*Macromol. Symp.* **2003**, *198,* 389-398

# *In Situ* Real-Time Monitoring of a Diglycidyl Ether of Bisphenol A Epoxy Resin Modified with Poly(etherimide)/Polysulphone Blends by Simultaneous Dielectric/Near-Infrared Spectroscopy

*G. Kortaberria, P. Arruti, I. Mondragon**

"Materials + Technologies" Group, Escuela de Ingenieria Tecnica Industrial,
Universidad del Pais Vasco/Euskal Herriko Unibertsitatea, Avda. Felipe IV, 1B.
20011, Donostia-San Sebastian, Spain

**Summary:** Simultaneous dielectric and near infrared measurements were performed in "real –time" to follow polymerisation reactions on blends of a diglycidyl ether of bisphenol A (DGEBA) epoxy resin with 4,4'-diaminodiphenylmethane (DDM) hardener and a mixture of polysulphone (PSU) and polyetherimide (PEI) as modifier. All the blends had a 10 wt% of PSU/PEI mixture. The effect of the PEI/PSU ratio in the mixture was studied. Monitoring of the α-relaxation (related to vitrification) was performed by dielectric measurements, while epoxy conversion was followed by near infrared spectroscopy. The effect of the PEI/PSU ratio on this behaviour was studied, as well as that of the curing temperature. Obtained results were compared with that of the blends with neat PSU and PEI as modifiers.

**Keywords:** curing, dielectric spectroscopy, epoxy, near infrared

## Introduction

*In situ* real-time monitoring for chemical and physical changes during processing of reactive polymer-forming materials is of crucial importance to scientist and engineers.

Dielectrometry has been developed by many authors as a non-destructive and convenient method for monitoring of thermosets curing. Many dielectric studies of epoxy-amine systems have been reported.[1-8] Several groups[9-12] have tried to relate the changes in dielectric properties to chemical and physical phenomena that occur during reaction.

Among a host of spectroscopic, dielectric and acoustic monitoring techniques, Fourier transform spectroscopy represents a particularly attractive choice owing to its possibility to offer molecular level information contained in the infrared portion of the electromagnetic spectrum. And while the use of conventional (off-line) FTIR spectroscopy to study reactive polymeric systems has been well documented in the literature[13,14] the use of *remote* FTIR for

DOI: 10.1002/masy.200350833

*in situ* monitoring of process has a much more recent origin. Only a handful of investigations of reactive systems have been conducted in the near infrared range, which extends from about 14.000 to 4000 $cm^{-1}$ and which contains weaker overtones of the fundamental absorptions.[15-23]

So the combined use of near infrared and dielectric spectroscopy becomes of particular interest in monitoring of the reactive processes. Both techniques working together enable to generate complementary information about chemical changes (from near infrared) and physical changes (from dielectric spectroscopy) associated with various phenomena that occur during processing of thermosets including vitrification, gelation and various relaxations.

Epoxy resins are often modified with thermoplastics or elastomers in order to improve their fracture toughness. Usually, a single modifier is employed but the possibility of exists for the simultaneous using of two or even more modifiers.

The main objective of this preliminary work is to study the effect of the modification of the DGEBA/DDM resin with PEI/PSU mixture at 10 wt% with different PEI/PSU ratios on the curing reaction, by using dielectric and infrared spectroscopy working simultaneously. Blends were cured at 100°C and 120°C in order to study the effect of the curing temperature.

## Experimental

The bifunctional epoxy matrix consisted of stoichiometric amounts of diglycidyl ether of bisphenol A (DGEBA) epoxy resin (DER 332, n=0.03, kindly supplied by Dow Chemical) and 4,4'-diaminodiphenylmethane DDM, HT 972), kindly provided by Ciba. The modifiers were polysulphone of bisphenol A (PSU Udel P-1700), kindly supplied by Amoco Chemical, and polyetherimide (Ultem 1000), provided by GE Plastics.

DGEBA-(PEI/PSU) mixtures containing different PEI/PSU ratios (25/75, 50/50, 75/25) were prepared by dissolution in methylene chloride. The solvent was evaporated in an oil bath at 90°C. Last solvent traces were removed in a vacuum oven at 90°C overnight.

Dielectric measurements were performed on a Solartron 1260 impedance gain-phase analyzer operable in the range from 0,1 Hz to 1 MHz, interfaced with a computer to the reaction cell used.

Fourier transform infrared spectroscopy was performed using a Nicolet Nexus-IR System 750 Spectrometer with spectral range coverage from 15.800 to 50 $cm^{-1}$. Near infrared data were obtained using a calcium fluoride beamsplitter, a white light source and PBSe or MCT-A detector. For simultaneous measurements, a large core (600/630 μm) low OH fused silica type 3M's multimode optical fibre was used.

## Results and Discussion

### Dielectric Spectroscopy

The advancement of the curing reaction of DGEBA/DDM resin modified with 10 wt% PEI/PSU mixture is followed. The effect of the PEI/PSU ratio is studied as well as that of the curing temperature. Obtained data are compared with those for blends of DGEBA/DDM with 10 wt% PSU and 10 wt% PEI. The main α-relaxation (related with the vitrification phenomena) is followed in time and frequency domains in order to study the effect of the curing in it.

Vitrification occurs when the curing resin changes from the gel to the glassy state. When the cure proceeds at constant temperature, as in this case, the time at which the increasing Tg of the system reaches the cure temperature defines this physical event. When this change occurs, the permittivity decreases until it reaches an assymptotic value. At the same time, the loss-factor curve presents a peak depending on the frequency, and after this peak it also reaches an assymptotic value. This peak, corresponding to the α-relaxation, occurs when $\varpi\tau$ (frequency-relaxation-time product) equals unity. This α-relaxation is the material relaxation process associated with glass transition, and is linked with cooperative segmental motions and with microscale density fluctuations.[24]

Figure 1 show permittivity and loss-factor vs cure time plots for the DGEBA/DDM resin modified with 10 wt% PEI/PSU (50/50) at 100°C. There can be clearly seen the fall in permittivity at the same time of the appearance of the peak, corresponding to the slowing down of the relaxations of the permanent electrical dipoles.[25]

Figures 2a, 2b and 3 show the effect of the modifier in this behaviour. Blends of DGEBA/DDM with 10 wt% PEI/PSU at several ratios (25/75, 50/50, 75/25) are compared with blends of DGEBA/DDM with 10 wt% PEI and 10 wt% PSU.

It can be seen that reaction advances faster in the case of the matrix modified with neat PEI, slowing down with the addition of PSU, until it is the slowest in the case of the matrix modified with neat PSU. This slowing down can be seen in the loss-peak and in the fall of permittivity. The reaction is retarded with the amount of PSU in the modifiers mixture.

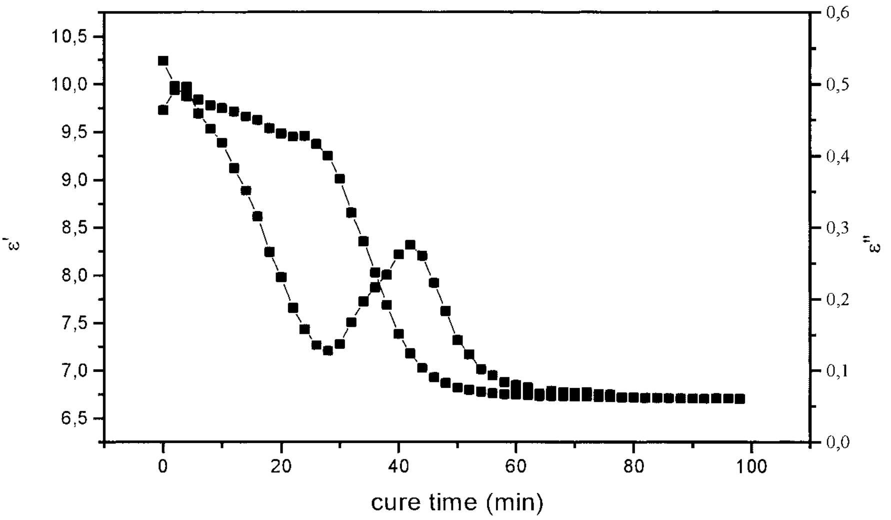

Fig. 1. dielectric loss and dielectric constant vs cure time plot for the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (50/50).

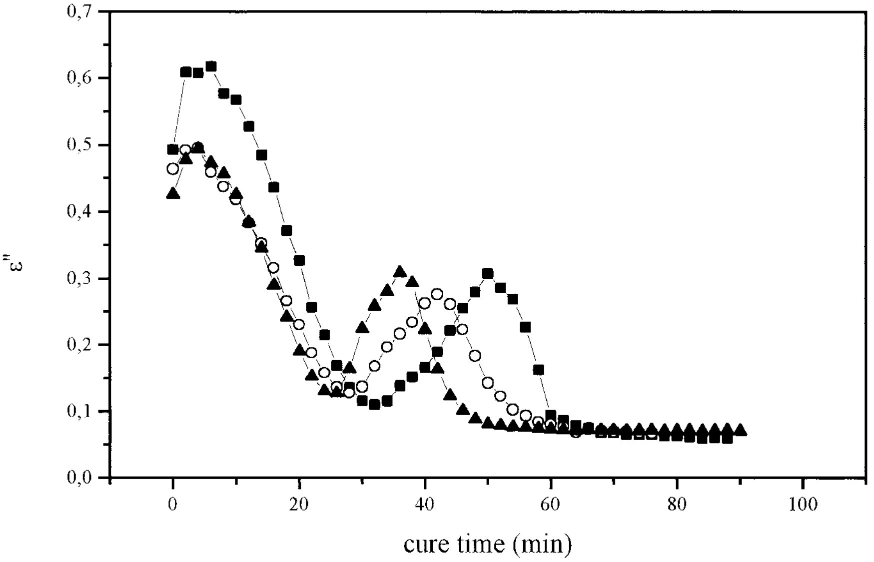

Fig. 2a. dielectric loss vs cure time plot for the DGEBA/DDM matrix modified with 10 wt% PEI (▲), 10 wt% PEI/PSU (50/50) (o), and 10 wt% PSU (■) respectively, at 100°C and 10 kHz.

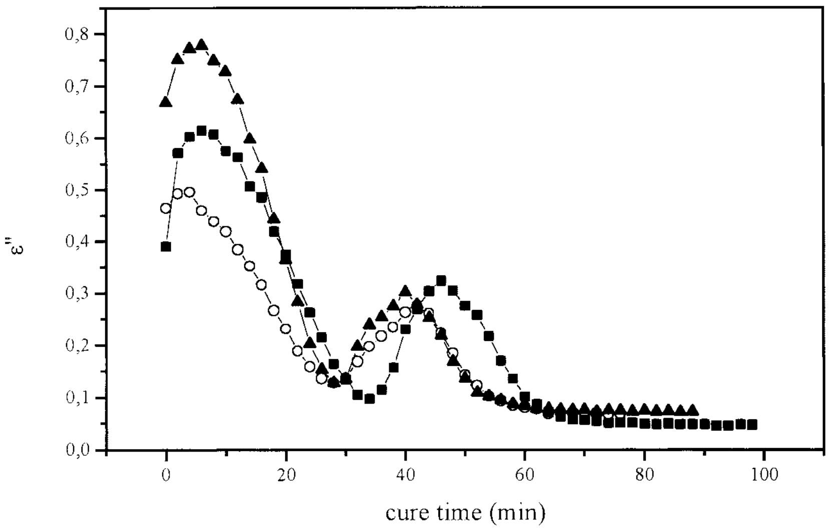

Fig. 2b. dielectric loss vs cure time plot for the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (75/25) (▲), 10 wt% PEI/PSU (50/50) (o), and 10 wt% PEI/PSU (25/75) (■) respectively, at 100°C and 10 kHz.

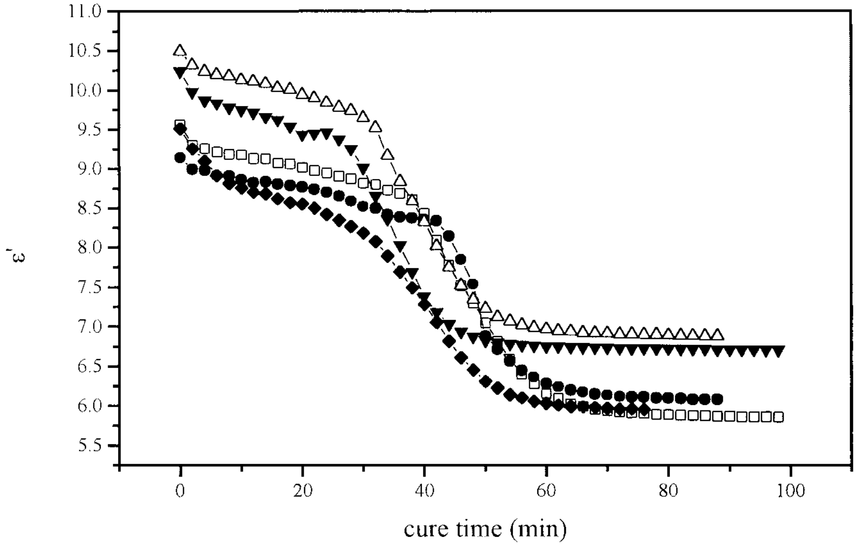

Fig. 3. dielectric constant vs cure time plots for DGEBA/DDM matrix modified with 10 wt% PEI (◆), 10 wt% PSU (●), 10 wt% PEI/PSU (75/25) (□), 10 wt% PEI/PSU (50/50) (▼), and 10 wt% PEI/PSU (25/75) (Δ) respectively, at 100°C and 10 kHz.

The effect of the cure temperature is shown in Figure 4, where loss factor and permittivity are measured for the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (50/50) at 100° and 120°C. The reaction is going faster with higher curing temperature.

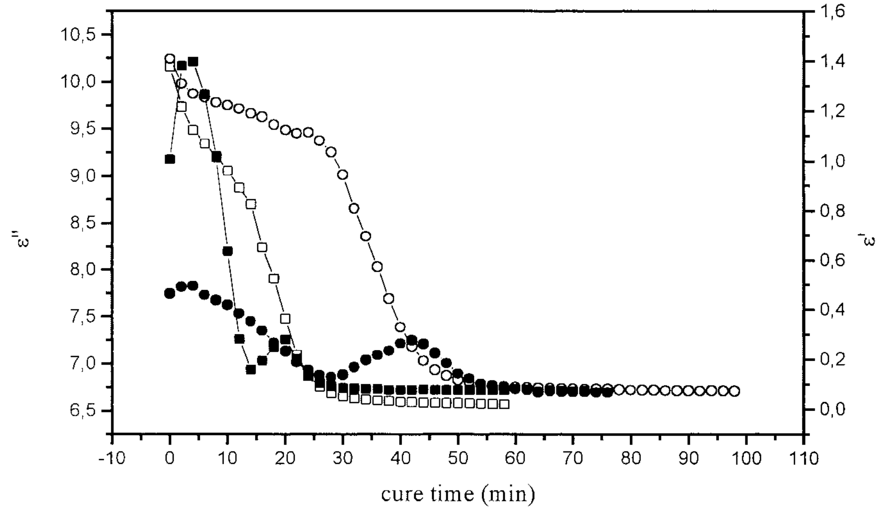

Fig. 4. dielectric loss and dielectric constant vs cure time plot. Dielectric loss at 100°C (●), dielectric loss at 120°C (■), dielectric constant at 100°C (o) and dielectric constant at 120°C (□).

The relaxational behaviour of the blends can be followed by studying the evolution of the imaginary impedance Z" in the frequency domain with cure time. Figure 5 shows the Z" vs frequency plot for the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (50/50) at 100°C. The relaxation peak of the Z" vs frequency plot appears from the high frequency region and moves to lower frequencies as the cure advances.[26]

During the cure, as the Tg of the resin becomes higher the medium becomes more viscous and so the chain segments have more difficulty in moving, and consequently dipoles need longer times for their orientation and relaxation. At the same time, the height of the peak increases and the width decreases, the distribution of relaxation times becoming narrower.

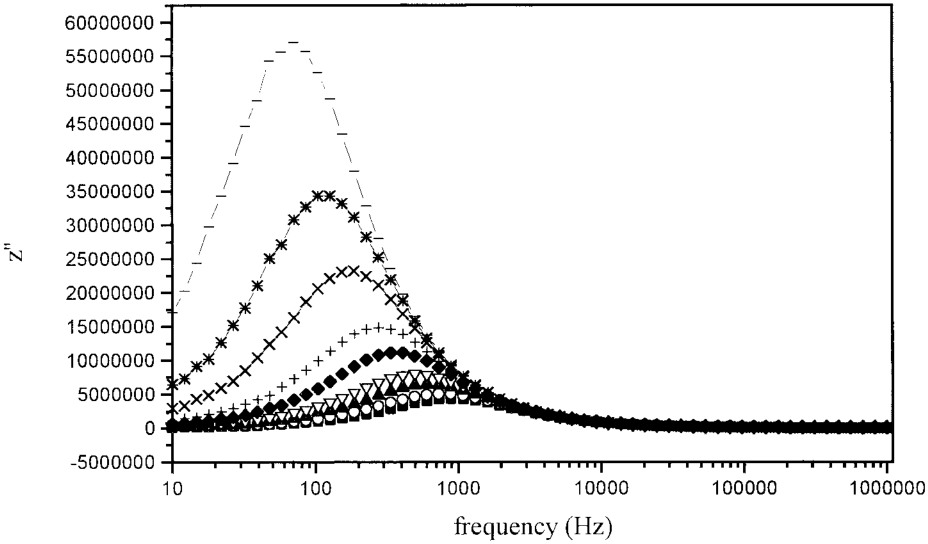

Fig. 5. imaginary impedance vs frequency plots for the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (50/50) at several cure times: 18 min (■), 20 min (o), 22 min (▲), 24 min (▽), 26 min (◆), 28 min (+), 30 min (×), 32 min (*) and 34 min (-).

## Near Infrared Spectroscopy

Figure 6 shows the evolution for the near infrared spectra with cure time, for the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (50/50) at 100°. The trend displayed by major peaks of relevance in epoxy/amine systems[27-29] are evident: decrease in epoxy absorption (6070 $cm^{-1}$, epoxy group stretching vibrations, first overtone), a decrease in amine absorption (5056 $cm^{-1}$, $-NH_2$ combination band of stretching and bending vibrations, and 6670 $cm^{-1}$, $-NH_2$ combination of symmetric and asymetric stretching vibrations).

The peak at 6070 was used to monitor the disappearance of the epoxy group in this study. Various reference peaks were examined and the most reproducible results were obtained using the peak at 5980 $cm^{-1}$, due to aromatic –C-H stretching first overtone band.

Figure 7 shows the epoxy conversion vs cure time plot for all the blends studied, cured at 100°C. The trend of the reaction advancement is similar to that shown by dielectric spectroscopy, i.e. being the reaction of the matrix modified with 10 wt% PEI is the fastest and the modified with 10 wt% PSU is the slowest. In the case of matrices modified with PEI/PSU mixtures, reaction advances more slowly by increasing the content of PSU in the mixture.

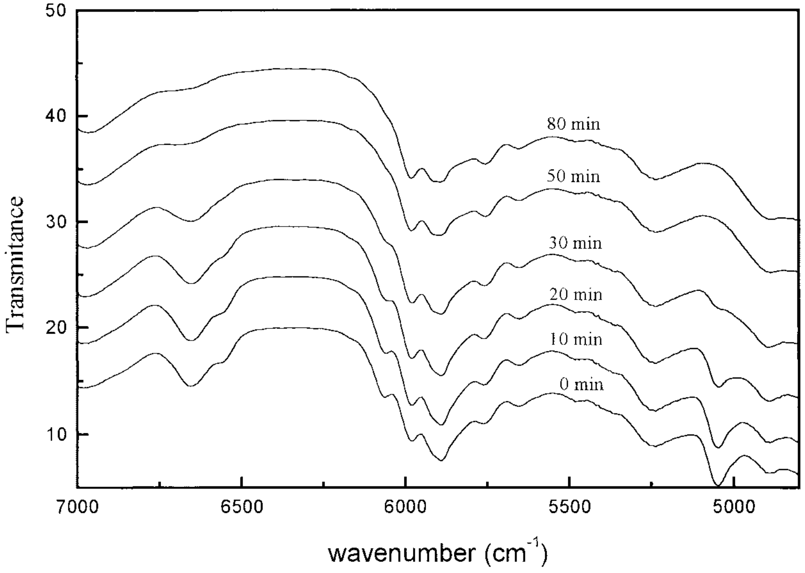

Fig. 6. near infrared spectra of the DGEBA/DDM matrix modified with 10 wt% PEI/PSU (50/50).

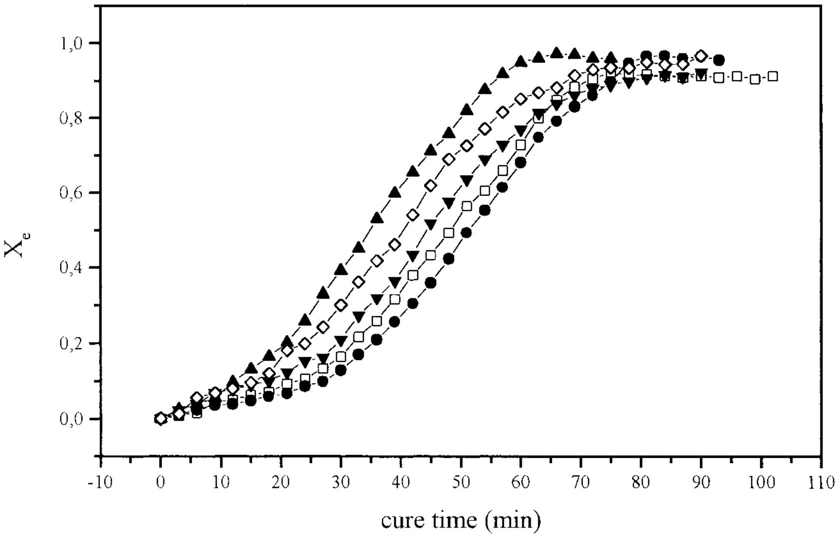

Fig. 7. epoxy conversion vs cure time plots for the DGEBA/DDM matrix modified with 10 wt% PEI (▲), 10 wt% PEI/PSU (75/25) (◇), 10 wt% PEI/PSU (50/50) (▼), 10 wt% PEI/PSU (25/75) (□), and 10 wt% PSU (●) respectively, cured at 100°C.

It is worth noting, however, that difference between the curing behaviour of all the systems studied is not very significant, so indicating that the reaction will not be very affected using PSU or PEI as modifier.

## Conclusions

*In situ* "real-time" simultaneous dielectric and near infrared measurements have been performed to follow polymerisation of thermoplastic-modified epoxy mixtures. Mixtures of two thermoplastic with different ratios have been used as modifier.

Monitoring of cure advancement have been carried out in order to study the effect of the thermoplastic and its amount on it. Measurements have been made at 100°C and 120°C, in order to show the effect of the cure temperature.

Dielectric and near infrared measurements are in quite well agreement indicating that the PSU thermoplastic slows down the cure reaction more than PEI. The bigger the amount of PSU in the mixture is, the slower the cure reaction advances, as it could be seen for the mixtures with PEI/PSU ratios of 25/75, 50/50, and 75/25, and for the mixtures with 10 wt% PEI and 10 wt% PSU. It is worth noting, however, that the differences between all the systems are not very significant, thus indicating that the use of PEI or PSU as modifier does not affect too much the reaction kinetics. The effect of the curing temperature is more significant, advancing the reaction much faster at higher curing temperatures. It can be concluded that the cure temperature is more determining than the kind of thermoplastic in our case.

The relaxational behaviour with cure time have been also shown in the frequency domain, in order to study the effect of the cure on the main relaxation of the resin. This α-relaxation goes towards low frequencies with the cure advancement, because the medium is more viscous and dipoles need longer times to orient and relax.

1. J. O. Simpson and S. A. Bidstrup, J. Polym. Sci.: Part B: Polym. Phys., 33, 55 (1995)
2. G. Levita, A. Livi, P. A. Rolla, and C. Culicchi, J. Polym. Sci.: Part B: Polym. Phys., 34, 2731 (1996)
3. J. Fournier, G. Williams, C. Duch, and G. A. Aldridge, Macromolecules, 29, 7097 (1996)
4. J. P. Elondou, Eur. Polym. J., 35, 1473 (1999)
5. J. P. Elondou, Eur. Polym. J., 35, 1481 (1999)
6. J. P. Elondou, O. Ayina, H. N. Nga, and J. F. Gerard, J. Polym. Sci.: Part B: Polym. Phys., 36, 2911 (1998)
7. S. Pichaud, X. Deuteurtre, and A. Fit, Polym. Int., 48, 1205 (1999)
8. T. Koike, J. Appl. Polym. Sci., 50, 1943 (1993)
9. G. Boiteux, P. Dublineau, M. Feve, C. Mathieu, G. Seytre, and J. Ulanski, Polym. Bull., 30, 441 (1993)
10. M. B. M. Mangion and J. P. Johari, J. Polym. Sci.: Part B: Polym. Phys.., 29, 1127 (1991)
11. M. G. Parthun and J. P. Johari, J. Polym. Sci.: Part B: Polym. Phys., 30, 655 (1992)
12. T. Koike, J. Appl. Polym. Sci., 44, 679 (1992)
13. S. Andjelic, J. Mijovic, and F. Bellucci, J. Polym. Sci.: Part B: Polym. Phys., 36, 641 (1998)
14. C. Vinh-Tung, G. Boiteux, G. Seytre, G. Lachenal, and B. Chabert, Polym. Comp., 17, 761 (1996)
15. M. Franco, I. Mondragon, and C. B. Bucknall, J. Appl. Polym. Sci., 72, 427 (1999)

16. M. Franco, M. A. Corcuera, J. Gavalda, A. Valea, and I. Mondragon, J. Polym. Sci.: Part B: Polym. Phys. 35, 233 (1997)
17. D. R. Day, T. J. Lewis, H. L. Lee, and S. D. Senturia, J. Adhesion, 18, 73 (1985)
18. L. K. H. Van Beek, in Progress in Dielectric, 7, 69 (1967)
19. D. A. Wasylyshyn and G. P. Johari, J. Polym. Sci.: Part B: Polym. Phys., 36, 2703 (1998)
20. G. M. Maistros, H. Block, C. B. Bucknall, and I. K. Partridge, Polymer, 33, 4470 (1992)
21. C. G. Delides, D. Hayward, R. A. Pethrick, and A. S. Vatalis, Eur. Polym. J., 28, 505 (1992)
22. G. Korkakas, C. M. Gomez, and C. B. Bucknall, Plast. Rubber Comp. Process. Appl., 19, 285 (1993)
23. I. Partridge and G. Maistros, High Perform. Polym., 8, 1 (1996)
24. B. D. Fitz and J. Mijovic, Macromolecules, 32, 4134 (1999)
25. S. Andjelic and J. Mijovic, Macromolecules, 31, 8463 (1998)
26. G. M. Maistros and C. B. Bucknall, Polym. Eng. And Sci., 36, 1517 (1994)
27. J. Mijovic, S. Andjelic, and J. M. Kenny, Polym. Adv. Tech., 7, 1 (1995)
28. G. A. George, P. Cole-Clark, N. St John, and G. Friend, J. Appl. Polym. Sci., 42, 643 (1991)
29. N. St John and G. A. George, Polymer, 33 (13), 2679 (1991)