

In-Line Analysis of the Influence of Monomeric and Oligomeric Hindered Amine on the Hydrolysis of Polycarbonate in a PC/ABS Blend

Vipin V. Rajan,^{1,2} Bernd Steinhoff,^{1,2} Ingo Alig,¹ Roy Wäber,¹ Jürgen Wieser¹

¹German Institute for Polymers (DKI), Department of Technology, Darmstadt 64289, Germany

²Dutch Polymer Institute (DPI), High Throughput Experimentation cluster, 5600 AX, Eindhoven, The Netherlands

Received 7 January 2010; accepted 26 April 2010

DOI 10.1002/app.32714

Published online 14 July 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The polycarbonate/polyacrylonitrile butadiene styrene (PC/ABS) blends lose mechanical properties when exposed to outdoor conditions. This is due to the ultraviolet (UV) induced photo-oxidation of the PC phase and the polybutadiene portion of the ABS. It is known that ABS can be stabilised against terrestrial light by the use of hindered amine in combination with a UV absorber. However, such hindered amine cannot be used when PC is present in a multi component polymer blend. The hydrolysis of PC is accelerated when a small amount of hindered amine light stabilisers (HALS) is incorporated in the resin and is exposed to elevated temperature. In this article the effect of monomeric and oligomeric hindered amine on the hydrolysis of PC during the compounding of PC/ABS blend in a twin screw extruder at 240°C is

observed by means of in-line UV-vis spectroscopy. Tinuvin 765 was used as monomeric hindered amine and Tinuvin 622 as oligomeric hindered amine. The molecular weight of the compounded sample was determined by gel permeation chromatography (GPC) and the rheological properties were observed using an online viscometer. It was found that the extent of hydrolysis induced by the oligomeric hindered amine is less compared to monomeric amine. It was also observed that polymeric hindered amine imparts better dispersion of the ABS phase into the polymer blend. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3532–3538, 2010

Key words: In-line monitoring; UV-vis spectroscopy; hydrolysis; hindered amine light stabilisers; PC/ABS blend

INTRODUCTION

One of the challenges when polymers are used in outdoor applications is that, the environment negatively influences their service life. This process is called weathering.^{1,2} The weathering of polymers can be defined as an irreversible chemical process induced by environmental parameters that leads to undesired changes of properties of the polymers, such as discolouration and loss of mechanical properties.^{3,4} Polycarbonate (PC)/ABS blends are widely used in demanding applications such as automotive parts, power tools and office equipments. Automotive specifications, in particular, are stringent regarding color retention for PC/ABS blends. However, adequate stabilization of PC blends against terrestrial light remains problematic.^{5–13} A high concentration of UV absorber is often used but it results in high cost for the PC blends.¹⁴ While the UV absorber is beneficial in shielding UV light, it does not act to scavenge radical species which arise from UV

induced or thermal induced degradation of the PC or the ABS components in the blends. The hindered amines are well known to be radical scavengers for many classes of polymeric materials.¹ These are extensively used to protect PC/ABS blends from photo-oxidation and thermo-oxidative degradation.^{15,16} The mechanism of action that is often used with HALS is the Denisov cycle,¹⁷ is depicted in Figure 1. Denisov describes a cyclic process wherein the active species are regenerated rather than consumed during the stabilization process. This theory suggests that the hindered amine oxidizes to form nitroxy radicals (NO•) that in turn react with the free radicals, which is normally an alkyl radical (R•) that is generated during photo-oxidation of the polymer to form an aminoether (NOR), a nonradical species. The aminoether (NOR) terminates peroxy radicals and, in the process, generates the nitroxy species (NO•) completing the cycle.¹⁷

However, hindered amines cannot be used in polymeric substrates which are sensitive to chemical reaction with the basic nitrogen atom in the light stabilizer.¹⁶ Such polymeric substrates include PC. Indeed a severe reduction in the mechanical properties is reported when hindered amines are incorporated into the PC/ABS blend during the compounding

Correspondence to: V. V. Rajan (vipinvrajan@hotmail.com).

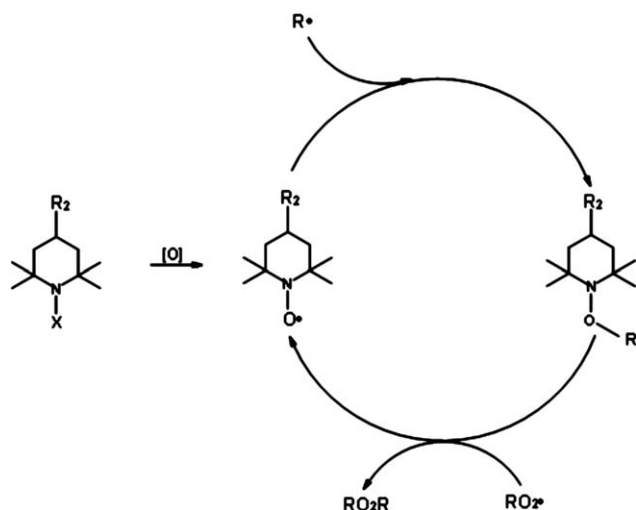


Figure 1 Stabilization mechanism of HALS in polymers, X = alkyl group.

stage.¹⁸ In this article an online measurement technique has been used to study the effect of stabilisers and processing parameters on polymer properties while compounding. The offline experiments are time consuming, but critical in determining the influence of processing on the resulting properties. Minimizing offline measurements and replacing them with real time monitoring using online instrumentation will give insight into the degradation of PC/ABS blend while it is being processed. Ultra violet-visible light (UV-vis) spectroscopy, which is very sensitive to color formation, has been proved to be a suitable method for *in situ* monitoring of polymer degradation in a laboratory setup.^{19–21} The online measurement provides a rapid, reliable, noninvasive and cost effective analysis methodology.^{22,23}

The objective of this article is to study the effect of monomeric and oligomeric hindered amine on the hydrolysis of PC during the compounding of PC/ABS blend in a twin screw extruder at 240°C. Tinuvin 765 (T765), monomeric HALS, and Tinuvin 622

(T622), oligomeric HALS, are used as the stabilisers for this study. These stabilisers are compounded with the PC/ABS and extruded to a film with a thickness of 0.35 mm. The effects of HALS on the polymer phase are monitored by an online UV-vis spectrometer during the compounding stage. GPC is used to measure the molecular weight after compounding. The effect of processing parameters and concentration of stabilizer on the rheological properties are observed using an online viscometer.

EXPERIMENTAL SECTION

Material

The polymer used in the investigation was PC (Calibre 300-10, Dow Benelux) and ABS (Magnum F641, Dow Benelux). A schematic overview of the stabilisers used is shown in Table I. The additives exhibit no significant absorption within the wavelength range used for the UV-vis spectroscopy, 350–900 nm.

The PC and ABS were firstly pre-blended with a weight ratio of 65/35. In a second step the preblend was compounded with the additives. As the amount of additives was quite small a masterbatch was prepared in ABS powder to ensure the required amount of additive was accurately fed. A small increase in the ABS content during compounding is therefore accounted when the additives are fed to the preblend. As the compounding of stabilisers with polymer and the online measurement of degradation using UV-vis spectroscopy is a continuous process it was practically not possible to change the stabilizer masterbatch each time the concentration of stabilizer is altered. A batch process with stoppage between each measurement while changing the stabilizer concentration can create serious errors in the online measurement system. Therefore, an alternate continuous method described above was preferred and the increase in ABS content is accounted while tabulating

TABLE I
Schematic Overview of the Stabilisers Used with Their Structure and Supplier

Name (Supplier)	Chemical structure
Tinuvin 622 [(283) _n g/mol], $M_n = 3100\text{--}4000$ g/mol (Ciba)	
Tinuvin 765 (509 g/mol) (Ciba)	

the results. The concentration of stabilizer used varies from 0 to 1 wt %.

Compounding experiments

A production size corotating twin screw extruder (ZSK-32 Mc MEGA Compounder, Coperion Werner and Pfleiderer GmbH) with 32 mm screws was equipped with gravimetric feeding units (DDW-MDI, Brabender). The barrel temperature was set to 240°C. Screw speed of 600 and 1200 rpm and a throughput of 35 kg/h were chosen. A standard screw configuration was used for the compounding. The extruder was equipped with a 3-way-melt divider. By this, one melt stream can be extruded into a film, a parallel second stream can be analysed with an online-rheometer with a slit die (Proflow, Thermo Electron Corporation) and a third melt stream can be pelletized.

The film extrusion line (Chill roll Type 136–350S, Dr. Collin GmbH, Germany) has a roll face width of 350 mm preceding a slit die with a width of 250 mm and a lip which is adjustable between 0.3 and 2 mm. The roller conveyor, following the chill roll has a length of 3300 mm and can be adjusted to throughput velocities between 0.5 and 5 m/min. The PC/ABS film extrusion was done at a velocity of 5 m/min and the thickness of the film with 0.35 mm.

Testing procedure

The molar mass of unaged polycarbonate in PC/ABS blends was determined by size exclusion chromatography (SEC; GPC) in tetrahydrofuran using toluene as internal flow marker. The GPC-setup consisted of a Waters 515 isocratic HPLC pump, a TSP AS 100 autosampler, a Waters UV 486 Detector operated at 254 nm and a Waters 410 differential refractometer. Three SDV columns (PSS, Polymer Standard Service GmbH, Mainz, Germany) with nominal pore sizes of 10^6 , 10^5 , and 10^4 Å (30×0.8 cm each) were used. Calibration was performed using narrow distributed polystyrene standards. Data acquisition and processing was performed using PSS WINGPC software version 6.2.

The online UV-vis spectroscopy consists of a MultiSpec 2-channel process spectrometer system (tec5 AG, Germany) equipped with a 1024 pixel diode array detector. The UV-vis transmission probes, Figure 2, measuring at the film are connected with the spectrometer by optical fibers.

The moisture content of PC was measured by aboni FMX Hydrotracer (HESS werkstoff-prüfgeräte, Richard HESS MBV GmbH, Germany). The sample is weighed and filled into the sample tray. A heater warms the sample to a chosen temperature, 175°C. The evaporating water reacts with the powdery reagent, calcium hydride, which transforms water into

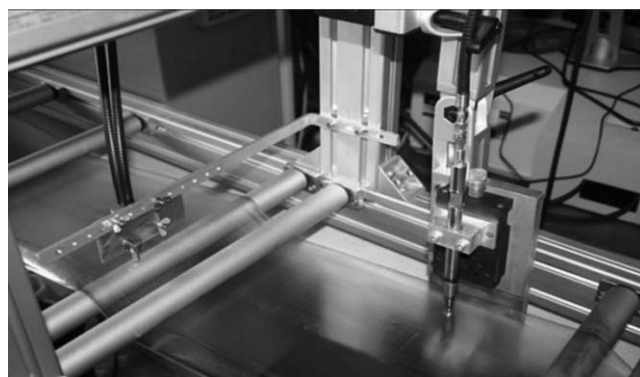


Figure 2 One of the UV-vis transmission probes (arrow) measuring on the running film. The second probe is mounted on the rear side of the film.

hydrogen. The concentration of hydrogen within the reactor atmosphere is a measure of the water content within the reactor. A gas sensor detects the hydrogen concentration.

The online viscosity was measured by the difference in pressure, when the melt was forced through a slit die at constant volume flow rate. Measurements can be made using a range of pre-set volume flow rates. Viscosity is defined as the ratio of true shear stress to true shear rate. All viscosity measurements were done at 190°C. Following equations were used to calculate the true shear rate and shear stress.

Apparent shear rate was calculated using the eq. (1),²⁴

$$\dot{\gamma}_{\text{app}} = \frac{6 \cdot V}{B \cdot H^2} \quad (1)$$

B is the width of the die in millimeters.

H is the thickness of the die in millimeters.

V is the volume flow rate in cubic millimeters per second.

The eq. (1) is valid only for Newtonian liquids. As plastics melts do not generally exhibit Newtonian behavior a correction procedure known as Weissenberg-Rabinowitsch correction method is applied to determine the true shear rate at the slit die and is given by eq. (2),²⁴

$$\dot{\gamma} = \frac{\dot{\gamma}_{\text{app}}}{3} \left(2 + \frac{d \log \dot{\gamma}_{\text{app}}}{d \log \tau} \right) \quad (2)$$

τ is the true shear stress and was calculated using the eq. (3),²⁴

$$\tau = \frac{HB}{2(H+B)} \times \frac{dp}{dl} \quad (3)$$

dp/dl is the longitudinal pressure gradient in pascals per millimeter measured using pressure transducers placed along the length of the die.

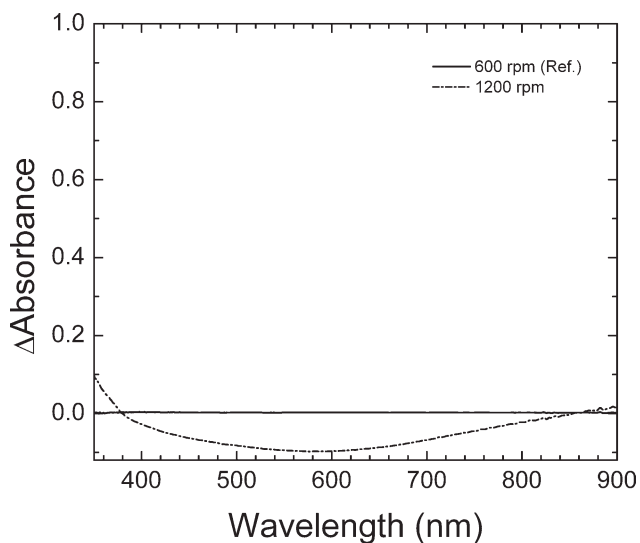


Figure 3 Variation of UV-vis spectra as a function of screw speeds.

RESULTS

Compounding of PC/ABS with UV stabilisers

In this section the compounding of PC/ABS at two different screw speeds without any additives as well as with two different UV stabilisers namely Tinuvin 622 and Tinuvin 765 and their effect on the PC phase is discussed. An online UV-Vis spectrometer is used to monitor the effect of these stabilisers on the polymer phase.

The effect of two different screw speeds, 600 and 1200 rpm, on the UV-vis spectra of the film without any additives is shown in Figure 3. Throughout the article, the curves are plotted as difference spectra which is obtained by subtracting the spectrum of the blend without additives and extruded at 600 rpm, reference spectrum, from the spectra of the blend extruded with or without additives at different conditions. The film compounded at 1200 rpm exhibit spectra of different shape. The film has absorbance values below the reference curve for wavelengths roughly between 500 and 700 nm. This is attributed to the better dispersion of the ABS phase within the blend and therefore less scattering at higher screw speeds. In the near infrared region, >700 nm, as well as for wavelength shorter than 500 nm, the absorbance increases remarkably. The increasing absorbance in the short wave length region corresponds to a yellow coloring of the film, which could be seen visually. The increasing absorbance in the short wavelength as well as in the near infrared region is caused by degradation products. Thermal degradation of the polymers is favored by the high melt temperature caused by the high shear and elongational forces at 1200 rpm.²⁵ As the compounding at 1200 rpm causes severe degradation of the film,

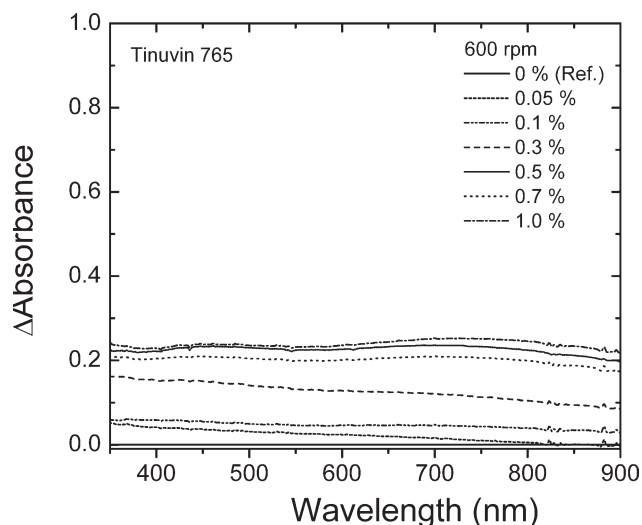


Figure 4 Variation of UV-vis spectra as a function of concentration of Tinuvin 765 at 600 rpm.

further compounding with additives is done only below this screw speed level.

The online UV-vis spectra for different concentrations of T765 are shown in Figures 4 and 5. In Figure 4 the screw speed of compounding was 600 rpm, whereas in Figure 5 three different screw speeds were used: 600, 800, and 1000 rpm at constant concentration of T765. At 600 rpm, Figure 4, an overall increase of absorbance is observed. This is attributed to the additional scattering due to the increased ABS content, since the additives are fed together with ABS powder. Visually, the samples are white and tough, no yellowing is observed. There is even no pronounced effect when compounding at 800 rpm, Figure 5. At 1000 rpm, there is decreased absorbance in the middle range of the spectrum. This is due to the better dispersion of the ABS phase within the

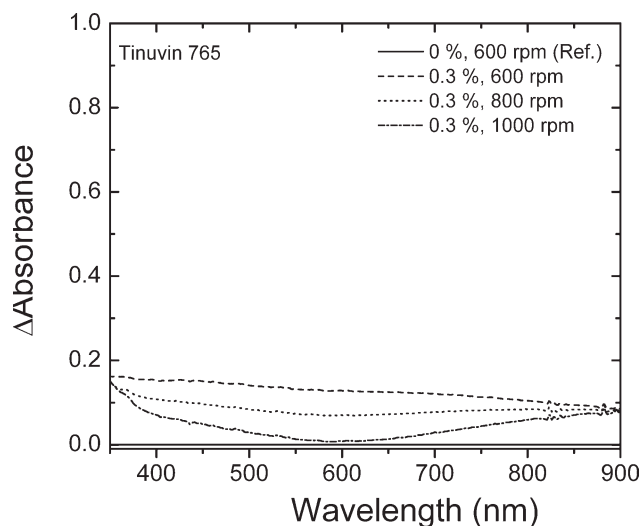


Figure 5 Variation of UV-vis spectra as a function of concentration of Tinuvin 765 at different screw speeds.

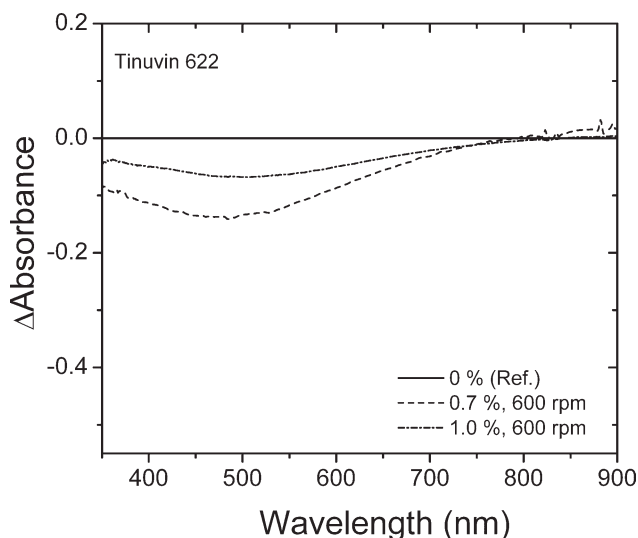


Figure 6 Variation of UV-vis spectra as a function of concentration of Tinuvin 622 at 600 rpm.

blend at higher screw speed which causes less scattering. Below 550 nm as well as above 650 nm the absorbance increases.

The effect of increasing concentration of Tinuvin 622 on the UV-vis spectra of the film when compounded at screw speeds of 600 and 900 rpm is shown in Figures 6 and 7, respectively. The curves have negative absorption below 750 nm however at near infrared region, >700 nm, the absorbance increases remarkably. At shorter wavelength also, <450 nm, the absorbance increases but still remains in the negative region. The low absorbance value in the wavelength region between 450 and 750 nm is attributed to the low scattering due to the better dispersion of ABS phase within the blend. The oligomeric additive acts also as a plasticiser in the polymer matrix which imparts better dispersion in the blend. It is also seen that the absorbance value in the mid wavelength region increases with increasing concentration of additive. This, in turn, is attributed to the additional scattering due to the increased ABS content, since the additives are fed together with ABS powder. Comparing Figures 6 and 7, 600 and 900 rpm, it is observed that the decrease in absorbance value in the mid wavelength region is more pronounced at higher screw speed, respectively. This is because of the less scattering due to the better dispersion of ABS phase within the blend at higher screw speed. It is also seen that at 600 rpm the absorbance in the near infrared region increases slightly but it remains close to the absorbance value of the reference spectrum, Figure 6. At 900 rpm a more pronouncing increase of the absorbance is found. It is assumed that at 600 rpm practically no degradation products are formed whereas at higher screw speed a small amount of degraded products

are formed. As the hydrolysis of PC phase produces low molecular weight products and these products are absorbed in the UV-vis spectroscopy in the lower or higher wavelength region. Therefore, the absolute value of UV-vis spectroscopy absorption in the lower or higher wavelength region is an indication of the amount of degraded products formed which in turn provides information regarding the hydrolysis of PC phase. As the absolute value of UV-vis absorption in the longer wavelength region is higher for higher screw speed, it gives sufficient information about the degradation occurred at 900 rpm. The elevated degradation at higher screw speed is because of the thermal degradation due to the increase in temperature based on the high shear force at higher screw speed.²⁶

Molecular weight determination

Molecular weight, M_w , of PC/ABS samples compounded with Tinuvin 765 and Tinuvin 622 at 600 rpm is measured at different concentration is depicted in Figure 8. It is seen that the molecular weight decrease is prominent for Tinuvin 765, whereas for Tinuvin 622 it is marginal. It is observed that for both stabilisers there is no decrease in molecular weight till a concentration of 0.5%. Afterwards there is a sharp decrease in molecular weight for Tinuvin 765 whereas for Tinuvin 622 it is negligible. The reduction of M_w finally corresponds to a value of 14% for the former whereas for the latter it is $<1.5\%$. With the trends for the molecular weight, the conclusions drawn from the online spectroscopy are very well supported. From the online spectroscopy measurements only trends and extend regarding the degradation of PC phase with Tinuvin 765

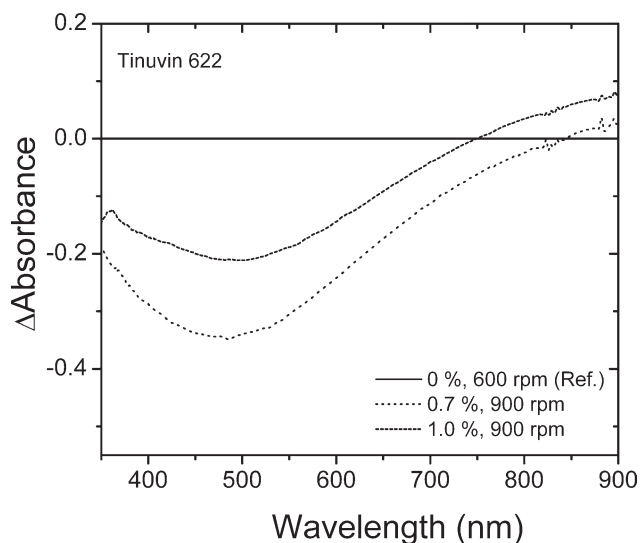


Figure 7 Variation of UV-vis spectra as a function of concentration of Tinuvin 622 at 900 rpm.

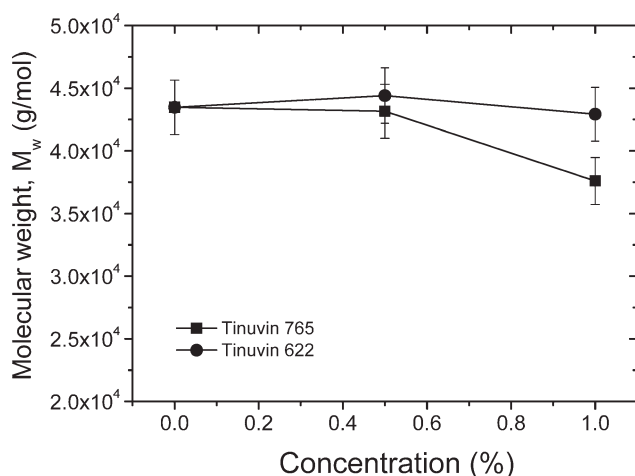


Figure 8 Molecular weight as a function of concentration of hindered amines.

and Tinuvin 622 can be obtained. To calculate the exact decrease in molecular weight with these stabilisers GPC have to be employed.

Effect of processing parameters

The effect of concentration of Tinuvin 622 on the viscosity of PC/ABS blend at different screw speeds is depicted in Figure 9. The viscosity decreases with increasing concentration of stabilizer and screw speed. The decrease in viscosity with increasing concentration of stabilizer is explained on the basis of the plasticisation effect of Tinuvin 622. The oligomeric part of the stabilizer acts as an internal lubricant and hence reduces the viscosity. These results very well correlates with the better dispersion observed with increased Tinuvin 622 content in the UV-vis spectra in the Figures 6 and 7. The increased degradation with screw speed is explained on the

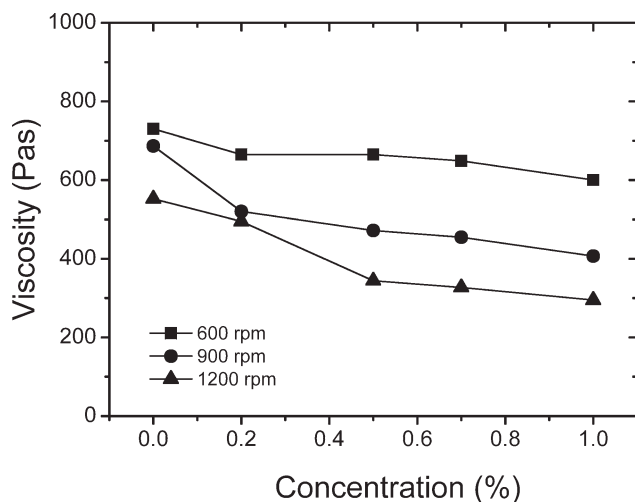


Figure 9 Viscosity of PC/ABS sample as a function of concentration of Tinuvin 622 at different screw speeds.

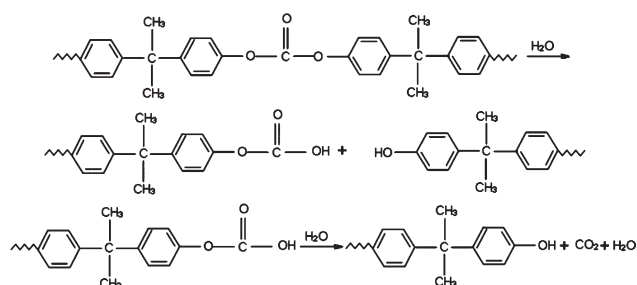


Figure 10 Mechanism of hydrolysis of polycarbonate with a weak base.

basis of additional heating of the melt due to shear and elongational deformation.²⁵ Lower viscosity is usually related with lower molar mass. The decrease in the viscosity with increased screw speed is an indication of the degradation occurred due to the explanation described earlier.

DISCUSSION

A comparative study on the degradative effect of monomeric and oligomeric UV stabilisers namely; Tinuvin 765 and Tinuvin 622 on the PC phase of the PC/ABS blend is measured by means of online UV-Vis spectroscopy and molecular weight determination.

It is known that hindered amines cannot be used in polymeric substrates which are sensitive to chemical reaction with the basic nitrogen atom in the hindered amine. A severe reduction in mechanical properties is reported when hindered amines are incorporated into PC/ABS blend during the compounding stage as the hydrolysis reaction in PC is accelerated by the presence of weak bases such as HALS at elevated temperature.¹⁷ There are remaining amounts of water in the PC even after drying before compounding and it is found to be 0.17% for all the compounding experiments performed in this research. The mechanism of hydrolysis of PC with a weak base to acid carbonate and its decarboxylation is described in Figure 10.^{26,27}

This process can be therefore described as a random chain scission with accumulation of phenolic chain ends. Generally, the degree of base-catalysed hydrolysis is markedly affected by the structure of the light stabilizer.

The UV-vis spectra and molecular weight determination studies show that the PC phase is less hydrolysed by Tinuvin 622, Figures 6–8—compared to Tinuvin 765, Figures 4, 5, and 8. As the hydrolysis of PC phase produces low molecular weight products and these products are absorbed in the UV-vis spectroscopy in the lower or higher wavelength region. Therefore, the absolute value of UV-vis spectroscopy absorption in the lower or higher wavelength region

is an indication of the amount of degraded products formed which in turn provides information regarding the hydrolysis of PC phase. From Figures 4–7 it is seen that the absolute value of UV-vis absorption at shorter, <450 nm, or higher wavelength, >700 nm, for Tinuvin 765 is higher than that of Tinuvin 622. The higher UV-vis absorption value for Tinuvin 765 is an indication of higher extent of hydrolysis and molecular weight reduction occurred during compounding. The lower reactivity of Tinuvin 622 with PC phase is explained on the basis of the basicity of the stabilisers. The basicity, expressed by the pKa value, of hindered amine compounds has a strong influence on the hydrolysis of the PC backbone. It is reported that the hydrolysis of PC is fast under basic conditions and increases with the basicity.^{16,28} Both Tinuvin 622 and Tinuvin 765 are tertiary amines but the basicity of both stabilisers is different. The basicity, pKa, of Tinuvin 765 and Tinuvin 622 is 9.0 and 6.5, respectively. As Tinuvin 765 has a higher basicity than Tinuvin 622 it is able to hydrolyse the PC backbone to a higher extent than Tinuvin 622.

CONCLUSIONS

The influence of the monomeric, Tinuvin 765, and oligomeric, Tinuvin 622, hindered amines on the hydrolysis of PC during the compounding of PC/ABS blend in a twin screw extruder at 240°C is studied using online UV-vis spectroscopy. This method turned out to be a powerful and nondestructive tool to get immediate information on degradation during the compounding experiments. It is observed in the spectra that the extent of degradation caused by Tinuvin 622 is less than that caused by Tinuvin 765. The molecular weight of the compounded samples determined by GPC very well agrees with the above observation. It was observed that the molecular weight of the PC decreases when Tinuvin 765 was used at a concentration level of 1% whereas no reduction in molecular weight is observed for Tinuvin 622 at the same concentration level. The lower basicity value of Tinuvin 622 favors less hydrolysis on the PC phase compared to Tinuvin 765 which has a higher basicity value. Another advantage observed for oligomeric HALS is the better dispersion of ABS phase into the blend. The polymeric additive acts as a plasticiser in the polymer matrix which imparts better dispersion in the blend. The

lower absorbance value in the mid wave length area and the reduced viscosity with the increased concentration Tinuvin 622 confirms the better dispersion.

This research forms part of the research program of the Dutch Polymer Institute (DPI), project #613. The authors thank Dr. Jan Torfs (Dow, Benelux) for his valuable discussion.

References

- Zweifel, H. *Stabilization of Polymeric Materials*; Springer-Verlag: Berlin Heidelberg, 1998.
- Wypych, G. *Handbook of Material Weathering*; 4th ed.; Chemtec Publishing: Toronto, 2008.
- Pickett, J. E. *Polym Prepr* 2007, 48, 621.
- Pickett, J. E. *Polym Prepr* 2001, 42, 424.
- Andrady, A. L.; Searle, N. D.; Crewdson, L. F. E. *Polym Degrad Stab* 1992, 35, 235.
- Hrdlovic, P. *Polym News* 2004, 29, 187.
- Pankasem, S.; Kuczynski, J.; Thomas, J. K. *Macromolecules* 1994, 27, 3773.
- Rivatton, A. *Polym Degrad Stab* 1995, 49, 163.
- Rivatton, A.; Sallet, D.; Lemaire, J. *Polym Photochem* 1983, 3, 463.
- Lemaire, J.; Gardette, J. L.; Rivatton, A.; Roger, A. *Polym Degrad Stab* 1986, 15, 1.
- Torikai, A.; Mitsuoka, T.; Fueki, K. *J Polym Sci Polym Chem* 1993, 31, 2785.
- Factor, A.; Chu, M. L. *Polym Degrad Stab* 1980, 2, 203.
- Factor, A.; Ligon, W. V.; May, R. *Macromolecules* 1987, 20, 2461.
- Diepens, M.; Gijssman, P. *Polym Degrad Stab* 2007, 92, 397.
- Lucarini, M.; Pedulli, G. F.; Lazzari, D.; Vitali, M.; Andrews, S. M. *Macromol Chem Phys* 2002, 203, 2239.
- Gaines, G. L., Jr. *Polym Degrad Stab* 1990, 27, 13.
- Denisov, E. T. *Polym Degrad Stab* 1991, 34, 325.
- Pryde, C. A.; Hellman, M. Y. *J Appl Polym Sci* 1980, 25, 2573.
- Kesters, E.; Vanderzande, D.; Lutsen, L.; Penxten, H.; Carleer, R. *Macromolecules* 2005, 38, 1141.
- Malinauskas, A.; Holze, R. *J Appl Polym Sci* 1999, 73, 287.
- Wang, Y.; Steinhoff, B.; Brinkmann, C.; Alig, I. *Polymer* 2008, 49, 1257.
- Coates, P. D.; Barnes, S. E.; Sibley, M. G.; Brown, E. C.; Edward, H. G. M.; Scowen, J. J. *Polymer* 2003, 44, 5937.
- Alig, I.; Fischer, D.; Lellinger, D.; Steinhoff, B. *Macromol Symp* 2005, 230, 51.
- Barnes, H. A.; Hutton, J. F.; Walters, K. *An Introduction to Rheology*; Elsevier Science: Amsterdam, The Netherlands, 1989.
- Rajan, V. V.; Wäber, R.; Wieser, J. *J Appl Polym Sci* 2010, 115, 2394.
- Schilling, F. C.; Ringo, W. M.; Sloane, N. J. A.; Bovey, F. A. *Macromolecules* 1981, 14, 532.
- Bair, H. E.; Falcone, D. R.; Hellman, M. Y.; Johnson, G. E.; Kelleher, P. G. *J Appl Polym Sci* 1981, 26, 1777.
- Schaller, C.; Rogez, D.; Braig, A. *J Coat Technol Res* 2009, 6, 81.