extractable additives because a small amount of additional additive could be extracted with CH_2Cl_2. Next, 1 gram of 1% cross-linked polymer (no prior SFE) was extracted using the traditional method. Again, the polymer sample was first dissolved in CH_2Cl_2 and then the polymer was precipitated using methanol. The filtered extract solution was analyzed. Table II also shows the concentration of additives in the 1% cross-linked polymer (sample 621) using the traditional solvent (CH_2Cl_2) extraction method. A comparison between the two methods (SFE versus LSE) shows that one can extract comparable amounts of additives from 1% cross-linked polymer via both the traditional solvent extraction method and the SFE method. However, only one polymer preparation was subjected to LSE and for a single time with CH_2Cl_2, whereas three polymer preparations were repeatedly studied via SFE. It should also be noted that the SFE results with this particular cross-linking were obtained with very low precision (shown in Table II). Summarizing to this point, Irganoxes were recovered in less than 50% yield, and Irgafos 168 surprisingly exceeded 100% recovery relative to what had been added during the synthesis of 1% cross-linked polymer in several cases. However, the results exhibited very poor precision within a sample and between samples, thus recoveries greater than 100% should not be seriously considered.

We next attempted to extract the same three additives from a 5%, 10%, and 20% cross-linked polymer via SFE, re-extraction of SFE raffeinates with CH_2Cl_2, and extraction of the fresh synthesized polymer with CH_2Cl_2. A cursory look at the data revealed that all three higher cross-linked polymers showed that no additives remained in the sample after the initial SFE method, the extraction precision was much higher, and the SFE results matched the LSE results.

Table III describes the extraction results with 5% cross-linking. Precision via SFE was good within a single polymer preparation (e.g., sample 596) in most cases. However, there appeared to be inconsistencies between sample preparations, especially for Irgafos 168. For example, sample 607 had almost double the

Table II. Average Mass of Additives Extracted from Various Preparations of 1% Cross-Linked PMMA via SFE

	Irganox 1010 (µg/g)	Irganox 1076 (µg/g)	Irgafos 168 (µg/g)
Sample 619*	80, 35[†]	332, 15[†]	757, 28[†]
Sample 620[‡]	207	611	1250
Sample 621[‡]	94, 111[§]	347, 470[§]	1017, 1433[§]

* Average of three extractions.
[†] Relative standard deviation value.
[‡] Average of two extractions.
[§] Results (µg/g) for the extraction of 1% cross-linked PMMA with CH_2Cl_2.

Table III. Average Mass of Additives* Extracted from Three Preparations of 5% Cross-Linked PMMA via SFE

	Irganox 1010 (µg/g)	Irganox 1076 (µg/g)	Irgafos 168 (µg/g)
Sample 596 (preparation #1)	138, 3[†], 131[‡]	214, 13[†], 182[‡]	759, 2[†], 735[‡]
Sample 604 (preparation #2)	292, 2[†], 155[‡]	685, 8[†], 351[‡]	740, 17[†], 423[‡]
Sample 607 (preparation #3)	311, 10[†]	599, 5[†]	1418, 7[†]

* Three independent extractions of the same sample.
[†] Relative standard deviation value.
[‡] One LSE of polymer with CH_2Cl_2.

Table IV. Average Mass of Additives Extracted in Triplicate from Three Independently Prepared 10% Cross-Linked PMMA Samples via SFE

	Irganox 1010 (µg/g)	Irganox 1076 (µg/g)	Irgafos 168 (µg/g)
Sample 597 (preparation #1)	238, 4*, 280[†]	535, 11*, 508[†]	910, 3*, 1071[†]
Sample 605 (preparation #2)	370, 8*, 241[†]	748, 7*, 417[†]	1319, 12*, 887[†]
Sample 608 (preparation #3)	301, 14*	852, 25*	1315, 18*

* Relative standard deviation value.
[†] LSE results from a single extraction of the same PMMA sample.

amount of Irgafos 168 as sample 596 and 604. A comparison of SFE and LSE results on sample 596 showed approximately the same numerical values. A comparison of the same data for sample 604 showed higher extractability for each additive via SFE than LSE (Table III). Re-extraction of the SFE raffeinate by LSE (unlike the 1% cross-linked case) yielded no additional additive extraction. Again, overall recoveries were much lower than expected for the Irganoxes.

Results for 10% cross-linked PMMA are shown in Table IV. Three polymer preparations were examined in triplicate by SFE. The discrepancy regarding additive extraction results between preparations is striking. The comparison of SFE results with LSE results revealed similar situations to that earlier described for 5% cross-linking (i.e., SFE yielded as good or better recoveries than LSE). The data for 20% cross-linked PMMA (Table V) appears to be the most consistent (e.g., high precision, good agreement between two preparations, and good agreement between SFE and LSE). Recoveries were again low for the Irganox additives, but Irgafos 168 exhibited near quantitative recovery.

The kinetics of extraction of variously cross-linked polymers were of interest to us. The extraction profiles of additives from 1% and 20% cross-linked PMMA (e.g., samples 619 and 598, respec-

tively) are shown in Figures 3A and 3B. The extraction profile of 20% PMMA exhibited more classical behavior than the 1% PMMA profile. After the passage of 20 g of CO_2, all extractable Irgafos 168 and Irganox 1076 were removed. Approximately twice that amount of CO_2 is required to exhaustively remove Irganox 1010. For 1% cross-linked PMMA, Irgafos 168 continued to be extracting after the passage of 90 g CO_2, and the Irganoxes appeared to be exhaustively extracted after 40–50 g of CO_2. Although the two PMMA samples were ground to a similar mesh size, the 1% polymer extraction appeared to be more diffusion-limited than the 20% polymer. An explanation for this observation is not readily apparent. It should also be noted that the absolute amount of each additive extracted was considerably less for 1% PMMA than 20% PMMA.

The low Irganox additive recoveries in all our samples were initially thought to arise from various analytical protocols. For example, it was felt that the low values were a result of the HPLC analysis protocol (e.g., column overload). We therefore reduced the extract solution injection volume from 50 to 20 µL, but this change did not have a significant effect on the percent recovery of any additive.

We tried to determine whether our pressurized fluid extraction using the optimized conditions was truly exhaustive. Therefore, an additional extraction was performed on a 1% cross-linked polymer sample, which had been extracted previously using what we thought were optimum conditions (e.g., 10% modifier). In this extraction, the concentration of modifier was increased from 10% to 15%, and other extraction conditions remained exactly identical. The HPLC analysis showed no detectable Irganox 1010 and 1076 in the second extract and less than 10% Irgafos 168.

The low recoveries for Irganox 1010 and 1076 were then

Table V. Average Mass of Additives Extracted in Triplicate from Two Independently Prepared 20% Cross-Linked PMMA Samples via SFE

	Irganox 1010 (µg/g)	Irganox 1076 (µg/g)	Irgafos 168 (µg/g)
Sample 598 (preparation #1)	242, 9*, 242[†]	515, 2*, 705[†]	951, 1*, 1279[†]
Sample 603 (preparation #2)	314, 3*, 263[†]	582, 8*, 448[†]	1064, 7*, 912[†]

* Relative standard deviation value.
[†] LSE results from a single extraction of the same PMMA sample.

Figure 3. Extraction profile of additives from (A) 1% cross-linked (film 619) and (B) 20% cross-linked PMMA (film 598).
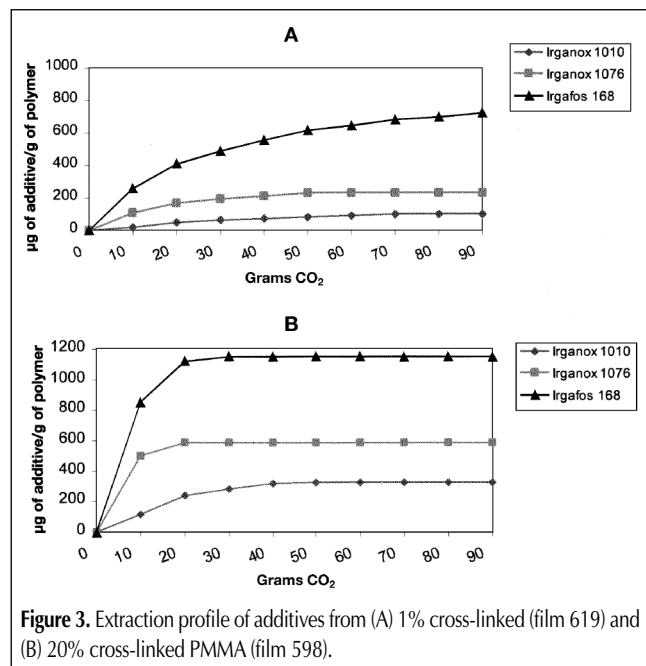
Table VI. Mass of Additive Extracted from the 20% Cross-Linked Polymers PEMA and PBMA

Sample	Additive	Average mass of additive extracted* (µg/g)
PEMA (synthesis #1)	Irganox 1010	403 (8)
	Irganox 1076	731 (8)
	Irgafos 168	340 (7)
PEMA (synthesis #2)	Irganox 1010	207 (19)
	Irganox 1076	421 (28)
	Irgafos 168	79 (7)
PEMA (synthesis #3)	Irganox 1010	342 (3)
	Irganox 1076	640 (5)
	Irgafos 168	170 (12)
PBMA (synthesis #1)	Irganox 1010	283 (5)
	Irganox 1076	766 (29)
	Irgafos 168	278 (12)
PBMA (synthesis #2)	Irganox 1010	267 (9)
	Irganox 1076	621 (4)
	Irgafos 168	276 (6)
PBMA (synthesis #3)	Irganox 1010	307 (12)
	Irganox 1076	669 (3)
	Irgafos 168	399 (10)

* Three replicates. Percent relative standard deviation in parentheses.

reasoned to have maybe come as a result of extensive swelling of the polymer in CO_2, resulting in a production of a preferred CO_2 flow pattern or reduced overall flow. The former situation would result in less of the matrix being examined and the latter would have resulted in insufficient modified CO_2. In order to test this notion, 1 g of 1% cross-linked polymer was measured for volume and subjected to optimum extraction conditions. After exposure to the extraction conditions, the volume was remeasured and found to have doubled. We did the same experiment with 20% cross-linked polymer, and the expanded volume after extraction was only approximately 10%. We therefore reasoned that the poor results with low-percent cross-linking may be caused by the plugging of the vessel by the swollen polymer, but this could not be the reason for the low Irganox recoveries observed with 20% PMMA. Consequently, another experiment was performed to study whether more free space in the vessel would have any effect on the results. We only studied 1% cross-linked polymer. A 10-mL stainless steel vessel was used instead of the 5-mL stainless steel vessel, which had been used in previous studies. Exactly 1 g of ground polymer and approximately 4 g of sand were mixed together as usual. The mixture was then introduced into the vessel and again the optimum impregnation conditions were employed. In both cases, the extraction vessel was not filled to capacity after the extraction. There was approximately 50% free volume using the 10-mL vessel, and there was only approximately 10% free volume using the 5 mL vessel. The results for the 50% free-volume vessel were a little higher (116 µg/g for Irganox 1010, 462 µg/g for Irganox 1076, and 1381 µg/g for Irgafos 168) than for the 10% free-volume vessel (94 µg/g for Irganox 1010, 347 µg/g for Irganox 1076, and 1017 µg/g for Irgafos 168). It should be mentioned at this point that the experiment for 50% free volume was performed just once for the 1% cross-linked polymer, and the results for 10% free volume were the average of three extraction/assay experiments.

Because we felt that our results were influenced in part by the polymer synthetic procedure, analogous acrylate polymers were prepared employing PEMA and PBMA. Each system was 20% cross-linked in the presence of 0.1% (w/w) of the three additives. The final polymer (PEMA and PBMA) was then subjected to SFE under the optimized conditions used for PMMA for the purpose of extracting the additives. Table VI gives the results for both polymers. Just as before, all analyses have had extensive replication. For example, synthesis #1 for PEMA yielded an average mass for Irganox 1010 of 408 µg/g of polymer. This number represents the average of three independent extractions of synthesis #1. Each extraction recovery result of synthesis #1 was the average of two chromatographic injections of the extract solution. The recovery results were slightly different for PEMA and PBMA relative to PMMA. The amount of each additive should have been 1000 µg/g if no additive degradation during synthesis nor unextracted additive remained in the polymer. The amount of extracted Irgafos 168 decreased considerably, whereas Irgafos 168 was nearly quantitatively recovered in all PMMA samples. Most recoveries were below 50% of the theoretical. An explanation for the dramatic decrease in Irgafos 168 recovery cannot be explained.

In summary, the purpose of this work was to evaluate the effect of polymer cross-linking on the extractability of antioxidants from PMMAs. Three additives were extracted with either supercritical fluid CO_2 or methylene chloride from the prepared samples of PMMA. For a 5%, 10%, and 20% cross-linked polymer, the SFE results matched the LSE results with CH_2Cl_2. Precision via SFE was better than LSE overall within a single PMMA preparation. Percent recoveries for the two Irganoxes were quite low, and Irgafos 168 was nearly quantitative regardless of the percent cross-linking. High-percent cross-linking yielded more consistent analytical data; however, the amount of additive extracted did not appear to vary significantly with cross-linking. An extension of the study to PEMA and PBMA gave similar results.

Acknowledgments

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