

ORIGINAL ARTICLE

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## Durability of isocyanate resin adhesives for wood V: changes of color and chemical structure in photodegradation

Received: August 7, 2007 / Accepted: January 16, 2008 / Published online: March 17, 2008

**Abstract** The effect of ultraviolet (UV) light irradiation on the color and chemical structure of water-cured polymeric diphenylmethane diisocyanate (PMDI) was investigated using a UV long-life fade meter. Control treatment was performed without UV light irradiation using a thermohygrostat for comparison. Two kinds of resin were used in this study: that to which only water had been added, and resin to which a small amount of polyol and water had been added. In addition, lauan (*Shorea* spp.) wood was used as a reference. The photodegradation of the resins over a period of up to 300 h was observed using a colorimeter and Fourier transform infrared (FT-IR) spectroscopy. When the resins were treated with UV light, the color difference ( $\Delta E^*ab$ ) of the resins increased significantly in a short time, and then reached a near-constant value. For lightness,  $L^*$  decreased rapidly for a few hours and then decreased gradually. The color darkened compared with that of the wood used. When treatment was performed without UV light irradiation,  $\Delta E^*ab$  and  $\Delta L^*$  of the resins showed negligible change. Based on the results of FT-IR analysis, severe degradation such as cleavage of the main chemical bond was hardly observed under UV light irradiation irrespective of the type of resin.

**Key words** Isocyanate adhesives · Durability · P-MDI · Photodegradation · Color

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Part of this report was presented at the 54th Annual Meeting of the Japan Wood Research Society, Sapporo, Japan, and at the 6th International Wood Science Symposium, Bali, Indonesia

### Introduction

Isocyanate resins consisting of polymeric diphenylmethane diisocyanate (PMDI) have come to be widely used as non-formaldehyde-based wood adhesives. Concomitantly, the durability and degradation of PMDI has become of interest. Generally, heat and moisture are thought to be the most serious degradation factors for wood adhesives. In our previous reports, the durability and degradation of emulsion-type PMDI have been investigated in regard to those degradation factors.<sup>1–5</sup> In an actual environment, however, various degradation factors including those factors would be at play. It is empirically known that the color of PMDI used on wood-based materials changes quickly under sunlight. It is possible that this color change has adverse effects, leading to degradation of the materials. Many studies regarding the photodegradation of polyurethanes consisting of PMDI have been reported.<sup>6–12</sup> However, studies of the photodegradation of water-cured PMDI assuming a unique curing system in wood adhesion have not been performed in detail. In this study, the photodegradation of water-cured PMDI when exposed to ultraviolet (UV) light for up to 300 h was investigated. The effect of UV light irradiation on the color change was examined using a colorimeter. The chemical structure of UV light-irradiated resin was observed using Fourier transform infrared (FT-IR) spectroscopy.

### Materials and methods

#### Materials

Emulsion-type PMDI (COSMONATE M-201W) and propylene oxide-based polyether polyol (Diol-400) were supplied by Mitsui Chemicals Polyurethanes (Chiba, Japan). The properties of PMDI are shown in Table 1. The properties of the polyol referred to here are the same as those described in previous reports.<sup>2,3</sup> To observe color change in

wood, 12 heartwood specimens of lauan (*Shorea* spp.) with a size of 50 (L) × 110 (T) × 4 (R) mm were prepared.

### Specimens

In this study, two types of cure system were adopted. As a standard, only water was added to PMDI at an isocyanate/hydroxyl (NCO/OH) ratio of 0.5. On the other hand, the polyol was added at an NCO/polyol-OH ratio of 25, and water was added to obtain a final NCO/OH ratio of 0.5. The systems contain in any event much water. This means that PMDI was mainly cured with water. The details of the formulations of the resins are shown in Table 2. Each resin was vigorously stirred for about 30 s using an agitator. The resin was applied to bakelite plates (60 × 110 × 1 mm), and the plates were placed between two flat glasses covered with polytetrafluoroethylene sheets. The thickness of each resin was adjusted to 1 mm by using a spacer made of a polytetrafluoroethylene. Twelve specimens of each resin were prepared and cured at 40°C for 24 h in an oven. The standard and the polyol-added resins are represented by the abbreviations ICW and ICWD4, respectively.

### UV light irradiation test

UV light irradiation test was performed using a UV long-life fade meter FAL-5 (Suga, Tokyo, Japan). This device has an irradiance of 366, 134, and 888 W/m<sup>2</sup> in the ultraviolet (300–400 nm), visible (400–700 nm), and infrared (700–3000 nm) light regions, respectively. In addition, the UV light has the strongest irradiance at 380 nm as produced by a carbon arc. During testing, the temperature of the black panel and the relative humidity (RH) were approximately 63°C and 20%–30%, respectively. Each six specimens of ICW, ICWD4, and wood were treated. After being placed under UV light for the scheduled duration, the specimens were removed and analyzed.

**Table 1.** Properties of polymeric diphenylmethane diisocyanate (PMDI)

Molecular weight	Viscosity <sup>a</sup> (Pa·s)	Specific gravity <sup>a</sup>	NCO (%)
500–1000	0.1–1.0	1.2–1.3	30–31

NCO, Isocyanate  
<sup>a</sup>At 25°C

**Table 2.** Preparation of resins

Resin	PMDI (g)	Polyol (g)	Water (g)	NCO/polyol-OH	Total NCO/OH
ICW	100	0	12.63	–	0.5
ICWD4	100	5.61	12.38	25	0.5

ICW, Water-cured PMDI; ICWD4, water-cured isocyanate resin containing polyol

### Test without UV light irradiation

The other six specimens were treated at the same temperature (63°C) and humidity (20%–30% RH) conditions by using a thermohygrostat PR-1G (Tabai, Osaka, Japan). After treatment for the scheduled duration, the specimens were removed and analyzed.

### Measurement of color

The treated specimens were vacuum-dried at 60°C for 15 h prior to measurement. To observe the color of resin visually, close-up photographs were taken intermittently using a digital camera (Nikon Cool Pix 995) under stable conditions. The shutter speed and F-number were 1/30 s and 8.2–10.3, respectively. The actual surface color of each specimen was evaluated using a colorimeter (Gardner color-guide 45/0, Toyo Seiki Seisaku-sho, Tokyo, Japan). The colorimeter sensor head was 20 mm in diameter, and the measurement was performed under a D65 light source and an observer angle of 10°. The CIELAB color parameters ( $L^*$ ,  $a^*$ ,  $b^*$ ) were used to express the color change. The differences in the lightness ( $\Delta L^*$ ) and color ( $\Delta E^*_{ab}$ ) were calculated using the following formulas:

$$\Delta L^* = Lt^* - Lr^*$$

$$\Delta E^*_{ab} = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2},$$

where  $Lt^*$  is the lightness of the treated resin,  $Lr^*$  is untreated resin as a reference, and  $\Delta a^*$  and  $\Delta b^*$  are the chroma differences based on the untreated resin. Five specimens were used for each treatment condition, and three locations in each specimen were measured.

### Fourier transform infrared spectroscopy

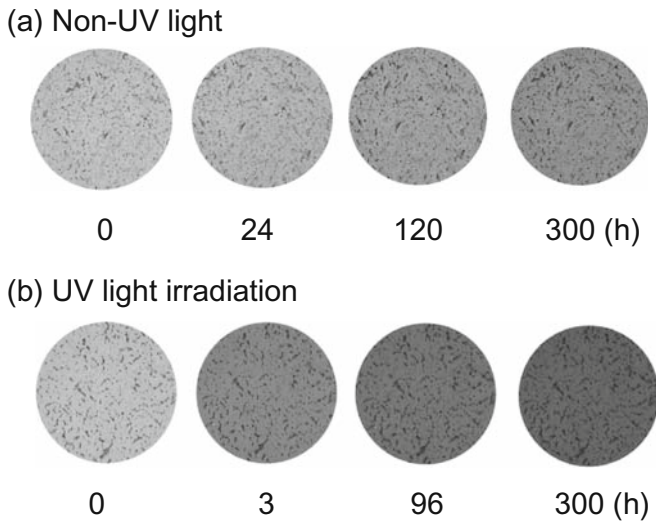
All infrared spectra of the treated resins were obtained using an FT-IR620 spectrometer (JASCO) employing the KBr pellet method, and were recorded by averaging 36 scans at a resolution of 4 cm<sup>-1</sup>.

## Results and discussion

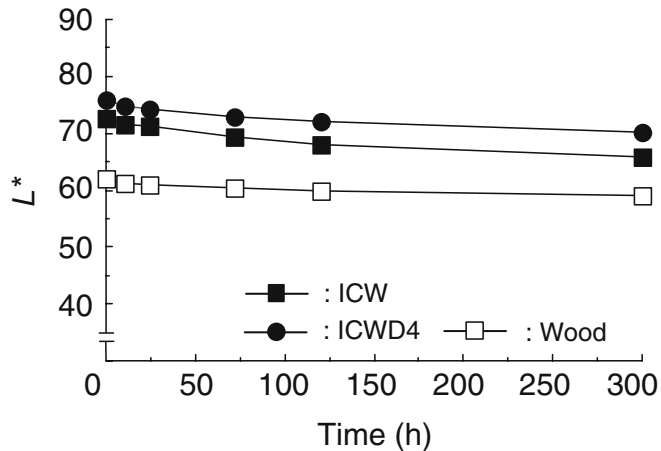
### Effect of UV light irradiation on color change

Figure 1 shows the intermittent photographs of ICW over 300 h. In the case of non-UV light irradiation (Fig. 1a), the color darkened slightly with treatment time. However, a marked change was not observed. When ICW was irradiated with UV light (Fig. 1b), the color darkened to a remarkable degree, with the color of the resin irradiated by UV light for 300 h turning dark brown. This indicated that the color of ICW was greatly affected by UV light irradiation.

To analyze the color change quantitatively, the surface color of each specimen was evaluated by using a colorimeter. Figure 2 shows the changes in  $L^*$  of each resin without UV light irradiation. The initial values of  $L^*$  for ICW,

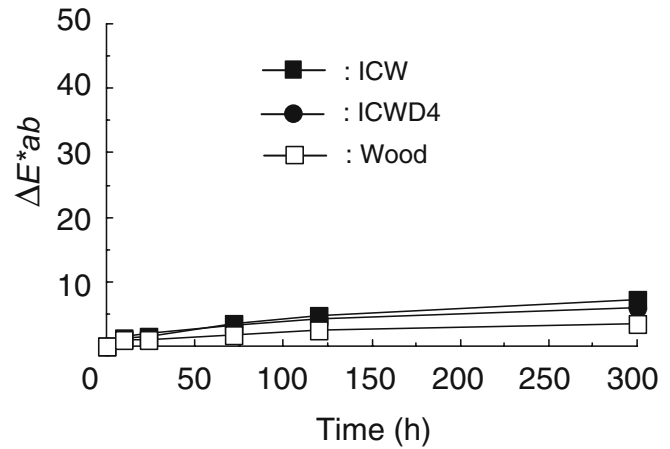


**Fig. 1a, b.** Effect of ultraviolet (UV) light on the color changes of water-cured isocyanate resin (ICW). **a** Control treatment, **b** treatment with UV irradiation

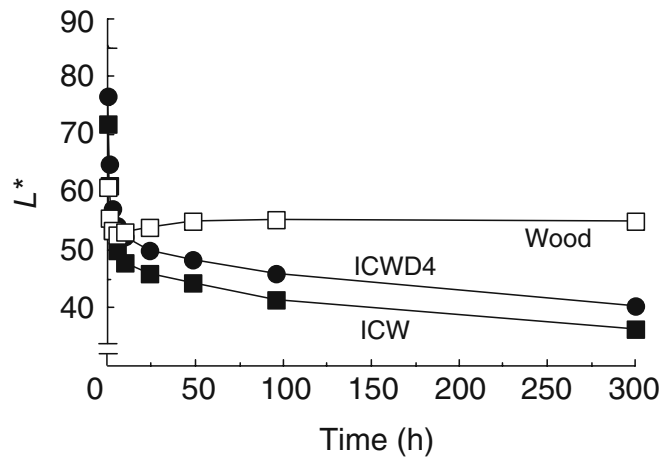


**Fig. 2.** Changes in lightness ( $L^*$ ) of samples without UV irradiation. ICWD4, Water-cured isocyanate resin with added polyol

ICWD4, and wood were 71.9, 76.6, and 60.9, respectively. Comparing ICW and ICWD4, the value of ICWD4 was a little higher than that of ICW. The difference between ICW and ICWD4 has to do with the presence or absence of the polyol. However, the effect of polyol on the  $L^*$  of PMDI needs further study. In any case, the lightness of the cured PMDI recorded a higher value than that of wood used. When the specimens were treated, each value decreased slightly with treatment time. The values of  $L^*$  for ICW, ICWD4, and wood at 300 h were 65.8, 70.2, and 60.0, respectively. Figure 3 shows the  $\Delta E^*_{ab}$  of each specimen without UV light irradiation. The value of wood increased slightly with time, and each value of ICW and ICWD4 also increased somewhat. The values of  $\Delta E^*_{ab}$  for ICW, ICWD4, and wood at 300 h were 7.15, 6.02, and 3.45, respectively. These results showed that the color of cured PMDI is much more likely to change than that of wood



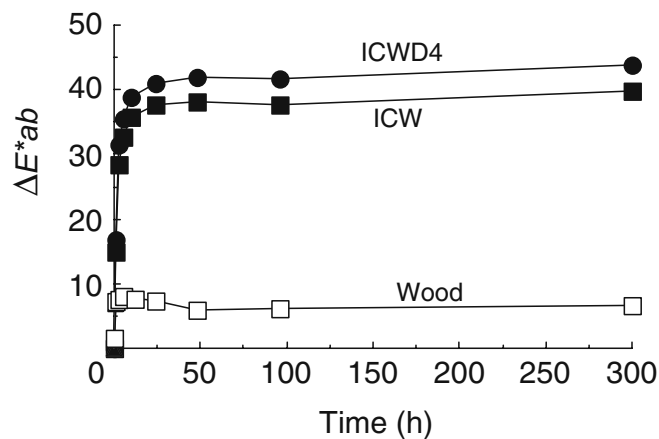
**Fig. 3.** Changes in color difference ( $\Delta E^*_{ab}$ ) of samples without UV irradiation



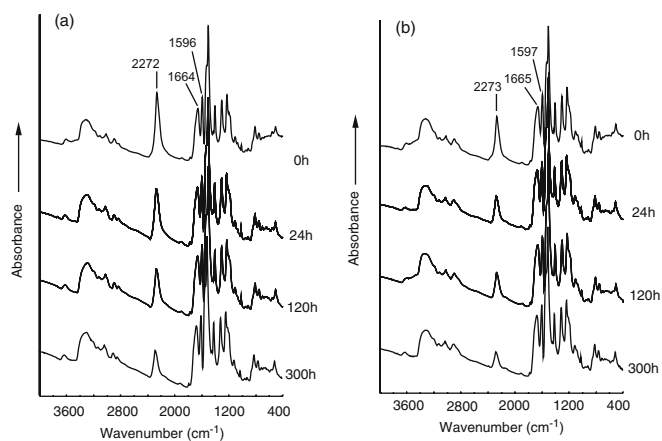
**Fig. 4.** Changes in lightness of samples irradiated with UV light

without UV light irradiation. However, large color change was scarcely observed.

Figure 4 shows the changes in  $L^*$  of the specimens that underwent UV light irradiation. The value of wood decreased rapidly in a short time and recovered slightly up to 50 h. The main cause of the initial change would be due to the degradation of extractives and lignin. Similar behavior was also reported by Nzokou and Kamdem.<sup>13</sup> After about 50 h, an almost constant value was recorded regardless of the treatment duration. In the case of cured PMDI, the values decreased drastically for a few hours, and then continued to decrease gradually with time. It was clear that the colors darkened compared with wood in a short time under UV light irradiation. Therefore, when PMDI is used in wood-based material, the color might come to stand out after a short time. As for ICW and ICWD4, each value decreased at a similar rate. Figure 5 shows the color difference of each specimen that underwent UV light irradiation. The  $\Delta E^*_{ab}$  of wood increased slightly over a short period, and soon reached a near-constant value. On the other hand, the  $\Delta E^*_{ab}$  of cured PMDI increased drastically over a short period, and then maintained a near-constant value about



**Fig. 5.** Changes in color difference of samples irradiated with UV light

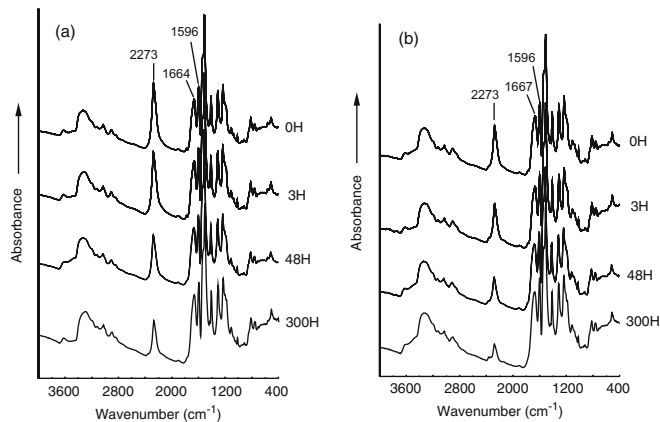


**Fig. 6a, b.** Fourier transform infrared (FT-IR) spectra of **a** ICW and **b** ICWD4 without UV irradiation

fourfold that of wood. It is well known that wood exposed to UV light is subject to surface degradation, which results in a large color change.<sup>14–17</sup> However, the present study demonstrated that the color change of cured PMDI was extremely large.

#### Effect of UV light irradiation on chemical structure

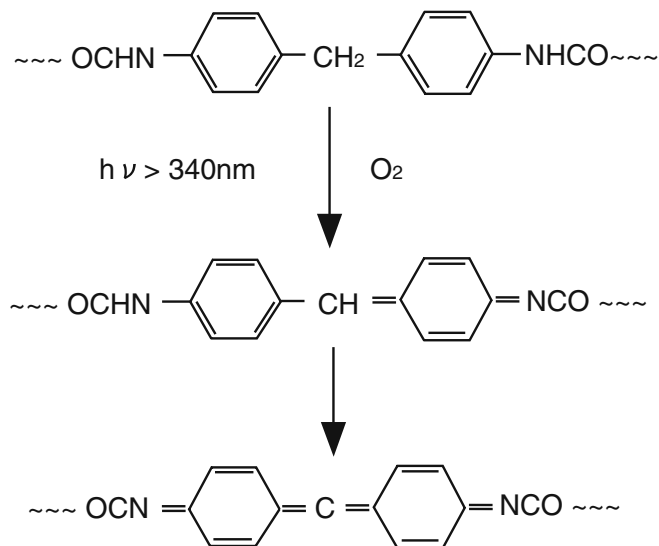
To observe the change of chemical structure of each resin, FT-IR measurements were performed. Figure 6 shows the infrared spectra of ICW (Fig. 6a) and ICWD4 (Fig. 6b) not having been exposed to UV light irradiation. In water-cured PMDI, the peaks of primary interest are 3200–3500  $\text{cm}^{-1}$  for the N–H stretching region, 2270–2280  $\text{cm}^{-1}$  for the isocyanate (NCO) group, and 1600–1800  $\text{cm}^{-1}$  for the C=O stretching region.<sup>1–3</sup> For ICW (Fig. 6a), the infrared spectrum of the untreated resin (0 h) recorded a strong peak at about 2272  $\text{cm}^{-1}$ , showing that the resin contains a considerable amount of unreacted isocyanate groups. In addition, absorption peaks were clearly identified at about 3300  $\text{cm}^{-1}$ , which was attributed to hydrogen-bonded N–H groups, and



**Fig. 7a, b.** FT-IR spectra of **a** ICW and **b** ICWD4 irradiated with UV light

1664  $\text{cm}^{-1}$ , which was attributed to disordered urea carbonyl groups.<sup>1</sup> The isocyanate absorption peak decreased gradually with treatment time. This indicated that unreacted isocyanate groups reacted with atmospheric moisture. Marked changes in other peaks were scarcely observed, regardless of treatment time. For ICWD4 (Fig. 6b), similar absorption peaks were identified in untreated resin. The peak height for unreacted isocyanate groups in untreated ICWD4 (0 h) was lower than that for untreated ICW (Fig. 6a). This indicated that the reactivity of the isocyanate group was enhanced by the addition of polyol.<sup>3</sup> When the treatment was performed, the isocyanate peak lowered gradually. However, other peaks hardly changed as in the case of ICW.

Figure 7 shows the infrared spectra of ICW (Fig. 7a) and ICWD4 (Fig. 7b) having undergone UV light irradiation. For ICW, the absorption peak at about 2273  $\text{cm}^{-1}$  decreased gradually with treatment time. However, marked changes in other peaks and the appearance of new peaks were scarcely observed. A similar trend was also observed in ICWD4. It is generally known that the coloring phenomenon of polyurethanes based on 4,4'-diphenylmethane diisocyanate (MDI) takes place through two main mechanisms.<sup>6,7,18</sup> Mechanism I is the reaction producing quinone-imide structures by photo-oxidation of the central methylene group. In this case, quinone-imide structure acts as a chromophore, leading to the change of its color. Mechanism II is the photo-Fries type reaction that leads to the formation of the aromatic amine. Photo-oxidation is predominant at wavelengths of 340 nm or higher, whereas the photo-Fries type reaction is predominant at wavelengths of 340 nm or less. In this study, water-cured PMDI would suffer mainly photo-oxidation as shown in Fig. 8, because the UV light has the strongest irradiance at 380 nm. As for the identification of quinone-imide structure using FT-IR, absorption bands at 1595 and 1650  $\text{cm}^{-1}$  are attributed to the quinone methide in polyurethane coatings.<sup>18</sup> Athawale et al.<sup>19</sup> observed that a peak at about 1600  $\text{cm}^{-1}$  has a major contribution from the quinoid rings in polyaniline film. Hari<sup>20</sup> reported that the absorption band at 1600  $\text{cm}^{-1}$  is attributed to the C=N vibration and the quinoid phenyl ring in aniline. Angela and



**Fig. 8.** Formation of quinone imide in water-cured polymeric diphenylmethane diisocyanate

Lothar<sup>21</sup> also identified the quinoid ring vibration at  $1590\text{ cm}^{-1}$  and the  $\text{N}=\text{C}$  vibration at  $1635\text{ cm}^{-1}$  in the polymerization of aniline. Based on the results of FT-IR spectra as shown in Fig. 7, the formation of the quinone structure was not detected. This is because the peaks derived from the quinone structure overlapped with existing peaks. Actually, the absorption peak at about  $1596\text{ cm}^{-1}$  in both resins was scarcely shifted regardless of treatment time. The photo-oxidation is not accompanied by a scission of molecules. In addition, cleavage of the main chemical bond such as urea linkages was hardly observed in the results of FT-IR spectra. Therefore, serious degradation causing a severe decrease of performance would not take place during the UV light irradiation for 300 h. The physical and mechanical properties of UV-light-irradiated PMDI will be reported in a future article.

## Conclusions

Changes in the color and chemical structure of water-cured PMDI were investigated under UV light irradiation. In cases where the resin was exposed to UV light,  $\Delta E^*ab$  increased markedly over a short period.  $L^*$  decreased rapidly in a few hours and then decreased gradually. A similar color change was observed in two types of resin. The color of the resins became very dark compared with that of the wood used. On the other hand,  $\Delta E^*ab$  and  $L^*$  decreased only slightly with treatment time for samples not having undergone UV light irradiation. The FT-IR spectra of UV-light-irradiated resins were similar to those that were not exposed to UV light. Therefore, serious degradation would not occur during UV light irradiation for 300 h.

When water-cured PMDI is exposed to UV light, it is important to pay attention to the drastic color change that occurs in a short period.

## References

1. Umemura K, Takahashi A, Kawai S (1998) Durability of isocyanate resin adhesives for wood I: thermal properties of isocyanate resin cured with water. *J Wood Sci* 44:204–210
2. Umemura K, Takahashi A, Kawai S (1999) Durability of isocyanate resin adhesives for wood II: effect of the addition of several polyols on the thermal properties. *J Appl Polym Sci* 74:1807–1814
3. Umemura K, Kawai S (2002) Effect of polyol on thermo-oxidative degradation of isocyanate resin for wood adhesives. *J Wood Sci* 48:25–31
4. Umemura K, Kawai S (2002) Durability of isocyanate resin adhesives for wood III: degradation under constant dry heating. *J Wood Sci* 48:380–386
5. Umemura K, Takahashi A, Kawai S (2002) Durability of isocyanate resin adhesives for wood IV: degradation under constant steam heating. *J Wood Sci* 48:387–393
6. Thapliyal BP, Chandra R (1991) Photostability of polyetherurethaneureas. *Polym Int* 24:7–13
7. Hoyle CE, Shah H, Moussa K (1996) Photolysis of methylene 4,4'-diphenyldiisocyanate-based polyurethane ureas and polyureas. *Polym Durability* 249:91–111
8. Shah H, Hoyle CE (1993) Photodegradation of MDI based polyurethane/urea elastomers. *Polym Mater Sci Eng* 68:74–75
9. Bajsic EG, Rek V, Sendjarevic A, Sendjarevic V, Frish KC (1996) The effect of different molecular weight of soft segments in polyurethanes on photooxidative stability. *Polym Degrad Stab* 52:223–233
10. Wilhelm C, Rivaton A, Gardette JL (1998) Infrared analysis of the photochemical behavior of segmented polyurethanes. *Polymer* 39:1223–1232
11. Furukawa M, Wakiyama K (1999) Deterioration of novel polyesterurethane elastomers in outdoor exposure. *Polym Degrad Stab* 65:15–24
12. Wilhelm C, Gardette J-L (1997) Infrared analysis of the photochemical behavior of segmented polyurethanes: 1 aliphatic poly(ester-urethane). *Polymer* 38:4019–4031
13. Nzokou P, Kamdem DP (2006) Influence of wood extractives on the photo-discoloration of wood surfaces exposed to artificial weathering. *Color Res Appl* 31:425–434
14. Hon DN-S, Clemson SC, Feist WC (1986) Weathering characteristics of hardwood surfaces. *Wood Sci Technol* 20:169–183
15. Pastore TCM, Santos KO, Rubim JC (2004) A spectrophotometric study on the effect of ultraviolet irradiation of four tropical hardwoods. *Bioresource Technol* 93:37–42
16. Minemura N, Umehara K (1979) Color conditioning of wood I (in Japanese). *Rep Hokkaido Forest Prod Res Inst* 68:92–145
17. Tolvaj L, Mitsui K (2005) Light source dependence of the photo-degradation of wood. *J Wood Sci* 51:468–473
18. Singh RP, Tomer NS, Bhadraiah SV (2001) Photo-oxidation studies on polyurethane coating: effect of additives on yellowing of polyurethane. *Polym Degrad Stab* 73:443–446
19. Athawale AA, Deore BA, Kulkarni MV (1999) Spectroscopic and electrochemical properties of poly(2,5-dimethyl aniline) films. *Mater Chem Phys* 60:262–267
20. Hari SN (1991) Structural determination of a semiconductive tetramer of aniline by IR, UV-visible, ESR, XPS and mass spectroscopy techniques. *J Mater Sci* 26:1683–1690
21. Angela Z, Lothar D (1997) Investigation of the electropolymerization of aniline by the in situ techniques of attenuated total reflection (ATR) and external reflection (IRRAS). *J Mol Struct* 410–411:165–171