

High-Resolution Thermogravimetric Analysis of Polyurethane/Poly(ethyl methacrylate) Interpenetrating Polymer Networks

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ABSTRACT: Thermal degradation of a series of polyurethane/poly(ethyl methacrylate) interpenetrating polymer networks and their constituent networks were studied by three modes of thermogravimetric analysis: the conventional method, the constant reaction rate method, and the dynamic rate technique. The best understanding of the degradation mechanism was achieved by the last method, which allows much better resolution of overlapping events. In addition, the weight losses correspond well with the results obtained from the constant reaction rate analysis, but are achieved in shorter times. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 287–295, 1998

Key words: High-resolution thermogravimetric analysis; interpenetrating polymer networks; polyurethane; poly(ethyl methacrylate)

INTRODUCTION

Thermogravimetric analysis is an important tool in the study of the complex thermal degradation pathways of polymers and polymer systems. The effects of additives, blending, and network structure on the degradation of polymers may be studied by measuring the weight change as the temperature of the sample is increased. However, to yield accurate and useful information, the individual decomposition weight losses must be well resolved. Factors affecting the resolution of successive weight losses are sample size and geometry, heating rate, and purge gas conditions. It has been shown that in thermogravimetric (TG) analysis the most effective method of enhancing resolution is by slowing the heating rate,^{1,2} which leads to longer experimental times. A relatively new technique, high-resolution thermogravimetric analysis (Hi-Res TGATM, TA Instruments), has

been introduced which provides increased resolution without increasing the required experimental time and, in many cases, decreases the time needed for analysis.

The application of high-resolution TG techniques to polymers has been demonstrated in a very limited number of articles.^{3–5} Lever et al.³ showed the enhanced resolution obtained in the analysis of an acrylonitrile–butadiene–styrene (ABS) copolymer. Salin and Seferis⁴ proposed a simplified method to extract kinetic information from the variable heating rate data produced by the high-resolution techniques. They found that keeping the initial heating rate constant and changing the resolution was the best approach. The activation energy, preexponential factor, and reaction order were determined for the two stages of ethylene vinyl acetate (EVA) copolymer decomposition, as well as the activation energy of poly(ether ether ketone) (PEEK) resin decomposition. Gill et al.⁵ demonstrated a number of applications of high-resolution TG analysis, including a high-resolution study of polytetrafluoroethylene (PTFE) and EVA.

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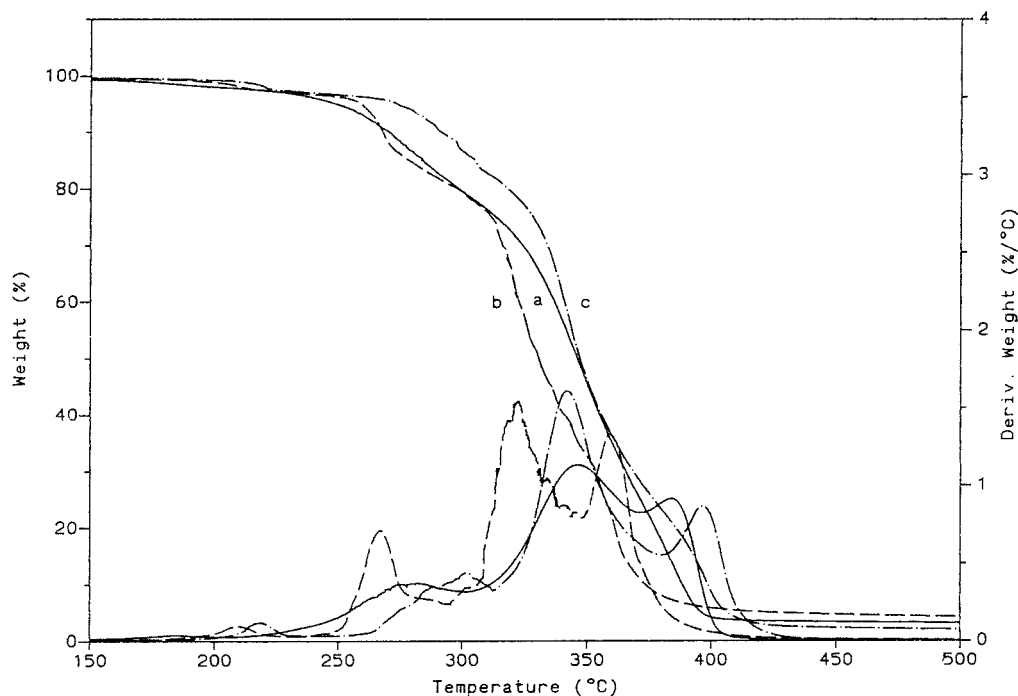


Figure 1 TG analysis of the PEMA network: (a) conventional, 1°C/min (420 min); (b) constant reaction rate, resolution -4; sensitivity 1 (319 min); (c) dynamic rate, resolution 4; sensitivity 2 (63 min).

In this study, the thermal degradation of a series of polyurethane/poly(ethyl methacrylate) interpenetrating polymer networks and their constituent networks were examined using three different modes of TG analysis: (1) conventional TG analysis, that is, a constant heating rate, (2) constant reaction rate, that is, constant preselected rate of weight change, and (3) dynamic rate, where the heating rate of the sample is continuously varied in response to changes in the rate of decomposition in order to maintain maximum resolution.

EXPERIMENTAL

Materials and IPN Preparation

The preparation of the poly(ethyl methacrylate) (PEMA) and polyurethane networks and the IPNs were described in more detail in previous articles.^{6,7} The PEMA network was formed by copolymerizing ethyl methacrylate (EMA, Aldrich, UK) with tetraethylene glycol dimethacrylate (TEGDM, BDH, UK), using azoisobutyronitrile as an initiator. The polyurethane (PUR) was formed from poly(oxypropylene glycol) (PPG 1025, BDH)

as the soft segment and either 1,1,3,3-tetramethylxylene diisocyanate (TMXDI, Cytec, UK) or toluene diisocyanate (TDI, Aldrich, UK) as the hard segment. The crosslinker used was trimethylol propane (TMP, Aldrich, UK) and the PUR catalyst was stannous octoate (SnOc, Aldrich).

Thermogravimetric Analysis

The polymer degradation characteristics were determined using a TA Instruments TGA 2950 thermogravimetric analyzer. Samples of 8–12 mg were analyzed in a nitrogen atmosphere from 100 to 520°C at heating rates of 1, 5, and 20°C/min for conventional analysis. A constant reaction rate TG analysis was conducted at an initial heating rate of 10°C/min with resolution and sensitivity settings as indicated in the text. High-resolution TG analysis was conducted at various resolution and sensitivity settings with an initial heating rate of 50°C/min.

RESULTS AND DISCUSSION

Homopolymer Networks

The degradation characteristics of the two PUR networks and the PEMA network were studied

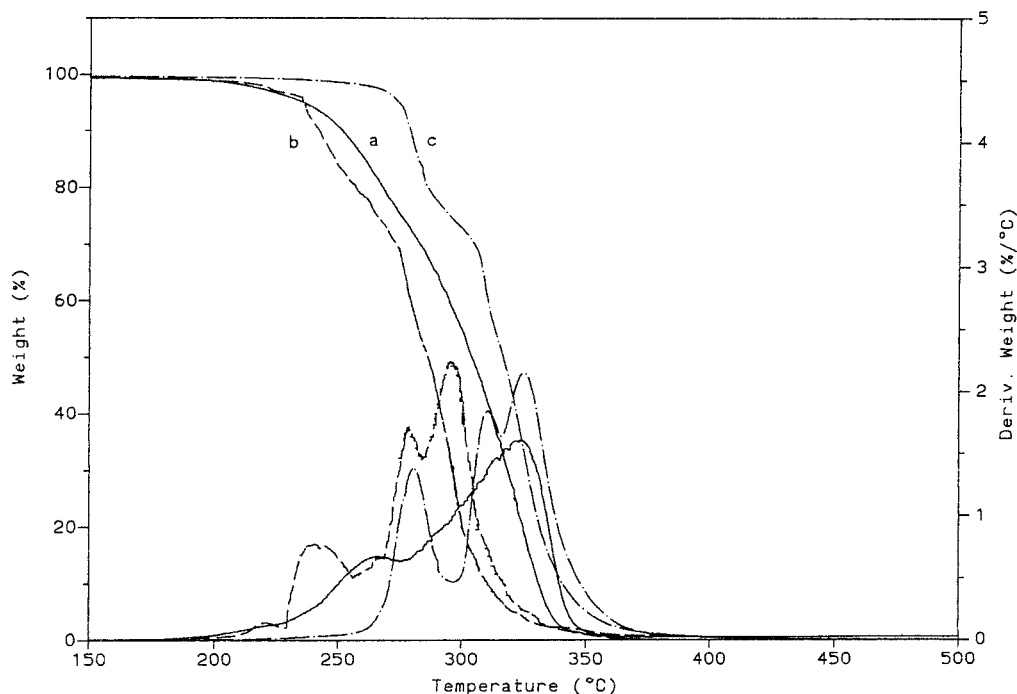


Figure 2 TG analysis of TDI/PPG PU network: (a) conventional, 1°C/min (420 min); (b) constant reaction rate, resolution -4; sensitivity 2 (319 min); (c) dynamic rate, resolution 4; sensitivity 2 (61 min).

using conventional, constant reaction rate, and dynamic rate thermogravimetric analyses. Figure 1 shows the TG analysis results for the PEMA network. The thermal degradation of PEMA has been reported to be very similar to that of PMMA.^{8,9} Kashiwagi et al.¹⁰ described the degradation of PMMA as proceeding in three steps: initially, scission of the head-to-head linkages; second, scissions initiated from vinylidene chain ends; and, finally, random scission within the polymer chains. The conventional TG curve shows some evidence of the three-stage weight loss for the decomposition of the PEMA network (Fig. 1), but the constant reaction rate TG curve clearly shows a three-step degradation. In the first step, 18.9% of the weight is lost; in the second, 45.7%, and, finally, the remaining 35.4% is lost. The dynamic rate TG analysis of PEMA at a resolution setting of 4 and sensitivity 1 showed some indication of the three-step mechanism, but by increasing the sensitivity to 2, the three regions of weight loss are more clearly defined (Fig. 1). The three weight-loss regions shown correspond reasonably to those indicated by the constant reaction rate TG analysis, that is, 18.1, 57.8, and 24.1%. This correlation between the constant reaction rate and the dynamic rate TG analysis

results gives an indication of the reliability of these results. This greatly enhanced resolution of the three steps was obtained in 63 min as compared to 319 min for the constant reaction rate experiment.

The thermal stability of PURs has been extensively studied.¹¹⁻¹⁴ In this article, PURs based on two different diisocyanates were studied by high-resolution TG. PURs are formed by the reaction of a polyether or polyester macroglycol, which forms the soft segments, with diisocyanates, which form the hard segments. The onset of the thermal degradation of the UR bond depends on the type of precursors used. Petrovic et al.¹¹ studied the thermal degradation of segmented PURs by TG analysis at 0.5, 1, and 2°C/min in nitrogen. They showed that the initial stages of weight loss were dominated by hard-segment degradation. The TG curve of a PUR produced from diphenylmethane diisocyanate (MDI) and poly(tetramethylene glycol) (MW = 1000) with a butanediol chain extender showed two distinct regions of weight loss, as reflected by the derivative weight loss curves. The first part of the degradation was split into two peaks: The first mass loss was ascribed to degradation beginning in the hard segments, and the second part, to degradation of the soft seg-

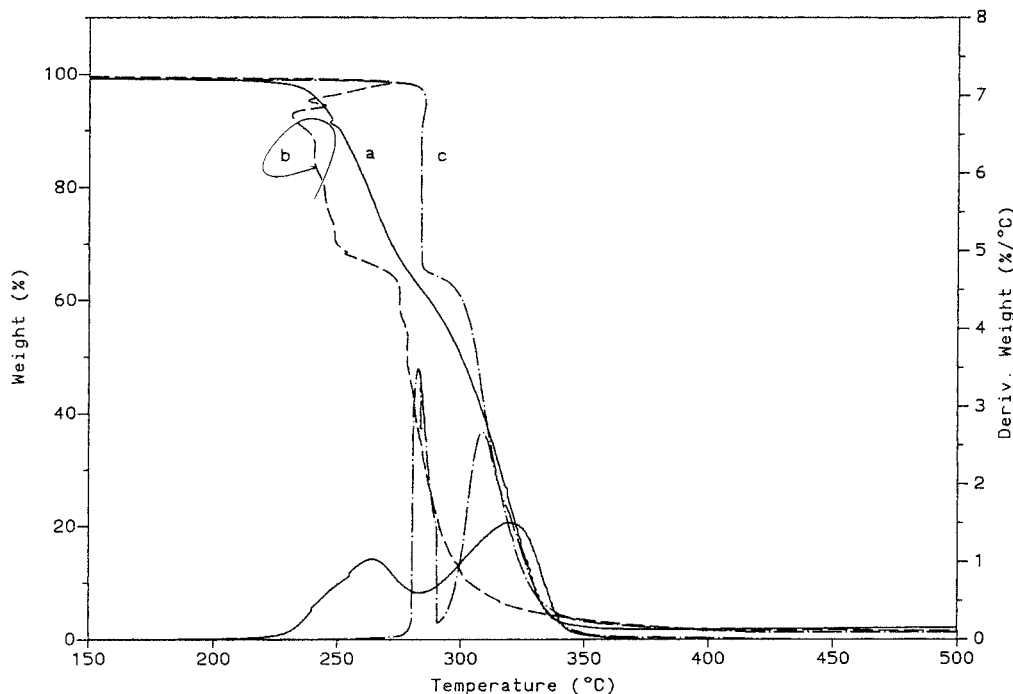


Figure 3 TG analysis of a TMXDI/PPG PU network: (a) conventional, 1°C/min (420 min); (b) constant reaction rate, resolution -4; sensitivity 1 (306 min); (c) dynamic rate, resolution 4; sensitivity 2 (52 min).

ments. The second region of the degradation process was the loss of all volatile material. Not all the PUR samples used by Petrovic et al.¹¹ showed the splitting of the first part of the weight loss. TG analysis of three series of polyetherurethaneurea (PEUU) elastomers was performed by Lee and Ko.¹³ They found that the PEUU elastomers exhibited two-stage degradation behavior at a heating rate of 20°C/min in a nitrogen atmosphere. The initial degradation was, again, shown to start with the hard segments and the thermal stabilities of the PEUUs were related to the microstructural ordering of the hard segments.

Weight-loss curves of a network PUR made from TDI hard segments and PPG 1025/TMP (3 : 1) soft segments by conventional, constant rate, and dynamic TG analyses are shown in Figure 2. While the 1°C/min conventional TG curve does not show any indication of the possible three weight-loss regions, the constant rate TG curve clearly shows a three-step weight loss. Degradation, possibly initiated in the hard segments, started at 188°C and this first region of decomposition resulted in a 23.6% weight loss. The degradation that then continued, probably in the soft segments, resulted in a further 25.5% weight loss, with the remaining 50.9% degrading above

286°C. Because of the long experimental time required for the constant rate study, dynamic rate TG analysis is preferable with its shortened experimental times. Figure 2 shows the dynamic rate TG curve at resolution 4 and sensitivity 2 settings. The curve at sensitivity 1 showed a shoulder in the derivative mass loss curve, which is indicative of a more complex process than can be seen from the conventional TG curves. Increasing the sensitivity to 2 enhances the resolution to such a degree that the three-step process, seen by constant rate TG analysis, is quite clear. The weight losses shown by dynamic rate TG analysis correspond well with those shown by the constant reaction rate analysis. They were initially 25.9%, then a further 22.5%, and, finally, 51.6%.

Analysis of another PUR showed a slightly different decomposition pattern. This PUR, made from TMXDI hard segments and PPG 1025/TMP (3 : 1) soft segments, showed a two-step degradation process in the conventional TG weight-loss curve. Decomposition started at 209°C and the first weight loss was 37.9%, followed by the remaining 62.1% (Fig. 3). The constant reaction rate TG curve again showed a two-step degradation process, which is made somewhat less clear because of temperature variations to obtain a con-

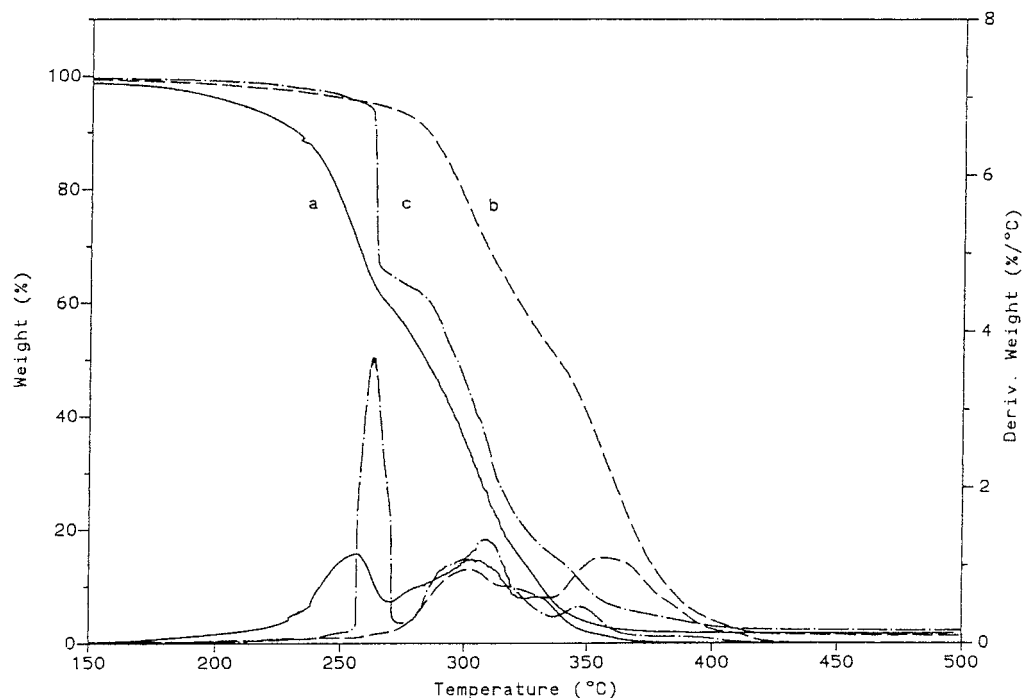


Figure 4 TG analysis of a 70 : 30 PUR/PEMA IPN: (a) conventional, 1°C/min (420 min); (b) conventional 20°C/min (21 min); (c) dynamic rate, resolution 4; sensitivity 2 (59 min).

stant rate. Dynamic rate TG analysis of the PUR also showed the two clearly resolved weight losses. Decomposition commenced at 275°C. The first weight loss was 35.0%, followed by the remaining 65.0% above 292°C. There was no indication of a third step, as was found for the MDI-based PUR.

Interpenetrating Polymer Networks

Interpenetrating polymer networks (IPNs) consist of two or more polymers, of which at least one was crosslinked in the presence of the other network. This synthesis procedure commonly results in a degree of forced mixing of the network segments. The IPNs investigated in this study consisted of TMXDI-based PUR and PEMA. The soft-segment: crosslinker ratio used was 3 : 1 (PPG 1025 : TMP) and 5 wt % TEGDM was used to crosslink the PEMA. The morphology and mechanical properties of this series of PUR/PEMA IPNs were already described by Hourston and Schafer.⁶ The tensile properties of the 70 : 30 PUR/PEMA IPN composition showed it to exhibit a synergistic effect. The stress at break and toughness index properties of this particular IPN exceeded those of either

the PUR or the PEMA homonetworks. Hourston and Schafer⁶ attributed this to both networks being continuous and to a high level of network interpenetration.

The TG analysis of the 70 : 30 PUR/PEMA (Fig. 4) and other IPNs using a number of high-resolution settings showed that a setting of resolution 4 and sensitivity 2 produced the most accurate results. Resolution 4, sensitivity 2 was, therefore, used for all subsequent analyses of these IPN materials. Figure 4 shows the 1°C/min, 20°C/min, and resolution 4, sensitivity 2 TG curves for the 70 : 30 PUR/PEMA IPN. The dynamic rate TG curve shows enhanced resolution of the degradation for the IPN. The initial weight loss that starts at 252°C, resulting in a 32.72% weight loss. This first loss is approximately equal to the weighted sum of the initial weight losses of the PUR and the PEMA networks, which are 35.0 and 18.1%, respectively. This is followed by a further two weight losses and, finally, two more weight-loss regions which can be attributed to both the PEMA and PUR degradations.

Figures 5 and 6 show the entire PUR/PEMA IPN series. It is immediately apparent that none

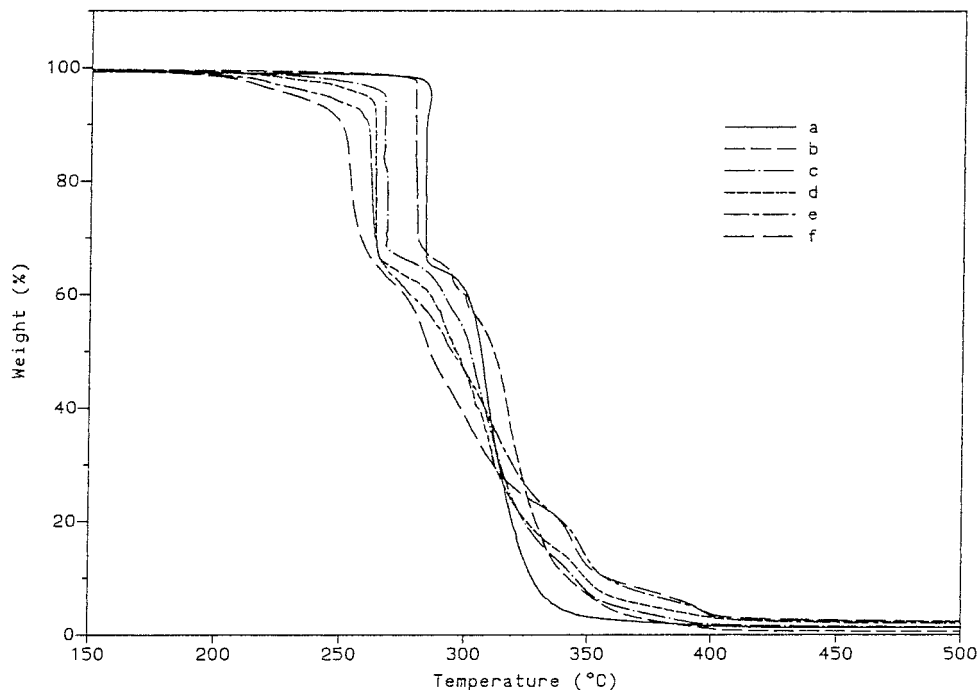


Figure 5 TG analysis of a PUR/PEMA IPN series. Dynamic rate, resolution 4; sensitivity 2: (a) PUR homopolymer network; (b) 90 : 10; (c) 80 : 20; (d) 70 : 30; (e) 50 : 50; (f) 40 : 60.

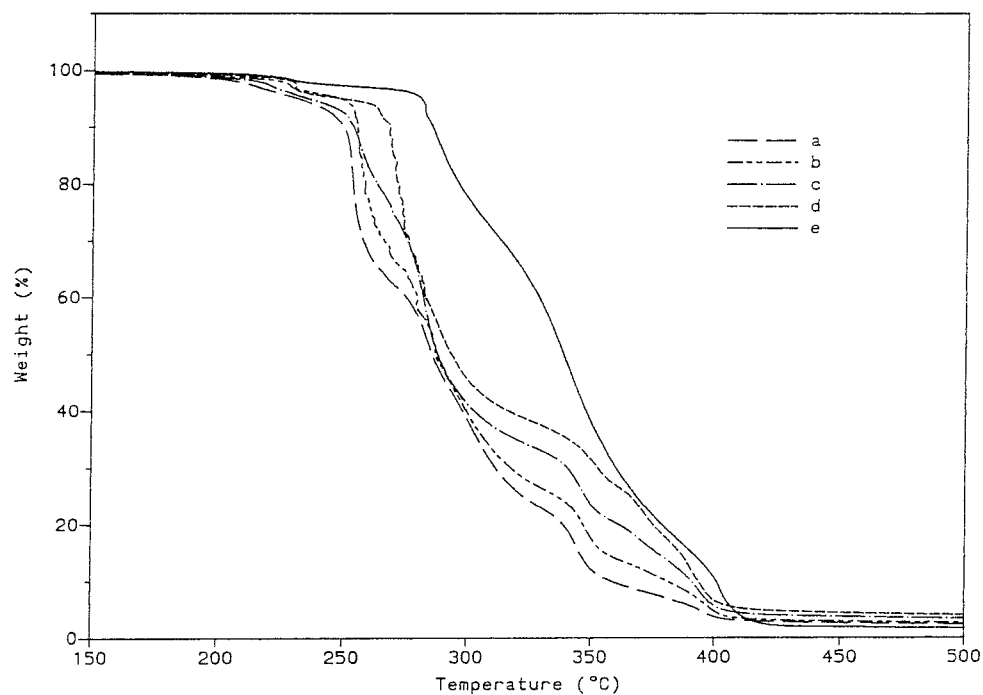


Figure 6 TG analysis of a PUR/PEMA IPN series. Dynamic rate, resolution 4; sensitivity 2: (a) 40 : 60; (b) 30 : 70; (c) 20 : 80; (d) 10 : 90; (e) PEMA homopolymer network.

Table I Degradation Initiation Temperature for the PUR/PEMA IPN Series

PUR/PEMA Ratio	Initiation Temperature for Initial Weight Loss (°C)
100 : 0	275
90 : 10	273
80 : 20	258
70 : 30	256
60 : 40	—
50 : 50	252
40 : 60	231
30 : 70	238
20 : 80	238
10 : 90	258
0 : 100	258

of the IPNs have the thermal stability of either of the homopolymers. TG analysis of a PUR/PMMA IPN by Kim et al.¹⁵ showed an increase in the weight retention with increasing PMMA content, and all of the IPNs showed a greater heat stability than that of the individual components. They attributed this to the presence of the unzipped PMMA monomer which acted as a radical scav-

enger for the radicals produced by the degrading PUR, thus delaying PUR degradation. Pandit et al.¹⁶ reported a decrease in the initial degradation temperature of a PUR/PS IPN as the polystyrene content was increased. They attributed this to an increase in the crosslink density by the formation of PS intranetwork bridges which led to the formation of strained bonds. TG analysis has also been used to analyze the thermal stability of castor oil-isophorone-diisocyanate¹⁷ and epoxy-PMMA¹⁸ IPNs.

In this series of IPNs, the initiation of degradation occurs at an earlier temperature as the PEMA content increases from 0 to 60% (Table I). Between the 40 : 60 and the 30 : 70 PUR/PEMA IPN compositions, Hourston and Schafer⁶ reported that the IPNs showed changes due to a difference in miscibility/morphology. TEM micrographs by Hourston and Schafer⁶ showed that with the 30 : 70 PUR/PEMA IPN a change in the matrix was observed from a cocontinuous morphology to a predominantly PEMA matrix with discontinuous PUR phases. It is at this component ratio that an increase in the weight retention was observed (Table I). From the 30 : 70 to the 10 : 90 PUR/PEMA IPN, the IPNs became more thermally stable and behaved more like the

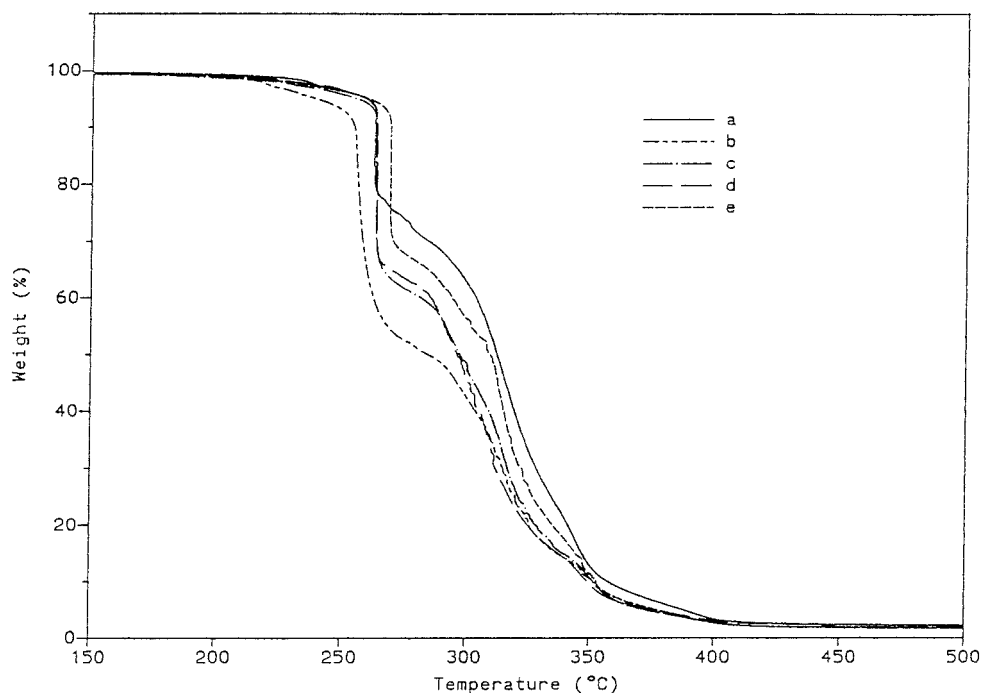


Figure 7 Effect of soft segment-to-crosslinker ratio (PPG : TMP) on a 70 : 30 PUR/PEMA IPN with 5% TEGDM. Dynamic rate, resolution 4; sensitivity 2: (a) 1 : 0; (b) 1 : 1; (c) 2 : 1; (d) 3 : 1; (e) 7 : 1 (molar ratios).

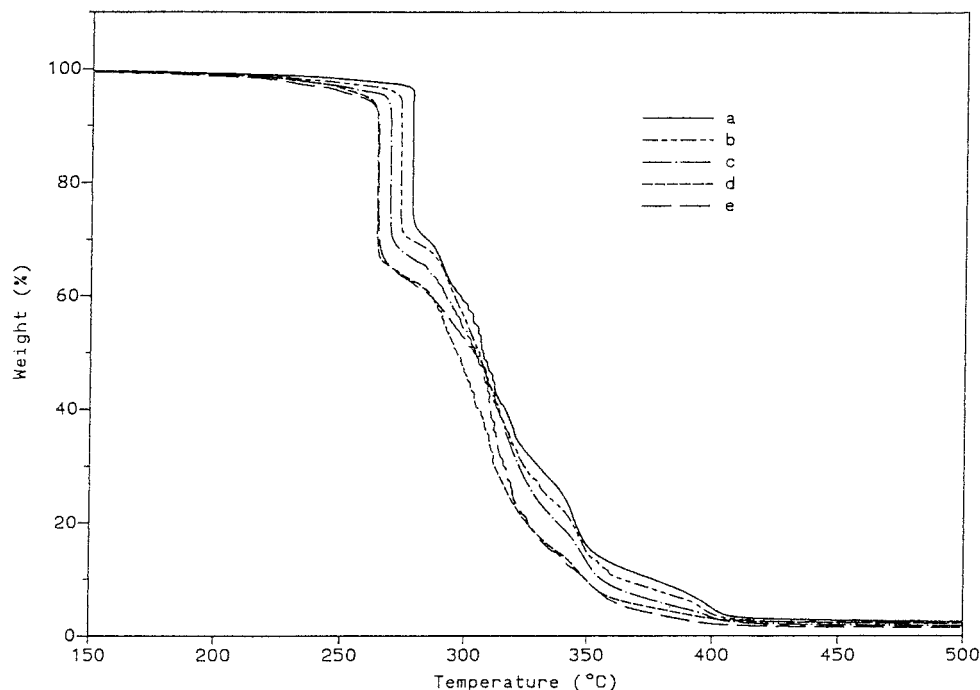


Figure 8 Effect of crosslinking on a 70 : 30 PUR/PEMA IPN with a soft segment to crosslinker ratio of 3 : 1. Dynamic rate, resolution 4; sensitivity 2: (a) 0%; (b) 1%; (c) 2.5%; (d) 5%; (e) 10% (molar ratios).

PEMA homopolymer. This is in agreement with the other results reported by Hourston and Schafer for this IPN series.⁶

Crosslinking of the first-formed network in an IPN restricts the phase domain size for the second polymer. Figure 7 shows the dynamic rate TG analysis of IPNs with a PEMA crosslink level of 5% TEGDM and varying PPG 1025/TMP ratios. The IPN with the PPG 1025/TMP of 1 : 1 was shown to be the least thermally stable. Decreasing the crosslinking level leads to more thermally stable IPNs and the 7 : 1 ratio IPN shows an increased initial weight retention over that of the linear polyurethane IPN (1 : 0).

The effect of the level of TEGDM crosslinking in the PEMA component is shown in Figure 8. Crosslinking leads to a decrease in the thermal stability of the IPNs, but little difference was observed at the higher crosslink levels between 5 and 10 wt % TEGDM.

CONCLUSIONS

High-resolution TG analysis offers a rapid technique for the analysis of polymers and polymer

systems. Improved resolution was obtained in most cases, which will allow a more thorough analysis of the degradation pathways of polymers, polymer blends, and IPNs. Good resolution of the individual degradation processes occurring in the IPNs themselves and the component networks was achieved for PU-PEMA-based IPNs.

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