NOTE

Mechanical Stability of Intumescent Chars

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ABSTRACT: Intumescent fire-retardant systems have been studied in detail from all points of view. However, all works passed around questions of mechanical stability of foamed chars produced during burning. In the present work, mechanical properties of intumescent chars has been discussed. Technique and method of such investigations have been supposed. It was supposed that mechanical stability of foamed chars correlates with high molecular fraction in char residue. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1827–1830, 1998

Key words: intumescence; foamed chars; fire-retardant polymers

INTRODUCTION

Among all fire-retardant additives, there exist a special class, intumescent fire-retardant systems.[1] When exposed to temperatures common during fires, intumescent polymeric compositions undergo an expansion to form a protective foamed char layer. This layer is, as a rule, 10–50 times thicker than the initial coating. Intumescent systems combine low weight of the coating and high efficiency of fire protection. For this reason, such systems found application fields of industry such as aircraft construction.

The main reason for the high efficiency of intumescent fire-retardant materials is the high thermoprotection properties of the foamed char cap[2]; and, as a consequence, efficiency depends on the char formation. This point has been discussed in detail.[3,4] Some aspects of char properties have been already discussed. In particular, it has been shown[5] that flammability of intumescent materials depends on the structure of coke cap. The process of liquid destruction products filtration through the pores char structure has been discussed in Gibov et al.[6] In Bourbigot et al.,[7] surface and bulk chemical structure of the char has been investigated. Chemical structure of foamed chars produced at different pyrolysis conditions has been discussed in Mashlyakovskii et al.[8]

In the present work, we intend to begin discussion about mechanical properties of foamed chars, in particular, their stability. These questions are very important because the efficiency of fire protection depends on these factors. Indeed, in the conditions of fire, char destruction can proceed not only by means of ablation and heterogeneous burning but also under external influence, such as wind. So we need to know how to create intumescent fire-retardant system with high mechanical stability.

It is known that mechanical properties of foams depend on their structure, porosity, and mechanical properties of the foam material. For the foamed chars pro-

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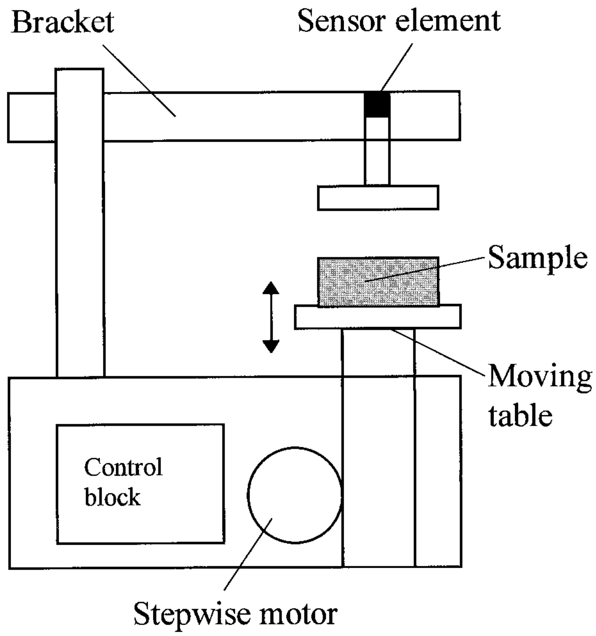

Figure 1 Structural scheme of the "Structurometr ST-1" device.

duced during burning, we can expect similar dependence; but in their order, these parameters will depend on conditions such as pyrolysis and initial chemical compositions. In the present work, we shall discuss these points and try to choose criterion of mechanical stability.

MATERIALS

Intumescent fire-retardant formulation on the base of carbamide–formaldehyde resin (Russian grade CFRLTCS) was used. As an intumescent additive, we used a blend of ammonium polyphosphate (Russian grade TU 6-18-22-101-87) and sorbitol (grade "NEOSORB," produced by Roquette Corp., France) at different ratios. Compositions were prepared by mixing of components with subsequent addition of catalytic agent (phosphoric acid). After mixing, the composition was put on the wood substrate. Solidification was done at 20°C at the air atmosphere in 24 h. The thickness of final coating was 0.3 mm.

Pyrolysis was made in the condition of constant heat flow from the radiation panel at the air atmosphere. Heat flow near the panel was 5 W/cm^2. This value corresponds to the heat flow from the flame in fires.[9] For the experiments carried at equal heat flow, all wood pieces with coating were placed on the foundation; and pyrolysis of all samples was made simultaneously.

EXPERIMENTAL

For experiments, we used a "Structurometr ST-1" device developed at the Moscow State Food Academy. A structural scheme of this device is shown in the Figure 1. A mobile table served for transference of the sample. The table moved by means of stepwise motor with a step of 0.01 mm. Such an approach allowed us to manage without a height position control system and avoid additional errors. The speed of moving can be varied in the range of 10 to 100 mm/min. The top plate was secured with a force sensor, which controlled the current effort of destruction (or deformation). The sensitive of sensor element is not worse than 0.01*N*. The area and shape of top plate was the same as wood substrate (3 cm disk diameter). In this work, all measurements were carried out at the constant speed 100 mm/min.

RESULTS AND DISCUSSION

First of all, we need to choose the approach to foamed char investigation. From the polymer foam theory, it is known[10] that for rigid polymer foams, there exist special mechanical criterion, the force of destruction. However, such an approach is not suitable in our case. First, values of destruction force for foamed chars are in some orders less then for common foams, and it can be expected that a mistake will be too high. Secondary, char has nonuniform structure in the coordinate of intumescence. To prove this point, let us consider (Fig. 2) a typical experimental curve for rigid polymer foam (curve 1) and foamed char (curve 2). One can see that curves have a qualitative distinguish in their behavior. In the case of foam, force rises up to the destruction force, and, after, it stays practically constant up to the point of full destruction. In the case of foamed char, this force rises during experiment. Moreover, we can emphasize the following two regions (showed on the plot): the first region corresponds to the destruction of char; the second region apparently corresponds to the destruction of pyrolysis zone. Because we did not allow the full degradation of the coating, after stopping the heat action, pyrolysis zone stays "freezing."

Now we should choose the criterion of mechanical stability. We can, of course, use the integral value, the

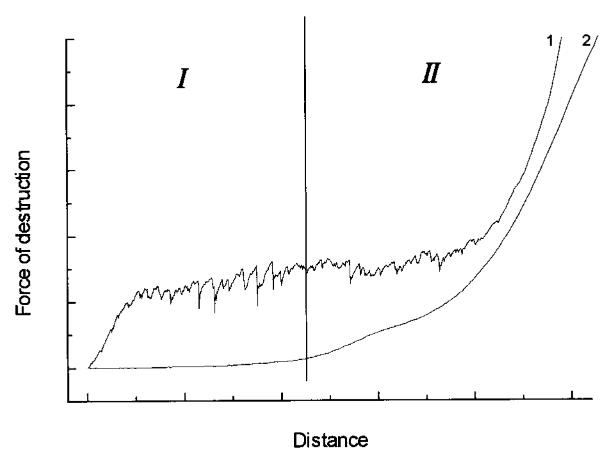

Figure 2 Typical curves of destruction: (1) rigid polymer foam; (2) foamed char.

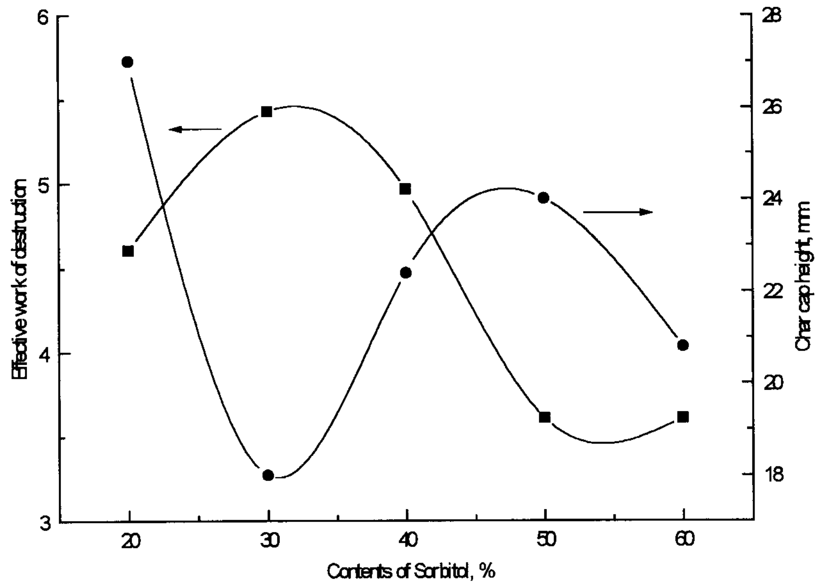

Figure 3 Effective work of destruction and char cap height for various contents of sorbitol.

full work of complete destruction of the char cap. However, this value can not adequately describe mechanical stability because chars have different heights (or expansion ratios). We suggest to choose a value of "effective" or "rescaled" work of destruction. In other words, full work should be divided on the char cap height. Criterion for mechanical stability in this approach will be effective work on the unit of surface area. Of course, this value will depend on the speed of destruction. To avoid misunderstandings in this work, this speed was constant.

Let us now try to use supposed criterion for examination of influence of various parameters on the mechanical stability of foamed chars and its connection with the expansion ratio. In Figure 3, data on the stability and char cap height versus the ratio of sorbitol in intumescence additive are presented. We can see that graphs clearly correlate, and the minimal expansion ratio corresponds to the maximum on the stability curve. We should note here that such contents of sorbitol (approximately 30%) correspond to the optimum ratio, derived from the data derived from differential thermal analysis.[11] Let us now conduct some analysis of Figure 3. It can be supposed that chars with minimal

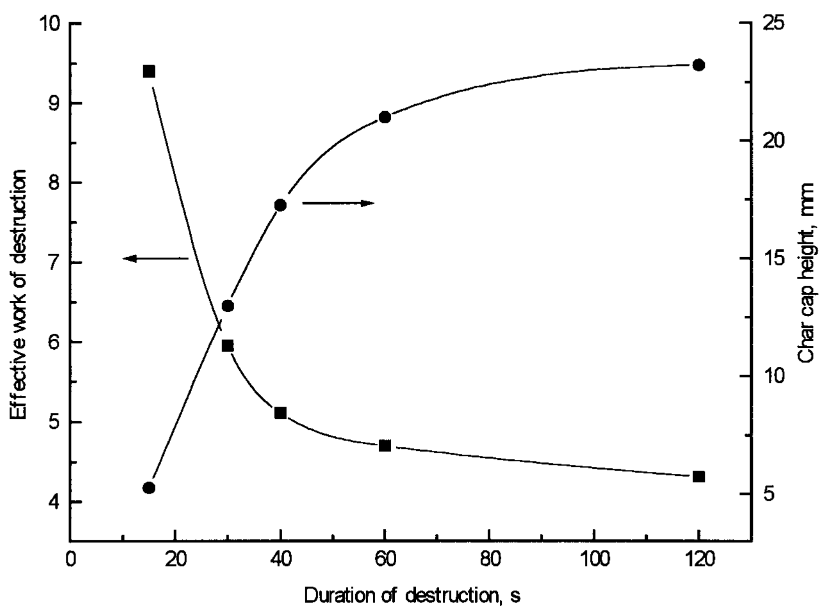

Figure 4 Effective work of destruction and char cap height versus duration of destruction.

height have structures that provide better thermoprotection than others because the conditions of destruction were the same for all samples. If this is the case, it can be expected that, in this char cap, a value of high molecular fraction will be more than for others. Of course, it is only a supposition. Such high molecular residue will strengthen the char cap. For this reason, effective destruction work should increase. The second reason is that it is known[12] that at optimal ratio of ammonium polyphosphate and polyol, formation of crosslinked structures at high temperatures proceed to a great extent. It should also increase the work of destruction.

The second point (about crosslinked phosphorus-containing structures) is rather understandable. In order to check the first one (about the influence of high-molecular polymer fraction), char stability as a function of pyrolysis duration has been investigated. Contents of sorbitol for all samples was constant and equal to the optimum ratio. These data are shown in Figure 4. One can see that when we increase duration of pyrolysis, effective work of destruction, in accordance with prediction, also increases. The similar picture was observed for the samples, exposed to various heat flows during equal time, as a varied parameter distance from the pyrolysis panel was used. As in the previous case, increasing the total power leads a decrease in mechanical stability.

CONCLUSIONS

For the first time, questions of mechanical stability of foamed chars has been discussed and investigated. Universal criterion for mechanical stability has been supposed. It has been shown that mechanical stability depends on the high molecular and crosslinked fragments in the char residue.

On the basis of this work, we can predict one main direction on how to create intumescent compositions with high mechanical properties introduction additives that promote formation of crosslinked structures at high temperature (e.g., on the base of polyphosphoric acid or organosilicon additives). So preliminary analysis indicates that addition of some silicon-containing compounds allows us to create compositions with high mechanical stability and thermoprotection properties.

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