Peel Adhesion of Natural Rubber Bonded to Polyethylene Terephthalate: Effect of Crosslinking on Rate/Temperature Response

G. R. Hamed[a]; W. Preechatiwong[a]

[a] College of Polymer Science and Polymer Engineering, The University of Akron, Akron, OH, USA

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G. R. HAMED* and W. PREECHATIWONG

*College of Polymer Science and Polymer Engineering,
The University of Akron, Akron, OH 44325-3909, USA*

Laminates consisting of natural rubber (NR) sandwiched between cloth fabric and polyester film were pulled apart at various rates and temperatures in a T-peel geometry. Peel energies for joints containing uncrosslinked or lightly-crosslinked NR did not obey simple time-temperature superposition. This behavior is attributed to strain-induced crystallization during peeling. However, when the rubber was highly crosslinked, strain crystallization seems to be absent, as peel energies now can be WLF shifted to form a mastercurve.

Keywords: Natural rubber; Peel adhesion; Anomalous rate/temperature response; Strain-crystallization

INTRODUCTION

Peel adhesion energies of single-phase, non-crystallizing elastomers adhered to rigid substrates obey time-temperature superposition [1–6]. Schematic data illustrating the principle are given in Figure 1, where peel energies, P, for a typical crosslinked, amorphous elastomer are shown at various test rates and temperatures. Test temperature increases for isotherms from top to bottom. Peel forces

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*Corresponding author. Tel.: 330-972-6831, Fax: 330-972-5290, e-mail: hamed@polymer.uakron.edu
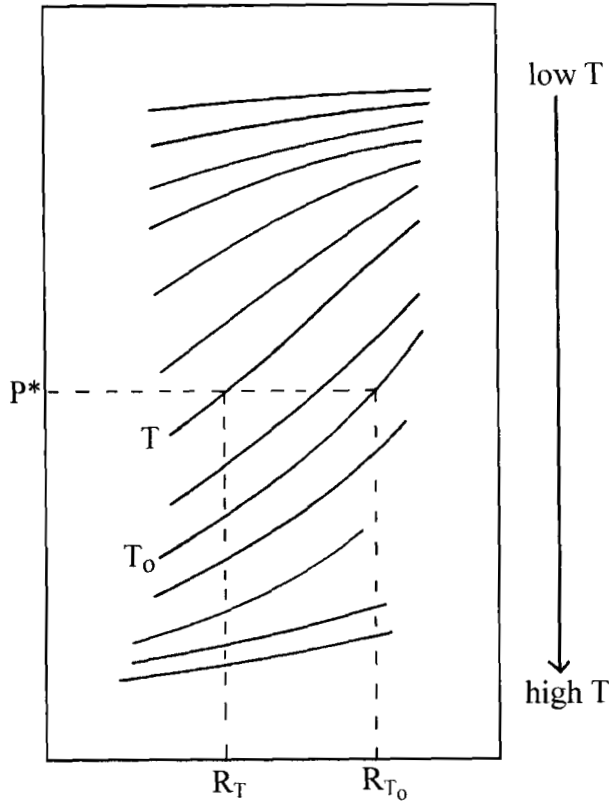
FIGURE 1 Schematic of peel energy at various test rates and temperatures for a crosslinked, amorphous elastomer adhered to a solid substrate.

are a *direct* measure of energy dissipation during fracture and they increase with increasing peel rate and decreasing temperature. Consider the value P^*, which is obtained by testing at arbitrary temperature, T, and rate, R_T, or at reference temperature, T_0, and R_{T_0}, *i.e.*,

$$P^* = P(R_T, T) = P(R_{T_0}, T_0)$$

The relaxation of a deformed (*e.g.*, peeling) elastomer is due to chain segmental mobility, which can be modeled by a "jump" frequency, φ. If N is defined as the number of relaxational "jumps" which take place

at the peel front during peeling at rate, R, then,

$$N \propto \frac{\varphi}{R},$$

and, hence,

$$N(R_T, T) \propto \frac{\varphi_T}{R_T}$$

and

$$N(R_{T_0}, T_0) \propto \frac{\varphi_{T_0}}{R_{T_0}}$$

It is now assumed that the same value (P^*) of the peeling energy will be obtained when N is the same at the two different test conditions, *i.e.*,

$$N(R_T, T) = N(R_{T_0}, T_0)$$

so that

$$\frac{R_{T_0}}{R_T} = \frac{\varphi_{T_0}}{\varphi_T}.$$

Note that, in order to have the same peel energy, the ratio of the macroscopic test rates at T_0 and T must be the same as the ratio of the molecular jump frequencies at these temperatures. We now define

$$a_{T_0} \equiv \frac{R_{T_0}}{R_T}.$$

Also, then

$$a_{T_0} = \frac{\varphi_{T_0}}{\varphi_T},$$

where a_T is termed the shift factor and $R_T a_{T_0}$, the reduced rate. Any temperature may be selected as the reference temperature, T_0, and data at each of the other temperatures may be shifted (*one* shift factor for each temperature) to give peel energies at T_0 and (reduced) rate, $R_T a_{T_0}$. The result is a mastercurve of peel energy *versus* reduced rate at temperature T_0 (Fig. 2). (Experimental peel data, corresponding to Figs. 1 and 2, for stereo-irregular polybutadiene adhered to glass, are shown in Ref. [4].)
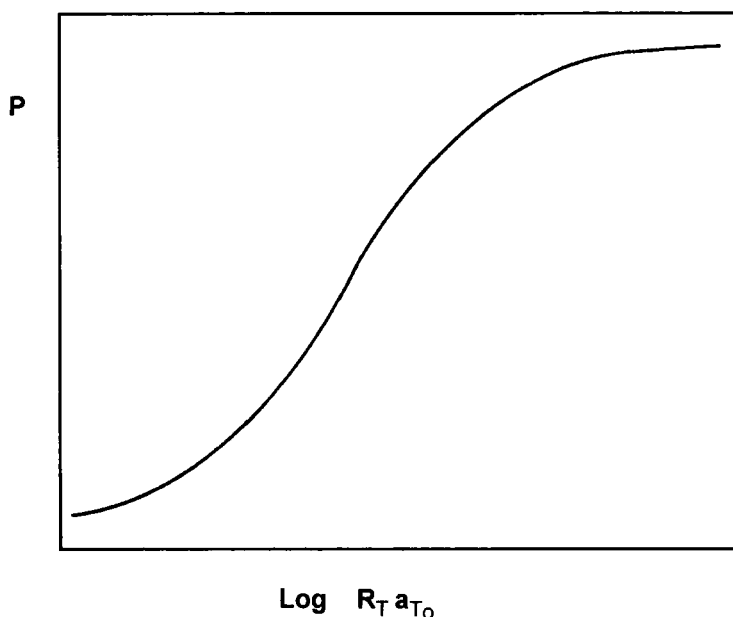
FIGURE 2 Peel energy mastercurve at T_0 generated by WLF shifting of curves in Figure 1.

Thus, even though *direct* testing of peel energy at T_0 may be limited to a relatively narrow range of test speeds, time-temperature superposition allows prediction of peeling energies: (1) at lower rates by shifting data at $T > T_0$ to the "left" and (2) at higher rates by shifting data at $T < T_0$ to the "right".

Shift factors for the peel energy of both uncrosslinked and crosslinked amorphous elastomers agree with values calculated from the universal WLF equation [7]:

$$\log a_{T_0} = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)}$$

$$c_1 = \frac{900}{c_2}$$

$$c_2 = 51.6 + (T_0 - T_g),$$

where T_g is the glass transition temperature.

In this paper, we study the peel energies at various test rates and temperatures of uncrosslinked and crosslinked natural rubber adhered to polyethylene terephthalate (PET) film (Mylar$^{®}$). When NR is sufficiently crosslinked, the results obey simple time-temperature superposition, but uncrosslinked and lightly crosslinked samples exhibit marked deviance from this principle.

EXPERIMENTAL

Prior to testpiece preparation, the natural rubber (CV60, Akrochem, Akron, OH, USA) was masticated for 10 minutes at 40 rpm in a laboratory internal mixer (Haake Rheocord) using a fill factor of 0.7. Masticated rubber was compression molded between cotton cloth (0.57 mm thick) and Mylar film (77 μm thick) at 140°C. Specimens with uncrosslinked rubber were molded for 20 minutes and those with crosslinked rubber for 2 hours. The crosslinking agent was Trigonox$^{®}$ 17/40B-pd (40% active n-butyl 4,4-di-(tert-butyl peroxy) valerate), and the final rubber thickness was 0.25–0.30 mm. Molded plaques were cut into 25 mm wide strips, which were T-peeled apart at various test rates and temperatures. Specimens were equilibrated at a test temperature for 15 minutes before peeling.

RESULTS AND DISCUSSION

Figure 3 shows peel energy *versus* peel rate at various temperatures for specimens with uncrosslinked NR. Results are qualitatively similar to those obtained by Gent and Petrich [1] for uncrosslinked SBR adhered to PET. Failure changes from visually interfacial (I, open symbols) at lower temperatures and higher peeling rates to visually cohesive (C, filled symbols) tearing within the rubber at higher temperatures and lower rates. Peeling is rather steady except for the transition region (half-filled symbols), where failure is stick–slip. The two half-filled data are average values of initiation and arrest peel energies. The locus of fracture alternates periodically between cohesive (stick) and interfacial (slip) for the datum ($\sim 280 - 60 \, \mathrm{J/m^2}$) at the lower rate, while
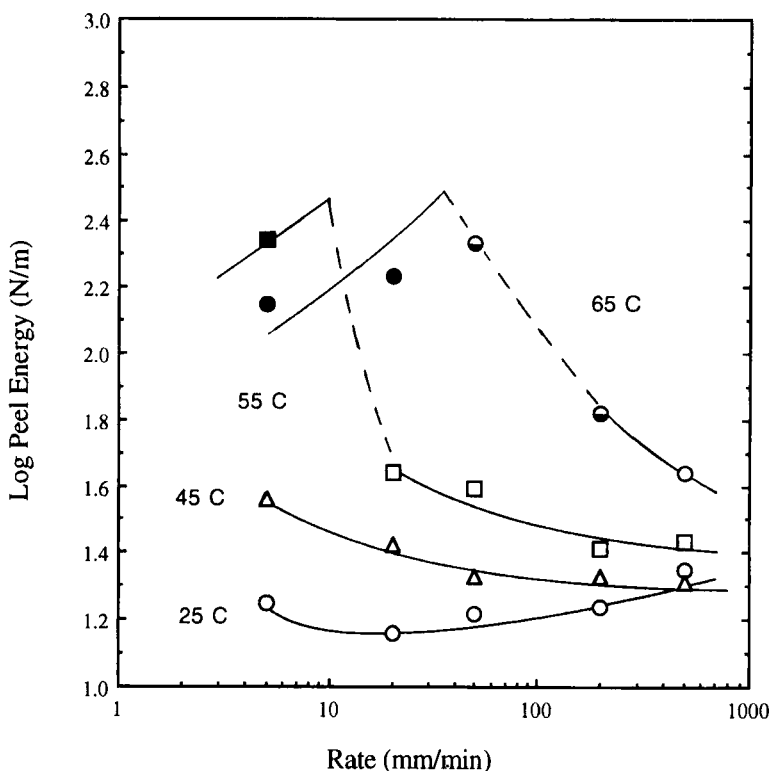
FIGURE 3   Peel energy at various test rates and temperatures for uncrosslinked NR/ PET. Filled symbols: cohesive failure; open symbols: NR/PET interfacial failure; half-filled symbols: stick – slip.

failure, though stick – slip, is all interfacial for the other data point $(\sim 136-40\,\mathrm{J/m^2})$.

Unlike SBR/PET, peel energies for NR do not superpose when shifted according to the universal WLF equation (Fig. 4, $T_0 = 25°\mathrm{C}$). Rather, peel strengths must be shifted much further (to the left) to form a smooth mastercurve (Fig. 5). Gent and Petrich proposed that the C/I transition was due to a change in response of the rubber from entanglement slippage at low rates to "elastic" entanglement coupling at high rates. The drop in peel energy was attributed to an abrupt change in deformation energy at the C/I transition rate. Below this rate, failure occurs by viscous flow of the rubber, involving large irreversible deformation and much energy dissipation. On the other
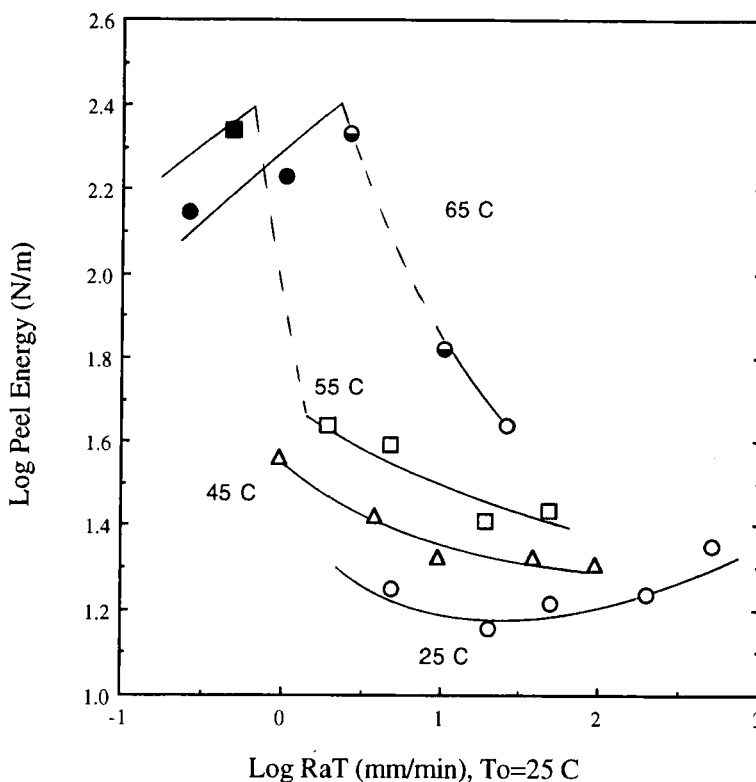
FIGURE 4 Data from Figure 3 shifted according to the WLF equation with $T_0 = 25°C$ and $T_g = -72°C$.

hand, above the critical rate, the elastomer responds in the rubbery plateau regime and "elastic" separation occurs; the rubber layer exhibits essentially no permanent deformation – characteristic of detachment with little energy loss.

Peel energies for lightly-crosslinked NR (0.475 phr peroxide) are shown in Figure 6. Under all conditions, failure is visually interfacial between the rubber and PET; network formation prevents failure by viscous flow. At any given temperature, peel energy increases with increasing test speed – the expected response for simple viscoelasticity. However, quite strikingly, normal time-temperature equivalence (as depicted in Figs. 1 and 2) is not obeyed. WLF shifting would further spread, and not superpose, the data. Indeed, the behavior is
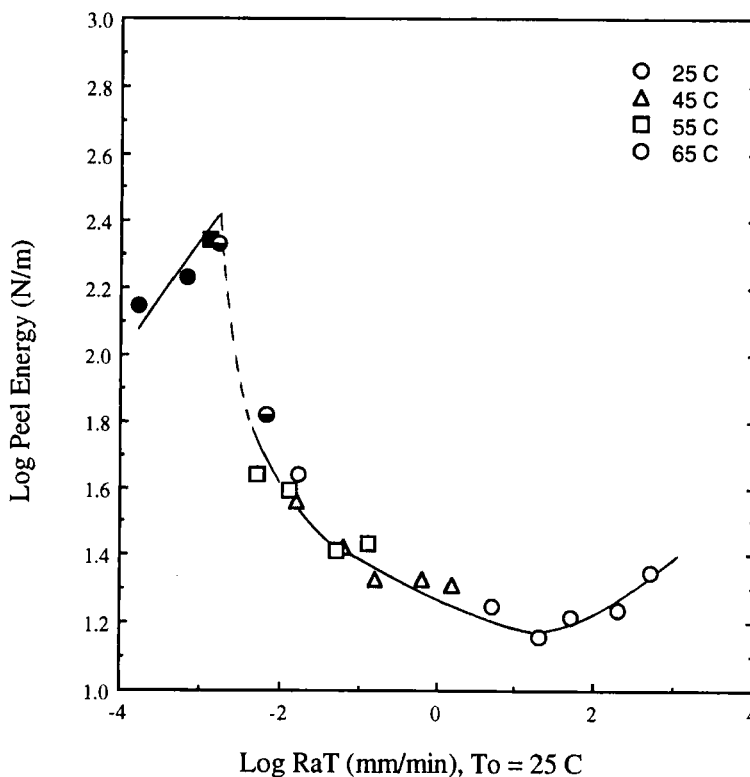
FIGURE 5   Data from Figure 3 experimentally shifted to form a smooth mastercurve with $T_0 = 25°C$.

"anti-WLF", with shifting of high temperature data *to the right* possible to form an apparent, but perhaps fictitious, mastercurve (Fig. 7). A crosslinked amorphous rubber has a simple viscoelastic (time-temperature) response. Elevating temperature decreases peel energy and is equivalent to a certain (from the WLF equation) lowering of test speed. For both changes, molecular jumps at the peel front are increased by the same amount – in the first case, because of an increased jump frequency and, in the second case, because the time for relaxation at the peel front is increased. Clearly, a process which greatly enhances peel strength at elevated temperature must be operative when peeling lightly-crosslinked NR.
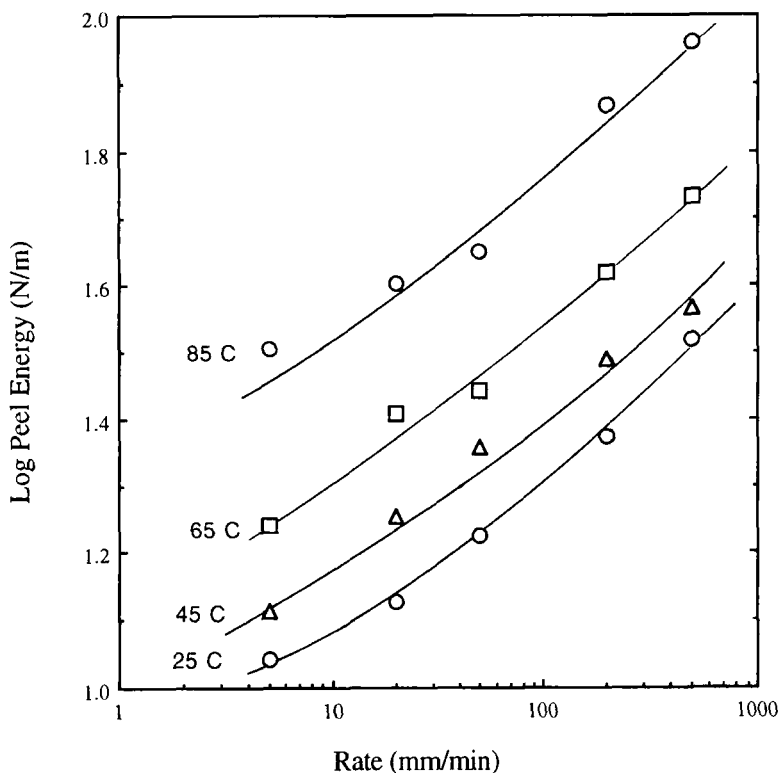
FIGURE 6 Peel energy at various test rates and temperatures for lightly-crosslinked (0.475 phr peroxide) NR/PET. Fracture is always visually interfacial between the NR and PET.

Specimens containing NR with two higher levels (0.95 and 1.9 phr) of peroxide also were tested. Results are shown in Figures 8 and 9. In both cases, mastercurves at $T_0 = 25°C$ could be formed by shifting peel energies at higher temperatures to the left (Figs. 10 and 11). Peel energies in Figure 11 (1.9 phr) were shifted according to the WLF expression.

Shift factors to form mastercurves for uncrosslinked and crosslinked NR are compared in Figure 12. We propose that the deviances of shift factors from WLF predictions are due to strain-crystallization, which influences segmental mobility and energy dissipation during peeling. Strain crystallization of NR is known to depend not only upon strain,
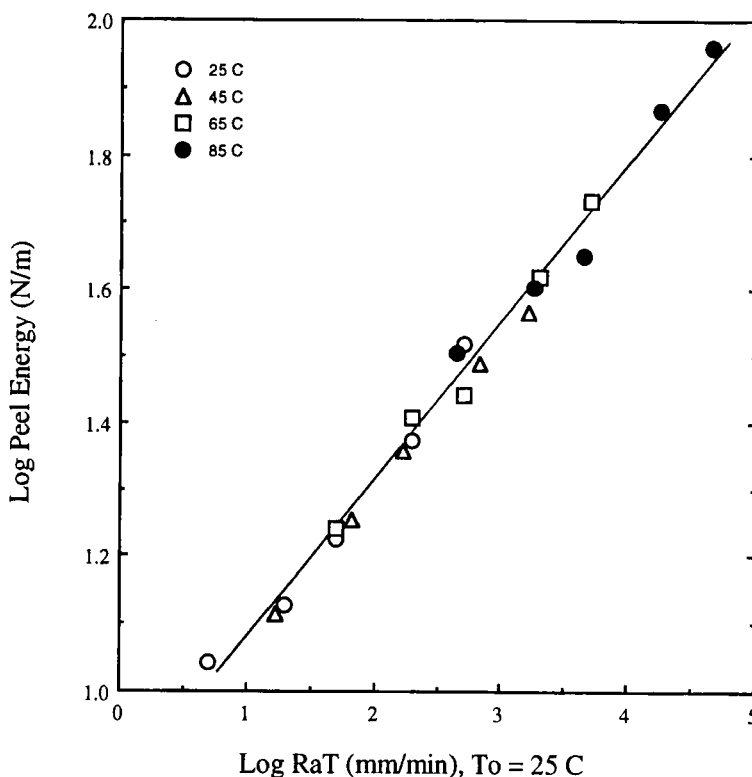
FIGURE 7   Data from Figure 6 experimentally shifted to form a mastercurve at $T_0 = 25°C$.

but also upon temperature, deformation rate, and degree of cross-linking [8]. If the strain rate, $\dot{\varepsilon}$, experienced by an elastomer during peeling is taken as approximately R/t, where R is peel rate and t is rubber layer thickness, then the range of $\dot{\varepsilon}$ used in the present experiments is about 20 to 2000 min^{-1}. It is difficult to determine exact strains during peeling, but examination of the peel front reveals high local strains during detachment of the uncrosslinked or lightly-crosslinked NR. We propose that these strains can be sufficient to cause crystallization. Sufficient crosslinking (1.9 phr peroxide) apparently inhibits crystallization, resulting in simple WLF shifting, as found previously for amorphous elastomers. Furthermore, the NR crosslinked with 1.9 phr of peroxide has the lowest peel forces and is
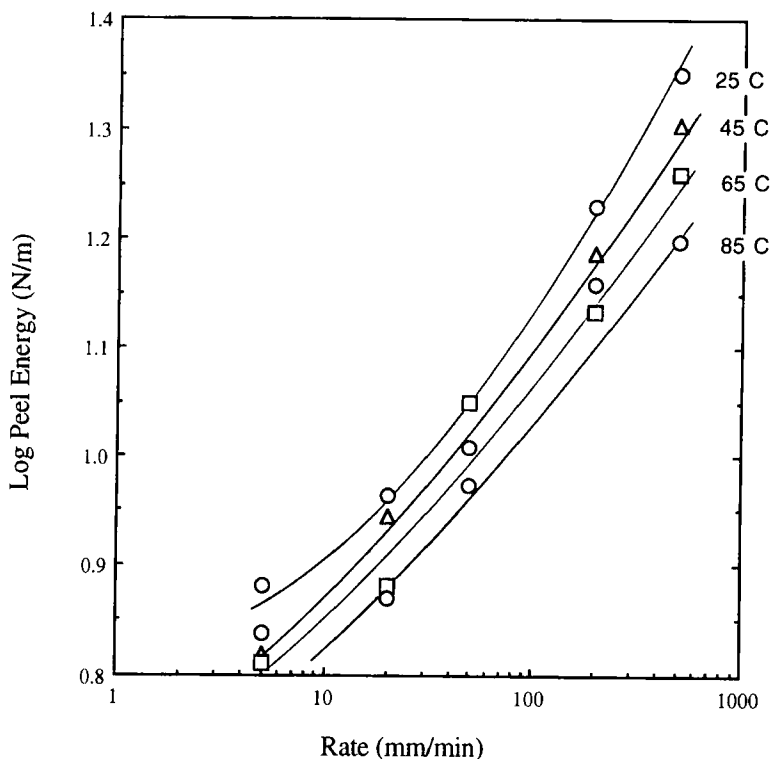
FIGURE 8 Peel energy at various test rates and temperatures for moderately-crosslinked (0.95 phr peroxide) NR/PET. Only visually interfacial fracture occurs.

expected to experience the lowest strains during detachment. This highly-crosslinked NR has low peel strength due to reduction in normal viscoelastic energy dissipation as well as the loss of strain crystallization.

For uncrosslinked NR, peel energies at elevated temperature must be shifted to anomalously low rates to superpose values with the response expected at 25°C. It is inferred that segmental mobility, *relative to that at 25°C*, increases more rapidly at higher temperatures than expected from simple viscoelasticity as predicted by the WLF equation. We hypothesize that this behavior is due to less strain crystallization of uncrosslinked NR at higher temperatures.

On the other hand, crosslinking causes an opposite effect on shifting. For the two less-crosslinked samples (0.475 and 0.95 phr
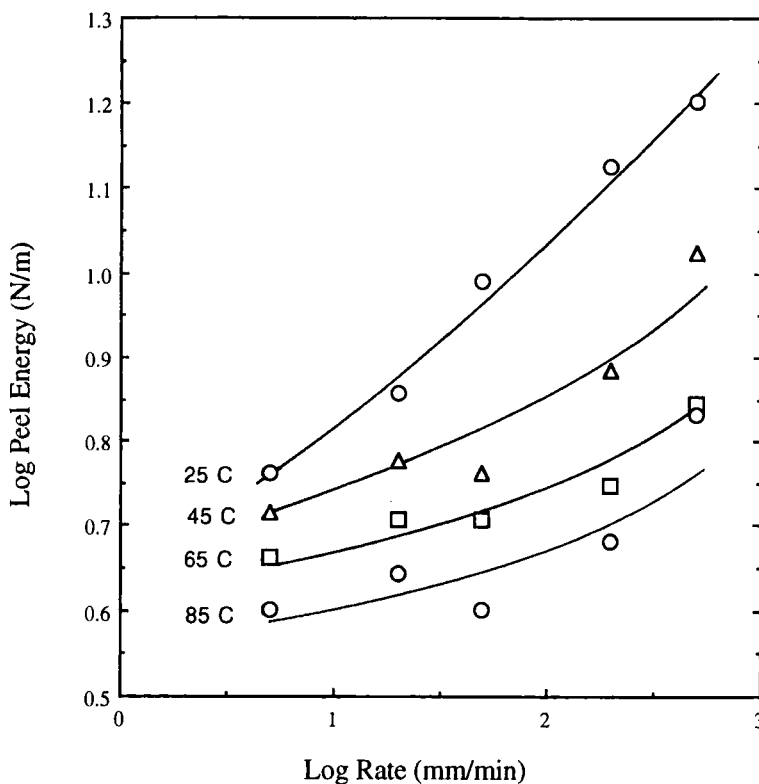
FIGURE 9   Peel energy at various test rates and temperatures for highly-crosslinked (1.9 phr peroxide) NR/PET. Interfacial fracture only.

peroxide), segmental mobility at elevated temperature, *relative to that at 25°C*, decreases more quickly than predicted by the WLF equation. For both the uncrosslinked and lightly-crosslinked samples, we assume that some strain crystallization occurs while peeling, at 25°C. During peeling, the rubber is amorphous as it "enters" the peel front. *While the rubber is amorphous*, its segmental mobility at elevated temperature will increase in accord with the WLF equation. For uncrosslinked NR, this increases entanglement slippage and reduces chain alignment, resulting in less strain crystallization and, hence, further chain mobility compared with that at 25°C. In contrast, for lightly-crosslinked NR, entanglement slippage is prevented because of network formation. Increased "WLF mobility" at elevated
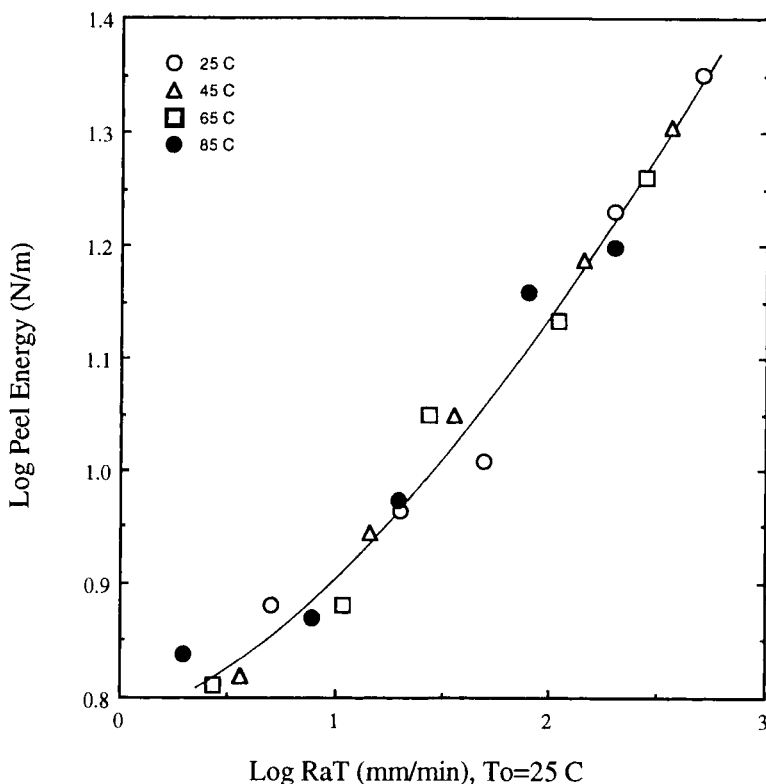
FIGURE 10 Data from Figure 8 experimentally shifted to form a mastercurve at $T_0 = 25°C$.

temperature facilitates chain alignment and increases strain crystal-lization, resulting, *overall*, in decreased chain mobility at detachment.

Although peel energies for uncrosslinked and crosslinked NR ex-hibit contrasting shifting behavior, in both cases peel energies after WLF shifting with $T_0 = 25°C$ are greater than expected. How can less strain crystallization of the uncrosslinked NR and more strain crys-tallization of the lightly-crosslinked NR both enhance peel energies at elevated temperatures? The answer may be due to differences in the way in which energy dissipation arises in the two cases. For the uncrosslinked NR, energy dissipation may arise principally from entanglement slippage and viscous flow, which would be hindered by crystallization. In effect, crystallites act as crosslinks. On the other
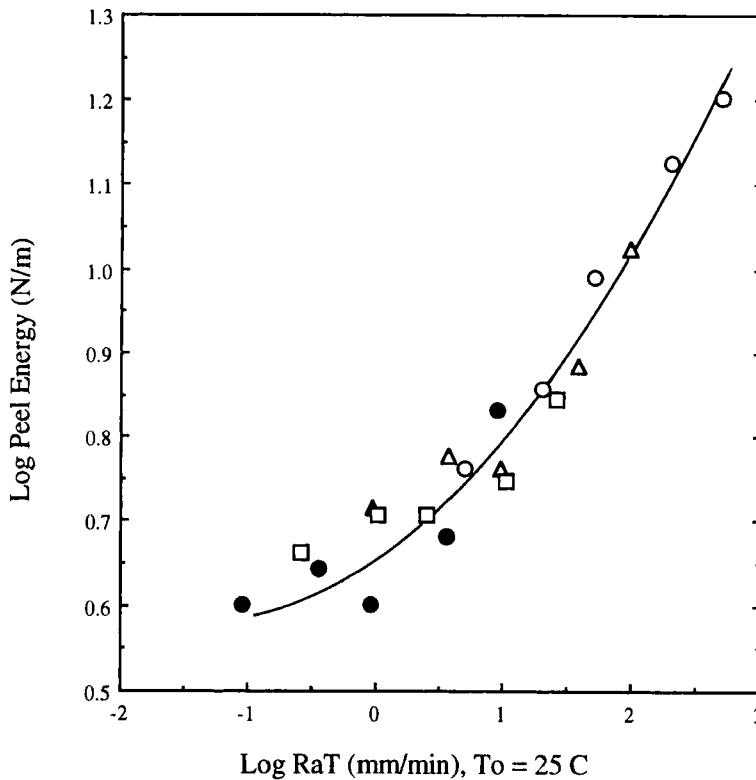
FIGURE 11 Mastercurve at $T_0 = 25°C$ from the data in Figure 9, generated by using WLF shift factors ($T_g = -72°C$).

hand, after crosslinking, entanglement slippage is absent, whether or not crystallization occurs. Now, the major contribution to energy dissipation could be strain crystallization, which is hypothesized to increase as temperature increases. Increased crystallization also has been invoked to explain the anomalously high tear strength of lightly-crosslinked NR at elevated temperature [9].

Strain-crystallization in crosslinked NR causes added energy dissipation [10]. However, it has not been established if dissipation is augmented when NR is deformed to *near* crystallization, where chains may be in the kinetic process of becoming crystalline. Even prior to actual crystallization, it seems reasonable that molecular motions could be significantly different in strained NR compared with those in
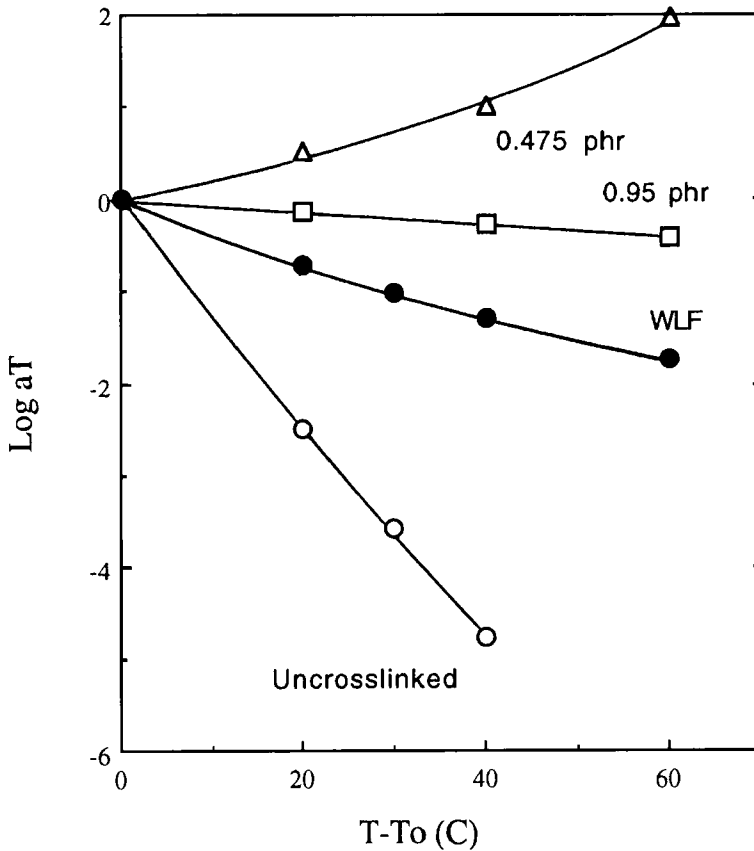
FIGURE 12   Shift factors used to construct the mastercurves in Figures 5, 7, 10 and 11.

a non-crystallizable network. Just the *propensity* for crystallization may account for the unusual peel behavior of NR. The difficult task of trying to determine strain-crystallization directly during peeling is needed to clarify the situation.

CONCLUSIONS

Previous workers have shown that, when peeling an uncrosslinked or lightly-crosslinked amorphous elastomer from a polyethylene

terephthalate (PET) film, peel strengths can be shifted to form mastercurves using shift factors in accord with the universal WLF equation. However, we have found that behavior is different when peeling natural rubber (NR) from PET. Although mastercurves can be constructed, WLF shift factors are only applicable when the natural rubber is highly crosslinked and peel forces are low. This is attributed to the lack of strain crystallization under these conditions. On the other hand, uncrosslinked and lightly-crosslinked NR appear to strain crystallize during peeling and this results in shift factors which deviate substantially from universal WLF values.

Acknowledgments

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