

Influence of Liquid Media on Lifetime Predictions of Nitrile Rubber

Gary S. Buckley,¹ C. Michael Roland²

¹Department of Physical Sciences, Cameron University, Lawton, Oklahoma 73505

²Naval Research Laboratory, Chemistry Division Code 6120, Washington, District of Columbia 20375-5342

Correspondence to: C. M. Roland (E-mail: mike.roland@nrl.navy.mil)

ABSTRACT: Evaluating a material's suitability for an application includes determination of its expected service lifetime. For alternative fuels, this entails assessing, *inter alia*, their effect on the durability of polymeric engine components, e.g., seals, gaskets, and O-rings. When this is governed by thermally activated chemical deterioration, the conventional approach to characterizing aging is laboratory measurements of property changes of the polymer subjected to accelerated conditions (usually higher temperatures), with the data analyzed by an Arrhenius analysis. However, this method is inefficient and time-consuming when the number of candidate alternative fuels is large. Herein, we test the hypothesis that the activation energy governing thermal oxidation of elastomeric engine components is independent of the fuel; thus, while the aging rate may vary, the effect of temperature is independent of the contacting liquid. Accelerated testing of the thermal oxidation of nitrile rubber O-rings were carried out in three liquids, including a fossil fuel and a bio-fuel. The activation energy obtained from changes in crosslink density, = 82 kJ/mol, was the same for all liquids and consistent with the broad range of literature values for similar compounds aged in air. This result suggests the possibility that estimates of the lifetime of polymeric engine components require only a single accelerated aging test, with the known activation energy used to predict the durability at the service temperature. This would represent at least an order of magnitude reduction in testing requirements. The extension of the approach to the general aging of polymers exposed to different environments is obvious. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40296.

KEYWORDS: ageing; elastomers; swelling

Received 2 October 2013; accepted 12 December 2013

DOI: 10.1002/app.40296

INTRODUCTION

Interest continues in developing alternatives to fossil fuels, including gasoline, jet, and diesel fuels, notwithstanding the many challenges, which include, among others, the availability of sufficient quantities, the potential effect of alternative fuels on the combustion dynamics, and their compatibility with engine components. This article addresses one aspect of the last, the effect of the fuel on the durability of polymeric components (e.g., rubber seals, gaskets, and O-rings). Since presently there is no alternative fuel "of choice," the compatibility of any candidate fuel with non-metallic engine parts must be determined empirically by aging tests and swelling/extraction measurements; however, to carry out the necessary experiments on every potential alternative fuel with each rubber component would be an extensive undertaking, especially given the myriad other requirements of a fuel. The approach examined herein is to circumvent the problem by using accelerated aging experiments that rely on the assumption that the effect of temperature on aging is a characteristic of the elastomer, independent of the fuel. This means that the activation energy, E_a , for thermal oxidative

degradation of the polymeric components is a material property, equivalent for different fuels and even consistent with the value measured in the absence of any liquid. If this assumption is verified, the prediction of lifetimes of non-metallic components exposed to an alternative fuel is reduced to a single accelerated aging measurement of the material in that fuel.

The fuel (or a solvent) in which a polymer compound is immersed can have a direct effect on aging through the degree of swelling, and hence expansion of the chain molecules. This expansion potentially increases the reactivity, as mechanical stress on the polymer chain acts in concert with thermal fluctuations to overcome the strength of backbone bonds¹; however, the effect is only significant for large stresses that distort bond lengths and angles. For elastomers, chain expansion can be accommodated by low energy conformational changes. Solvents can also play a role through their effect on antioxidants and other additives, both directly and by extraction.²⁻⁴ Another possible mechanism for a fuel-dependent aging rate is the potential influence of contaminant species in the fuel, particular metals, on the oxidation susceptibility of the polymer.^{5,6} So generally,

the rate of oxidative degradation is expected to be affected by swelling and solvent extraction, but not necessarily its temperature-dependence. That is, while aging of the polymer *per se* can depend on the fuel, the only requirement for our method is that the effect of temperature on the aging rate is not affected; thus, a material-specific temperature coefficient can be used to extrapolate short-term laboratory aging data to service lifetimes. The extrapolation of the single test result in order to predict the service life can be done without the need to determine E_a of the material in each potential fuel. The number of experiments for any candidate fuel would thus be reduced more than tenfold.

For our study, we chose commercial O-rings based on nitrile rubber (NBR). A random copolymer of acrylonitrile and butadiene repeat units, the polarity of NBR makes it a common material for sealing components in gasoline engines. The polymer is unsaturated, and the reactivity of the double bonds governs its heat resistance and oxidative stability.^{7–9} There is a wealth of published accelerated aging results on NBR compounds. In our experiments, the degradation process was accelerated by carrying out the aging at elevated temperature. The assumption was made that oxygen availability was not a rate-determining factor, as supported by the isotropic oxidation of samples, which were exposed to continuous air flow during the aging. Over a relatively short time scale (few weeks), property deterioration was induced and quantified, and the results analyzed using the Arrhenius equation

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where $k(T)$ is the reaction rate at a temperature T (in Kelvin) at which a property of the material is changing due to aging, k_0 is a material constant, and R ($=8.314$ J/deg mol) is the gas constant. The obtained value of E_a enables extrapolation of short time, high temperature property changes to the changes expected for long-time, lower-temperature exposure. Application of the Arrhenius equation to accelerated aging data has a long history in the field of rubber.^{10–14} Gillen et al.¹⁵ reviewed the Arrhenius method of lifetime prediction, including consideration specific to the aging of O-rings.¹⁶ Thermal oxidation of NBR increases the degree of crosslinking,⁹ so the typical property changes are increased hardness and reduced elongation. Even when more than one reaction occurs, it has been shown, specifically for NBR,^{17–19} that the Arrhenius method can be applied, yielding an effective activation energy. To simplify the present study, we neglect the effect of extraction of antioxidants, stabilizers, plasticizers, etc. from the NBR, on the assumption that engine components have been in extended use prior to introduction of a new fuel type. This means that the relevant aging herein is that occurring after any induction period associated with transient changes in material composition. We apply the Arrhenius analysis to aging data for different solvents. This requires determination of the time constant for property loss at a number of temperatures in each solvent. If our hypothesis is correct, the obtained E_a is independent of the fuel, and only a single test—one aging experiment at one temperature—would be required to predict the service life in any other liquid. Many

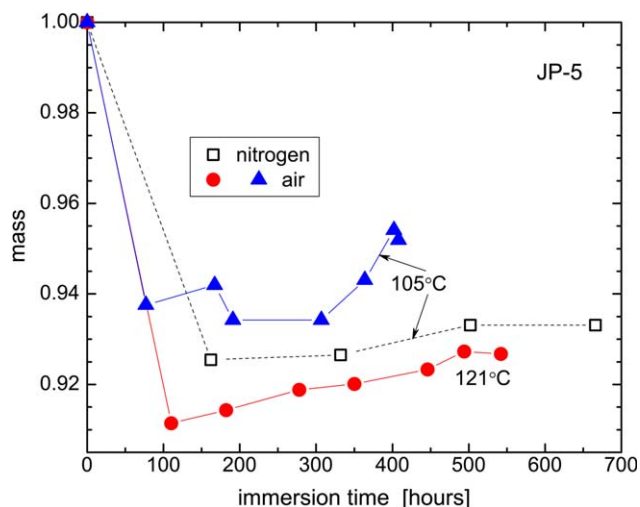


Figure 1. Mass change of NBR sample immersed in JP-5 jet fuel at the indicated temperatures and purged with nitrogen or air. The small increase in the presence of nitrogen is ascribed to residual oxygen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

standardized tests are based on such single point measurements; however, exposure to an arbitrary temperature for an arbitrary time cannot yield service life predictions, unless the activation energy is known.

EXPERIMENTAL

Aging was carried out in three solvents: JP-5 jet fuel (MIL-DTL-5624), a mixture of alkanes, naphthenes, and aromatic hydrocarbons; Camelina, a biofuel from the *Camelina sativa L.* plant²⁰; and the solvent dodecane. In each of the three liquids, 4–5 aging temperatures were employed. Samples in the form of O-rings (Mil-Spec 29513-210; 3.5 mm wide; 25.7 mm outside diameter) were immersed in a given liquid in round bottom flasks maintained at a fixed temperature, with a continuous stream of air bubbled through the solvent. Temperature stabilization over the course of an aging period was $\pm 2^\circ\text{C}$ or better; reported temperatures herein are the time-weighted averages. At various intervals, samples, typically three, were removed for testing. Swelling in toluene was used to determine the crosslink density. Mechanical measurements employed an Instron 5500R, with a nominal tensile strain rate of 0.4 s^{-1} . The O-rings were held in a fixture with rollers to eliminate pinching. Subsequent to the tensile testing, swelling measurements were carried out on the O-rings using toluene. The swelling of the O-rings was isotropic, indicating the absence of any heterogeneous aging due to diffusion-limited oxidation.²¹

RESULTS

Aging of NBR in the presence of solvents is at least a two-step process. Initially, the liquid swells the compound, extracting additives (e.g., plasticizers and stabilizers) and any uncrosslinked polymer; this causes a reduction in mass. To minimize leakage during service, elastomeric engine components should have low compatibility with fuels, including alternative fuels.^{22,23} The

Table I. Time for Onset of Thermal Oxidation Dominance of Aging Response ($T = 130^{\circ}\text{C}$)

Liquid	JP-5	Camelina	Dodecane
Induction time (hr)	45	130	190

O-rings swelled moderately in the three liquids of the present study: less than 10% in Camelina, less than 20% in dodecane, and less than 50% in JP-5. Concurrent with the fluid extraction of the elastomer compound, oxidation increases the mass as reaction products bond to the polymer. The net result is an initial loss of material, followed by a steady increase in mass at longer times. This is illustrated in Figure 1, showing the weight change of O-rings immersed in JP-5 jet fuel that is purged with either air or nitrogen; in the absence of oxygen, the extraction process dominates. Similar behavior was observed in Camelina and dodecane: an initial weight loss followed by a slow increase thereafter.

Our objective is to determine any effect of the liquid on the activation energy for thermal oxidative degradation. The aging process directly affects both the modulus and the failure strain, ϵ_{brk} . For the application of interest herein, the aging behavior of polymeric components subjected to changes in liquid exposure, the induction time is irrelevant, since the materials will be far enough along in their lifetime that extractable components of the compound will be gone. (JP-5, Camelina, and dodecane all extract on the order of 8.5–9.0% of the mass of the samples prior to the onset of significant oxidation.) Thus, to characterize the effect of the liquid on the aging behavior we consider only longer times. Representative induction periods for 130°C , determined by the intersection of linear extrapolation of short- and long time property changes, are listed in Table I. The aging data after the induction phase can be described as a first-order rate process,

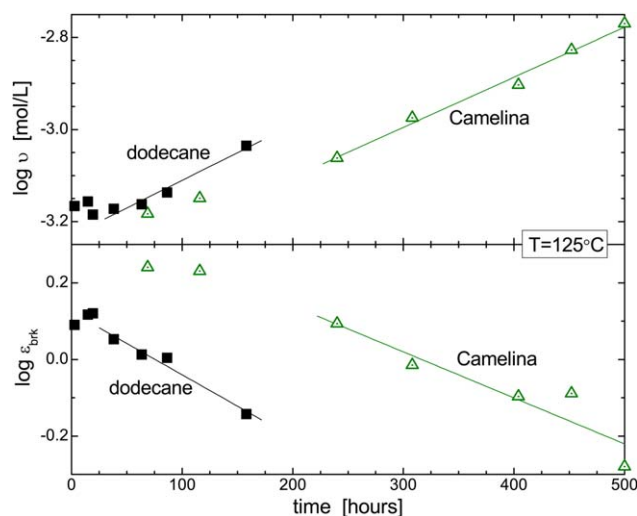


Figure 2. Comparison of aging of NBR in two liquids at the indicated temperature, as reflected in changes in the number density of network chains (top) and the failure strain (bottom). The fitted line defines the aging rate following an induction period that depends on both the liquid and temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with representative results shown in Figure 2 for Camelina and dodecane at 125°C . Note that while the degree of aging in the two liquids is quite different, the aging rates beyond the induction phase are similar. An aging time constant is determined from the slope at longer times of these semi-logarithmic plots.

Figure 3 shows the change at longer times in the elongation to break after aging in JP-5 at four temperatures. Although ϵ_{brk} is systematically reduced by thermal oxidation, there is a complication, in that this quantity does not vary linearly with the degree of crosslinking. This is seen in Figure 4 showing the failure strain of various elastomers^{12,24,25} including the present data for NBR, as a function of modulus during aging in air. In all cases the aging mechanism is oxidative crosslinking, which is proportional to the compound modulus²⁶; however, whereas the modulus continues to increase monotonically, the failure strain begins to level off at higher degrees of crosslinking. The nitrile samples of the present study show similar behavior, with data for JP-5 at 130°C included in Figure 4. This disconnect between crosslinking and failure strain is due to the latter's being driven by the "weakest link" in randomly crosslinked networks; that is, failure occurs upon rupture of the shortest network chains.^{26,27} At very low degrees of crosslinking, a similar lack of proportionality between modulus and failure strain would also be observed.²⁸ Unlike ϵ_{brk} , the modulus of a rubbery polymer remains proportional to the number density of network chains, ν , to very high degrees of crosslinking. ν is also more directly connected to the oxidation process, and thus it is the parameter chosen herein to quantify the degradation.

Swelling experiments were done to determine crosslink density. The polymer volume fraction in the swollen state ranged from $\sim 37\%$ for the unaged O-rings to values after aging exceeding 50%. These polymer concentrations are sufficiently high that, notwithstanding their swollen state, the chain segments experience steric constraints (excluded volume interactions) with

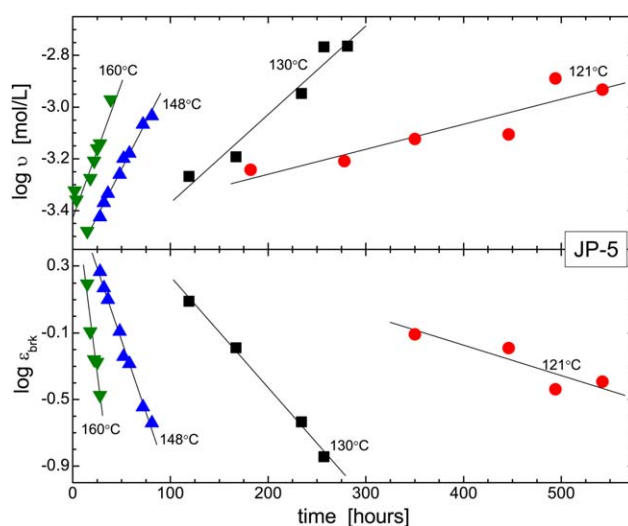


Figure 3. Change in the crosslink density (top) and elongation to failure (bottom) in JP-5 fuel at various temperatures. The slope of the fitted lines defines the aging rate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

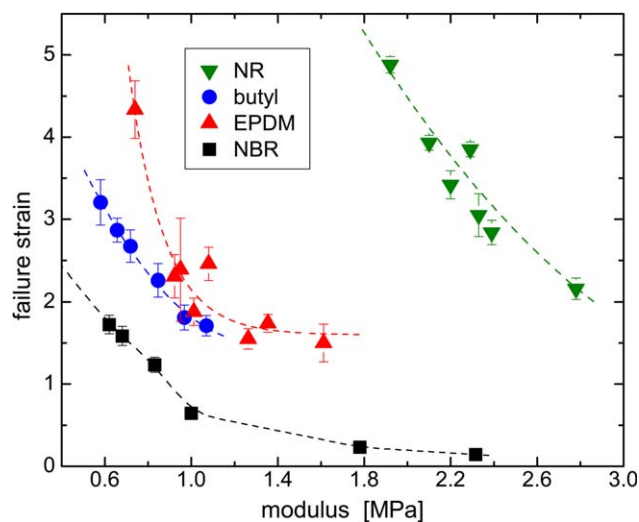


Figure 4. Failure strain versus modulus for elastomers subjected to oxidative crosslinking.^{12,18,19} At high degrees of degradation the elongation levels off, while the modulus continues to increase. The error in the data points does not exceed the symbol size. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

neighboring segments. These interactions limit fluctuations of the chains, and under such conditions the network can be assumed to deform affinely (i.e., proportionality between macroscopic and microscopic strains). The relationship between the network chain concentration and swelling is then given by

$$v = \frac{\ln(1 - v_r) + v_r + \chi v_r^2}{V_s(2v_r/f - v_r^{1/3})} \quad (2)$$

In eq. (2) v_r is the volume fraction of polymer in the swollen sample, V_s the solvent molar volume (=106.1 mL/mol), χ the polymer–solvent interaction parameter (=0.45), and f the functionality of the network junctions (assumed to be 4). The opposite assumption from affine behavior, that the network chains freely fluctuate from their average positions, would give twofold larger v .²⁶ Representative results for v from eq. (2) versus aging time are shown in Figure 3. The slopes of the semi-logarithmic plots define the temperature-dependent rate constant, $k(T)$.

We are now in position to test the premise that lifetime predictions for NBR undergoing oxidative degradation can be made using an activation energy that is independent of the solvent or contacting liquid. The kinetics of the changes in the network chain density was calculated according to

$$v = v_0 \exp[k(T)t] \quad (3)$$

where v_0 is the value for the virgin material and t is time. In Figure 5 $k(T)$ is plotted versus reciprocal temperature [eq. (1)], with the slopes yielding the activation energies listed in Table II. There is no significant difference in E_a for the three liquids.

DISCUSSION

After an induction period associated with extraction from the elastomer of small molecule components and unattached chains, oxidative crosslinking becomes the dominant mechanism for

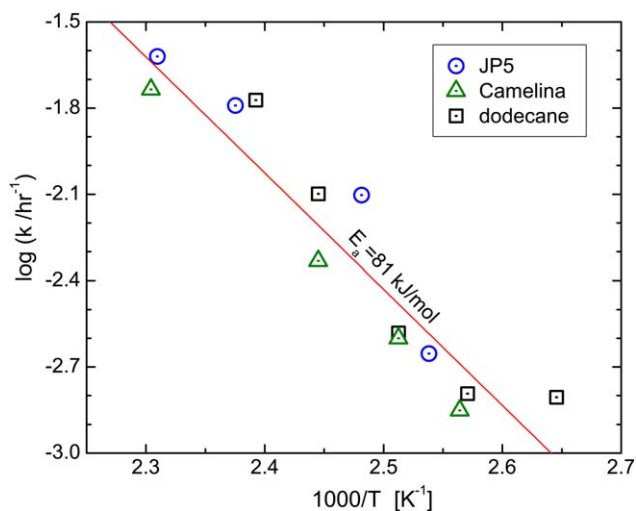


Figure 5. Arrhenius plot of the rate constant describing the change of crosslinking in NBR O-rings exposed to the indicated solvents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

changes in the properties of the NBR. The rate of oxidative degradation depends on the fluid in which the material is immersed; moreover, the constrained conditions of O-rings during service could affect swelling and hence aging behavior. However, we find herein that the effect of temperature on the aging is independent of the nature of the absorbed liquid. The mean value of the activation energy determined for the present material, $E_a = 82$ kJ/mol, is consistent with literature values, which generally fall in the range from 74 to 92 kJ/mol^{17,19,29,30} for the dry material aged in air. Since the oxidative behavior of NBR depends on the chemical composition (acrylonitrile content) of the copolymer,^{31,32} generic values of E_a for NBR are not useful for lifetime predictions. However, an activation energy can be determined for a given compound that will be “universal” for that material (i.e., independent of fluid), at least over the studied range of temperatures. Of course, at very high temperatures ($\geq 160^\circ\text{C}$), additional chemical reactions can arise, causing significant changes in E_a .^{18,33}

The utility of a temperature-insensitive activation energy is that for any candidate alternative fuel, its influence on aging of non-polymeric engine components can be assessed from measurement of $k(T)$ at a single temperature. The temperature selected can be sufficiently high that property changes due to aging transpire rapidly; this can enable efficient screening of potential replacement fuels.

Table II. Arrhenius Activation Energies for NBR O-Rings

Liquid	E_a (kJ/mol)
	Crosslink density
JP-5	81 ± 18
Camelina	81 ± 2
Dodecane	83 ± 17

SUMMARY

It was determined that the activation energy for oxidative degradation of a particular NBR O-ring has a value, 82 kJ/mol, that is invariant to the immersion liquid. This result, if generally valid, means that this E_a can be employed to extrapolate laboratory-determined aging rate, to yield a prediction for the lifetime of the component at the service temperature in any liquid of interest. The efficiency of this approach to estimating service lifetimes is important in situations such as alternative fuel development, in which the number of candidates is large and thus there is a need to minimize testing.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research. GSB acknowledges a fellowship through the Office of Naval Research and financial support through a Cameron University research grant.

REFERENCES

1. Beyer, M. K.; Clausen-Schaumann, H. *Chem. Rev.* **2005**, *105*, 2921.
2. Degteva, T.G.; Kuzminskii, A.S. *Rubber Chem. Technol.* **1956**, *29*, 1266.
3. Miller, D. E.; Gozdoff, M. M.; Shaheen, F. G.; Dean, P. R. Rubber Division National Meeting, Cincinnati, OH, 1988, Paper No. 63.
4. Hashimoto, K.; Maeda, A.; Hosoya, K.; Todani, Y. *Rubber Chem. Technol.* **1998**, *71*, 449.
5. Dunn, J. R. *Rubber Chem. Technol.* **1978**, *51*, 686.
6. Brown, R. *Physical Testing of Rubber*, 3rd ed.; Chapman & Hall: London, **1996**.
7. Grassie, N.; Heaney, A. *Rubber Chem. Technol.* **1975**, *48*, 678.
8. Datta, R. N.; Huntink, N. M.; Datta, S.; Talma, A. G. *Rubber Chem. Technol.* **2007**, *80*, 436.
9. Kuczkowski, J. A. *Rubber Chem. Technol.* **2011**, *84*, 273–295.
10. Chabba, S.; van Es, M.; van Klinken, E. J.; Jongedijk, M. J.; Vanek, D.; Gijsman, P.; van der Waals, A. C. L. M. *J. Mater. Sci.* **2007**, *42*, 2891.
11. Malek, K. A. B.; Stevenson, A. J. *Nat. Rubber Res.* **1992**, *7*, 126.
12. Mott, P. H.; Roland, C. M. *Rubber Chem. Technol.* **2001**, *74*, 79.
13. Wall, L. A.; Flynn, J. H. *Rubber Chem. Technol.* **1962**, *35*, 1157.
14. Sircar, A. K. *Thermal Characterization of Polymeric Materials*, 2nd ed., Academic Press: NY, **1997**.
15. Gillen, K. T.; Celina, M.; Clough, R. L.; Wise, J. *Trends Polym. Sci.* **1997**, *5*, 250.
16. Gillen, K. T.; Bernstein, R.; Wilson, M. H. *Polym. Degrad. Stab.* **2005**, *87*, 257.
17. Budrugaec, P. *Polym. Degrad. Stab.* **1992**, *38*, 165.
18. Budrugaec, P.; Segal, E. *Thermochim. Acta* **1991**, *184*, 25.
19. Roland, C. M. *Plast. Rubber Compos.* **2009**, *38*, 349.
20. Moser, B. R. *Lipid Technol.* **2010**, *22*, 270.
21. Gillen, K. T.; Keenan, M. R.; Wise, J. *Die Angew. Makro. Chem.* **1998**, *262*, 83.
22. Corporan, E.; Edwards, T.; Shafer, L.; DeWitt, M. J.; Klingshirn, C.; Zabarnick, S.; West, Z.; Striebich, R.; Graham, J.; Klein, J. *Energy Fuels* **2011**, *25*, 955.
23. Gormley, R. J.; Link, D. D.; Baltrus, J. P.; Zandhuis, P. H. *Energy Fuels* **2009**, *23*, 857.
24. Buckley, G. S.; Fragiadakis, D.; Roland, C. M. *Rubber Chem. Technol.* **2011**, *84*, 520.
25. Giller, C. B.; Roland, C. M. *Macromolecules* **2013**, *46*, 2818.
26. Roland, C. M. *Viscoelastic Behavior of Rubbery Materials*; Oxford Univ. Press: New York, **2011**.
27. Bueche, F. *Physical Properties of Polymers*; Wiley-Interscience: New York, **1962**.
28. Roland, C. M. *Rubber Chem. Technol.* **2013**, *86*, 351.
29. Wise, J.; Gillen, K. T.; Clough, R. L. *Polym. Degrad. Stab.* **1995**, *49*, 403.
30. Morrell, P. R.; Patel, M.; Skinner, A. R. *Polym. Test.* **2003**, *22*, 651.
31. Goh, S. H. *Thermochim. Acta* **1987**, *113*, 387.
32. Pazur, R. J. *Rubber Chem. Technol.*, to appear.
33. Jovanovic, V.; Budinski-Simendic, J.; Samardzija-Jovanovic, S.; Markovic, G.; Marinovic-Cincovic, M. *Chem. Ind. Chem. Eng. Quart.* **2009**, *15*, 283.