

Properties of UV-Curable Coatings for Wood Floorings as a Function of UV Dose

Byoung-Hoo Lee, Jae-Hoon Choi, Hyun-Joong Kim[†], Jong-In Kim*, and Jong-Young Park*

Laboratory of Adhesion & Bio-Composites, Department of Forest Products, Seoul National University, Seoul 151-921, Korea

*Department of Forest Products, Korea Forest Research Institute, Seoul 130-712, Korea

Received September 28, 2002; Accepted February 26, 2004

Abstract: We have investigated the viscoelastic properties and strengths of cured films of UV-curable urethane acrylate coatings as a function of the UV dose. In this study, the value of T_g increased with increasing UV dose, but the logarithmic damping ratio, which is related to the hardness, decreased accordingly. The tensile strengths increased with increasing UV dose. For the aliphatic and aromatic urethane triacrylate coatings, there was no significant improvement in the tensile strength over 0.44 J/cm^2 . For the mixture of aliphatic and aromatic coatings (50:50 wt%), the tensile strength increased with increasing UV dose up to 0.74 J/cm^2 .

Keywords: UV-curable coating, viscoelasticity, logarithmic damping ratio, urethane coating, wood flooring

Introduction

A broad definition of ultraviolet (UV)-curable coatings would be coatings that are cured into a solid when exposed to high-intensity UV radiation. A more technical and chemical definition would be coatings that are cured by free radical-initiated chain-growth polymerization in unsaturated monomers and oligomers [1].

UV-Curable and waterborne coatings have been replacing solvent-based coatings because of their lower toxicity and environmental advantages. UV-Curable coatings are used widely in many industrial applications, e.g., for wood floorings and furniture, in automotive parts, and in printing inks and adhesives [2]. An important ecological advantage is that only the reactive products are used, which means that there is no solvent recovery problem and much less pollution. Energy consumption is also low. Curing is performed at room temperature, which means that heat-sensitive substrates can be used. Conceivably, the most important advantage is the economic aspect. Curing occurs at a high speed, manipulation and installation are easy, and only minimal amounts of floor space and manpower are required. A further advantage is that the finished product is of high quality [3].

In the wood industry, the long-term value of wooden floorings depends to a high degree on its surface characteristics. Untreated or uncoated surfaces lose their aesthetic appearance quickly and rapidly deteriorate under constant use.

The application of clear coatings is the easiest and most common method for protecting wood flooring materials against environmental factors, such as moisture, ultraviolet light, and mechanical and chemical degradation, in addition to enhancing their distinctive appearances. Indeed, the properties of clear coatings are quite critical and definitely affect the materials' performance and service life [4-8].

In addition, continuous variations of atmospheric humidity lead to changes in the volume of the wood flooring. Therefore, the coating on the wood flooring must have excellent cured-film flexibility as well as hardness and resistance to abrasion and fluids (e.g., alcohol) when it is cured [3].

In a curing system that uses UV radiation, the UV dose is related to the basic properties (e.g., flexibility, hardness) of the cured films as well as the surface viscoelasticity. Efficient curing means that, for all applications, conditions should be created where a minimal UV dose (measured in J/cm^2 on the substrate surface) or a minimum UV exposure time can be applied to obtain the desired degree of curing [9].

[†] To whom all correspondence should be addressed.
(e-mail: hjokim@snu.ac.kr)

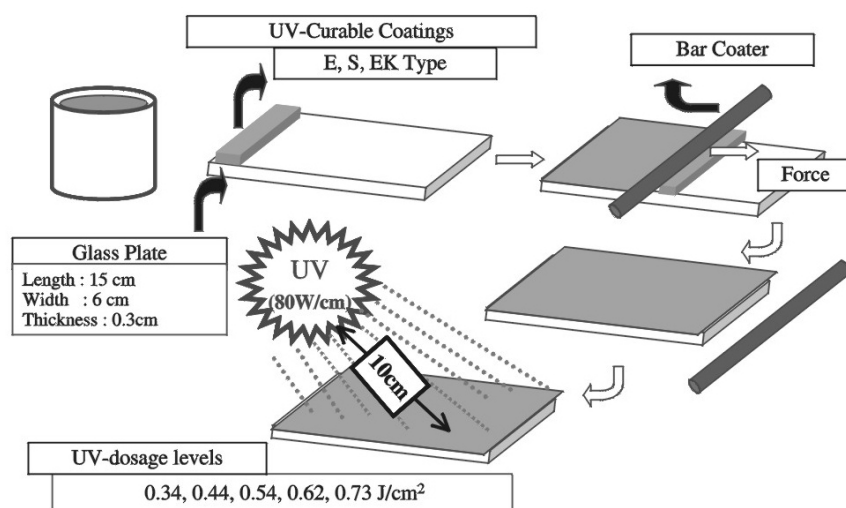


Figure 1. Curing process.

The most commonly used UV-curable formulations contain unsaturated acrylates. The main types of acrylic oligomers are epoxy acrylates, polyester acrylates, polyether acrylates, urethane acrylates, and silicone acrylates. A previous study reported that urethane acrylates are formed by reacting isocyanates with hydroxy-functionalized acrylate monomers. The incorporation of polyols, polyester polyols, or polyether polyols into the urethane acrylates leads to a variety of modified structures. Flexible films are obtained when long-chain glycols are used to modify the urethane moiety. Hard films can be produced when highly branched multifunctional polyols are employed. As a class of compounds produced by versatile chemistry, urethane acrylates offer a wide choice of excellent application properties. Flexibility, abrasion resistance, toughness, good adhesion to difficult substrates, chemical resistance and excellent weathering resistance are film properties that can be obtained by a suitable selection of aromatic or aliphatic urethane acrylates [9].

The viscoelastic properties of the bulk of a polymer material, such as coatings, plastics, and adhesives, are measured by using a dynamic mechanical thermal analyzer (DMTA) and an advanced rheometric expansion system (ARES) [10-12]. However, it is difficult to measure the viscoelastic properties of a cured film on the substrate because the cured film adheres to the substrate, and the viscoelastic behavior is restricted as a result of the substrate [13].

In this study, urethanes containing one polymerizable group, such as acrylate, were selected as the UV-curable oligomers. These compounds are used as UV-curable coatings for wood floorings. UV-Curable urethane acrylate coatings not only protect the flooring materials but they also preserve the aesthetic appearance of the flooring. Until now, little attention has been paid to the viscoelastic properties of cured films. In addition, the viscoelastic

properties of the cured film on a glass plate were obtained using a rigid-body pendulum tester that uses a cylinder-type pendulum to simulate the performance of the cured film on the wood flooring.

The aim of this study was to investigate the viscoelastic and mechanical properties of UV-curable urethane acrylate coatings as a function of the UV dose.

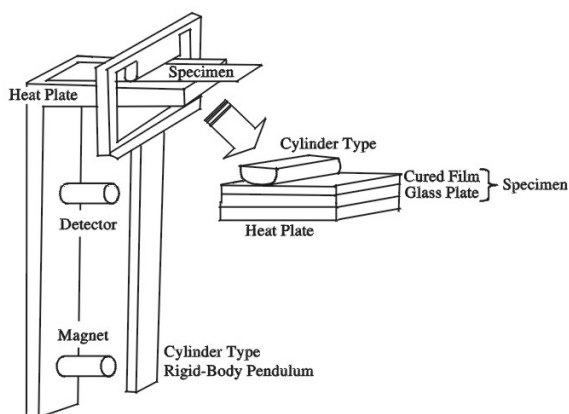
Experimental

Materials and Curing Process

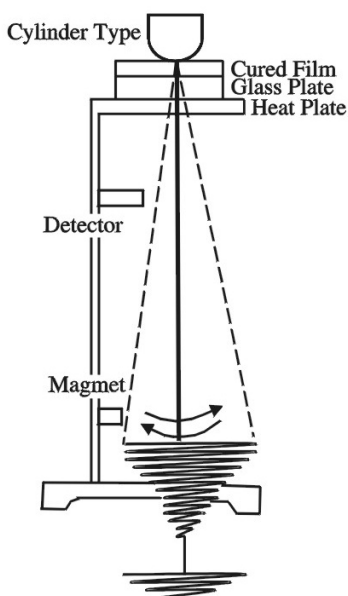
The three UV-curable top coatings used in this study were all based on a urethane acrylate system. This UV-curable urethane acrylate system consisted of three main components: firstly, isophoron-di-isocyanate (IPDI)-based aliphatic urethane triacrylate ($M_w = 1500$) oligomer or toluenedi-isocyanate (TDI)-based aromatic urethane triacrylate ($M_w = 2000$) oligomer; secondly, reactive diluent monomers; thirdly, a photo-initiator and other additives used to obtain the UV-curable coatings. The reactive diluent monomers were 2-hydroxypropyl acrylate (HPA), 1,6-hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA), trimethylol propane triacrylate (TMPTA), dipentaerythritol hexaacrylate (DPHA), and propoxylated glycerol triacrylate (PGTA). The photo-initiator was 2-hydroxy-2-methylprophenone. The non-volatile content and specific gravity of the UV-curable coatings were 95 wt% and 1.1, respectively. The viscosity was 75 KU, as measured by a Krieb- Stormer Viscosimeter.

The aliphatic urethane triacrylate coating is referred to herein as "S". The aromatic urethane triacrylate coating is referred to herein as "EK". The mixture of S and EK (50:50 wt.%) is referred to herein as "E".

Figure 1 depicts the curing process. Each UV-curable coating was coated onto glass plates using a bar coater



I. Rigid-body pendulum System



II. Oscillation of pendulum

Figure 2. The rigid-body pendulum system.

(No. 22). The sizes of the glass plates used for measuring the mechanical properties and the viscoelastic properties were $15 \times 6 \times 0.3$ cm and $7.6 \times 2.4 \times 0.1$ cm, respectively.

The UV dose levels used were 0.34, 0.44, 0.54, 0.62, and 0.73 (J/cm^2). The approximate cured-film thickness was 40 ± 2 μm . The UV-cured film was carefully peeled from the glass plate and then cut into a rectangular shape (5 cm \times 0.5 cm \times 40 μm) to measure its mechanical properties.

Viscoelastic Property

The viscoelastic property of the cured film was measured using a Rigid-Body Pendulum-Type Physical Pro-

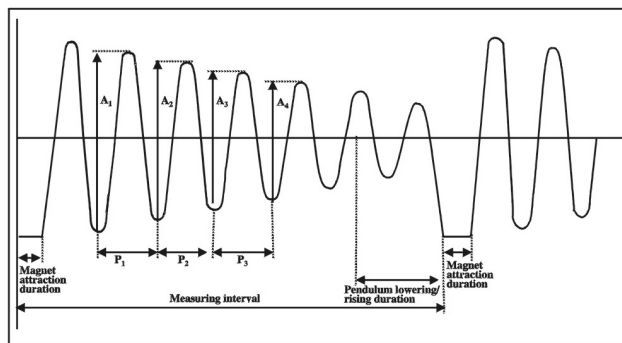


Figure 3. Oscillation of the pendulum for a rigid-body pendulum system [13].

erties Testing Instrument (A & D Co., Ltd., Japan). This instrument can be used to evaluate the physical properties of organic polymer materials and coatings under operation temperatures in the range from $-100 \sim 400^\circ C$ [13]. As shown in Figures 2 I and II, the glass plate, covered with the cured film, was fixed to a hot plate (or a cooling/heating block) to test the viscoelastic properties. The cylinder edge, the fulcrum of the swing of the pendulum, was set vertically on the cured film surface. A free vibration was applied subsequently to the pendulum. By analyzing this vibration, the viscoelasticity, e.g., measured as the logarithmic damping ratio (Δ), can be evaluated [14,15].

In this study, the logarithmic damping ratio at various temperatures was obtained by heating the heat plate from 30 to $150^\circ C$ at a heating rate of $10^\circ C/min$.

The oscillation pattern of the pendulum is shown in Figure 3. The logarithmic damping ratio (Δ) was obtained using the formula.

$$\Delta = [\ln(A_1/A_2) + \ln(A_2/A_3) + \ln(A_3/A_4) + \dots + \ln(A_n/A_{n+1})] / n \quad (1)$$

where A is the amplitude of oscillation, as shown in Figure 3.

The logarithmic damping ratio is related to the degree of chemical networking (crosslinking), physical networking (entanglement), and physico-chemical networking (absorption) of segments in the polymer structure, and to the interface between the cured film and the substrate [13].

Because the softness of the cured film surface increases upon increasing the heat plate temperature, the amplitude (A) of oscillation of the pendulum touching the surface decreases. This effect corresponds to the structural change that occurs during the transition process from the hard to the soft state of the cured film. The term T_g is defined by the temperature of the maximum logarithmic damping ratio, as shown in Figure 4. At any temperature, the lower the value of the logarithmic damping ratio, the higher the cured film hardness [13].

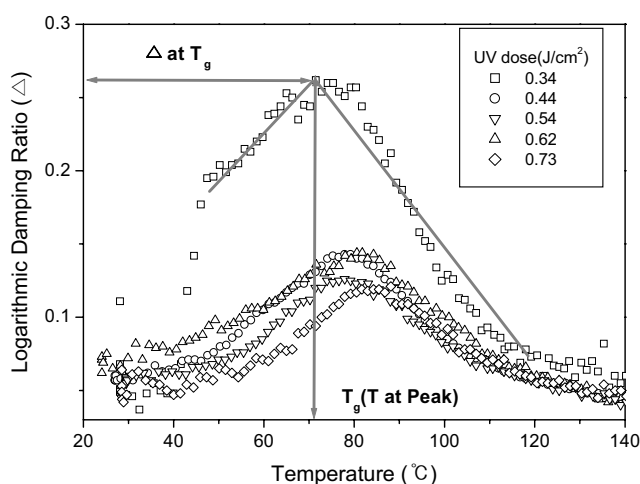


Figure 4. Surface-viscoelastic properties of a cured film of UV-curable coatings as function of the UV dose (S type).

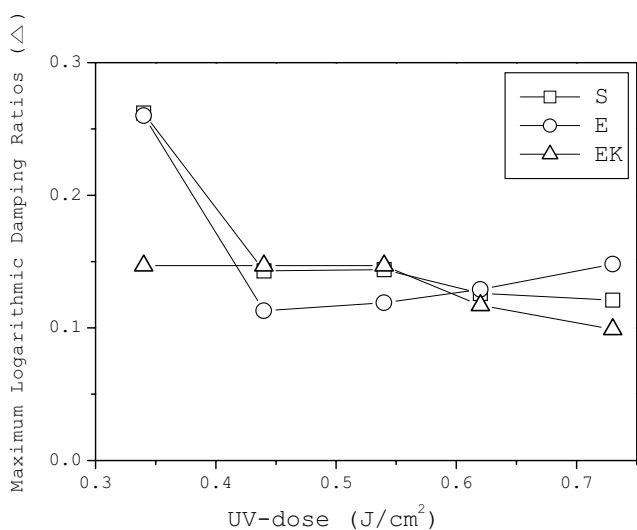


Figure 5. Surface glass transition temperature of a cured film as a function of the UV dose.

Mechanical Properties

The tensile strength and elastic modulus were measured using a Universal Testing Machine (Zwick Co., NICEM at Seoul National University). The film size was $5 \text{ cm} \times 0.5 \text{ cm} \times 40 \mu\text{m}$. The distance between grids was 4 cm. The crosshead speed during tensile testing was 2 mm/min.

Results and Discussion

Surface and Mechanical Property

The viscoelastic properties of the cured film as a function of UV dose are shown in Figures 5 and 6.

Viscoelastic cured films exhibit a combination of elastic and viscous behavior simultaneously. While all substances are viscoelastic to some degree, this behavior is especially

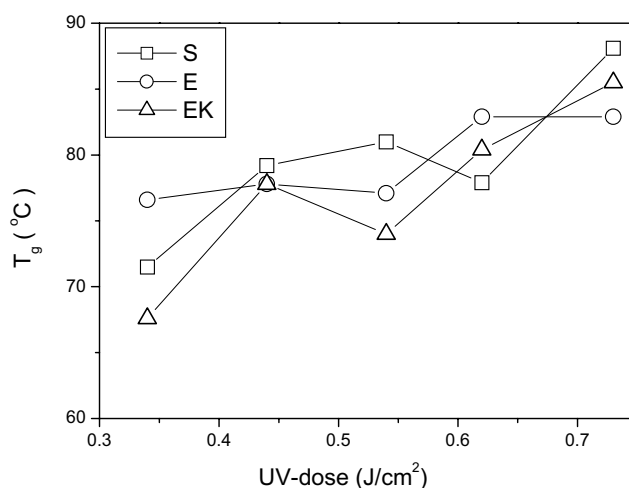


Figure 6. Logarithmic damping ratio of a cured film as a function of the UV dose.

prominent in polymers. Generally, viscoelasticity refers to both the time and temperature dependence of the mechanical behavior [16].

As shown in Figures 5 and 6, the values of T_g and the logarithmic damping ratios, related to viscoelasticity, are $67.6 \sim 88.1^\circ\text{C}$ and $0.099 \sim 0.262$, respectively.

The basis for the T_g is the onset of coordinated molecular motion in the cured film. In general, the cross-link density of a cured film increases with increasing UV dose. The coordinated molecular chain motion of amorphous portions of the cured film decreases as a result of increasing the degree of cross-linking [16]. For cured films, the T_g constitutes their most important mechanical property. As shown in Figure 5, the value of T_g increases with increasing UV dose.

In previous studies [17,18], it was found that the structural shape and geometry of a polymer are generally reflected by the value of T_g . The T_g of an amorphous polymer is an excellent probe of its chain stiffness, which is related to its hardness [17]. It is well known that the hardness decreases upon increasing T_g [19]. In addition, Ali and coworkers, Bashar and coworkers, and Shiryayeva and coworkers [20-22] have all reported the relationship between the UV dose and the hardness of a UV-cured film; they have clearly demonstrated that the hardness increases with increasing UV dose.

The logarithmic damping ratio between the cylinder edge of the pendulum and the surface of the cured film is complex, and it depends on the viscoelastic properties.

As shown in Figures 1, 5, and 6, the logarithmic damping ratio, which is related to the hardness, decreased upon increasing the UV dose, but the hardness increased accordingly.

Previous studies [20,23] have explained that the pendulum hardness, which is a physical property of the cured film, is expected to show some correlation with the

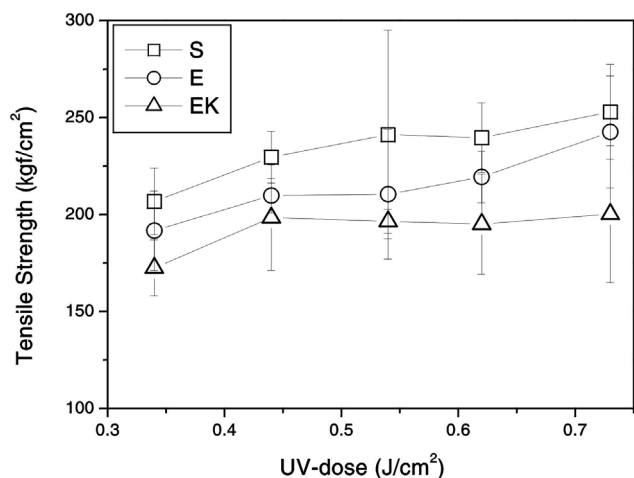


Figure 7. Tensile strength of a cured film as a function of the UV dose.

values of T_g . In addition, the pendulum hardness increases with an increasing value of T_g while the flexibility decreases. Bashar and coworkers and Wurtz and coworkers attributed the increased hardness to the increased cross-link density of the cured film [21,23]. Depending on the region of viscoelastic behavior, the mechanical properties of polymers differ greatly.

The tensile strength of UV-cured film as a function of UV dose are shown in Figure 7. The figure shows that the tensile strength increased with increasing UV dose.

Christmas and coworkers [24] reported the relationship between the UV dose and the tensile strength of cured film at various levels of peak irradiation. They showed, as expected, an increase in the tensile strength as the UV dose increased. In addition, the increased strength is related to increased values of T_g .

The criterion of a second-order transition temperature is that the temperature-dependent conformational entropy, S_c , becomes zero. If S_0 is the conformational entropy for a non-crosslinked system, then S_R is the change in conformational entropy due to adding cross-links [16, 25],

$$S_c = S_0 + \Delta S_R = 0 \quad (2)$$

Because cross-linking decreases the conformational entropy, qualitatively it may be concluded that the transition temperature is raised. The final relation may be written

$$[(T(x') - T(0)) / T(0)] = [(KMx' / \gamma) / (1 - (KMx' / \gamma))] \quad (3)$$

where x' is the number of cross-links per gram, M is the mer molecular weight, and γ is the number of flexible bonds per mer, backbone, and side chain. The quantity K is found by experiment and, interestingly enough, it appears to be independent of the polymer.

An alternate relation dates back to the work of Ueberreiter and Kanig [16,26]:

$$\Delta T_{g,c} = Zx' \quad (4)$$

where the change in the glass transition temperature upon with increasing cross-linking, $\Delta T_{g,c}$, is equal to the product of the cross-link density, x' , and a constant, Z . The strength is related to cross-linking.

Liaw and coworkers reported that the tensile strength of films increases upon increasing both T_g and the UV dose [21,27]. The tensile strength values ranged from 252.90 to 172.47 kgf/cm². In the S and EK cases, there was no significant improvement in tensile strength over 0.44 J/cm², but, in the E case, the tensile strength increased upon increasing the UV dose up to 0.74 J/cm².

Conclusions

This study was performed to assess the viscoelastic properties and strengths of cured films as a function of the UV dose.

The results obtained are summarized as follows:

- 1) The surface T_g increased upon increasing the UV dose, but the logarithmic damping ratio, which is related to the surface hardness, decreased accordingly.
- 2) The tensile strength increased upon increasing the UV dose.
- 3) In the S and EK cases, there was no significant improvement in the tensile strength over 0.44 J/cm².
- 4) In the E case, the tensile strength increased upon increasing the UV dose up to 0.74 J/cm².

Acknowledgment

B.-H. Lee and J.-H. Choi are grateful for graduate fellowships provided by the Ministry of Education through the Brain Korea 21 Project.

References

1. W. Fibiger, in *Coating Technology, III. Industrial Coatings*, 3rd Edn., W. Fibiger and A. C. Boyce Eds., pp.VII-1, ITE Consultants, Canada (1998).
2. M. Hirose, J. Zhou, and F. Kadowaki, *Colloids Surf., A*, **153**, 481 (1999).
3. M. Philips, in *Paints, Coatings and Solvents*, 2nd Edn., D. Stoye and W. Freitag, Eds., pp. 135-262, Wiley-VCH, Weinheim (1999).
4. S. J. Kim, H. S. Park, K. C. Lee, S. K. Kim, and E. K. Park, *J. Ind. Eng. Chem.*, **3**, 63 (1997).

5. H. S. Park, J. P. Wu, and H. K. Kim, *J. Ind. Eng. Chem.*, **3**, 282 (1997).
6. H. S. Park, E. K. Park, S. K. Kim, and P. W. Shin, *J. Ind. Eng. Chem.*, **5**, 59 (1999).
7. F. Masson, C. Decker, T. Jaworek, and R. Schwalm, *Prog. Org. Coat.*, **39**, 115 (2000).
8. S. T. Chang and P. L. Chou, *Polym. Degrad. Stab.*, **69**, 355 (2000).
9. R. Mehnert, A. Pincus, I. Janorsky, R. Stowe, and A. Berejka, *UV & EB Curing Technology & Equipment*, pp. 1-159, Wiley & Sons, Chichester (1998).
10. T. Kajiyama, K. Tanaka, and A. Takahara, *Macromolecules*, **30**, 280 (1997).
11. C. S. Powell and D. S. Kalika, *Polymer*, **41**, 4651 (2000).
12. T. D. Fornes, P. J. Yoon, H. Keskkula, and D. R. Paul, *Polymer*, **42**, 9929 (2001).
13. T. Tanaka, *Instruction Manual*, A&D Co., Ltd. (1999).
14. S. Ushiyama, *J. Jpn Soc. Colour Material*, **51**, 403 (1978).
15. S. H. Lee, Y. H. Park, S. K. An, and J. O. Lee, *Polymer (Korea)*, **25**, 15 (2001).
16. L. H. Sperling, *Introduction to Physical Polymer Science*. 3rd Edn., pp. 295-362, Wiley-Interscience, New York (2001).
17. N. Cordeiro, M. N. Belgacem, A. Gandini, and C. P. Neto, *Industrial Corps and Products*, **10**, 1 (1999).
18. K. M. I. Ali and T. Sasaki, *Radiat. Phys. Chem.*, **46**, 383 (1995).
19. R. Schwalm, L. Huling, W. Reich, E. Beck, P. Enenkel, and K. Menzel, *Prog. Org. Coat.*, **32**, 191 (1997).
20. M. A. Ali, M. A. Khan, and K. M. I. Ali, *Radiat. Phys. Chem.*, **47**, 295 (1996).
21. A. S. Bashar, M. A. Khan, and K. M. I. Ali, *Radiat. Phys. Chem.*, **48**, 349 (1996).
22. G. V. Shiryaeva, V. V. Bydanova, V. A. Khoromskaya, and T. A. Bolshakova, *Radiat. Phys. Chem.*, **46**, 995 (1995).
23. C. Wuertz, A. Bismarck, J. Springer, and R. Koniger, *Prog. Org. Coat.*, **37**, 117 (1999).
24. B. Christmas, G. Mendoza, and R. Buehner, in *Proc. RadTech 2000 conference. THE WORD OF UV/EB*, pp. 721-740, Baltimore Convention Center, Baltimore (2000).
25. E. A. DiMarzio, *J. Res. Natl. Bur. Stand. (U.S.)*, **68A**, 611 (1964).
26. K. Ueberreiter and G. Kanig, *J. Chem. Phys.*, **18**, 399 (1950).
27. D. J. Liaw and B. Y. Liaw, *Polymer*, **42**, 839 (2001).