Tetrafunctional Epoxy Resins: Modeling the Curing Kinetics Based on FTIR Spectroscopy Data

PELLEGRINO MUSTO, EZIO MARTUSCELLI, GIUSEPPE RAGOSTA, PIETRO RUSSO, PAOLA VILLANO

Institute of Research and Technology of Plastic Materials, National Research Council of Italy, via Toiano, 6, 80072 Arco Felice (NA), Italy

ABSTRACT: The curing kinetics of two thermosetting systems based on a tetrafunctional epoxy resin was investigated by Fourier transform infrared spectroscopy. Two formulations were studied, in which the hardener was an aromatic diamine and a carboxylic dianhydride, respectively. The quantitative evaluation of the epoxy conversion was based on spectra collected in the near-infrared range ($8000-4000$ cm^{-1}) as well as in the medium infrared range ($4000-400$ cm^{-1}). The kinetic parameters evaluated in the above frequency intervals were significantly different. The reasons for such a discrepancy are discussed critically. Several kinetic models, based on the widely employed Kamal approach, were applied to verify their predictive capability. Satisfactory results were obtained for the amine-cured system, particularly with a modified equation taking into account the autocatalytic nature of the process as well as a limiting diffusional effect. Less accurate results were achieved for the anhydride-cured system. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 532–540, 1999

Key words: FTIR spectroscopy; FT-NIR spectroscopy; epoxy resins; curing kinetics; modeling

INTRODUCTION

Tetrafunctional epoxy resins are highly crosslinked thermosets characterized by a wide range of desirable end properties such as light-weightness, high elastic modulus, high T_g values, excellent resistance to chemicals, and, finally, good thermal and thermooxidative stability. All these properties are responsible for their use as matrices for the formulation of high-performance composites used in the aerospace and military industry. In particular, tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM), cured with 4,4'-diaminodiphenyl sulfone (DDS), represents one of the most widely used matrices for fibrous composites in aerospace applications.

Generally, the physical, electrical, transport, and ultimate mechanical properties of epoxy resins depend strongly upon the curing process. Therefore, a clear understanding of the curing mechanism and the ability to develop suitable kinetic models to simulate the curing reaction are essential to predict and to control the end properties of the crosslinked material.

For epoxy–amine systems, three main reactions may take place, either simultaneously or sequentially, depending on the reactants' reactivity and on the process temperature: the addition of primary and secondary amine groups to the oxirane ring and the etherification of the epoxy group with a pendant hydroxyl group. The first two steps are catalyzed by the presence of hydroxyl functionalities added to the formulation as accelerators and/or created by the amine reactions. This effect accounts for the autocatalytic nature of the curing process.

Besides the multifunctional amines, a further, widely employed family of epoxy hardeners is that of carboxylic dianhydrides. These are generally less reactive than are amines, but also less toxic and yield resins with a reduced tendency to absorb atmospheric moisture.[1]

Owing to the reduced reactivity of the epoxy/anhydride systems, they require the presence of a third component acting as a catalyst, which is generally a tertiary amine.[2–4] The curing mechanism in this case is still not completely understood, due to the occurrence of secondary reactions at high temperatures.[5] The most probable are etherification between epoxy and hydroxyl groups and homopolymerization of the epoxy prepolymer[5–7]; both of them adversely affect the ultimate properties of cured materials, decreasing their final crosslinking density.

Owing to the technological relevance of epoxy-based formulations, a considerable amount of experimental and theoretical work has been performed in prior years to gain a deeper understanding of the mechanism and kinetics of the curing process. The techniques employed to monitor the curing reaction can be grouped into direct and indirect methods. The direct methods allow the evaluation of the concentration of one or more reactive groups as a function of time. They include gel permeation chromatography (GPC),[8] nuclear magnetic resonance (NMR),[9] electron paramagnetic resonance,[10] Fourier transform infrared spectroscopy (FTIR),[11–13] and Raman spectroscopy.[14]

Indirect analysis gives only an assessment of the degree of cure by monitoring, as a function of time, a physical property directly correlated with the reactants' conversion. In this area, most of the work has been performed by differential scanning calorimetry (DSC),[15] which is based on the assumption that the rate of heat evolution during curing is proportional to the rate of polymerization. Other widely employed indirect techniques include rheology, dielectric spectroscopy, and ultrasonic measurements.

In particular, among the various molecular spectroscopy techniques, FTIR offers several advantages. First, it allows one to monitor the curing process over the whole conversion range. In fact, although during curing the material undergoes several state transitions from fluid to rubbery to glass, these transitions have limited influence on the vibrational spectrum. Second, by selecting the appropriate signals, it is possible to monitor simultaneously the concentration profiles of the various reacting species present in the system, which is the only way to obtain direct mechanistic information. A third important consideration arises when working in the near-infrared (NIR) range, which extends between 10.000 and 4000 cm^{-1}. This radiation travels very efficiently through commercially available optical fibers, thus allowing an *in situ* remote monitoring of the process.[16]

In the present contribution, FTIR spectroscopy was employed to investigate the isothermal curing kinetics of a typical TGDDM/DDS formulation both in the medium infrared range (MIR) and in the NIR frequency range. The aim of the investigation was to compare the results obtained in the above regions of the electromagnetic spectrum and to refine the kinetic models proposed in the literature to the experimental results obtained herein.

Preliminary results on the TGDDM/methyl nadic anhydride are also presented, along with a tentative kinetic modeling of the reaction process. These latter data were obtained in the presence of a tertiary amine catalyst and in the NIR frequency range.

EXPERIMENTAL

Materials

The epoxy resin used was a commercial-grade tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM) supplied by Ciba Geigy (Basel, Switzerland) and was cured by 4,4′-diaminodiphenyl sulfone (DDS) or methyl nadic anhydride (MNA) in the presence of benzil dimethylamine (BDMA). The latter reagents were Aldrich (Milwaukee, WI) reagent-grade products and were used without further purification. The chemical formulas of the system components are reported below:

TGDDM: tetraglycidyl 4,4' diamino diphenyl methane

DDS: 4, 4' diamino diphenyl sulfone

MNA: methyl nadic anhydride

BDMA: benzil dimethyl amine

Figure 1 FTIR transmission spectra in the 4000–450 cm^{-1} wavenumber range of the TGDDM/DDS formulation before and after the curing process (traces A and B, respectively).

Techniques

FTIR spectra in the MIR wavenumber range (Fig. 1) (4000–400 cm^{-1}) were collected on thin films (5–15 μm) of the uncured resin, obtained by casting 10% wt/wt acetone solutions onto KBr disks. Most of the solvent was allowed to evaporate at room temperature, and final drying of the samples was performed in a vacuum oven at 70°C for 1 h. No traces of residual solvent were detectable spectroscopically. In the NIR wavenumber range (8000–4000 cm^{-1}), 0.50-mm-thick samples were employed, obtained by squeezing a drop of the reactive mixture between two quartz windows, separated by an appropriate spacer.

All the spectra were obtained at a resolution of 4 cm^{-1}, using a Perkin–Elmer System 2000 spectrometer. The instrument was equipped with a deuterated triglicyne sulfate detector (DTGS) and germanium on a KBr beam splitter. The frequency scale was internally calibrated to an accuracy of 0.01 cm^{-1} by a He/Ne reference laser.

The temperature measurements were carried out in a SPECAC 80100 temperature chamber directly mounted in the spectrometer and purged con-

tinuously with dry nitrogen. This unit was driven by an Eurotherm 071 temperature controller to an accuracy of ±0.5°C. Isothermal curing was carried out at 140°C for the TGDDM/DDS system and at 120°C for the TGDDM/MNA system.

Techniques

FTIR spectra in the Mir wavenumber range (4000–400 cm^{-1}) were collected on thin films (5–15 μm) of the uncured resin, obtained by casting 10% wt/wt acetone solutions onto KBr disks. Most of the solvent was allowed to evaporate at room temperature, and final drying of the samples was performed in a vacuum oven at 70°C for 1 h. No traces of residual solvent were detectable spectroscopically. In the NIR wavenumber range (8000–4000 cm^{-1}), 0.50-mm-thick samples were employed, obtained by squeezing a drop of the reactive mixture between two quartz windows, separated by an appropriate spacer.

All the spectra were obtained at a resolution of 4 cm^{-1}, using a Perkin–Elmer System 2000 spectrometer. The instrument was equipped with a deuterated triglicyne sulfate dectector (DTGS)

and germanium/KBr beam splitter. The frequency scale was internally calibrated to an accuracy of 0.01 cm^{-1} by a He/Ne reference laser.

The temperature measurements were carried out in a SPECAC 80100 temperature chamber directly mounted in the spectrometer and purged continuously with dry nitrogen. This unit was driven by an Eurotherm 071 temperature controller to an accuracy of $\pm 0.05°C$. Isothermal curing was carried out at 140°C for the TGDDM/DDS system and at 120°C for the TGDDM/MNA system.

Quantitative Analysis of the Infrared Spectra and of the Kinetic Data

The relative conversion, α, of the epoxy groups in the various investigated systems was determined in the usual way:

$$\alpha = \frac{C_0 - C_t}{C_0} = 1 - \frac{C_t}{C_0} \tag{1}$$

and by the hypothesis of validity of the Beer–Lambert relation:

$$\alpha = 1 - \frac{\bar{A}_t}{\bar{A}_0} \tag{2}$$

where C is the concentration, A represents the absorbance, and the subscripts 0 and t denote reaction times zero and t, respectively. Furthermore, $\bar{A}$ corresponds to the absorbance of the analytical peak corrected for the sample thickness. In the MIR range, a thickness correction was accomplished by use of the invariant peak at 1513 cm^{-1} (a ring semicircle stretching mode of the diphenylmethane unit) as an internal standard. In the NIR range, due to the design of the sample holder, no thickness variation was observed during curing and the thickness correction was unnecessary.

In the MIR range, the analytical peak was the oxirane ring deformation at 916 cm^{-1} (see Fig. 2). The peak area was used, according to the conclusions drawn in ref. 17. In the NIR interval, two characteristic oxirane absorptions are observed at 6064 and at 4524 cm^{-1}. The one at higher frequency is due to the first overtone of the terminal CH$_2$ stretching mode, while the peak at lower frequency has been attributed to a combination band of the second overtone of the epoxy ring stretch at 916 cm^{-1} with the fundamental C—H stretch at about 2725 cm^{-1}.[17] The 6064 cm^{-1} peak is considerably overlapped with the complex

Figure 2 MIR spectra in the wavenumber range 1100–850 cm^{-1}, collected at different times for the curing process carried out at 140°C on the TGDDM/DDS system.

profile due to the CH stretching modes at lower frequency. However, in the TGDDM/DDS system, the 4524 cm^{-1} peak is complicated by the interference of a primary amine contribution occurring at about the same frequency. Therefore, the 6064 cm^{-1} peak was preferred, and its intensity was evaluated by difference spectroscopy according to the procedure described in detail in ref. 17. In the TGDDM/MNA system, no interference was observed for the 4524 cm^{-1} band, whose area was used for the estimation of the relative conversion. The spectra collected during the isothermal curing of the TGDDM/DDS system in the MIR and NIR frequency ranges are reported, respectively, in Figures 2 and 3.

The analysis of the kinetic data was performed as follows:

- The raw conversion (α) versus time (t) curves (see Fig. 4) were smoothed to reduce the data scattering which would produce an excessive error when the derivative curves are calculated [i.e., ($d\alpha/dt$) versus α]. The smoothing function used throughout was an asymmetric sigmoid function of the type

$$y = Min + \frac{Max - Min}{1 - \left(\dfrac{x}{x_{1/2}}\right)^{-P}} \tag{3}$$

Figure 3 Three-dimensional (absorbance − wavenumber − time) NIR spectra relative to the curing of the TGDDM/DDS system at 140°C.

Nonlinear least-squares regression analysis of the experimental data allowed the evaluation of the adjustable parameters *Min*, *Max*, $x_{1/2}$, and *P*. In all cases, a very satisfactory fit was obtained (see Fig. 4), with a correlation factor, r^2, between 0.996 and 0.999.

- The first derivative of the smoothed curves was numerically evaluated to obtain $(d\alpha/dt)$ versus *t*, and, hence, the $(d\alpha/dt)$ versus α curves. The estimation of the kinetic parameters was carried out by nonlinear least-squares regression of the model equations [Eqs. (4)–(6)] over the $(d\alpha/dt)$ versus α curves. Finally, the simulated derivative profiles were numerically integrated by the Runge–Kutta fourth-order method to obtain the conversion profiles predicted by the models to be compared with the experimental data.

RESULTS AND DISCUSSION

Kinetic Models

Kinetic modeling of the curing process can be approached in two ways: mechanistic or phenomenological. The mechanistic approach consists of considering the complete set of reaction steps which constitutes the overall mechanism and in writing the single-rate equations for each step. A complex system of simultaneous differential equations is obtained, which, whenever possible, is solved numerically. The solutions yield the absolute values of the kinetic constants of each step, which allow the simulation of the concentration profiles of all the reactive species involved in the process. If the system of differential equations is not amenable to numerical integration, a number of simplifying assumptions is adopted. This approach is complicated from a computational point

Figure 4 Relative conversion, α, as a function of time for the curing of the TGDDM/DDS formulation at 140°C: (●) MIR data; (○) NIR data. The continuous lines represent the curves obtained by the smoothing procedure.

Figure 5 (■) Experimental $(d\alpha/dt)$ versus α curves relative to the curing of the TGDDM/DDS system at 140°C as monitored by MIR spectroscopy. The continuous line represents the curve obtained by best-fitting the experimental data with eq. (6).

of view, especially when side reactions play an important role in the process.

A more straightforward method consists of using empirical or semiempirical model equations, which are more compact in form and have been successfully employed for several thermosetting systems. These models do not bring any direct mechanistic information but can be very useful for predictive purposes.

A widely employed kinetic expression is due to Kamal et al.[18]:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^m)(1 - \alpha)^n \qquad (4)$$

where α is the extent of conversion of epoxy groups, K_1 and K_2 are Arrhenius-type rate constants, and m and n are empirical power-law exponents, whose sum represents the overall reaction order. This rate equation takes into account the autocatalytic nature of the curing process with the term $K_2\alpha^m$, while K_1 represents the kinetic constant of the uncatalyzed process.

Several simplifications have been suggested in the literature, among which a widely employed one makes use of the observation that, in general, the curing reaction of epoxy resins is a second-order process, that is, $m + n = 2$. With this assumption, eq. (4) reduces to

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^{2-n})(1 - \alpha)^n \qquad (5)$$

In this form, the Kamal equation does not take into consideration the fact that, as the conversion increases and the T_g of the material approaches the reaction temperature, the process becomes diffusion-controlled. Thus, the reaction rate decreases considerably and goes to zero before reaching full conversion. In general, the final conversion is strongly dependent on the reaction temperature. This effect could be accounted for by substituting the term $(1 - \alpha)$ on the right side of eqs. (4) and (5) with the term $(\alpha_{max} - \alpha)$, where α_{max} represents the final conversion reached at the investigated temperature. Thus,

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha^{2-n})(\alpha_{max} - \alpha)^n \qquad (6)$$

In the present contribution, the above-discussed kinetic models were applied to the TGDDM/DDS system cured at 140°C and to the TGDDM/MNA system cured at 120°C to evaluate their ability to simulate the real process.

Analysis of the Modeling Results

In Figure 4 are reported the $\alpha - t$ experimental data, along with the relative smoothed curves for the system TGDDM/DDS 100/30 wt/wt. In particular, curve A refers to the data collected in the MIR interval, while curve B is relative to the NIR frequency range

The $(d\alpha/dt)$ versus α curves relative to the MIR data and to the NIR data are shown in Figures 5 and 6, respectively, along with the curves simulated by the equation model (6). The theoretical conversion profiles obtained with the three equation models (4), (5), and (6) are compared with the experimental data in Figures 7 and 8. With respect to the data collected in the MIR range, it may be observed that models (4) and (6) give essentially the same conversion profile in the time range investigated. Detectable differences are found in the case of the curve obtained with model (5) $(m + n = 2)$, which shows a closer fit to the data up to about 0.65 ordinate units. However, toward the plateau region, the latter curve tends to diverge, while the former two, and, in particular, the one obtained by eq. (6) $(m + n = 2; \alpha_{max})$, display the correct behavior.

With respect to the NIR data, only the simulations obtained by models (4) and (6) are reported, since the model with $m + n = 2$ fits the experimental data very poorly. Conversely, both models 4 and 6 gave a very satisfactory fit; a comparison

Figure 6 (■) Experimental ($d\alpha/dt$) versus α curves relative to the curing of the TGDDM/DDS system at 140°C as monitored by NIR spectroscopy. The continuous line represents the curve obtained by best-fitting the experimental data with eq. (6).

between the two demonstrates that the model which takes into account the limiting final conversion better describes the system behavior toward the plateau region.

In summary, the more suitable kinetic model appears to be eq. (6), which, in fact, is also the more complete, since it contains the autocatalytic effect as well as the diffusional term. The general Kamal equation, instead, describes accurately the system's behavior only in the early stages of the

Figure 7 Comparison among the experimental $\alpha - t$ curves and the predictions of the various kinetic models, relative to the TGDDM/DDS system cured at 140°C, as monitored in the MIR interval: (●) experimental data points; (continuous line) model (4); (dashed line) model (5); (dotted line) model (6).

Figure 8 Comparison among the experimental $\alpha - t$ curves and the predictions of the various kinetic models, relative to the TGDDM/DDS system cured at 140°C, as monitored in the NIR interval: (●) experimental data points; (continuous line) model (4); (dotted line) model (6).

curing process, deviating appreciably as the diffusional effects begin to play a significant role. Therefore, although from a predictive point of view this model cannot be considered accurate over the whole conversion range, it could be usefully employed to detect the onset of diffusion control, that is, the onset of vitrification, as the point in the $\alpha - t$ diagram at which departure between the theoretical and experimental curves occurs. A further limitation of such a model is that overall reaction orders ranging between 5 and 9.5 are obtained (see Table I), which clearly have no mechanistic significance. Thus, eq. (4) is to be regarded as purely empirical and, as such, cannot provide any mechanistic information.

A further relevant observation is that the same TGDDM/DDS formulation, cured at the same temperature, shows a considerably different kinetic behavior depending on whether the data were collected in the MIR or in the NIR frequency ranges. The rate of the curing process is slower for the NIR data in comparison to the MIR results: If we consider the simulations of model (6) (see Table I), both K_1 and K_2 are twice in the MIR with respect to the NIR results. Also, the final conversion attained in the MIR experiment is considerably higher than that achieved in the NIR test (0.69 versus 0.58).

The two main differences between the NIR and the MIR experiments are the sample thickness (0.5 mm in the NIR and up to 15 μm in the MIR) and the

Table I   Kinetic Parameters Evaluated According to the Different Model Equations

System	TGDDM/DDS[a] 100/30	TGDDM/DDS[b] 100/30	TGDDM/MNA/BDMA[b] 100/80/0.56
T_{cure}	140°C	140°C	120°C
α_{max}	0.692	0.581	0.600
$K_1{}^c$	0.002561	0.001282	0.063340
$K_2{}^c$	0.092254	0.220259	2.0565
m^c	1.56	2.00	1.86
n^c	3.60	7.50	6.38
$K_1{}^d$	1E-9	—	0.04928
$K_2{}^d$	0.010801	—	0.002595
n^d	1.65	—	2
$K_1{}^e$	0.003321	0.001417	0.105027
$K_2{}^e$	0.026438	0.014274	0.035403
n^e	1.03	1.30	1.18

[a] MIR data.
[b] NIR data.
[c] Equation (4).
[d] Equation (5).
[e] Equation (6).

sample support (a quartz window in the NIR and a KBr window in the MIR). Accordingly, the kinetic effect could be related either to a thickness effect or to a catalytic activity of KBr in the curing process. Upon consideration of the extent of the change in curing rate, we incline to favor the second hypothesis. A catalytic effect of the KBr window has already been proposed to explain the faster curing rates observed by FTIR spectroscopy with respect to calorimetric techniques in the case of bifunctional[19] and tetrafunctional[20] epoxies cured with anhydrides. To our knowledge, this is the first time that the same behavior is reported for amine-cured epoxy resins.

On the basis of the above considerations, NIR spectroscopy should be preferred over MIR spectroscopy for kinetic analysis, since the latter may give unrealistically high values of the kinetic parameters. This conclusion seems relevant since, to date, most of the experimental work was carried out in the MIR frequency range.[21]

The kinetic parameters evaluated so far compare quite favorably with those from isothermal calorimetric measurements. For instance, Barton[22] reported, for a 100/32.8 TGDDM/DDS formulation, K_1 values ranging from 0.015 to 0.110 min^{-1} at temperatures ranging from 172 to 217°C. An activation energy of 80.4 kJ mol^{-1} was evaluated from the above data, which yielded a K_1 value at 140°C equal to 0.00278 min^{-1}. Analogously, according to the Barton's analysis, K_2 at 140°C was equal to 0.0185 min. Although the differences among the spectroscopic and calorimetric rate constants are modest, they are believed to be significant. A critical comparison between them to establish which set of values is the most reliable is considered very relevant since, up to now, the calorimetric parameters are employed almost universally for predictive purposes in designing the processing schedules. A forthcoming article will be entirely devoted to this issue.

Preliminary results on the TGDDM/MNA system are reported in Figure 9. In light of the conclusions drawn for the amine-cured system, the conversion profile was determined by NIR spectroscopy.

It is worth noting that the adopted models are less realistic for an anhydride-cured system, since, in this case, the curing process cannot be considered autocatalytic. However, fitting by these models has been attempted, since the Kamal approach has been considered of general applicability and has been employed successfully for a wide range of thermosetting systems.[23]

As expected, the coincidence of the predicted curves with the experimental data is worse than in the case of the TGDDM/DDS system (see Figs. 7 and 8). In particular, all three models describe quite accurately the kinetic behavior of the system up to α values of about 0.5. Afterward, models (4) and (5) deviate markedly, while model (6) represents, once again, the best compromise over the

Figure 9 Comparison among the experimental $\alpha - t$ curves and the predictions of the various kinetic models, relative to the TGDDM/MNA system cured at 120°C, as monitored in the NIR interval: (⊙) experimental data points; (continuous line) model (4); (dashed line) model (5); (dotted line) model (6).

whole conversion range. In summary, model (6) can still be considered a reliable approximation for predictive purposes. It is clear that more sophisticated models are necessary to improve their simulation capabilities, but their development will require a clearer understanding of the complex reaction mechanism of the curing process. In this respect, MIR and NIR spectroscopy are expected to play a fundamental role, and work is in progress in our laboratory along these lines.

CONCLUSIONS

In the present contribution, we carried out an isothermal kinetic analysis by NIR and MIR spectroscopy on two TGDDM-based epoxy formulations. Several kinetic models were applied to test their capability to correctly simulate the kinetic behavior of the systems under investigation. The conclusions drawn may be summarized as follows:

- For the TGDDM/DDS system, reasonably good results were obtained by all the employed models. However, the best fit between the experimental data and the model predictions is achieved by using a modified Kamal equation which takes into account both the autocatalytic nature of the curing process and the limiting diffusional effect at high conversions.

- No agreement has been found between the MIR and NIR data. In particular, higher values of the curing rate and of the final conversion were obtained by the MIR analysis. This effect was tentatively attributed to a catalytic activity of the KBr substrate used as window material in the MIR experiment.

- The models employed are less realistic for anhydride-cured systems and, in fact, they give a poorer representation of the experimental results. However, the modified Kamal equation which takes into account the diffusional effect can still be considered a useful approximation for predictive purposes.

REFERENCES

1. Rhodes, M. S. SAMPE J 1993, 29, 7.
2. Khanna, U.; Cha, M. J. J Appl Polym Sci 1993, 50, 1635.
3. Park, W. H.; Lee, J. K. J Appl Polym Sci 1998, 67, 1101.
4. Park, W. H.; Lee, J. K.; Kwon, K. J. Polym J 1996, 5, 407.
5. Bokare, U. M.; Ghi, K. S. J Polym Sci Polym Chem Ed 1980, 18, 857.
6. Morgan, R. J.; Mones, E. T. J Appl Polym Sci 1987, 33, 999.
7. Tsou, A. H.; Peppas, N. H. J Polym Sci Polym Phys Ed 1988, 26, 2043.
8. Rogers, M. G. J Appl Polym Sci 1972, 16.
9. Soika, S. A.; Moniz, W. B. J Appl Polym Sci 1976, 20, 1977.
10. Shmorhun, M.; Jamieson, M. A.; Simha, R. Polymer 1988, 29, 1960.
11. St John, N. A.; George, G. A. Polymer 1992, 33, 2679.
12. Min, B.-G.; Stachurski, Z. H.; Hodgkin, J. H.; Heath, G. R. Polymer 1993, 34, 3620.
13. Tadros, R.; Timm, D. C. Macromolecules 1995, 28, 7441.
14. Strehmel, B.; Younes, M.; Strehmel, V.; Wartewig, S. Prog Colloid Polym Sci 1992, 90, 83.
15. Prime, R. B. Polym Eng Sci 1973, 131, 365.
16. Mijovic, J.; Andjelic, S. Polymer 1995, 36, 3783.
17. Musto, P.; Martuscelli, E., Ragosta, G.; Russo, P.; Scarinzi, G., submitted for publication in Polymer.
18. Kamal, M. R.; Sourour, S. Polym Eng Sci 1973, 13, 59.
19. Woo, E. M.; Seferis, J. C. J Appl Polym Sci 1990, 40, 1237.
20. Corcuera, A.; Mondragon, I.; Riccardi, G. C.; Williams, R. J. J. J Appl Polym Sci 1997, 64, 157.
21. Mertzel, E.; Koenig, J. L. Adv Polym Sci 1986, 75, 73–112.
22. Barton, J. M. Br Polym J 1986, 18, 37.
23. Dell'Erba, R.; Martuscelli, E.; Musto, P.; Ragosta, G.; Leonardi, M. Polym Networks Blends, 1997, 7, 1.