Notes

Acid Catalysis in the Phenolic Resin Vulcanization of Unsaturated Rubbers

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It has long been known that unsaturated rubbers[2] including EPDM elastomers[3] can be vulcanized with phenol–formaldehyde resins, and that the resulting vulanizates exhibit heat- and air-aging characteristics superior to those of sulfur-cured stocks.[4]

One of the deficiencies of the phenolic resin vulcanization of unsaturated rubbers had been the undesirably slow rate of reaction. It was not until metal halides were introduced as accelerators or catalysts into the vulcanization system that significant progress was made in the field of resin vulcanization.[5] These accelerators were similar to those Lewis acid catalysts used in the Friedel–Crafts reaction, such as the halides of group III–VIII metals. In our study on the nature of acid catalysis in the phenolic resin vulcanization of an EPDM elastomer we found synergism when the mixture of a BrØnsted acid and a Lewis acid was used as catalyst. It is the purpose of this note to report our findings.

Experimental Section

Nordel 1070, an EPDM elastomer, was obtained from E. I. du Pont de Nemours and Co. Phenolic resin SP-1055 was from Schenectady Chemicals, Inc. Benzenesulfonic acid and trichloroacetic acid were Eastman White Label. Reagent grade $SnCl_2 \cdot 2H_2O$ was obtained from Mallinckrodt, and reagent grade cuprous chloride and zinc chloride were obtained from Allied Chemicals.

The kinetics of the cross-linking reaction was studied by following the torsional modulus change at 180° recorded in the Monsanto oscillating disk rheometer (odr). Prior to odr measurements, 100 parts of the EPDM elastomer Nordel 1070 was milled with 12 parts SP-1055, 50 parts carbon black SAF, one part stearic acid, and required amounts of acid catalysts.

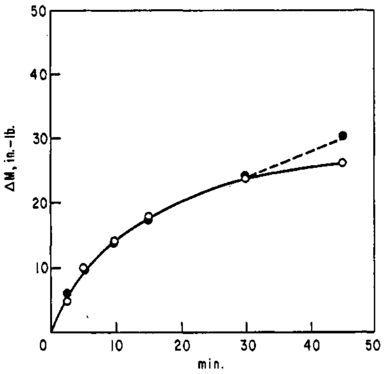

Figure 1. Effects of mixed BrØnsted acid catalysts on vulcanization rate of Nordel 1070 at 180°: ○, combination of four parts $PhSO_3H \cdot H_2O$ and four parts CCl_3CO_2H; ●, summation of the torsional modulus changes ΔM catalyzed by four parts $PhSO_3H$ and four parts CCl_3CO_2H.

Results and Discussion

Effects of various acid catalysts, either BrØnsted acid or Lewis acid, on the stress–strain properties of EPDM elastomers vulcanized with phenolic resins imply a parallelism between the catalytic activity and acidity of acid catalysts.[6]

When the mixture of a BrØnsted acid and a Lewis acid is used as catalyst, synergism may be observed in phenolic resin vulcanization. This is in interesting contrast to the nearly additive effect of the combination of two BrØnsted acids on the kinetics of cross-linking reactions. These effects are illustrated in Figures 1, 2, and 3.

The combination of $ZnCl_2$ or CuCl and a BrØnsted acid does not give rise to discernible synergistic effects; thus, it appears that not all Lewis acids are effective cocatalysts with

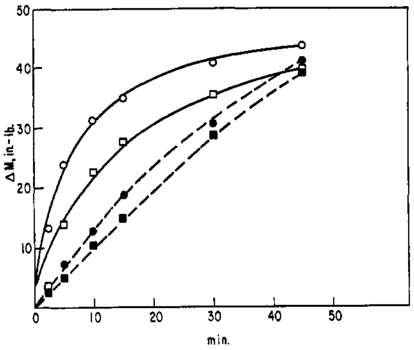

Figure 2. Effects caused by combination of $SnCl_2 \cdot 2H_2O$ and CCl_3CO_2H on the vulcanization rate of Nordel 1070 at 180°: ○, mixture of one part $SnCl_2 \cdot 2H_2O$ and four parts CCl_3CO_2H; □, one-half part $SnCl_2 \cdot 2H_2O$ and four parts CCl_3CO_2H; summation of torsional modulus changes ΔMcata lyzed by ●,one part $SnCl_2 \cdot 2H_2O$ and four parts CCl_3CO_2H; ■, one-half part $SnCl_2 \cdot 2H_2O$ and four parts CCl_3CO_2H.

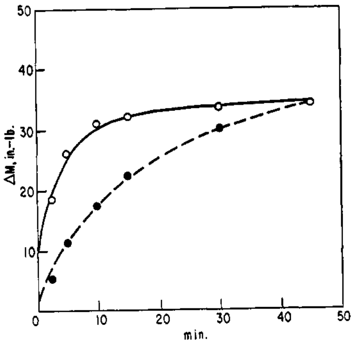

Figure 3. Effects of the combination of $SnCl_2 \cdot 2H_2O$ and $PhSO_3H \cdot H_2O$ on the vulcanization rate of Nordel 1070 at 180°: ○, one part $SnCl_2 \cdot 2H_2O$ and four parts $PhSO_3H \cdot H_2O$; ●, summation of torsional modulus changes ΔM catalyzed by one part $SnCl_2 \cdot 2H_2O$ and four parts $PhSO_3H \cdot H_2O$.

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(1) Contribution No. 239.

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(6) Unpublished results of M. C. Chen.

Brønsted acids. It is interesting to note that while CCl_3CO_2H has less catalytic activity than $PhSO_3H \cdot H_2O$, the combination of $SnCl_2 \cdot 2H_2O$ and CCl_3COOH provides a greater synergistic catalytic effect than the combination of $SnCl_2 \cdot 2H_2O$ and $PhSO_3H \cdot H_2O$.

The synergism caused by mixed acids may well be ascribed to dual-acid formation, since in certain cases the formation of dual acids of enhanced acidity has been recognized.[7] It must be mentioned that during the course of this investigation Pierce and Frick independently observed synergistic catalytic activity caused by mixing certain metal salts and carboxylic acids in the cross-linking reaction of cellulose with formaldehyde or methylolamide agents.[8]

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Comments on the Proposed Existence of Local Order in Amorphous Polymers below Their Glass-Transition Temperatures as Deduced from Calorimetric Studies

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The appearance of endothermal peaks in the dta, dsc, and heat capacity curves for the glass transitions of several amorphous polymers and the dependence of the endothermal peak heights and positions on the thermal histories of the samples investigated have recently been interpreted[1–4] as evidence for the existence of local intermolecular order in the polymers below the glass-transition temperature, T_g; order which is absent above T_g. When a glassy polymer is heated for a period of time above T_g and then either slowly cooled through the glass transition or quenched to below T_g and annealed, subsequent heating of the sample at a constant rate more rapid than the previous cooling rate[5–7] results[1–7] in an endothermal peak near T_g. For a given cooling rate, the endothermal peak height increases and moves to higher temperatures with an increase in the time of annealing below T_g[1,5] and with an increase in the annealing temperature.[1,4]

Several workers[1–4] have attributed the above-mentioned calorimetric behavior of amorphous polymers in the glass-transition region to the local ordering of the segments of neighboring polymer chains. They[1,3,4] envision the ordering process at temperatures below T_g as a parallel alignment of those portions of neighboring chains having identical configurations and conformations to form a small crystalline area in the otherwise amorphous solid. Upon heating through the glass transition, these crystalline regions are said to be disrupted at the onset of substantial polymer backbone motion, resulting in the observed endothermal peaks at, or slightly above, T_g. It is our view that such an interpretation (crystalline-like order produced by annealing below T_g) of the thermal-history-dependent calorimetric behavior of amorphous polymers in the glass-transition region is invalid, and we qualitatively suggest an alternative explanation based on the dynamic conformational characteristics of polymer chains and the nonequilibrium nature[5–7] of the glassy state of polymers.

The rotational isometric-state model[8] of polymer chains is adopted, where it is assumed that each backbone bond in the chain is constrained to a small number of rotational states (usually three). The frequency of occurrence or the probability of finding a given backbone bond in any of its rotational states depends[8,9] on the rotational states of the adjacent backbone bonds (nearest-neighbor interdependence). Intramolecular and intermolecular excluded-volume effects[9] are assumed to be absent in the undiluted bulk polymer.

Above T_g, each polymer chain is relatively free to adopt any of the myriad of possible rotational isomeric conformations consistent with the restriction that each backbone bond is only able to assume a small number of rotational states. As the temperature is lowered to T_g, the rate of rotational isomerism about each backbone bond is drastically reduced[5] until large-scale backbone motions become severely restricted below the glass transition due to the increased viscous drag at these increased densities (or due to the lack of sufficient free volume[10] to permit these rotational isomerisms). This increase in the viscous drag resisting rotational isomerism stems from the increased cooperativity[5] between the motions of neighboring chains which is made necessary by the increased density (or decreased free volume[10]) below the glass transition. Consequently, as the temperature is dropped rapidly from above T_g through the glass transition, the conformation of each chain becomes further removed[5,6] from its equilibrium conformation at the temperature in question.

The following three predictions are the logical results of the model of bulk amorphous polymers presented above: (i) the customary discontinuity in the heat capacity should be observed at T_g when the cooling and heating rates through the glass transition are equal, (ii) an endothermal peak should appear near T_g when the heating rate exceeds the cooling rate through the glass transition, and (iii) an exothermal peak should appear near T_g when the cooling rate through the glass transition exceeds the heating rate. When the rates of cooling and heating through the glass transition are equal, each chain is removed from its equilibrium conformation to the same extent[5,6] at the same temperature in both legs of the thermal cycle, thus the absence of thermal peaks near T_g. Heating through T_g at a rate exceeding the cooling rate through the glass transition results in each chain adopting a conformation closer to its equilibrium conformation, which corresponds to a lower energy, on the cooling leg of the cycle. Hence, an endothermal peak in the heating leg of the cycle appears near T_g where the chains are more rapidly able to approach their equilibrium conformations. The reverse reasoning predicts the appearance of an

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