Influence of Solvent and Filler on Some Physical Properties of a Fluoroelastomer

MARIA CRISTINA RIGHETTI,¹ GIUSEPPE AJROLDI,² MANUELE VITALI,³* GIOVANNI PEZZIN⁴

¹ Centro di Studio per la Fisica delle Macromolecole-CNR, Via Selmi 2, 40126 Bologna, Italy

² Via Campiglio 9, 20133 Milano, Italy

³ Dipartimento di Chimica, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

⁴ Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, 35131 Padova, Italy

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ABSTRACT: Samples of virgin and a crosslinked fluorinated rubber, containing different amounts of carbon black and solvated with methylethyl ketone, have been investigated by differential scanning calorimetry. Although the polymer-solvent interaction increases with decreasing temperature, a process of solvent separation was observed for all of the systems. This process can be attributed to a T_g regulation effect in which solvent crystallization occurs only when the crystallization temperature is higher than the T_g of the system. The interaction between rubber and filler, approximately temperature independent, was found to not influence the glass transition of the rubber-methylethyl ketone systems, even when the carbon black content is on the order of 35 wt %. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 377–384, 1999

Key words: fluorinated rubbers; swelling; fillers; glass transition temperature (T_{g})

INTRODUCTION

The marked dependence of the glass transition temperature (T_g) on diluent concentration in binary polymer-diluent mixtures, a well-established experimental fact, has been the subject of several thermodynamic treatments.¹⁻⁵ In this context, the term polymer has a broad meaning: the macromolecular structure can be linear, branched, or crosslinked. The latter structural variable was considered years ago by ten Brinke et al.,⁶ who extended the Couchman thermodynamic theory³ to swollen crosslinked polymers.

This extension modification of the theory indicates that the initial negative slope $(dT_g/dw_1)_{w_1=0}$ (where T_g is the glass transition temperature of the mixture and w_1 is the weight fraction of the solvent) increases in absolute value with increasing crosslinking degree. Some experimental results have confirmed this behavior.⁶

The aforementioned findings are relevant also from an industrial standard. In the automotive industry, for example, crosslinked rubber items like O-rings, gaskets, and fuel hoses are in contact with gasoline or other liquids, which results in swelling of the rubber. To avoid significant dimensional variations, the solvent take-up usually must be minimized by using specialty rubbers, such as fluoroelastomers. The fuel resistance of these materials is quite good, and their swelling ratio is low, but unfor-

Correspondence to: M. C. Righetti.

^{*} Present address: Ciba Specialty Chemicals, Via Pila 6/3, 40044 Sasso Marconi (BO), Italy.

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tunately their T_g is often not adequate for lowtemperature applications. For example, for a random vinylidene-fluoride/hexafluoropropene (VDF/HFP) copolymer 79/21 mol %, the T_g is approximately -23° C, so the requirement for a rubber elastic behavior down to low temperatures (typically down to -40° C) is not fulfilled unless special rubber types are used. However, Streit,⁷ in his work on the leakage temperature of fuel injectors, has shown that a very modest swelling can be beneficial, as it shifts the leakage temperature down by some 20°C without impairing the O-ring performance.

Moreover, industrial rubber items are not only crosslinked, but are also filled with carbon black, other inorganic fillers, or a suitable mixture of both. As shown by Kraus,⁸ the volume fraction of fillers can affect swelling through an interaction between polymer and fillers; the stronger the interaction, the higher the constraint against swelling. Consequently, the industrial practice requires knowledge not only of the effect of the degree of crosslinking on the T_g for the polymer–diluent system, but also of how this dependence is changed by filler type and loading.

The purpose of this article is to investigate the effect of filler concentration on the T_g of a swollen crosslinked and filled fluoroelastomer rubber. Because such rubbers are commonly used in the automotive industry [in the past two of the authors⁹ have determined the glass transition dependence on solvent concentration of a VDF/HFP uncrosslinked copolymer swollen with methylethyl ketone (MEK)], it seems worthy to investigate the same system after crosslinking of the rubber and as a function of the carbon black concentration.

The solvent used was MEK, which is a good solvent for these polymers, so the T_g -MEK concentration curve can be obtained over a large concentration range. The relationship, once determined, should in principle be easily translated to other solvents, including the poor ones, for which the rubber swelling is low. As a matter of fact, the T_g of a binary polymer–solvent mixture is dependent mainly on the T_g of the solvent used. Because the T_g of many simple liquids is between -180 and -140° C¹⁰ (T_g of MEK is -162° C¹⁰), it is reasonable to apply the T_g-w_1 equation obtained for a good solvent like MEK to a poor solvent as well (clearly in the composition range in which the poor solvent and the polymer are

	Formulation (phr)		
Ingredient	To	T_1	T_2
Tecnoflon	100	100	100
$M1^{a}$	4	4	4
$M2^{b}$	1.5	1.5	1.5
MgO	3	3	3
Ca(OH) ₂	6	6	6
MT black	0	30	60
Volume swelling ratio ^c	5.10	4.10	3.60

^a Commercial Ausimont master containing the crosslinking agent.

^b Commercial Ausimont master containing the accelerant. ^c Defined as the ratio of the volume of the swollen polymer to the volume of the dry polymer measured at 30°C.

miscible), if its glass transition temperature is close to that of the model solvent investigated.

EXPERIMENTAL

Materials

The VDF/HFP copolymer rubber investigated (Tecnoflon® FKM) and the solvent 2-butanone or MEK are commercial products supplied by Ausimont S.p.A. (Bollate, Italy) and Carlo Erba (Milan, Italy), respectively. Molecular weight and molecular weight distribution were measured by GPC analysis in tetrahydrofuran at 30°C; a five-column set (precolumn, 10³, 10⁴, 10⁵, and 10⁶ Å) was used. The following weight averages were obtained: $M_n = 95,300$ and $M_w = 294,300$; the polydispersity index is $M_w/M_n = 3.1$. The limiting viscosity number, measured in 2-butanone at 30°C by a dilution Ubbelohde viscometer, is 90.8 mL g⁻¹.

The fluororubber was crosslinked by conventional ionic vulcanization (bisphenol AF as crosslinker and a phosphonium salt as accelerant) and additioned with different amounts of carbon black MT (Table I). The compounding procedure was close to that recommended by ASTM D 3182; milled rubber sheets were crosslinked at 170°C for 10 min, and the plaques so obtained (13 × 13 × 2 mm) were postcured for 24 h (8 h heating + 16 h isotherm) at 250°C.

The crosslinking degree, as measured by equilibrium solvent swelling,¹¹ was obtained in 2-bu-



Figure 1 Volume swelling ratio *Q* as a function of the quantity $\phi/(1 - \phi)$ at 0°C (\Box), 30°C (\triangle), and 50°C (\diamond).

tanone at 30°C, following the ASTM D 471 standard. Raw data, corrected for the soluble fraction, are reported in the last row of Table I. For the sake of comparison, a few mixtures of the uncrosslinked Tecnoflon® FKM and MEK were also investigated.

Calorimetric Analysis

Calorimetric data on the samples were obtained by using a Perkin–Elmer DSC 7 differential scanning calorimeter, driven by a Unix computer. A liquid nitrogen ("cold finger") subambient apparatus was used as cooling accessory to extend the temperature range down to -180 °C. The instrument was calibrated with high-purity standards



Figure 2 Calorimetric curve of a mixture fluororubber T_1 -MEK (solvent weight fraction 0.242).

(indium, cyclohexane, n-decane, n-heptane) at 20°C min⁻¹. Dry helium was used as a purge gas. The polymeric mixtures were prepared directly in aluminum 50 μ L capacity pans by adding appropriate amounts of MEK to weighted amounts of polymer (with the total sample mass ranging from 10 to 20 mg); the pans were then sealed and weighed. Before performing the measurements, the polymeric mixtures were left to equilibrate at least 15 days. Additional equilibration time did not modify the DSC results. The samples, transferred in the calorimetric furnace kept at room temperature, were then rapidly quenched (actual average cooling rate of -40° C min⁻¹), and the calorimetric curves were recorded in the temperature range from -180 to 30° C, at a scanning rate of 20°C min⁻¹. Excellent reproducibility of the second and subsequent scans on selected samples was obtained. No evaporation of solvent was found after the measurements. The T_g was taken as the fictive temperature; that is, the T_g defined by the intersection of the extrapolated pretransition and posttransition enthalpy data.¹² (Integration of the calorimetric curves was done with the Perkin-Elmer software package.) The specific heat increment Δc_p values were calculated from the calorimetric curves as the distance between the two extrapolated baselines at the fictive T_{σ} .

RESULTS AND DISCUSSION

The fluororubbers investigated in this work were crosslinked with a standard industrial recipe. The crosslinking degree obtained in this way can be considered as medium crosslinking; the M_c value is estimated to be between 10,000 and 15,000.¹¹ The rubbers contain variable amounts of carbon



Figure 3 Calorimetric curve of a mixture fluororubber T_0 -MEK (solvent weight fraction 0.605).



Figure 4 T_g of the mixtures as a function of nominal weight fraction $(w_{1(\text{nom})})$ of MEK: uncrosslinked fluororubber (\bullet), sample T_0 (\diamond), sample T_1 (\triangle), sample T_2 (\Box). The T_g of pure MEK is also shown (\blacksquare).¹⁰

black, and the main scope of the work was to investigate the possible carbon black influence on the rubber-solvent interaction.

The latter is known to be temperature dependent, as expected and shown in Figure 1, where the volume swelling ratio Q (defined as the ratio of the volume of the swollen polymer to the volume of the dry polymer) is plotted, following the Kraus treatment,⁸ versus $\phi/(1 - \phi)$, where ϕ is the volume fraction of the fillers calculated with respect to the volume of the dry rubber. In the present case, not only the carbon black but also two of the components of the vulcanization recipe, MgO and $Ca(OH)_2$, were considered as fillers in the calculation of ϕ . Because the Q data decrease rapidly (by as much as 20%) with increasing filler concentration, filler-rubber interactions are clearly present. The effect of temperature on swelling degree is also quite clear, with the mutual solubility of rubber and solvent decreasing on average by about 8% when the temperature increases from 0 to 50°C. This means that the polymer-solvent interaction is decreasing with increasing temperature; that is, the Flory interaction

parameter χ^{11} is increasing with temperature. A rough estimate of the change of χ with temperature can be obtained by the Flory–Rehner equation¹¹

$$\chi(T) = a\chi(T_0) + 0.5(1-a) \tag{1}$$

where T_0 is a reference temperature and

$$a = \left(\frac{Q(T)}{Q(T_0)}\right)^{5/3} \left(\frac{\rho(T)}{\rho(T_0)}\right) \left(\frac{V_1(T)}{V_1(T_0)}\right)$$
(2)

with V_1 the molar volume of the solvent and ρ the polymer density. Because a value of $\chi = 0.290$ was calculated from the second virial coefficients from osmometric measurements in MEK at 30°C for fractions,¹³ the values $\chi(0^{\circ}C) = 0.265$ and $\chi(50^{\circ}C)$ = 0.307 can be calculated from the *Q* data.

The trend of χ with temperature is also confirmed by intrinsic viscosity measurements carried out on the virgin uncrosslinked material at temperatures between -20 and 56°C. The viscosity number decreases from 102 to 83.5 mL g⁻¹, indicating that coil expansion decreases with increasing temperature.

Moreover, it must be noted that the temperature influence on Q seemingly is not substantially affected by changes of the filler concentration, as indicated by the curves of Figure 1 being clearly similar in shape. It is tempting to conclude that the temperature-independent polymer-filler interactions do not influence the temperature-dependent polymer-solvent interaction.

One of the interesting results obtained in this work is related to the fact that when the T_g of the solvated polymer is higher than the crystallization temperature T_c of the pure MEK, the only transition revealed by the DSC measurements is the T_g of the polymer–solvent mixture. On the other hand, when T_g is lower than T_c , both the T_g of the system and the separation of part of the solvent are revealed by DSC. A melting peak is in fact found in the heating scan, at a temperature higher than the T_g , and the peak corresponds to the fusion of pure MEK ($T_m = -86.5^{\circ}$ C). Figure 2 shows an example of this behavior, which is common to all formulations.

As expected, the amount of solvent that separates from the solvated polymer in the cooling process is a function of both the initial solvent concentration and the cooling rate. Some experiments carried out at different cooling rates have shown that



Figure 5 Weight fraction of the free separated MEK $(w_{1(\text{sep})})$ versus the nominal weight fraction $(w_{1(\text{nom})})$ (a) and corrected weight fraction of the free separated MEK $(w_{1(\text{sep,corr})})$ versus the corrected weight fraction $(w_{1(\text{corr})})$ (b) (see text); symbols are as in Figure 4.

the amount of MEK separated in the cooling step is inversely proportional to the cooling speed.

In many cases, however-particularly when samples of high MEK concentration are investigated-a broad crystallization minimum is present in the heating scan that follows a quick cooling, as shown in Figure 3. The sum of the area of the crystallization exotherm in the cooling process and of the area of the crystallization occuring during the heating step is equal (within experimental error) to the melting endotherm area, demonstrating that the two processes must be considered real crystallizations. Figure 3 shows that the fusion of the separate MEK can be characterized by a double melting peak, a feature observed only when the cold crystallization phenomenon is present in the heating stage. The narrower peak, centered at -86.5°C, (and thus identical to that of pure MEK) must be attributed to the solvent separated in the cooling step, whereas the broad melting peak centered at about -91°C appears to be typical of the small MEK crystallites that are separating from the polymer-solvent system in the cold crystallization process that occurs between -120 and

 -95° C. As a matter of fact, the areas of the two peaks of cold crystallization and melting at -91° C are the same, within experimental error.

The effect of crystal size on the melting point depression of liquids separated from crosslinked polymers was first reported long ago for polystyrene swollen in several solvents and for rubber swollen in benzene.¹⁴ Recently, similar results have been reported for the system poly(vinyl alcohol)–water¹⁵ and polyacrylamide–water.^{16,17}

Because, as pointed out previously, the polymer–solvent interaction increases with decreasing temperature, the observed solvent separation must be attributed to a T_g regulation effect.^{16,17} Thus segregation of the solvent can occur only when its crystallization temperature is higher than the T_g of the system.

The T_g -composition curves for the four series of samples of different composition are plotted in Figure 4 against the nominal diluent weight fraction $w_{1(\text{nom})}$, where $w_{1(\text{nom})}$ is defined as the weight fraction of the total MEK, unseparated and separated. It is possible to calculate the real solvent concentration at the T_g of the mixture by subtracting from the total the amount of free



Figure 6 T_g of the mixtures as a function of solvent weight fraction (w_1) ; symbols are as in Figure 4.

MEK obtained from the DSC fusion peak area. For samples in which the cold crystallization phenomenon occurs, the area of the crystallization peak is subtracted from the total melting area, keeping in mind that this separation take places above T_g . A plot of the weight fraction of the free solvent separated in the cooling step $w_{1(sep)}$ against $w_{1(\text{nom})}$ is shown in Figure 5(a). It seems that when $w_{1(\text{nom})}$ exceeds 0.4, the free solvent amount increases rapidly for the crosslinked rubber-MEK systems. Moreover, the quantity of solvent that separates in the crosslinked mixtures is higher than that of the uncrosslinked system. In the former case the added fillers could act as nucleating agents, favoring the MEK crystallization process.

Because the real concentration of the solvent at T_g is known, it is possible to plot T_g as a function of the real w_1 , as shown in Figure 6. It is worth noting that for crosslinked samples, the T_g tends to level out at an approximately constant value. As far as MEK crystallization is concerned, it has been observed that supercooling effects play a considerable role, owing to the marked difference between the melting point and the crystallization

temperature (which ranges from -100 to -120° C, depending on the cooling rate). It appears from Figure 6 that an increase in carbon black content brings about, at constant w_1 , a lower T_g . If, however, a new weight fraction of the solvent $w_{1(corr)}$ is used by taking into account only the unseparated solvent amount and the rubber (plus the crosslinking agent and the accelerant) and by excluding the fillers [carbon black, MgO, and Ca(OH)₂], then the data for all four series fall on the same curve, as shown in Figure 7. Moreover, in Figure 5(b), in which $w_{1(sep, corr)}$ is plotted as a function of $w_{1(corr)}$, the three curves concerning the crosslinked FKM–MEK systems approach each others and tend to overlap.

CONCLUSIONS

Despite the interaction between rubber and filler, the latter does not influence the T_g of the rubber– MEK system, even though the content of carbon black can be as high as 35 wt %. The composition



Figure 7 T_g of the mixtures as a function of solvent correct weight fraction $(w_{1(corr)})$; symbols are as in Figure 4. The solid line corresponds to the T_g curve calculated according to eq. (3).



Figure 8 Specific heat increment Δc_p as a function of w_1 (a) and specific heat increment $\Delta c_{p(\text{corr})}$ as a function of $w_{1(\text{corr})}$ (b) (see text): uncrosslinked fluororubber (\bullet), sample T_0 (\diamond), sample T_1 (\triangle), sample T_2 (\Box). The Δc_p of pure MEK is also shown (\blacksquare).¹⁸

dependence of the T_g in binary polymeric systems is analyzed using the entropic Couchman equation^{3,4}

$$T_{g} = \frac{w_{1}\Delta c_{p1}T_{g1} + w_{2}\Delta c_{p2}T_{g2}}{w_{1}\Delta c_{p1} + w_{2}\Delta c_{p2} + (\Delta s_{m}^{l} - \Delta s_{m}^{g})}$$
(3)

where w_i is the weight fraction of component *i*, T_{gi} is its glass transition temperature and Δc_{pi} its specific heat increment at T_{gi} , and Δs_m^l and Δs_m^g are the entropies of mixing in the liquid state and the glassy state, respectively. As noted previously,⁴ the difference $(\Delta s_m^l - \Delta s_m^g)$ can be considered as an adjustable parameter that indicates the strength and the type of interactions between the mixture components. According to the Wunderlich rule,¹⁸ Δc_{p1} was estimated to be approximately 0.64 J g⁻¹ K⁻¹. The curve calculated from eq. (3) by taking $T_{g1} = 111$ K,¹⁰ $T_{g2} = 257$ K, and $\Delta c_{p2} = 0.20$ J g⁻¹ K⁻¹ and by assuming (Δs_m^l $-\Delta s_m^g) = 0$, is shown in Figure 7. The excellent agreement between calculated and experimental T_g data up to $w_{1(\text{corr})} = 0.5$ seems to indicate that strong and specific interactions are absent in the polymer-diluent system under investigation. The departure from a monotonic decrease shown by

the experimental T_g data in the range 0.5 $< w_{1(\text{corr})} < 1.0$ is a feature common to other plasticized polymer systems, as previously reported⁴ and discussed.

Of some interest are the curves of Figure 8, in which the specific heat increments at the T_g are plotted against both w_1 and $w_{1(\text{corr})}$. The values Δc_p and $\Delta c_{p(\text{corr})}$ are different because they have been calculated in different ways: Δc_p refers to the system comprising unseparated solvent and rubber (plus crosslinking agent, accelerant, and fillers), whereas $\Delta c_{p(\text{corr})}$ does not take the fillers into account. Although the Δc_p data are more scattered than the relative T_g data, it is clear that the fillers do not affect the T_g and the specific heat increment of the FKM–MEK systems.

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