

FTIR Analysis of a Polycarbonate Blend After Hygrothermal Aging

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ABSTRACT: Fourier transform infrared spectroscopy was used to detect changes or degradation in chain structure of PC/ABS specimens after being exposed to three hygrothermal conditions. The two main absorbance peaks of interest are associated with carbonyl and hydroxyl groups due to the oxidation of butadiene in the ABS component. The changes to these groups were evident in earlier work during thermal aging of this blend but were not found in this hygrothermal study. However, the increase in intensity within the hydroxyl region for two of the conditions was attributed to bulk water diffusion in the material. When viewed together with results published earlier by our research group, the changes driven by bulk moisture diffusion are reversible. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41316.

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INTRODUCTION

Polycarbonate/Acrylonitrile-Butadiene-Styrene (PC/ABS) blends are widely used to mould thin-walled plastic housings for electronic devices. The blends are preferred alternatives to polycarbonates because of their higher processibility and water resistance. Given the intent to further decrease the wall thickness of components, the user community is particularly interested in understanding the durability of these blends due to prolonged exposure to combined high humidity and elevated temperature conditions. The present work is an extension of our earlier work on the moisture absorption of PC/ABS polymer blend.¹ In that paper, the response of PC/ABS to five hygrothermal or hot-wet conditions was reported. Under these conditions, it was postulated that their responses depended on two competing physical mechanisms: moisture absorption and structural recovery/mechanical relaxation associated with physical aging. We also reported that the relative humidity and aging temperature during hygrothermal aging have opposite effects on the two parameters used to characterize moisture diffusion, i.e., the equilibrium moisture content and the coefficient of diffusion. Moreover, the diffusion mechanism in four hygrothermal conditions was found to be different from the behaviour observed for samples immersed in distilled water at room temperature. Although water absorption and interactions with the polymer structure are generally considered to be physical mechanisms, it is possible that the polymer structure undergoes chemical degradation at higher humidity and temperature conditions.

In this study, the Fourier transform infrared reflectance (IR) technique has been applied to detect modification or degradation of the blend structure after water sorption. To the best of the authors' knowledge, most of the studies on PC^{2–7} and ABS^{8–12} alike have applied this technique to characterize structural changes due to thermal aging but there is minimal IR data on the effects of moisture absorption on either single polymer system.¹²

EXPERIMENTAL

Material Preparation and Procedure

The material used in this work is the same as that in our earlier work.¹ It consisted of commercial grade of 75 : 25 PC/ABS from SABIC (formerly, GE Plastics), designated as Cycloy C6600. The blend has a melt flow rate of 21.5 g/10 min at 260°C with 2.16 kgf in accordance to the ASTM standard.¹³ The weight average molecular weight (M_w) of the blend was found to be 45,000 by Jordi FLP using gel permeation chromatography with RI (GPC-RI) and GPC-Fourier transform infrared spectroscopy (FTIR) techniques. The size of the molecules in solution was found to be the same and could not be resolved using GPC. Moreover, GPC-FTIR confirmed that they were eluting at the same time.

Moulded sheets of the material were cut to size in accordance to ASTM D570-98 Standard.¹⁴ Test samples were cut in the form of a bar with nominal dimensions of 76.2 mm (3 in.) by 25.4 mm (1 in.) by the thickness of the sheet, 2.84 mm

Table I. Values of $\Delta A_D/A_0$ (%) and Comparison of Changes in IR Regions After Hygrothermal Conditioning

		Hygrothermal condition			
		80°C/dry ^a	65°C/50% RH	50°C/93% RH	RT/immersed
IR Region	Butadiene (960 cm ⁻¹)	Decrease	38 (subtle decrease)	12 (negligible change)	9 (negligible change)
	Carbonyl (1770 cm ⁻¹)	Increase	7.2 (negligible change)	1.2 (negligible change)	9.8 (negligible change)
	Hydroxyl (3100–3500 cm ⁻¹)	Increase	17 (negligible change)	587 (increase)	698 (increase)

RT room temperature

^aFrom Ref. [16].

(0.11 in.). Cut edges were smoothed so as to be free from cracks and were polished slowly to avoid heating the surfaces.

All test samples were subjected to the following conditioning treatment: (a) storing in a desiccator for 48 h before testing in accordance to the ASTM D 618-08 Standard conditioning guidelines;¹⁵ (b) drying in an oven at 135°C for 10 minutes to erase previous thermal history;¹⁶ and (c) weighing of dry sample mass. In total, the samples were exposed to three different conditions: (i) 65°C and 50% relative humidity (RH); (ii) 50°C and 93% RH; and (iii) at room temperature fully immersed in distilled water. Hygrothermal aging for conditions (i) and (ii) was conducted inside environmental chambers with the samples standing on one end in grooves machined into an aluminum block such that both surfaces of each sample were equally exposed to their conditioning environment. Samples fully immersed in water were rested on one end inside an enclosed container.

IR scans were conducted on samples exposed to conditions (i) and (ii), which corresponded to the lowest and highest equilibrium moisture content, and compared with the fully immersed condition (iii). Simultaneously, another set of samples conditioned in the same three environments was weighed for gravimetric experiments.

In the gravimetric measurements, the conditioned samples were weighed at the following set schedules; after 1, 3, 7, and 10 days following conditioning, and then once every week thereafter. Two samples were taken from the same conditioning environment for IR scans. Samples removed for the IR scans were not reused. Moreover, an unaged sample was also used as a reference for comparing the IR scans of conditioned samples.

Apparatus

A Bruker Optics Tensor27 FTIR attached to a Hyperion microscope with an (attenuated total reflectance) ATR-II 20× objective was used to obtain the infrared spectrum. The objective consisted of a germanium tip, approximately 100 μm in diameter. FTIR data was averaged over 100 scans, and the resolution in wavelength was 4 cm⁻¹.

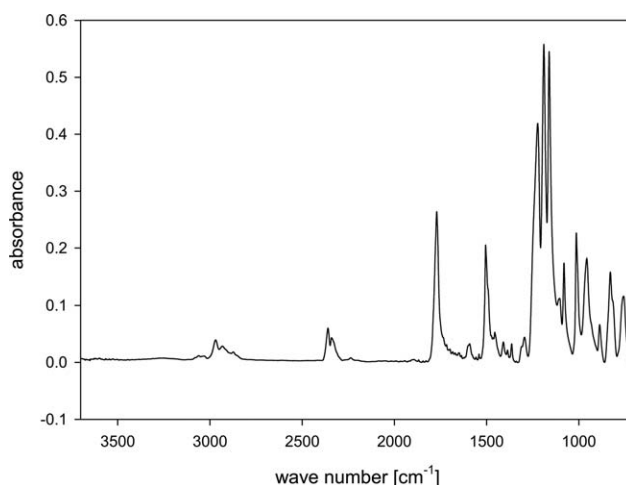
RESULTS AND DISCUSSION

Gravimetric measurements reproduced the same moisture uptake behavior observed in the measurements reported in our earlier work,¹ therefore confirming that the equilibrium moisture contents of samples exposed to conditions (i) and (ii) are

related to the lowest and highest contents, respectively (as per Table I in Ref. [1]).

Figure 1 shows the absorbance spectrum of the PC/ABS material with its thermal history erased, which is consistent with the spectrum of PC/ABS reported in the work of Kuczynski et al.¹⁷ The spectrum also appears very similar to that of the PC component given in the study of Balart et al.,¹⁸ which is reasonable since the blend has a larger component of PC.

As a brief review, the characteristic IR frequencies in the PC/ABS spectrum¹⁷ can be correlated to the molecular structures of the mer groups of the constituent materials shown in Figure 2. Characteristic of PC is the carbonate linkage (or the carbonyl functional group, C=O). The infrared absorption band for the carbonyl group occurs near 1770 cm⁻¹, but with contributions from *trans-trans* (*t-t*) conformers at 1767 cm⁻¹ and *trans-cis* (*t-c*) at 1785 cm⁻¹.¹⁹ The terms *trans-trans* and *trans-cis* refer to the conformation of the carbonate linkage. The stretching of the C–O bond occurs around 1150 to 1250 cm⁻¹ and for the methyl groups is in the 2850 to 3000 cm⁻¹ region.⁶ The stretching of the C–C bond in the phenyl group (benzene ring) is found at approximately 1600 cm⁻¹. This band can also be deconvoluted into *t-t* and *t-c* conformers at 1594 and 1604 cm⁻¹, respectively.¹⁹ Characteristic of polyacrylonitrile is the C≡N bond which is seen approximately at 2250 cm⁻¹,¹¹ and the characteristic polybutadiene region occurs at

**Figure 1.** FTIR scan of unaged PC/ABS.

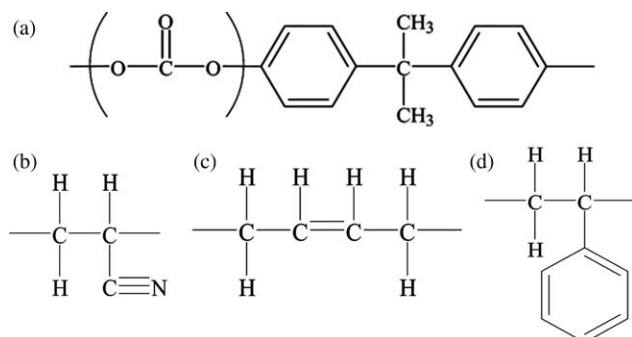


Figure 2. Molecular structure of (a) polycarbonate (b) polyacrylonitrile (c) polybutadiene and (d) polystyrene.

960 cm^{-1} .¹⁰ The presence of polystyrene is noted by the phenyl group, which also exists in PC.

ABS is easily oxidized, and during oxidation, carbonyl and hydroxyl degradation products are formed, as reported by, for example Motyakin and Schlick,¹⁰ Rjeb et al.,²⁰ and Gugumus.²¹ The oxidation process of butadiene leads to the formation of carbonyl (around 1770 cm^{-1}) and hydroxyl groups (between 3000 and 3500 cm^{-1}) during the degradation of ABS.¹⁰ Thermal treatments also cause an increase in the absorbance intensities of the carbonyl bond around 1770 cm^{-1} ,² as well as a shifting of the carbonate population from a high-energy, *trans-cis* arrangement to a lower-energy, *trans-trans* arrangement.^{2,3}

Figures 3–5 show the progressive changes in the FTIR spectra for the hygrothermally aged samples when fully immersed at room temperature, at $50^\circ\text{C}/93\%$ RH, and at $65^\circ\text{C}/50\%$ RH, respectively.

The C=O bond in the carbonate linkage has a very high dissociation energy, as indicated by Li and Huang,²² which makes it suitable for monitoring. Upon closer inspection of the carbonyl region (1770 cm^{-1}) for the three hygrothermal conditions, no appreciable changes were found. For example, the carbonyl region is enlarged in Figure 5 for the samples at $65^\circ\text{C}/50\%$ RH.

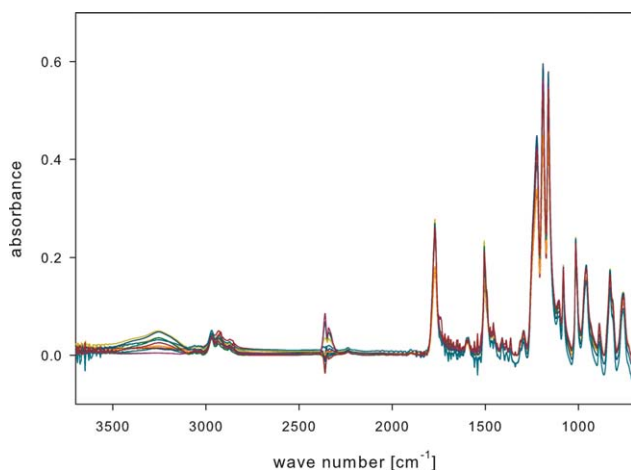


Figure 3. Progressive ATR-FTIR spectra of hygrothermally aged samples fully immersed at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The absorbance intensities in the carbonyl region (normalized to the reference peak height) for the three hygrothermal conditions are overlaid in Figure 6.

Figure 7 shows a subtle decrease in the absorbance intensity in the butadiene region at the $65^\circ\text{C}/50\%$ RH condition. The normalized peak absorbance intensity of polybutadiene region for the three hygrothermal conditions is illustrated in Figure 8.

Our group had reported earlier¹⁶ that for PC/ABS samples aged at 80°C without hygrothermal exposure, the absorbance intensities of the hydroxyl and carbonyl regions increased but that was accompanied by a decrease in the absorbance intensity of the butadiene region. These changes have been attributed to the oxidation of ABS at 80°C , which is close to the T_g of ABS in the blend. However, the results of the current study revealed that the presence of moisture unexpectedly modified the aging response of the blend. The changes in IR regions for the different hygrothermal conditions are compared in Table I.

The samples that were fully immersed at room temperature and at $50^\circ\text{C}/93\%$ RH showed no appreciable changes in the carbonyl and the butadiene regions. Such changes would be associated with oxidation of butadiene for the period of conditioning. Although these conditions are well below $T_{g,PC}$ for physical aging or relaxation to occur (the glass transition for the polycarbonate component, $T_{g,PC}$, of this same PC/ABS blend occurred at approximately 110°C),¹⁶ it was surprising that the presence of moisture does not appear to affect the carbonyl bonds. It is as if the hygrothermal conditions are not severe enough for oxidation to occur, not only because the temperatures are lower as compared to the physical aging study at 80°C ,¹⁶ but also due to the lower concentration or lack of oxygen.

A plausible explanation is that when fully immersed under water, the lack of oxygen prevented oxidation. Similarly, the oxygen concentration in the $50^\circ\text{C}/93\%$ RH condition is too low to support detectable levels of the oxidation process. Moreover, the difference of aging in air and water for polypropylene has shown similar findings.²³

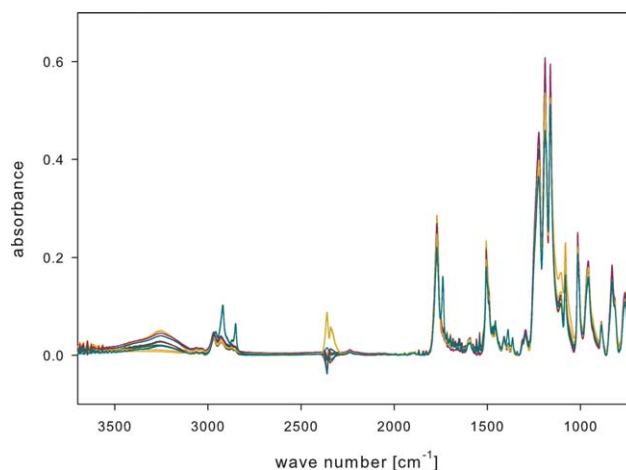


Figure 4. Progressive ATR-FTIR spectra of hygrothermally aged samples at $50^\circ\text{C}/93\%$ RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

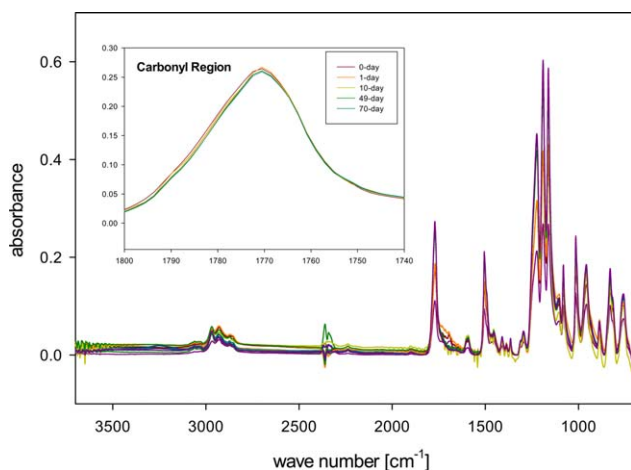


Figure 5. Progressive ATR-FTIR spectra of hygrothermally aged samples at 65°C/50% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

At the end of the study, the last absorbance spectrum for each hygrothermal condition, along with the unaged spectrum are plotted in Figure 9 to superimpose all the results. The hydroxyl region (3100–3500 cm^{-1}) of Figure 9 has been enlarged to better illustrate the absorbance intensity changes in this region.

A reasonable question then is “If oxidation is suppressed, what caused the hydroxyl region (between 3100 and 3500 cm^{-1}) to increase in absorbance, as is seen in the enlarged insert in Figure 9, but not in the carbonyl region?” Although further investigations are necessary, one possible explanation for the appearance of the broad band in the spectrum is the stretching of hydroxyl groups formed through hydrogen bonding.^{24–26} The IR spectrum shown in Figure 9, however, illustrates the final profiles of the three hygrothermal conditions in comparison to the unaged state. As compared to the two conditions of 50°C/93% RH and fully immersed at room temperature which are very similar, the presence of hydroxyl groups was not observed at 65°C/50% RH even though the temperature at this condition is the highest among the three conditions. As Figure 9 shows,

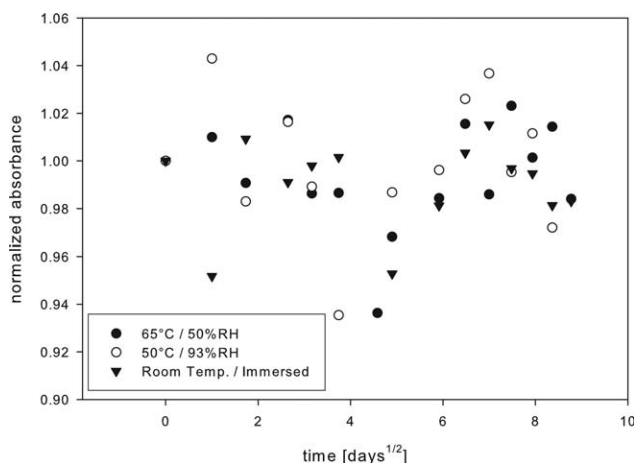


Figure 6. Effect of hygrothermal aging on the normalized peak absorbance intensity of carbonyl region for the three hygrothermal conditions.

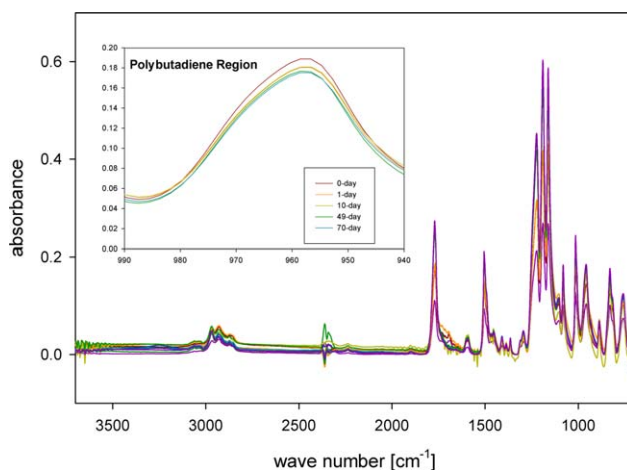


Figure 7. Absorbance of polybutadiene region (960 cm^{-1}) at 65°C/50% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the hydroxyl groups in the other two hygrothermal conditions approximately reach the same point of saturation. Since the equilibrium moisture in these two conditions are comparable (0.39% at 50°C/93% RH and 0.41% when fully immersed at room temperature), it is therefore more likely that the difference in behaviour is due to the higher water concentrations in these two environments which led to higher levels of hydroxyl ions. Similar findings have been reported by Yang et al.²⁷ when using FTIR spectroscopy to study water diffusion in poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

Since polycarbonate is a major component in this blend, it would be useful to highlight the relevant findings from numerous reports of polycarbonate hydrolysis in the literature.^{12,28–32} The hydrolysis of PC at moderate temperatures below its glass transition temperature is known to cause chemical aging of the material³⁰ resulting in carbonic acid, which further yields phenolic end groups by releasing carbon dioxide.^{12,31,32} Although hydrolysis is more likely at high temperatures and relative humidity, some studies on polycarbonate have suggested that

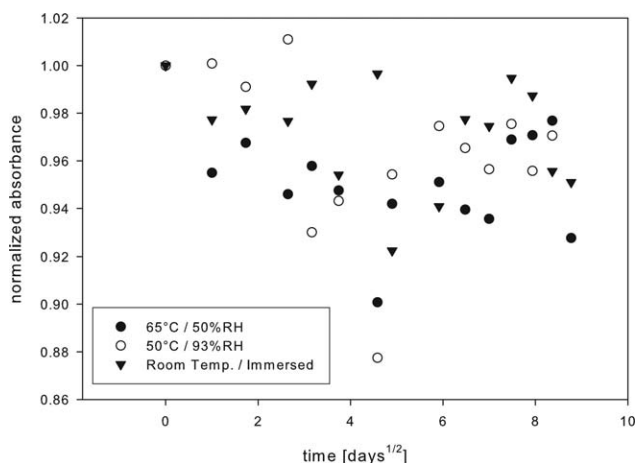


Figure 8. Effect of hygrothermal aging on the normalized peak absorbance intensity of polybutadiene region for the three hygrothermal conditions.

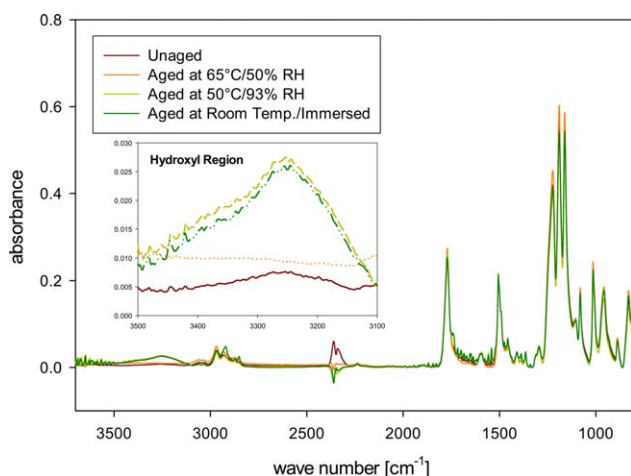


Figure 9. ATR-FTIR spectra of unaged and hydrothermally aged samples after 77 days of aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrolysis may occur under less severe conditions.^{29,31,33} In the current study, however, no increase was observed in the intensity of the carbonyl region (1770 cm^{-1}), as discussed before. This may be explained by the fact that the polycarbonate component of PC/ABS blend has a carbonate linkage ($\text{C}=\text{O}$) that appears as a large peak in the carbonyl region of the IR spectra of unaged samples, Figure 1.

Since the hydrolysis of PC leads to molecular weight losses, most of the authors have measured molecular weight change of PC using gel permeation chromatography (GPC).^{12,28,29,32} Mechanical and thermal property changes of PC caused by hydrolysis have also been investigated.^{30,31} Pryde and Hellman¹² also studied chemical behaviour of PC using two IR and UV spectrometric methods. They observed the formation of new phenolic end groups at 3605 cm^{-1} . In this work, hydrolysis of PC has not been detected using IR. Since hygrothermal conditioning of the blend material is complicated by physical aging mechanisms of two polymer components, a more extensive evaluation will require examining properties such as molecular

weight and mechanical properties.³² This will be a subject of interest in our future work.

To quantify the changes in IR scans, the numerical difference between the scans was analyzed by subtracting the reference spectrum from subsequent spectrums. The spectra were analyzed in the range $900\text{--}1050\text{ cm}^{-1}$, $1700\text{--}1850\text{ cm}^{-1}$, and $3000\text{--}3500\text{ cm}^{-1}$ for butadiene, carbonyl, and hydroxyl regions, respectively. This analysis technique follows earlier reports by other authors including Heymans and Dequenne.³⁴

The procedure applied is best described by using an example: in this case, the carbonyl region of the 77-day band for the condition of $65^\circ\text{C}/50\%\text{ RH}$ (Figure 10). If the difference between the two peaks at the absorbance of 1770 cm^{-1} on the reference curve is denoted by A_0 and the absorbance of the difference spectrum (difference between the reference curve and the curve after 77 days of hygrothermal aging) is represented by ΔA_D (depicted in Figure 10), the ratio $\Delta A_D/A_0$ shows the modification in the band within the carbonyl region. This parameter has been calculated in percentage for three regions in three hygrothermal conditions and is also tabulated in Table I. The comparison of the values shown in Table I also confirms the changes observed for the three regions, where relatively high values are denoted as either increases or decreases in the band and very low values are referred to as negligible changes.

CONCLUSIONS

The ABS component of the PC/ABS blend appears to be structurally stable under the high humidity and temperature conditions tested. IR scans of the butadiene region absorption spectrum showed minimal changes to the chain structure after aging. This is especially evident when the observations of this study are quantified and compared against the findings of similar experimental work conducted under $80^\circ\text{C}/\text{dry}$ condition, where the changes were easily detected by FTIR scans. Although there was no evidence of the oxidation of butadiene in this study, the increase in the hydroxyl region occurred for only two conditions, i.e., fully immersed at room temperature and at $50^\circ\text{C}/93\%\text{ RH}$. This is attributed to the presence of bulk water diffused into the material. It would be reasonable to infer that the effects of water ingress in PC/ABS are reversible.

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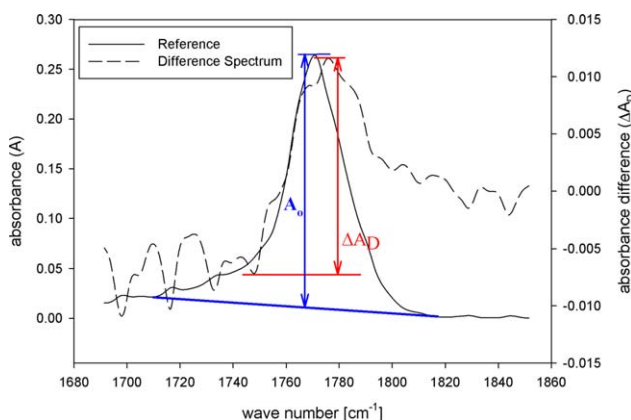


Figure 10. Reference spectrum and difference spectrum for the carbonyl region after 77 days of hygrothermal aging at $65^\circ\text{C}/50\%\text{ RH}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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