Effects of Coffee on the Stability of Accelerated Aged Poly(acrylonitryle-butadiene-styrene)

Piotr Rytlewski,[1] Krzysztof Moraczewski,[2] Marian Żenkiewicz[2]

[1]Institute for Engineering of Polymer Materials and Dyes, 87–100 Toruń, Poland
[2]Department of Materials Engineering, Kazimierz Wielki University, 85-064 Bydgoszcz, Poland
Correspondence to: P. Rytlewski (E-mail: prytlewski@ukw.edu.pl).

ABSTRACT: In food chemistry coffee is nowadays accepted as a rich source of compounds possessing antioxidant and radical scavenging activities. The aim of this work was to assess the influence of coffee on degradation properties of poly(acrylonitryle-butadiene-styrene) (ABS). Content of instant extract coffee powder varied from 0.1 to 0.5 wt %. The injection moulded samples were accelerated aged by means of heat treatment, UV-Vis irradiation, and immersion in salt water. The influence of coffee on ABS properties were characterized by oxidation induction time (isothermal OIT), oxidation induction temperature (dynamic OIT), Fourier transform-infrared spectroscopy (FT-IR), UV-Vis spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG), and dynamic mechanical analysis (DMA). It was found that coffee effectively acted as an antioxidant, color, and structure stabilizer, maintaining mechanical properties close to the nonaged as compared with aged ABS. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39887.

INTRODUCTION

Due to various chemical structures, synthesis methods, additives used, and environmental factors polymer materials have different resistance to degradation processes. Most of them require introducing stabilizers, mainly to inhibit photo- and thermal-oxidation reactions. Antioxidants retarding polymer oxidative degradation are the compounds which deactivate free radicals or react with hydroperoxides. These compounds like phenol, amine, or pyrimidine derivatives comprise labile hydrogen atoms,[1,2] Exemplary antioxidants used in polymer processing are shown in Figure 1. As a result of the transfer of a hydrogen atom from antioxidant to deactivated macromolecule stable and nonreactive radical is formed. The effectiveness of the deactivation process is high when reaction rate of radicals with antioxidant is greater than with macromolecules.

Knowing the fundamental mechanisms of photo- and thermo-degradation one can propose new antioxidants to improve polymer stability against aging processes. Generally, the antioxidants should satisfy the following requirements: be of solid state to limit migration, be miscible with polymers, have high thermal stability, be nontoxic, especially when used in food packaging, and relatively inexpensive.[3,4] All these requirements would be satisfied in the case of extract coffee powder. Coffee contains effective plant antioxidants, such as chlorogenic acids, phenolic

acids, polyphenols, and alkaloids. Among the many coffee compounds few selected are presented in Figure 2.[5] Content of coffee may vary mainly due to the species of coffee tree (e.g. *Coffea arabica*, *Coffea canephora*, Robusta) and their origin. The seasonal rainfall and sun exposure can also be a factor here. Despite the controversial effects of coffee on human health, coffee is nowadays accepted as a rich source of compounds possessing antioxidant and radical scavenging activities in human body. This inspired the authors of this work to test stabilization effects of coffee on some properties of ABS.

Acrylonitrile-butadiene-styrene (ABS) terpolymer is an important engineering material. Copolymerization of styrene and acrylonitrile carried out in the polybutadiene latex medium is one of the basic methods for manufacturing ABS. This copolymer combines properties of each component: acrylonitrile enhances hardness and chemical resistance, butadiene acts as plasticizer while increasing impact strength, and styrene improves thermal and processing properties.[6,7] However, ABS was selected to test coffee antioxidant properties because of its high susceptibility to various degradation processes, mainly photo- and thermo-degradations. This copolymer is known to be very sensitive to photodegradation when exposed to sunlight, also at longer wavelengths.[8,9] The oxidative chemical transformation of ABS involves reaction in polybutadiene segments and
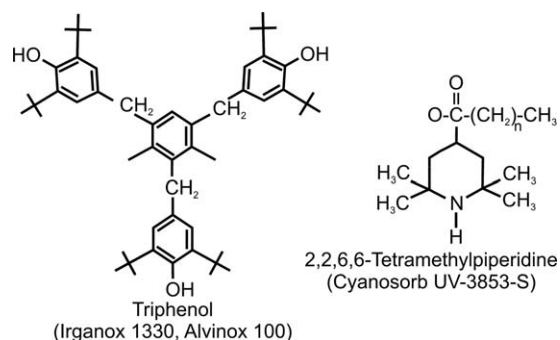
Figure 1. Exemplary antioxidants used in polymer processing.

in the styrene-acrylonitryl marcophase.[3,10–12] The oxidation of polybutadiene causes an induced oxidation of the polystyrene block in the styrene-acrylonitryle macrophase. The main effect of this reaction is formation of highly absorbing oxidation products that are responsible for the yellowing of ABS.

The objective of this work was to asses stabilizing effects of coffee on some properties of ABS subjected to UV-Vis, heat, and salt water aging treatments. For that reason accelerated aging procedures were proposed and samples were tested by means of spectroscopic and thermoanalysis measurements. Due to proving the stabilization effects of coffee on some properties of ABS patent application was previously submitted to Polish Patent Office.[13]

EXPERIMENTAL

Materials
The following materials were applied:

- Acrylonitrile-butadiene-styrene (ABS), type Terluran GP-35 Natural (Styrolution GmbH, Germany). Its density was 1.04 g/cm^3 and melt volume rate 55 cm^3/10 min (10 kg, 220°C).
- Instant coffee powder, 100% natural coffee of the mixed grades of Arabica and Robusta (Nescafé, Poland).

Sample Preparation and Aging Procedure
A single-screw extruder of the W25–30D type (IPTSz "Metalchem", Toruń, Poland), equipped with a folding screw,
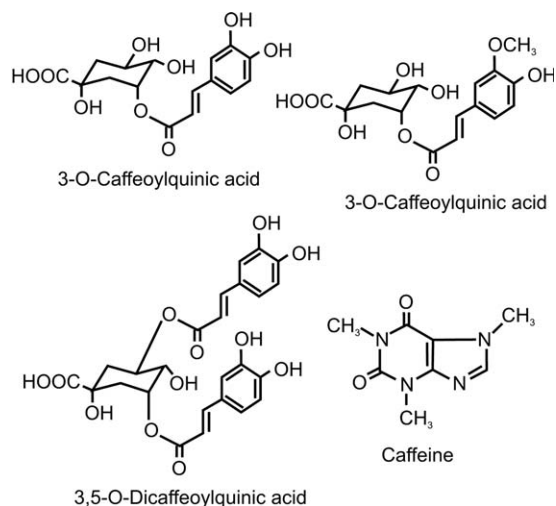
Figure 2. Some phenolic compounds and caffeine.

was used to obtain granulated ABS containing: (i) 0 wt % of coffee (further referred to as sample A), (ii) 0.1 wt % of coffee (sample B), (iii) 0.3 wt % of coffee (sample C), and (iv) 0.5 wt % of coffee (sample D). Before the extrusion, the mechanically mixed components were dried at 90°C for 24 h. The temperatures of barrel heating zones I, II, III, and of the die of the extruder were set to 170, 180, 190, and 190°C, respectively. The samples for the tests were obtained by injection moulding of the granulated blends, using a laboratory injection moulding press of the type TRX 80 Eco 60 (Tederic Inc., Taiwan). Injection moulded samples in the shape of bars with dimensions 100 × 10 × 4 mm were subjected to aging procedure and then to testing.

Investigations of aging processes occurring in polymer materials in natural environment can take many years before degradation effects will be measurable. For that reason many various testing methods and standards for accelerated aging of polymer materials were proposed.[14–17] In natural environment photo- and thermal-degradations proceed simultaneously, and thus are classified as oxidative degradation. In this study, procedure of accelerated aging was proposed in the following steps:

- UV-Vis irradiation using laboratory chamber type SunSet CPS+ (Atlas, Germany) equipped with xenon lamp. Samples were irradiated during 8 h at power of 765 W/m^2 and at temperature of 60°C;
- heat treatment using laboratory oven (samples were stored for 8 h at 120°C);
- salt water immersion (samples were stored in salt water for 8 h at 50°C).

These three aforementioned 8 h treatments constituted together one aging cycle (total of 24 h). The samples were subjected to the 6, 12, and 24 aging cycles. Considering the type of a sample (A, B, C, or D) and number of aging cycles, the samples discussed in this work are designated as A0, A6, A12, A24, …, D0, D6, D12, D24.

Measurements
Oxidation induction time (isothermal OIT) was determined using Q 200 calorimeter (TA Instruments) under the following conditions: start temperature: 40°C, final temperature 150°C, scan rate 10°C/min; N$_2$ to O$_2$ switch over after 3 min at 150°C (gas flow rate 50 cm^3/min). Oxidation induction temperature (dynamic OIT) was determined as onset temperature for increase in heat flow measured for the samples heated from 50 to 280°C in an oxygen atmosphere. Both types of OIT values were determined according to ISO standard.[18]

UV-Vis spectra were recorded on a spectrometer Evolution 220 (Thermo Scientific) equipped with an integrating sphere. Fourier transform-infrared (FT-IR) spectra were recorded in a reflective absorbance mode (ATR-FTIR) using a Nicolet iS10 spectrometer (Thermo Scientific), at a constant spectral resolution of 2 cm^{-1}, in the range of 4000 to 600 cm^{-1}, and after acquiring 30 scans. The spectra were baseline corrected to compensate for variations in instrument background and next to the intensity of C≡N from acrylonitryle phase at 2238 cm^{-1}.

This assumption is based on other studies on degradation of ABS.[8,19]

Differential scanning calorimetry (DSC) measurements were performed using a Q 200 calorimeter (TA Instruments) under nitrogen flow. Typically, a 4 mg amount of a polymer was placed on an aluminium pan for sampling. The samples were successively: quenched to $-50°C$, heated to $200°C$ at a rate of $10°C/min$, annealed at $200°C$ for 3 min, cooled to $-50°C$ at a rate of $10°C/min$, and reheated to $200°C$ at a rate of $10°C/min$. The transition temperature points (T_1, T_2), and their total enthalpy (H) were determined.

The change in weight of the samples was measured using a thermogravimetry (TG) analyzer Q 500 (TA Instruments). The analysis was done under nitrogen atmosphere at a heating rate of $10°C/min$ from 27 to $700°C$.

Dynamic mechanical analysis (DMA) of the studied samples was performed using a DMA analyzer Q 800 (TA Instruments). The bar-shaped samples were examined in a single cantilever mode, at a constant frequency of 1 Hz and controlled amplitude of 15 μm, as a function of temperature ranging from 27 to $180°C$.

RESULTS AND DISCUSSION

Oxidation Induction Time and Temperature

To verify expected antioxidant properties of coffee oxidation induction time (isothermal OIT) was determined. Dependencies of heat flow versus storing time of the studied samples in oxygen at $150°C$ are presented in Figure 3. It was found that isothermal OIT value was nearly three times greater for sample D than for sample A. It was also noticed that during isothermal storing heat flow into the samples increased with increasing content of coffee. Since the OIT measurement process is held isothermally, the samples with coffee needed more heat to maintain the set temperature of $150°C$ (higher heat flow observed in Figure 3). The difference in heat flow can result from the fact that oxidation reactions are accompanied by heat
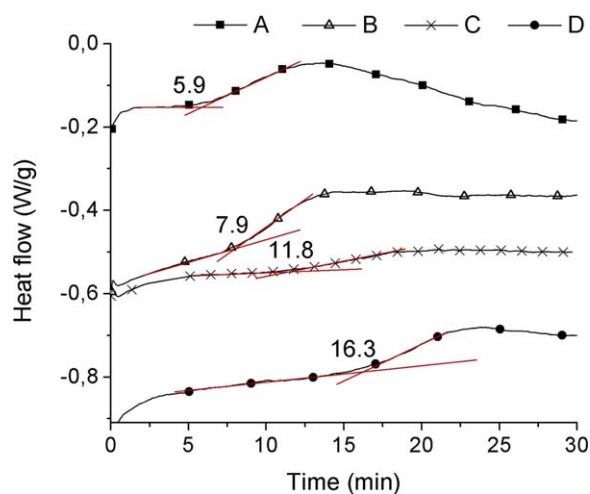
emission. Emitted heat compensates heat flow into the samples to maintain isothermal temperature. The heat emitted due to oxidation reactions in samples containing coffee is lower and needed to be compensated by external heat flow to maintain the set isothermal temperature. On the other hand, heat emitted during thermo-oxidation needs to be compensated by lower heat flow in order to maintain the set isothermal temperature. Thus, the observed increase in heat flow with increasing coffee content can confirm that these samples emitted less heat, and in consequence, coffee effectively inhibited exothermic oxidation reactions. The difference in heat flow levels could be also explained by difference in ABS structure affected by coffee, and thus by different heat capacity constants of the studied samples. However, FT-IR and DSC analysis did not show significant changes in ABS structure affected by coffee. Highly linear dependence (20 min/wt %) between isothermal OIT and coffee content was noticed, and one can assume direct influence of coffee on oxidative stability of ABS (Figure 4). Increasing resistance to thermal oxidation with increasing content of coffee was also noticed when the samples were heated from 50 to $280°C$ in an oxygen atmosphere. The oxidation induction temperature (dynamic OIT) was 175.5, 186.2, 187.9, and $200.4°C$ for the samples A, B, C, and D, respectively. In other report,[20] the value of dynamic OIT for neat ABS samples ranged from 205 to $224°C$ depending on the injection moulding conditions. However, it was determined under an airflow, at rate of 100 mL/min, and for other grade of ABS.

UV-Vis Spectroscopy

UV–Vis spectroscopy supplied information about the presence of absorbing groups (chromophores) in molecules mainly responsible for the color of the sample. The absorption of UV-Vis radiation by polymeric materials involves transitions of electrons in s, p, and n-orbital from the ground state to higher energy states. According to literature reports concerning polymer degradation,[9,21] species absorbing in the region of 300 to 500 nm are macromolecules containing conjugated double bonds and unsaturated bonds linked with carbonyl groups. These degradation products are also considered to be responsible for the yellowing of aged polymers. Absorbance of accelerated-aged neat ABS and ABS with 0.5 wt % coffee content versus wavelength are presented in Figures 5 and 6,
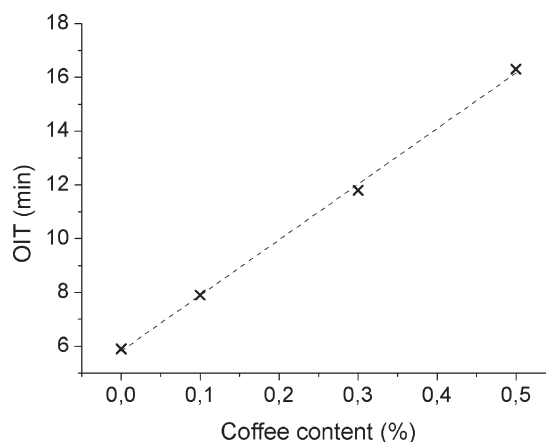

Figure 3. Oxidation induction time (isothermal OIT) for samples A, B, C, and D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Dependence of coffee content on isothermal OIT.

Figure 5. UV-Vis spectra for samples A0, A6, A12, and A24.

Figure 7. Relative absorption change (ΔAbs) at 400 nm for samples A, B, C, and D.
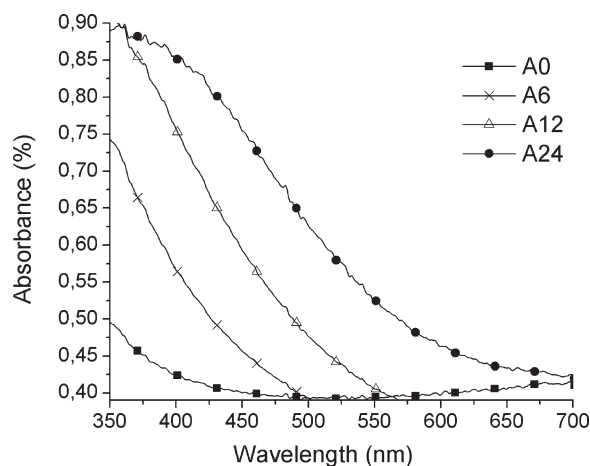
respectively. In all spectra an increase in absorption was detected, without showing any defined maximum. The observed absorption increase followed by aging cycles indicates that absorbing degradation products (e.g. conjugated double bonds and unsaturated bonds linked with carbonyl groups) appeared in all studied samples. However, this change was less pronounced for the samples containing coffee (Figure 6). For quantitative calculations, the relative absorption change at 400 nm versus the number of aging cycles is presented in Figure 7. The wavelength of 400 nm lays in between the previously mentioned absorption range and is frequently selected and associated with degradation products containing conjugated double bonds and unsaturated bonds linked with carbonyl groups responsible for polymer yellowing.[7,21] Relative absorption change (ΔAbs) was defined as a ratio of absorption intensity of aged sample and absorption intensity of nonaged sample. This approach was implemented to show quantitatively a change in absorption spectra reflecting the changes in chemical structure of the samples subjected to various numbers of aging cycles. Thus, when greater than 1, ΔAbs reflects the chemical alterations resulted from aging process. While the samples differ with coffee content one can estimate the potential of coffee as a stabilizing agent against degradation manifested in sample discoloration.
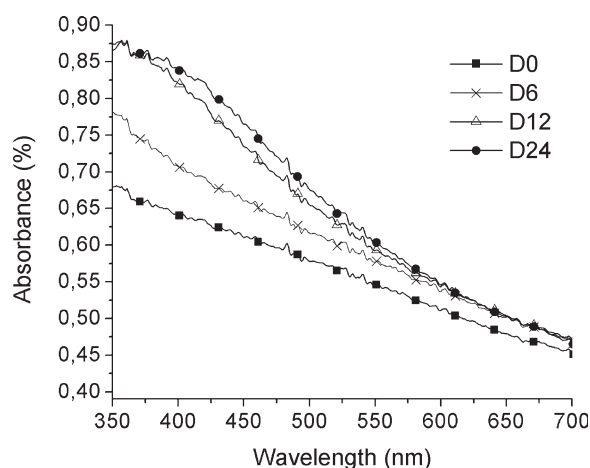
However, degradation and subsequent discoloration in ABS is confined to the thin surface layer of the specimen and is controlled by the rate of oxygen diffusion through the polymer.[22] As follows from Figure 7, the values of ΔAbs are increasing with increasing number of aging cycles. However, the values of ΔAbs are significantly lower for ABS containing coffee (samples B, C, and D) than for neat ABS (sample A) subjected to the same number of aging cycles. It indicates that thermo- and photo-oxidation leading to chromophoric group formation is more efficient in ABS than in ABS blended with coffee. Additionally, it can be concluded that increasing the coffee content above 0.3 wt % (sample C) is not necessary to obtain better color stability of ABS surface because no significant difference as compared with 0.5 wt % (sample D) was revealed.

FT-IR Spectroscopy

Degradation induced changes can be followed by observing the appearance of new absorption bands in the hydroxyl (3600–3200 cm^{-1}) and carbonyl (1800-1600 cm^{-1}) regions, and changes in the peaks attributed to butadiene (910 and 965 cm^{-1}), acrylonitryl (2238 cm^{-1}), and styrene (1602 and 1494 cm^{-1}) components in ABS. It is well known that ABS is very sensitive to oxidative-degradation processes. Especially butadiene part of ABS is highly affected by degradation process and thus initiates induced oxidation of the polystyrene component.[3]

Evaluation of IR spectra of samples A0, A6, and D6 shows that rubber double bands at 910 cm^{-1} and 965 cm^{-1}, attributed to poly(1,2-butadiene) and poly(*trans*−1,4-butadiene), respectively, rapidly decreased (Figure 8). This considerable decrease confirms strong degradation of butadiene phase, especially poly(*trans*−1,4-butadiene) represented by peak at 965 cm^{-1} which almost totally disappeared after 12 and 24 aging cycles. The change of the peak corresponding to poly(1,2-butadiene) was less pronounced and peak at 910 cm^{-1} was still visible even after 24 aging cycles. Generally, there was no perceptible difference in these two butadiene peaks for samples subjected to 12 and 24 cycles. However, lower number (6) of aging cycles revealed some stabilizing effect of coffee on ABS butadiene phase. As follows from Figure 9, the peak at 965 cm^{-1}
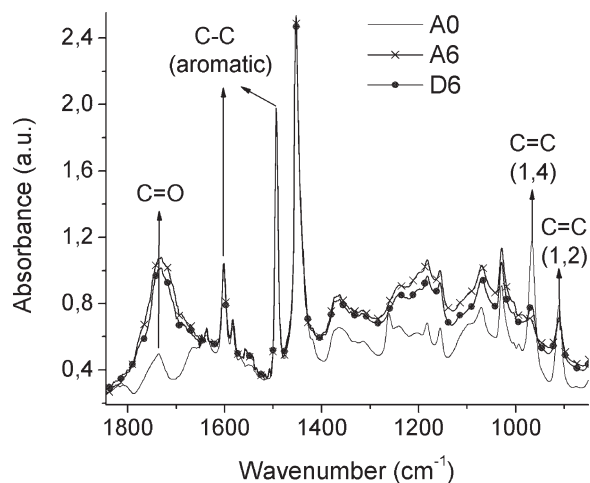

Figure 6. UV-Vis spectra for samples D0, D6, D12, and D24.

Figure 8. FTIR spectra for samples A0, A6, and D6.

Figure 10. The carbonyl absorption band for the samples A0, A6, B6, C6, and D6.

attributed to poly($trans-1,4$-butadiene) reduced to a lower extend with increasing coffee content. The same trend was observed for absorption band of poly(1,2-butadiene) at 910 cm^{-1}; however, this butadiene form was generally more resistant to degradation process and stabilizing effect of coffee was less pronounced although also discernible.

The broad peak at about 1735 cm^{-1} was attributed to carbonyl groups resulted from oxidative degradation. It is seen that sample A6 was more intensively oxidized as compared with sample D6 subjected to the same number of aging cycles (Figure 8). Generally, changes in chemical structure of aged samples were very intensive at six aging cycles and then varied slightly with increasing number of aging cycles. As a result of aging, bands at 1772, 1716, and 1688 cm^{-1}, due to α- and β-unsaturated carbonyl groups, developed (Figure 10). The various types of carbonyls like esters, acids, ketones, aldehydes, etc., formed during accelerated aging process are responsible for these new shoulders and for widening of the analyzed carbonyl peak. The stabilizing effect of coffee on ABS oxidation is discernible for samples subjected to six aging cycles varied with coffee content
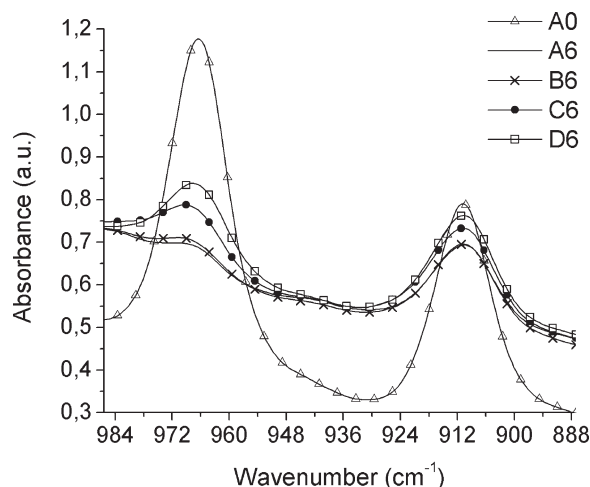
(Figure 10). The neat ABS sample aged with six cycles (sample A6) underwent intensive oxidation, thus has a high and wide carbonyl peak. However, this increase was less pronounced with increasing content of coffee. The same tendency is observed for hydroxyl groups formed under aging, which are represented by a broad signal with maximum at 3410 cm^{-1} (Figure 11). This absorption band was very intensive for neat ABS subjected to six aging cycles, whereas increasing content of coffee has contributed to its reduction. On the other hand, the tendency reverts when subjecting the samples to 12 or 24 aging cycles. Then carbonyl and hydroxyl peaks increased with increasing content of coffee. Thus, although coffee delays initiation of thermo-oxidation, as proved by isothermal and dynamic OIT measurements and confirmed by FT-IR analysis for samples subjected to six aging cycles, it can also contribute to accelerated aging once the degradation is initiated.

In order to precisely determine the influence of coffee on the reduction of isothermal and dynamic OIT values, by means of FT-IR analysis, lower than six aging cycles should be applied to
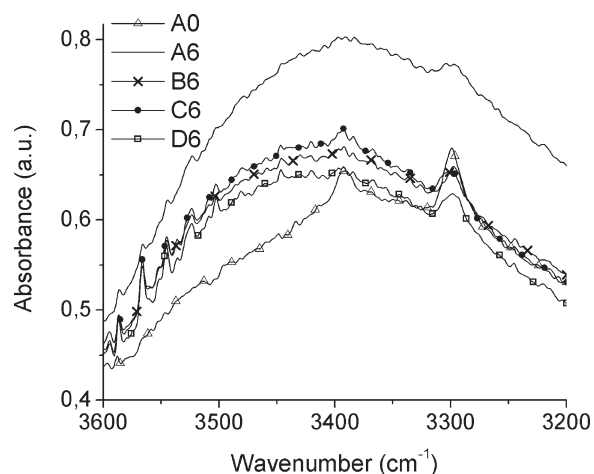

Figure 9. The butadiene absorption bands for the samples A0, A6, B6, C6, and D6.
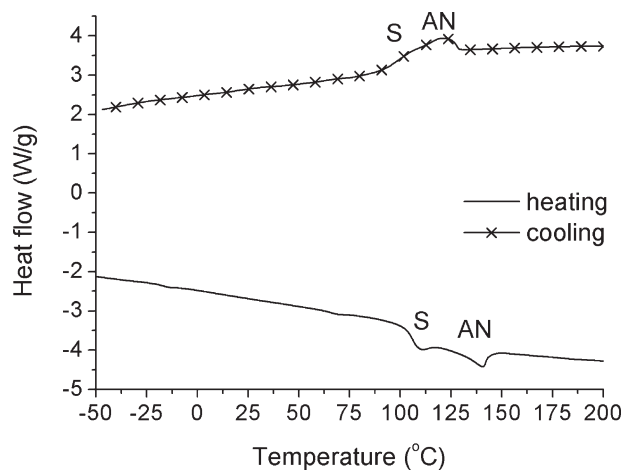

Figure 11. The hydroxyl absorption band for the samples A0, A6, B6, C6, and D6.

Figure 12. DSC curve for neat ABS.

Figure 13. DSC curves for samples A0 and D0. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

capture the start of oxidation reactions. For this purpose, the effects of thermo-, photo-, and alkaline degradation of ABS containing coffee should be investigated separately; this however is beyond the scope of this article and will be the subject of further examinations.

DSC Analysis

DSC analysis was performed to evaluate the effect of aging on the structural stability of studied samples. Due to the butadiene (B), styrene (S), and acrylonitrile (AN) blocks of ABS copolymer, three different transitions can be expected. The hardly detected broad glass transition of butadiene is reported to be at around $-53°C$[20] or even at about $-80°C$.[23] Although various heating and cooling rates (5, 10, and 20°C /min) were applied, glass transition of butadiene phase was not detected for neat ABS in this range of temperature. Thus, the attention was paid to transitions related to S and AN blocks. A typical DSC curve of the ABS is shown in Figure 12. There is apparent glass transition of S (at about 110°C) phase followed by melting of AN crystallites (at about 140°C). In order to eliminate the effects of different thermal history of aged samples and to distinguish between S and AN phase transitions, DSC analysis was performed for the second heating cycle.

Coffee in ABS caused an increase in total enthalpy of S and AN transitions for nonaged samples whereas did not affect their characteristic transition temperatures T_1 and T_2 for S and AN components, respectively (Figure 13 and Table I). As a result of aging total transition enthalpy of S and AN, and AN melting
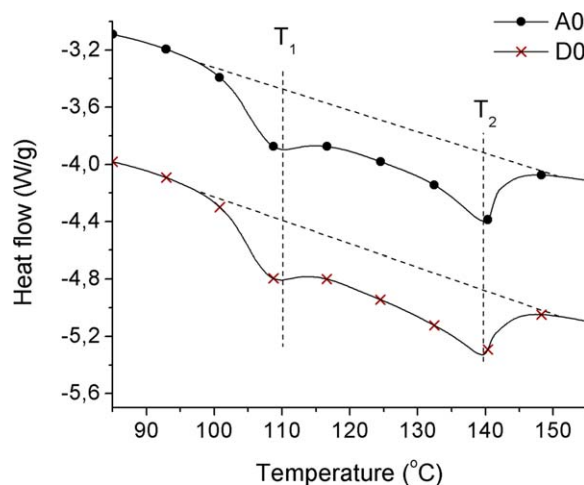
temperature (T_2) decreased for neat ABS (Figure 14 and Table I). On the other hand, these changes were less pronounced for ABS containing coffee, especially for sample D subjected to 24 aging cycles. Thus, omitting the physical interpretation of the changes in DSC curves, one can assume stabilizing effect of coffee on S and AN structure of ABS. Since the changes in DSC curves resulted from accelerated aging are more significant for neat ABS than for ABS containing coffee, it can confirm stabilization effect of this natural compound for S and AN phases in ABS.

TG Analysis

Generally, significant differences in mass loss (Δm) of the studied samples under nitrogen flow were not detected. It was noticed that samples degraded in the same temperature range from about 346 to 480°C (Figure 15). The main difference was manifested in mass derivative with respect to temperature (dm/dT) which reflects the rate of mass loss at current temperature (DTG curves). The general tendency was that the maximum value of DTG curves increased with increasing content of coffee and with increasing number of aging cycles. However, these changes were not considerable. Figure 15 shows TG and DTG curves for the samples A0 and D24 which varied the most with coffee content (0 and 0.5 wt %) and aging cycles (0 and 24). The rates of mass loss represented by the maximum of DTG curve were of about 2.0 and 2.2%/°C for samples A0 and D24, respectively. This slight increase in degradation rate could be effected by coffee

Table I. Transition Temperatures of Styrene (T_1) and Acrylonitrile (T_2) phases, and Total Enthalpy (H) for S and AN Transitions in Samples A, B, C, and D

| Aging cycles	T_1 [°C]				T_2 [°C]				H [J/g]			
	A	B	C	D	A	B	C	D	A	B	C	D
0	110.4	110.8	110.1	110.0	139.8	139.9	139.7	139.5	85.0	94.7	92.0	90.0
6	108.6	109.1	110.3	110.0	135.8	137.7	139.2	139.5	83.1	82.9	83.3	88.8
12	108.8	109.3	109.3	108.8	136.6	134.9	138.2	139.1	77.3	78.7	81.6	87.5
24	108.4	108.6	109.3	109.4	136.3	133.7	138.1	138.7	72.3	71.6	76.1	86.3
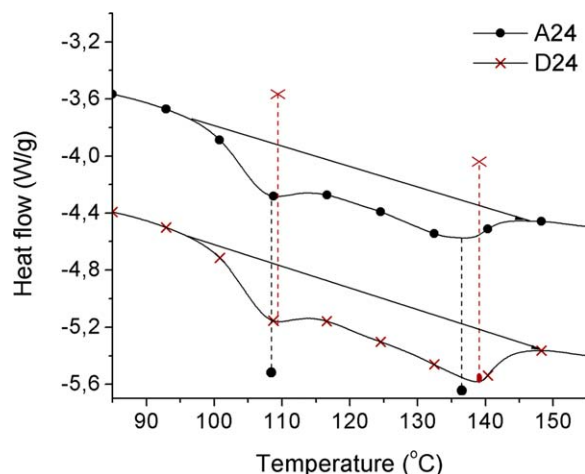
Figure 14. DSC curves for samples A24 and D24. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which starts to decompose above 210°C, whereas in aged samples it can result from degradation products.

DMA Analysis

The degradation induced breaking of carbon double bonds is often associated with crosslinking of ABS butadiene phase. This crosslinking is reported to be responsible for increase in stiffness and decrease in impact strength of aged ABS.[22,24] The decrees of carbon double bonds in butadiene phase of aged ABS was revealed by FTIR measurements, whereas DMA analysis can indirectly confirm the effect of its crosslinking based on an increase in storage modulus reflecting sample stiffness. As follows from Figure 16 storage modulus of the samples subjected to 24 aging cycles determined at room temperature significantly increased from about 1100 to about 1700 MPa. In order to assess stabilization effect of coffee on ABS attention has to be paid to the only first six aging cycles. In that case, values of storage modulus increased to about 1630, 1590, 1590, 1530 MPa for samples A6, B6, C6, and D6, respectively. These results are generally in line with those obtained for butadiene phase
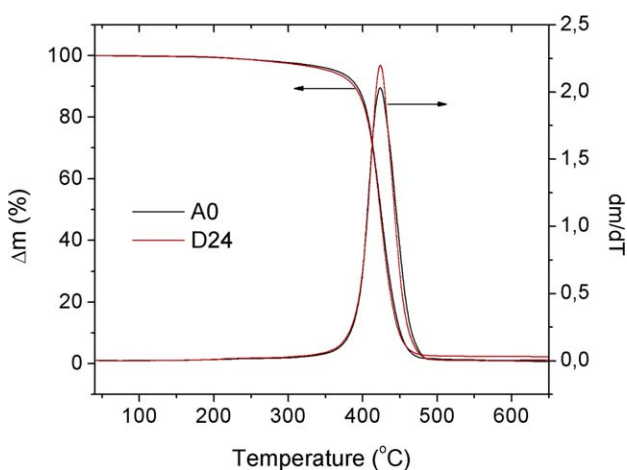
Figure 15. TG and DTG curves for samples A0 and D24. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

based on FT-IR analysis. Coffee inhibited breaking of butadiene double bonds, and thus also reduced degree of crosslinking, which is reflected by lower values of storage modulus for samples containing coffee. The shift of glass transition toward higher temperatures was probably caused by this crosslinking of butadiene component, which resisted the movements of styrene-acrylonitrile mirophases.

CONCLUSIONS

Measurements of oxidation induction time proved that the samples containing coffee underwent thermal oxidation with delay, proportional to the increase in coffee content. The value of isothermal OIT was almost three times greater for sample containing 0.5 wt % of coffee than for neat ABS. As confirmed by FT-IR studies, the addition of coffee has stabilized the structure of ABS subjected up to six aging cycles. Coffee also affected the color of the samples which was revealed in the UV-Vis spectra. It is well known that also phenolic antioxidants used in processing are affecting the color of polymers. Aging cycles caused more intensive change in the UV-Vis spectra for neat ABS than for ABS containing coffee. Although coffee delays initiation of thermal oxidation, as proved by isothermal and dynamic OIT measurements and confirmed by FT-IR analysis for samples subjected to six aging cycles, it can also contribute to accelerated aging once the degradation is initiated, as concluded from FT-IR analysis. From the viewpoint of common industrial applicability the delay in oxidation induction time and increase in induction oxidation temperature is a key issue, since elimination of polymer degradation is practically inevitable. For that reason, coffee can be used as a natural antioxidant of vegetable origin, thus being safe to be used in food packaging. Additionally, coffee effectively acted as color and structural stabilizer, maintaining mechanical properties closer to nonaged ABS.

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