# Studies of Rigid Poly(vinyl chloride) (PVC) Compounds. III. Correlation of Compounding Energy with Fusion Level

C. H. CHEN, R. D. WESSON, J. R. COLLIER,* and Y. W. LO

Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803

## SYNOPSIS

The major contributors to the compounding energy of a poly(vinyl chloride) (PVC) sample in the Haake torque rheometer are starting temperature, rotor speed, and totalized torque. In this study, the compounding energy was calculated by using an energy balance in the internal mixer reported by Pedersen. The fusion levels of the PVC samples, which were prepared in the Haake torque rheometer at various blending conditions (starting temperature = variable, rotor speed = 60 rpm, and totalized torque = 10 kg-m-min), were determined by DSC and a capillary rheometer. The compounding energy was then correlated with the fusion level. The simple total energy balance can be applied to correlate the compounding energy with the fusion level of the PVC compound prepared in the Haake torque rheometer.

## INTRODUCTION

Internal mixers and various continuous extruders have been commonly used to mix polymer compounds and blends in industry. Compounding and blending of polymers is of increasing importance and becoming more attractive because of the fact that the mechanical properties of polymers can be improved through these processes. Internal mixers have been used to process poly(vinyl chloride) (PVC) compounds for many years due to their flexibility, particularly because frequent product and formulation changes are common.

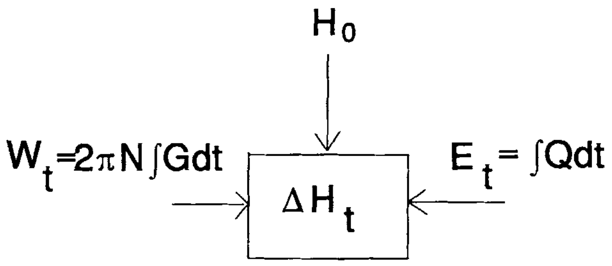
Van Buskirk et al.[1] used the automatic integration of Rheocord torque–time curves to study the independent variable "unit work" (*Wu*) for quantifying mixing in a torque rheometer with a Rheomix 750 (Banbury-type mixer/sensor) and a Rheomix 600 (cam-type rotors in the mixer/sensor). Dealy[2] reviewed the reports that were related to the energy conservation in plastics processing, especially in the areas of extrusion, injection-molding, and heat recovery. He also applied the second law of thermodynamics for energy analysis. Menges and Grajewski[3] studied the flow process in an internal mixer by using colored mixtures at various mixing conditions. They also developed a model which can be used to calculate the variation of the internal wall temperatures. White et al.[4] applied a hydrodynamic lubrication theory to analyze the flow in internal mixers and twin-screw extruders. Pressure fields and mean fluid patterns were also computed in their report.

The compounding energy consumed in an internal mixer can be calculated using the concept that the energy transfer in the mixing process can be obtained from the total energy balance.[3] Pedersen[5] illustrated a simple energy balance for a torque rheometer as shown in Figure 1. The compounding procedure involves compaction of the PVC resin particles into a fixed volume during mixing and heating. The amount of work (mechanical energy) going into the PVC sample is contributed by the torque necessary to turn the noninterchangeable, counterrotating, and nonintermeshing rotors at the preset rpm. The amount of heat transferred into the PVC sample is mainly a function of the PVC sample and bowl temperature. The melt temperature at any time ($t$) is dependent upon the work and heat transferred into, or out of, the PVC sample. In this article,

---

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 58, 1101–1105 (1995)
© 1995 John Wiley & Sons, Inc. CCC 0021-8995/95/071101-05



$H_t = H_o + E_t + W_t$ , $T_{melt,t} = H_t / mC_p$
$H_o = mC_pT_o + P_oV$ , $Q = UA(T_{bowl} - T_{melt,t})$
where: $H_o$ = Initial enthalpy of material, (J).
$H_t$ = Enthalpy of material at time t, (J).
$E_t$ = Amount of heat transferred by time t, (J).
$W_t$ = Amount of work generated by time t, (J).

m = Charge size, (kg).
$C_p$ = Heat capacity of material, (J/kg°C).
$P_o$ = Pressure upon charging, ($N/m^2$).
V = Bowl volume, ($m^3$).
$T_o$ = Temperature before charging, (°C).

t = Time, (mins).
Q = Rate of heat transfer, (J/min).
U = Overall heat transfer coefficient, ($J/m^{2}$°Cmin).
A = Bowl surface area, ($m^2$).
T = Temperature, (°C).
G = Torque, (kg-m).

**Figure 1** Simple total energy balance for a torque rheometer.[5]

the compounding energy has been correlated with the fusion level of the PVC sample by basing the determination of the compounding energy on the total energy balance, which is illustrated in Figure 1.

## EXPERIMENTAL

### Preparation of PVC Compounds

The material used in this study is a suspension-dry PVC masterbatch powder containing 100 parts of PVC grain particles, 1.5 parts of process aid (K12ON), 1.0 part wax (XL165), 1.0 part calcium stearate, and 1.5 parts heat stabilizer (T-137). All masterbatch samples without compounding were supplied by the Dow Chemical Co.

To determine the influence of temperature on the fusion level, PVC samples with various fusion levels were prepared in the Haake torque rheometer, equipped with an electrically heated mixing head. The rotor speed was set at 60 rpm, and the sample weight was always 65 g. Samples were charged into the mixer at 160, 170, 180, 190, and 200°C and removed when 10 kg-m-min totalized torque was reached in the Haake torque rheometer. Table I illustrates the digital data from the Haake torque rheometer at a preset bowl temperature of 180°C. The $T_2$ is the melt temperature of the PVC sample at time $t$.

### DSC Thermal Analysis

PVC compounds prepared by the Haake torque rheometer were cut randomly into small pieces, weighted approximately 10 mg, and then characterized by a Seiko 220C automatic cooling differential scanning calorimeter. The samples were heated from room temperature to 270°C, at 20°C per min. Three DSC measurements from each Haake preparation were conducted for each PVC compound in order to obtain an average value for the heat of fusion. This average value was used to determine the fusion level of the PVC compound.

### Capillary Rheological Analysis

The viscoelastic property of all processed PVC samples was characterized by the zero-length capillary entrance pressure drop at 180°C. To put samples into the barrel with a diameter of 20 mm, all PVC samples were cracked into small pieces by a hammer. The test conditions are summarized in Table I. The rheological measurements were performed on the advanced capillary extrusion rheometer system (ACER 2000, Polymer Laboratory, now Rheometrics) equipped with a pressure transducer and a measuring range of up to 700 MPa. The entrance pressure drop was read by the pressure transducer every 4 s. An average value was obtained after approximately 150 entrance pressure drop data points were measured. A "zero-length" capillary die was used. To minimize the possibility of slip and maximize the amount of internal deformation, a flat entry was selected for the zero-length capillary.[6,7] To melt rigid PVC compounds, PVC samples were put in the barrel at an isothermal temperature (180°C) for 25 min before the measurement.

## THEORETICAL METHOD, RESULTS, AND DISCUSSION

Based on the total energy balance,

$$H_t = H_0 + W_t + E_t \qquad (1)$$

which is shown in Figure 1, the compounding energy is calculated and correlated with the experimental results. The initial enthalpy of the material, $H_0$, is mainly a function of the material. Here, $H_0$ is con-

**Table I Digital Data from the Haake Torque Rheometer at a Preset Bowl Temperature of 180°C**

| Time (min:s) | Torque (mg) | TTQ (kg · m · min) | R1 (rpm) | T1 (°C) | T2 (°C) | T3 (°C) | T4 (°C) | T5 (°C) | P1 (psi) | P2 (psi) | P3 (psi) | P4 (psi) | P5 (psi) | R2 (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0:0 | 11 | 0.0 | 60 | 26 | 175 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0:6 | 11 | 0.0 | 60 | 26 | 175 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 0:12 | 11 | 0.0 | 60 | 26 | 175 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0:18 | 11 | 0.0 | 60 | 26 | 175 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0:24 | 11 | 0.0 | 60 | 26 | 175 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 0:30 | 11 | 0.0 | 60 | 26 | 174 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 0:36 | 11 | 0.0 | 60 | 26 | 165 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 0:42 | 11 | 0.0 | 60 | 26 | 157 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0:48 | 37 | 0.0 | 60 | 26 | 155 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0:54 | 3454 | 0.4 | 60 | 26 | 137 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1:0 | 2180 | 0.7 | 60 | 26 | 142 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1:6 | 1722 | 0.9 | 60 | 26 | 148 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1:12 | 1439 | 1.0 | 60 | 26 | 153 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1:18 | 1253 | 1.2 | 60 | 26 | 157 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 1:24 | 1157 | 1.3 | 60 | 26 | 159 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1:30 | 1077 | 1.4 | 60 | 26 | 162 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 1:36 | 1018 | 1.5 | 60 | 26 | 164 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 1:42 | 981 | 1.6 | 60 | 26 | 166 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 1:48 | 965 | 1.7 | 60 | 26 | 168 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 1:54 | 938 | 1.8 | 60 | 26 | 169 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2:0 | 917 | 1.9 | 60 | 26 | 170 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2:6 | 906 | 2.0 | 60 | 26 | 171 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2:12 | 901 | 2.1 | 60 | 26 | 172 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2:18 | 912 | 2.1 | 60 | 26 | 173 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2:24 | 901 | 2.2 | 60 | 26 | 174 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2:30 | 938 | 2.3 | 60 | 26 | 175 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2:36 | 965 | 2.4 | 60 | 26 | 176 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2:42 | 1002 | 2.5 | 60 | 26 | 177 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 2:48 | 1093 | 2.6 | 60 | 26 | 178 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2:54 | 1221 | 2.7 | 60 | 26 | 179 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:0 | 1370 | 2.9 | 60 | 26 | 180 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3:6 | 1727 | 3.0 | 60 | 26 | 181 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:12 | 2143 | 3.2 | 60 | 26 | 182 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:18 | 2378 | 3.5 | 60 | 26 | 184 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:24 | 2420 | 3.7 | 60 | 26 | 186 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:30 | 2452 | 3.9 | 60 | 26 | 187 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:36 | 2468 | 4.2 | 60 | 26 | 188 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:42 | 2490 | 4.4 | 60 | 26 | 189 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 3:48 | 2452 | 4.7 | 60 | 26 | 190 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3:54 | 2452 | 4.9 | 60 | 26 | 191 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 4:0 | 2490 | 5.2 | 60 | 26 | 191 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 4:6 | 2522 | 5.4 | 60 | 26 | 193 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 4:12 | 2527 | 5.7 | 60 | 26 | 193 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 4:18 | 2490 | 5.9 | 60 | 26 | 194 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4:24 | 2458 | 6.2 | 60 | 26 | 194 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4:30 | 2410 | 6.4 | 60 | 26 | 195 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4:36 | 2372 | 6.7 | 60 | 26 | 196 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 4:42 | 2330 | 6.9 | 60 | 26 | 196 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4:48 | 2287 | 7.1 | 60 | 26 | 197 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4:54 | 2255 | 7.4 | 60 | 26 | 197 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 5:0 | 2228 | 7.6 | 60 | 26 | 198 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5:6 | 2207 | 7.8 | 60 | 26 | 198 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5:12 | 2186 | 8.0 | 60 | 26 | 198 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5:18 | 2170 | 8.2 | 60 | 26 | 198 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5:24 | 2148 | 8.5 | 60 | 26 | 199 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5:30 | 2127 | 8.7 | 60 | 26 | 199 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5:36 | 2111 | 8.9 | 60 | 26 | 199 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 5:42 | 2106 | 9.1 | 60 | 26 | 199 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 5:48 | 2090 | 9.3 | 60 | 26 | 200 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |
| 5:54 | 2079 | 9.5 | 60 | 26 | 200 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6:0 | 2063 | 9.7 | 60 | 26 | 200 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6:6 | 2058 | 9.9 | 60 | 26 | 200 | 26 | 26 | 26 | 0 | 0 | 0 | 0 | 0 | 1 |

**Table II Enthalpy of the PVC Sample at Time $t$, $H_t$, for Various Starting Temperatures (Where $W = H_0 + W_t$)**

| Starting Temperature | $H_t$ |
|---|---|
| 160°C | $W - 372UA\Delta t$ |
| 170°C | $W - 241UA\Delta t$ |
| 180°C | $W + 32UA\Delta t$ |
| 190°C | $W + 67UA\Delta t$ |
| 200°C | $W + 92UA\Delta t$ |

sidered as the same for each compounding condition, since a unique PVC sample was used for all the compounds. The amount of work generated at time $t$, $W_t$, is equal to the integration of torque ($G$) by time:

$$W_t = 2\pi N \int G\,dt \tag{2}$$

where $N$ = rotor speed (rpm) and $G$ = torque.

The torque ($G$) is an instantaneous force required to cause the material to flow,[8] and it is expressed as

$$Torque = 2\pi R^2 L\tau \tag{3}$$

where $R$ = rotor radius (m), $L$ = rotor length (m), $\tau$ = instantaneous shear stress (Pa), and $t$ = time (min).

If eq. (3) is substituted into eq. (2), then

$$W_t = 2\pi N \int 2\pi R^2 L\tau\,dt \tag{4}$$

Since the PVC sample was removed from the Haake torque rheometer when a 10 kg-m-min totalized torque was reached, the amount of work transferred into the system can also be considered as the same for each case. Therefore, the only different term for each case is the amount of heat transferred at time $t$, $E_t$, into the system:

$$E_t = \int Q\,dt \tag{5}$$

The rate of heat transfer, $Q$, is expressed as

$$Q = UA(T_{\text{bowl}} - T_{\text{melt},t}) \tag{6}$$

where $U$ = overall heat transfer coefficient (J/m$^2$ °C min), $A$ = bowl surface area (m$^2$), $T_{\text{bowl}}$ = preset bowl temperature (°C), and $T_{\text{melt},t}$ = melt temperature of PVC sample at time $t$ (°C). By substituting eq. (6) into eq. (5), then

$$E_t = \int UA(T_{\text{bowl}} - T_{\text{melt},t}) \tag{7}$$

Equation (7) can be expressed as the following formula:

$$E_t = \int UA(T_{\text{bowl}} - T_{\text{melt},t})\,dt = \sum UA(T_{\text{bowl}} - T_{\text{melt},t})\,\Delta t \tag{8}$$

If we substitute $T_{\text{bowl}}$ = 180°C and $T_{\text{melt},t}$ = various with time (see Table I) into eq. (8), then

$$H_t = H_0 + W_t + 32UA\,\Delta t \tag{9}$$

Using a similar procedure, we can obtain the $H_t$ for the different bowl temperatures: 160, 170, 190, and 200°C, as shown in Table II.

When the compounding energy, $H_t$, ($Y$-axis) is plotted vs. various bowl temperatures ($X$-axis), we can obtain one S-shaped fusion curve similar to experimental results as illustrated in Figure 2. Figure 2 illustrates experimental results vs. the mathematical result based on a simple total energy balance in a torque rheometer. It is apparent that the simple total energy balance based on Figure 1[5] can be applied to correlate the compounding energy with the fusion level of the PVC compound prepared in the torque rheometer.

## CONCLUSIONS

The simple total energy balance based on Figure 1[5] can be applied to correlate the compounding energy

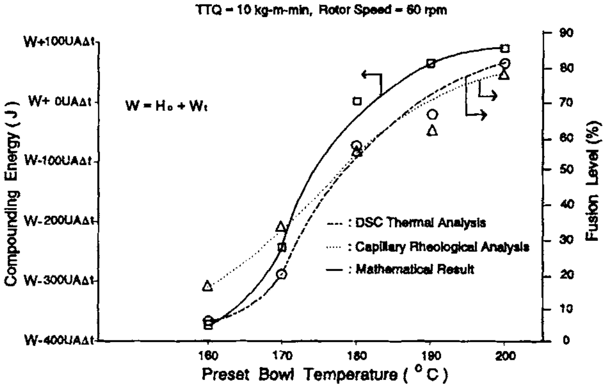


**Figure 2** Experimental results vs. the mathematical result based on a simple total energy balance in a torque rheometer.

with the fusion level of the PVC compound prepared in the Haake torque rheometer. Both DSC thermal analysis and capillary rheological analysis can be used to evaluate the fusion level of PVC compounds.

The authors would like to thank The Dow Chemical Co. for sponsoring this research.

## REFERENCES

1. P. R. Van Buskirk, S. B. Turetsky, and P. F. Gunberg, abstracted by W. T. Blake, *Haake Buchler Technical Abstract,* TA-56, Haake, Saddle Brook, NJ (1978).
2. J. M. Dealy, *Polym. Eng. Sci.,* **22,** 528 (1982).
3. G. Menges and F. Grajewski, *Int. Polym. Process.,* **3,** 74 (1984).
4. J. L. White, J. K. Kim, W. Szydlowski, and K. Min, *Polym. Compos.,* **Oct.,** 368 (1988).
5. T. C. Pedersen, *Soc. Plast. Eng. Vinyl RETEC,* 31 (1991).
6. R. J. Krzewki and E. A. Collins, *J. Macromol. Sci.-Phys., B,* **20,** 443 (1981).
7. R. J. Krzewki and E. A. Collins, *J. Macromol. Sci.-Phys. B,* **20,** 465 (1981).
8. *Haake Buchler Technical Bulletin,* TB-826, Haake, Saddle Brook, NJ (1984).

*Received February 27, 1995*
*Accepted May 19, 1995*