

DEGRADATION BEHAVIOUR OF POLYMERIC MATERIALS FOUND IN AUTO SHREDDER RESIDUE WASTES*

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The thermogravimetry of a series of 50/50 mixtures of polypropylene, acrylonitrile/butadiene/styrene, polyvinyl chloride and polyurethane polymers have been studied as representative of the major polymeric materials found in automobile shredder residues. The weight loss behaviour of these polymeric mixes have been compared with the results calculated from the individual polymeric components. This comparison of the thermogravimetry curves and the calculated kinetic parameters indicates that interactions occur between the individual polymers when heated together. The extent of these interactions are dependent upon the polymeric mixtures being considered, but in most cases the changes in the degradation kinetic parameters were not large.

Keywords: automobile shredder residue, kinetics, polymeric materials

Introduction

The recycling of materials from discarded automobiles has been a viable and economical enterprise for many years. However, in recent years, due to the demands for improved fuel efficiency, the heavier recyclable metals are being replaced by lighter weight plastics which currently end up in landfill sites. Increased landfill tipping fees and the shift to increased plastic usage may soon make the metal shredding industry non economical. Consequently new technologies are being investigated to use this waste, commonly referred to as Automobile Shredder Residue (ASR), to produce useful products or resources. One approach is to employ inert gas pyrolysis to produce recoverable chemical feedstocks and reduce the quantities destined for landfill sites. However, in order to optimize these pyrolysis conditions a knowledge of the possible chemical in-

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teractions between the wide variety of plastics used in automobiles and found in ASR is desirable. In this paper we describe the preliminary results obtained with a sample of ASR and several mixed polymer systems as studied by dynamic thermogravimetry.

Experimental

Materials

The ASR employed in this study was obtained in a systematic manner for use in a characterization study of ASR currently being produced from shredding operations in the provinces of Quebec and Ontario [1].

The four automotive polymeric samples evaluated in this study were:

- Himont's PRO-FAX SV-152, polypropylene copolymer recommended for automotive applications (designated PP).
- Dow's Magnum Acrylonitrile/Butadiene/Styrene plastic resin recommended for interior automotive components (designated ABS).
- B. F. Goodrich's Geon, polyvinyl chloride resin (designated PVC).
- An automotive polyurethane foam received from Curon Canada Ltd., suppliers to the auto industry (designated PU).

Methodology

The thermogravimetry experiments were conducted using a TA Instruments 951 TG balance controlled by a TA Instruments 2100 controller. All experiments were conducted in nitrogen at a flow rate of 50 ml·min⁻¹. Heating rates of 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 deg·min⁻¹ were employed throughout. Kinetic data from the weight loss processes were analyzed by the Kissinger [2] and the Ozawa-Flynn Wall method [3, 4] which have been shown to be [5, 6] reliable techniques for evaluating degradation kinetics.

Results and discussion

The thermogravimetric weight loss curves for the ASR material and the four automotive polymers employed in this study are shown in Fig. 1. These curves were determined at a heating rate of 5 deg·min⁻¹. From these curves it can be seen that the composition of the ASR material is a complex mixture of substances some of which can be tentatively assigned to the various polymers shown in this figure. According to data obtained from the resin suppliers to the automotive industry [7] the following represents the plastic composition of the typical US

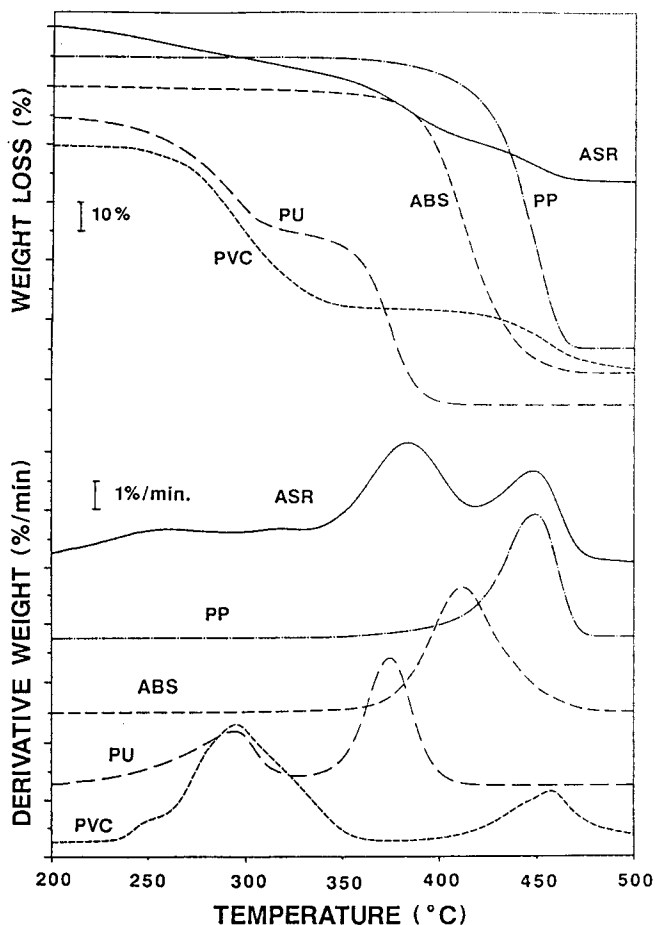


Fig. 1 Experimentally determined thermogravimetric and derivative weight loss curves for ASR(—), PP(- · - ·) ABS(- - - -), PU(— — —) and PVC(· · · · ·) determined at a heating rate of 5 deg·min⁻¹ in nitrogen

automobile manufactured in 1980 and which would be scrapped in 1990: PU 27%, PP 17%, PVC 12%, ABS 9% and others 35%. An attempt to match the ASR to this data was not very successful. However a compositional fit to the ASR data was obtained by the use of the TA Instruments File Modification Utility Program employing the following composition: PU 55%, PP 30% and fibrous material 15%. (The fibrous material was sound deadening material taken from a 1977 Oldsmobile Regency 98). However due to polymer interaction as will be noted in this study the following experimental mix was found to give the best fit to the

ASR data: PU 34%, PP 47% and fibres 19%. Clearly therefore polymer/polymer interactions are occurring during the thermal degradation of polymer mixes found in ASR.

The pyrolyses of the individual polymers were on the whole relatively simple and straight forward and showed no major deviations from the data reported in the literature. The derived kinetic parameters obtained in this study are summarized in Table 1 using isoconversion data corresponding to a weight loss of approximately 5% into each weight loss segment. It is evident from Fig. 1 that both the PP and ABS samples degrade by single one step processes while both the PVC and PU are characterized by two stage processes. In the case of the PVC the initial stage has been shown to be associated with the loss of hydrogen chloride to give polyenes which subsequently degrade during the second stage to give lower molecular weight fractions [8]. In the case of PU the initial stage has been attributed to the formation of isocyanates and substituted amines, while at higher temperatures lower molecular weight nitrogen containing species are produced [9].

Table 1 Kinetic mass loss data for the individual polymers

Polymer	Isoconversional data (taken 5% into the stage)				Kissinger data	
	1st stage		2nd stage		1st stage	2nd stage
	$E / \text{kJ}\cdot\text{mol}^{-1}$	$\log A / \text{min}^{-1}$	$E / \text{kJ}\cdot\text{mol}^{-1}$	$\log A / \text{min}^{-1}$	$E / \text{kJ}\cdot\text{mol}^{-1}$	$E / \text{kJ}\cdot\text{mol}^{-1}$
PP	161.0	10.61	–	–	161.1	–
ABS	169.4	11.81	–	–	159.4	–
PVC	116.1	9.55	144.1	11.96	129.5	227.3
PU	104.9	8.77	161.1	12.70	146.3	174.5

The purpose of this study, however, was to determine the possible interactions that could occur between the different polymer systems present in a typical ASR mixture. For example, does the hydrogen chloride gas generated from the degrading PVC influence the weight loss processes of the other polymer systems, and what reactive effects do the isocyanate species produced by PU have on the other polymer degradation processes. In order to obtain some idea of these effects 50/50 w/w mixtures of the four polymer systems were prepared by blending together equal weights of these polymers in a laboratory Wiley mill. The TG curves of these mixes were then determined, and the results compared with those obtained for the individual polymers. To facilitate the comparisons, the experimentally determined curves were compared with calculated weight loss curves derived from the individual weight loss curves by the use of the TA Instruments File Modification Software program. Comparison of these calculated curves with the experimentally observed weight loss curves in the differential form

is presented in Fig. 2. If no interactions were occurring between the two polymers in each mix, the calculated and the experimental curves should coincide. The fact that differences are noted indicates that some form of interaction must be occurring.

In the case of the PP/ABS mix the experimentally observed curve is similar to the calculated curve which would suggest that there does not appear to be a great deal of interaction between the degrading processes in the case of these two polymers. Meanwhile in the case of the PP/PVC mixture some interactions appear to be occurring as can be seen from the differences noted between the experimental and calculated curves. For example it appears that the onset of the loss of

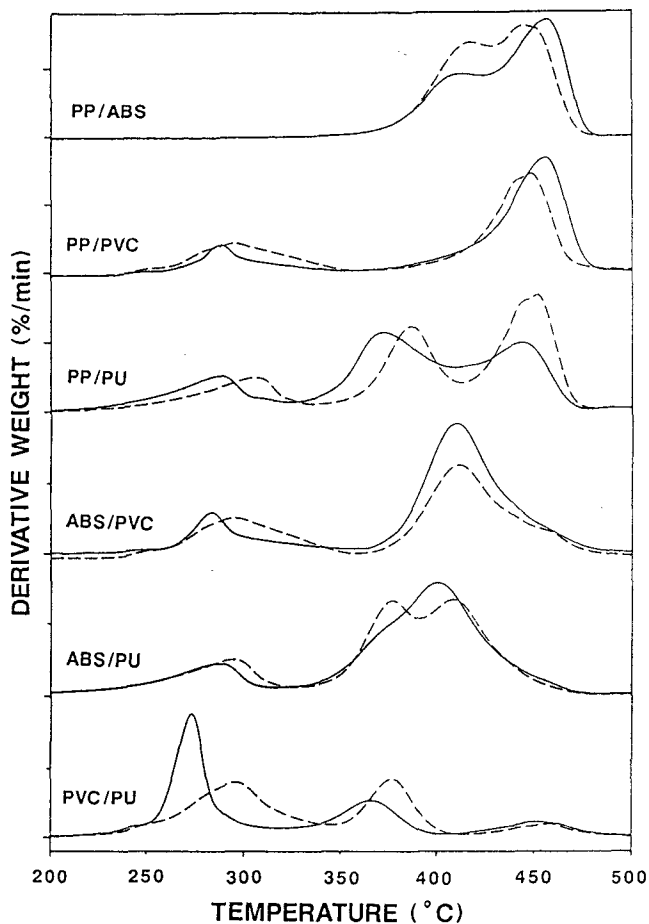


Fig. 2 Experimentally determined (—) and calculated (---) derivative weight loss curves for 50/50 polymer mixes of PP/ABS, PP/PVC, PP/PU, ABS/PVC, ABS/PU and PVC/PU determined at a heating rate of $5 \text{ deg}\cdot\text{min}^{-1}$ in nitrogen

hydrogen chloride occurs in a more discrete temperature range in the presence of PP than was noted for the neat PVC, while the weight loss associated with the PP was retarded and peaks at a higher temperature than was noted for the neat PP. This latter effect may be attributed to the formation of a char residue, a characteristic of the degradation of PVC. This char then retards the evolution of the volatile degradation products from PP. The PP/PU mix shows slightly different interactive characteristics. For example, it would appear that the onset of both stages of the PU degradation as well as that of the PP are enhanced, in that they appear to be occurring at lower temperatures than would be predicted from the behaviour of the individual polymers.

The behaviour of the ABS/PVC mix in many ways resembles that of the PP/PVC mix, i.e. the hydrogen chloride is evolved in a narrower temperature range while the weight loss associated with the ABS is retarded slightly. In the case of the ABS/PU mix the extent of the interactions appear to be only marginal with the weight losses tending to occur slightly earlier than would be anticipated based upon the behaviour of the individual polymers. Because of the two stage nature of the degradation of the individual polymers, PVC and PU, the possible occurrence of complex interactions in the case of a PVC/PU mixture is not unexpected. The onset of HCl evolution as well as the other stages of degradation all appear to be enhanced in the mix than would be predicted based upon the behaviour of the individual polymers. However, not only are there changes in the weight loss processes but it can be anticipated that chemical reaction is also possible between the acidic HCl and the basic amine products and could give rise to a wide range of new degradation products.

Clearly, therefore, a comparison of the experimental and calculated curves shown in Fig. 2 indicates, that in most of the polymer mixes studied, some form of interaction is occurring. However, the magnitude of the interaction is greatly dependent upon the type of polymer mixture being considered, with PVC and PU generating very reactive breakdown products.

In addition to examining the weight loss curves it is also possible to compare the weight loss kinetics obtained experimentally with the values obtained for the individual polymers. Because of the complexity of the weight loss curves shown in Fig. 2, the simplest approach is to compare the weight loss kinetics of these mixtures by applying the Kissinger method [2]. This data is presented in Table 2 for the polymer mixes and the individual polymers. Based upon these kinetic results it would appear that interaction between the polymers can once again be detected although surprisingly the kinetic effects in many cases are not large.

For example in the case of the PP/ABS mix the apparent activation energy (E) for ABS appears to be unaffected by the presence of the PP while that for the PP fraction is increased due to the presence of the ABS. In the case of PP/PVC mix, meanwhile, although the weight loss curves indicated changes in the evolution of HCl the kinetic E value determined from the peak rates for HCl evolution remained unaltered. Meanwhile the values for the PP and polyene fractions

decreased by 37 and 74 kJ respectively. The kinetic data for the PP/PU mix shows little difference between the values observed with the individual polymers with the possible exception of the PP fraction which has increased in a similar manner to that noted for the PP/ABS mix. The data for the ABS/PVC mix, meanwhile, reflects that obtained for the PP/PVC mix in that the E value for the HCl evolution remains the same as that of the individual polymer, while that for the ABS degradation remains unaltered but once again, however, there is a decrease in E for the polyene of 69 kJ. In the case of the ABS/PU mix meanwhile, only a slight increase in the E values for both components is noted in comparison with the individual polymers. Finally in the case of the PU/PVC mix although the degradation process is the most complex with both polymers contributing two stages, the

Table 2 Comparison of Kissinger calculated apparent activation energies for the polymers and their mixes

	Experimental mix		Individual polymers		
	Peak temp*/ °C	E / kJ·mol ⁻¹	Peak temp*/ °C	E / kJ·mol ⁻¹	Polymer
PP/ABS	412.1	162.9	411.8	159.4	ABS
	456.0	197.7	448.4	161.1	PP
PP/PVC	287.8	133.1	294.6	129.5	PVC
	430.2	124.4	448.4	161.1	PP
	455.2	153.7	456.6	227.3	PVC
PP/PU	288.2	154.8	295.0	146.3	PU
	371.3	174.4	374.5	174.5	PU
	443.9	189.2	448.4	161.1	PP
ABS/PVC	283.3	129.1	294.6	129.5	PVC
	409.4	165.6	411.8	159.4	ABS
	447.5	158.2	456.6	227.3	PVC
ABS/PU	287.3	162.4	295.0	146.3	PU
	366.5	171.5	374.5	174.5	PU
	400.2	171.9	411.8	159.4	ABS
PU/PVC	273.3	127.6	294.6	129.5	PVC
	—	—	295.0	146.3	PU
	365.8	162.9	374.5	174.5	PU
	450.7	223.2	456.6	227.3	PVC

*Value at a heating rate of 5 deg·min⁻¹

actual Kissinger kinetic analysis reveals results which are not exceptionally different from those noted for the individual polymers.

Conclusions

The composition of ASR has been shown to be a complex mixture of polymeric materials which can be reconstituted with some degree of success in the laboratory using TG weight loss experiments. Analysis of the thermogravimetry curves of binary mixtures of some of the polymers found in ASR indicates that interactions are likely when these mixed polymers are pyrolysed together in a resource recovery process. The degree of interaction and influence of the pyrolysis products produced however, is greatly dependent upon the polymers present and the reactivity of their degradation products (i.e. HCl, isocyanates, polyenes and amines). This preliminary study has provided interesting results on relatively simple binary polymer mixes and will be broadened in scope to cover more complex polymer mixtures, more typical of those found in ASR and other mixed plastic waste streams.

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Zusammenfassung — Eine Reihe von 50/50-Gemenge aus Polypropylen, Acrylnitril/Butadien/Styrol, PVC und Polyurethanpolymeren als typische Vertreter von Automobil-Häckselresten wurden thermogravimetrisch untersucht. Das Gewichtsverlustverhalten dieser Polymergemenge wurde mit den für die reinen Polymerkomponenten errechneten Resultaten verglichen. Dieser Vergleich von TG-Kurven und errechneten kinetischen Parametern zeigt, daß beim Erhitzen der Gemenge Wechselwirkungen zwischen den einzelnen Polymerkomponenten auftreten. Das Ausmaß dieser Wechselwirkungen hängt von der Zusammensetzung der Gemenge ab, jedoch sind die Änderungen der kinetischen Parameter für die Zersetzung in den meisten Fällen nicht groß.