# Rheological Study of the Solidification of Photopolymer and Dispersed Nanotube Systems

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### ABSTRACT:

We herein describe a set of rheological measurements that were carried out in order to characterize the solidification of photopolymers. The solidification depends on the length of time of exposure to UV light, and the intensity of that light, which reduces with distance from the irradiative surface. Liquid prepolymer was solidified inside the gap of a parallel disk rheometer by irradiation of the prepolymer with UV light through a fixed quartz disk. The rheological time-dependent changes were measured and analyzed for both unidirectional and oscillatory shear. The results were compared with those obtained by direct measurement in the absence of shear. When the thickness of the sample was less than 0.1 mm, the analysis for unidirectional shear flow yielded a reasonable agreement for both critical exposure and solidified depth. When the thickness was greater than 0.1 mm, the application of unidirectional shear delayed the start of the solidification but then caused it to occur more rapidly. This dependence of the solidification on the thickness of the sample was more significant for dispersed systems of nanotubes and for dynamic measurements made under oscillatory shear. The increase in viscosity due to photopolymerization was also estimated, and its effect was discussed.

#### ZUSAMMENFASSUNG:

Wir beschreiben eine Reihe von rheologischen Messungen, die durchgeführt wurden, um die Verfestigung von Photopolymeren zu charakterisieren. Die Verfestigung hängt von der Zeit, in der die Probe der UV-Strahlung ausgesetzt ist, und der Lichtintensität ab, die mit dem Abstand von der Strahlungsquelle abnimmt. Das flüssige Prepolymer wurde durch die Bestrahlung des Prepolymers durch eine feste Quartzscheibe im Spalt eines parallelen Platten-Rheometers verfestigt. Die zeitabhängigen rheologischen Änderungen wurden gemessen und analysiert sowohl für Scherung mit konstanter Schergeschwindigkeit als auch für oszillatorische Scherung. Die Resultate wurden mit denen verglichen, die durch direkte Messung ohne Scherströmung gewonnen wurden. Wenn die Probendicke kleiner als 0.1 mm ist, führt die Analyse der Ergebnisse für eine stationäre Scherströmung zu einer guten Übereinstimmung sowohl für die kritische Bestrahlung als auch für die Verfestigungstiefe. Wenn die Probendicke größer als 0.1 mm ist, verzögert die Anwendung einer Scherung mit konstanter Schergeschwindigkeit den Beginn der Verfestigung, führt danach jedoch zu einer beschleunigten Verfestigung. Diese Abhängigkeit der Verfestigung von der Probendicke war für disperse Systeme mit Kohlenstoffnanorörchen bedeutend bei dynamischen Messungen unter oszillatorischer Scherung. Die Zunahme der Viskosität aufgrund der Photopolymerisation wurde ebenfalls abgeschätzt und der Effekt diskutiert.

#### Résumé:

Nous décrivons ici un ensemble de mesures rhéologiques qui ont été faites dans le but de caractériser la solidification de photopolymères. La solidification dépend de la durée d'exposition à la lumière UV et de l'intensité de cette lumière qui diminue avec la distance calculée depuis la surface irradiante. Un liquide pré-polymérique a été solidifié à l'intérieur de l'entrefer d'un rhéomètre équipé de disques parallèles en irradiant le pré-polymère avec une lumière UV à travers un disque de quartz. Les changements rhéologiques au cours du temps ont été mesurés et analysés en cisaillement oscillatoire et continue. Les résultats ont été comparés avec ceux obtenus par mesure directe en l'absence de cisaillement. Lorsque l'épaisseur de l'échantillon est inférieure à 0.1 mm, l'analyse en cisaillement continu conduit à un accord raisonnable pour l'exposition critique et la profondeur de solidification. Lorsque l'épaisseur est supérieure á 0.1 mm, l'application d'un cisaillement continu retarde le début de la solidification mais ensuite induit une solidification plus rapide. Cette dépendance de la solidification avec l'épaisseur de l'échantillon est plus importante pour les systèmes dispersés de nanotubes et pour les mesures dynamiques effectuées avec un cisaillement oscillatoire. L'augmentation de la viscosité associée à la photopolymérisation a aussi été estimée et son effet est discuté.

KEY WORDS: photopolymer, solidification, exposure, shear flow, nanotubes

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If  $E_s(t) \le E_1$  then  $\eta/\eta_1 \cong 1$ . The constant *n* is related to the magnitude of the range of  $\zeta$  in which the viscosity increases. If *n* is large, the prepolymer increases in viscosity within a narrow range of  $\zeta$ and is therefore rapidly solidified. In the next step,  $\zeta$  is defined as  $e(x,t)/E_2$  instead of  $E_s(t)/E_2$  and Equations 26 and 28 are used to give the moment as follows

$$M = \frac{\pi R^4 \omega \eta_i}{2D_p} \left/ \left\{ (1 + \varepsilon) (H - h^*) - \frac{1}{n+i} (\varsigma (h^*, t)^{n+i} - \varsigma (H, t)^{n+i}) \right\}$$
(29)

Thus

$$h^* = H\left(1 - \frac{M_o}{M}\right) - \Delta \tag{30}$$

where

$$\Delta = \frac{D_p}{(1+\varepsilon)(n+1)} \left( \varsigma(h^*,t)^{n+1} - \varsigma(H,t)^{n+1} \right)$$
(31)

The first term in the denominator of Equation 29 is approximately H -  $h^*$  because of  $\epsilon \ll 1$ , and indicates the liquid layer thickness. The second and third terms in the denominator indicate the contribution of increasing viscosity that occurs in the liquid layer from  $x = h^*$  to x = H. Equation 31 includes the unknown values of solidified depth  $h^*$  in  $\zeta(h^*,t)$  and depth of penetration  $D_n$ . However, the exposure  $e(h^*,t)$  is  $E_{\lambda}$  and so  $\zeta(h^*,t)$ = 1. If  $E_s(t)$  is lower than  $E_2$ ,  $h^*$  = 0, and  $\zeta(h^*, t)$  =  $E_{s}(t)/E_{s}$ . The depth of penetration  $D_{p}$  cannot be obtained because  $h^*$  is unknown in Equation 3. The solidified depth h obtained from Equation 8 is therefore used as the first approximation of  $h^*$ , thereby enabling  $D_p$  and  $\Delta$  to be obtained in order that  $h^*$  may be calculated. As mentioned above, a large value of n in Equation 28 results in a rapid viscosity increase in a narrow range of  $\zeta$ , and gives a small value for  $\Delta$  in Equation 31. The method of characterization proposed in Section 2.3 corresponds to this limiting case of n >> 1 and  $\Delta \cong 0$ . In Figure 10a, the solidified depth h<sup>\*</sup> calculated from Equation 30 is plotted with h calculated from Equation 8. The correction  $\Delta$  is approximately 10 % of *H*. This modest degree of correction suggests that the rheological method in Section 2.3 can provide a reasonable set of values for the characterization of solidification.

The influence of shear on photopolymerization is important not only in rheological measurements, but also in applications such as coating. Further research must therefore be carried out in order to improve our understanding of the influence of shear on the photopolymerization reaction. Improvements, such as a combination with optical measurement, would make the rheological method more useful for the characterization of photopolymers.

### 3 CONCLUSIONS

The critical exposure E, and the rate of change of solidified depth h were obtained from the results of rheological and direct measurements. In the analysis of solidification under unidirectional shear flow there were reasonable agreements on E, and h with direct measurement when the sample thickness in the rheometer H was less than 0.1 mm. For H larger than 0.1 mm, the rheological method gave a higher critical exposure and a faster increase in h than direct measurement. In other words, when H was greater than 0.1 mm unidirectional shear initially delayed the start of the solidification and then caused it to occur more rapidly. This influence of H on solidification was more significant in dispersed systems of CNTs. On the other hand, for all values of H, dynamic measurements under oscillatory shear showed a significant difference in critical exposure and solidified depth from those values obtained by direct measurement.

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