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THERMAL AND DEGRADATION BEHAVIOR OF FIQUE FIBER REINFORCED THERMOPLASTIC MATRIX COMPOSITES

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Abstract

The influence of untreated and treated fique fibers on the crystallization process and thermal degradation of different thermoplastic matrix composites has been evaluated. The fique fibers have been treated with different chemicals according with the type of thermoplastic matrix employed. Additionally, a copolymer of poly(propylene) with maleic anhydride (MAPP) has been used as compatibilizer. The treatments introduce an increment on the thermal stability of fique fibers respect to untreated fibers. Crystallization is affected by the presence of fique fibers showing important differences for each type of composites. Fiber presence has an important influence on the matrix morphological characteristics, as observed by dynamical mechanical analysis.

Keywords: crystallization, esterification, fique fibers, polymer matrix (POM), poly(propylene) (PP), thermal stability

Introduction

Vegetable fibers are increasingly finding application for polymeric reinforcements because of their characteristics such as low cost, low abrasion, high disposability, recyclability and biodegradability [1–3]. Some fibers present a moderate specific strength and modulus [4]. There are many studies concerning to natural fibers as sisal [5–6], jute [7–8] or flax [9]. However, a great amount of other natural fibers can also be employed to produce composite materials.

Fique fibers are native from Colombia being extracted by mechanical techniques from leaves of plants with the same name. The fique plants are also cultivated in different regions around South America.

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When semicrystalline thermoplastics polymers (TP) are used as matrix, the interfacial morphological features can be affected due to the direct influence of the fibers on the crystallization process [10–12]. These featured changes can lead to variations on melting and crystallization temperatures or even on degree and type of crystallization, important factors to determinate the mechanical properties [13].

Fique fibers present a predominant polar character due to OH groups on their structure [14]. On the contrary, thermoplastic matrices as poly(propylene), PP, are highly non polar polymers [15]. For enhancing the interactions at the fiber-matrix interface, surface modification [16–20] or coupling agent adding [21–24] have been tried.

Some studies have reported the mechanical behavior of thermoplastic composites reinforced with natural fibers [25–28]. However, relatively few studies reporting the thermal behavior of these composites have been published [29–31].

In the present study, the influence of fique fibers and that of fibers modified with different treatments such as maleic anhydride (MA), propionic acid (PA), glycydylmethacrylate (G) or formaldehyde (F), as well as the use of a copolymer of poly(propylene) and maleic anhydride (MAPP) as compatibilizer, on the thermal behavior of thermoplastic composites has been analyzed. Both poly(propylene) and polyoxymethylene have been used as matrices. Thermal stability has been studied by thermogravimetric analysis. Thermal studies have been carried out by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

Experimental

Materials

Compañía de Empaques S.A. (Medellin, Colombia) supplied the fique fibers. Thermoplastic matrices employed were PP (Novolen 2300 K, density: 0.91 g cm^{-3}, *MFI*: 4 g 10 min^{-1} at 190°C) and POM (Ultraform S2320, density: 1.41 g cm^{-3}, *MFI*: 11 g 10 min^{-1} at 190°C). The fibers were cleaned and thereafter chopped with a mesh size of 4 mm, thus obtaining an average length of 2.9 mm. For PP composites, chemical agents employed for treatment of the fique fiber for PP composites were MA, Fluka, PA, Fluka, and MAPP copolymer (Eastman, Epolene 43) as compatibilizer. For POM composites, the chemical agents used were F, Panreac and G, Fluka, and MAPP copolymer was also employed as compatibilizer.

Fiber surface modification

For all treatments, the fibers were immersed in a solution of the agent used. A catalyst was employed in specific cases, as for F and G treatments. After treatment, the fibers were washed first with the respective solvent, and then with distilled water. The treated fibers were then dried at 105°C for 24 h. The main details of the different treatments are presented in Table 1. The formaldehyde treatment was developed according with the process described by Hua *et al*. [32].

Table 1 Modification treatment conditions applied on fique fibers

Treatment type	Solvent	Catalyst	Reaction time/h	T/°C
MA	acetone	–	25	55
PA	distilled water	–	1	room
F	distilled water	$ZnCl_2$	0.17	room
G	distilled water	H_2SO_4	1	room

Compatibilizer addition

A MAPP copolymer was mixed with each matrix by melt mixing using a Haake Rheomex CTW 100 mixing chamber, operating at a screw speed of 15 rpm and at 180 and 190°C for PP and POM matrices, respectively. The mixtures were then pelletized for ulterior processing.

Composite processing

A Haake Rheomex CTW 100 twin-screw extruder was employed to compound fique fiber with thermoplastic matrices. Mixing was carried out at 180 and 190°C for PP and POM matrices, respectively, at a screw rate of 15 rpm.

Composites plates were performed by compression molding. For PP composites, molding was carried out at 180°C and 10 bars for 5–10 min, while for POM composites 190°C and 15 bars during 5–10 min were used. Plates were obtained after cooling from melt to room temperature at 4°C min^{-1}.

Test methods

Thermogravimetry (TG) was employed to analyze the thermal stability of fibers and composites. The measurements were performed using a Setaram 92–12 thermoanalyzer. A heating rate of 10°C min^{-1} and nitrogen atmosphere were used. The peak temperatures, T_p and T_{pc}, are defined as the temperatures corresponding to the temperature peak in each region of the DTG curve for fique fibers and composite materials, respectively.

A differential scanning calorimeter, Perkin Elmer DSC-7, was used to monitor the thermal behavior of composites during crystallization. The samples were heated to 180°C for PP or 190°C for POM, at a heating rate of 10°C min^{-1} and then cooled to room temperature at a cooling rate of 4°C min^{-1}. Then, a second heating scan was carried out at 10°C min^{-1}.

The normalized crystallization degree, X_R, was determined as follows:

$$X_R = 100\frac{\Delta H}{\Delta H_M}$$

where ΔH is the melting enthalpy for composite sample and ΔH_M is the melting enthalpy of neat matrix.

Dynamical mechanical analysis of rectangular samples measuring 60×12×3 mm was carried out using a Metravib viscoanalyser with a three-point bending device. A heating rate of 3°C min^{-1} and a frequency of 10 Hz were used.

Optical observations were made using a Zeiss Axioplan 2 Hal 100 with cross polarizers in order to investigate the crystallization process in the fiber surfaces. The samples were maintained at 220°C for 10 min and then cooled at 4°C min^{-1} to the crystallization temperature: 125°C for PP composites and 145°C for POM composites with untreated fibers, respectively.

Results and discussion

Thermogravimetric analysis

The thermal behavior of fique fibers has been reported in a previous work [14]. The fibers present three mass loss regions: 60–105, 220–350 and 350–600°C. The first region corresponds to the release of moisture present in the fique fiber. The other regions are associated to the decomposition of the fiber constituents such as hemicellulose, lignin and cellulose.

Table 2 Thermogravimetric behavior of untreated and treated fique fibers

Treatment type	Mass loss_1/%	T_{p1}/	T_{p2}/	T_{p3}/
			°C	
Untreated	6.7	64.9	301.3	355.8
MA	3.5	63.4	309.5	368.2
PA	3.7	65.8	335.5	386.0
F	5.5	74.1	336.1	386.0
G	3.2	67.4	342.3	390.5

Table 2 shows the mass losses in the 60–105°C region and also the three-peak temperatures (T_p) for untreated and treated fibers at the three different loss regions. The different systems employed to enhance the fiber/matrix adhesion have an important effect on the thermal stability of the fique fibers. Thus, the peak temperatures in all degradation regions experiment a slight increment with treatment, in special with PA, F and G compounds. On the other hand, a 18–47% reduction in the moisture content is observed as a function of the treatment used. The peak temperatures in this region experiment a slight increment with respect to that for the untreated fiber, specially with F or G treatments, possibly due to the presence of new groups in the fiber surface reducing the moisture access to the fiber.

Concerning to the second and third degradation regions, the main variations are associated with higher decomposition peak temperatures, thus indicating that the thermal stability of the treated fibers increases. Authors as Nada *et al*. [33] reported comparable results with cellulose treated with a process as cyanoethylation. The results observed in the different degradation regions may be associated with the presence of groups that restrict the segmental mobility but also to fiber crystallinity variations, that can be load to variation on the fiber stiffness [34].

Table 3 Thermogravimetric behavior of different PP composites with 20 mass% untreated fiber

Treatment type	T_{pc_1}/	T_{pc_2}/	T_{pc_3}/
		°C	
Neat PP	–	–	473
Untreated	310	387	451
PA	340	389	486
MAPP	344	393	476

TG curves for both PP and untreated fiber/PP composites and also for both POM and untreated fiber/POM composites are presented in Figs 1 and 2, respectively. The untreated fiber/PP composites present a region associated with the fiber constituents decomposition appearing as shoulders at 250–400°C. Table 3 shows a summary of changes registered on peak temperatures for PP composites (T_{pc}) in each decomposition region.

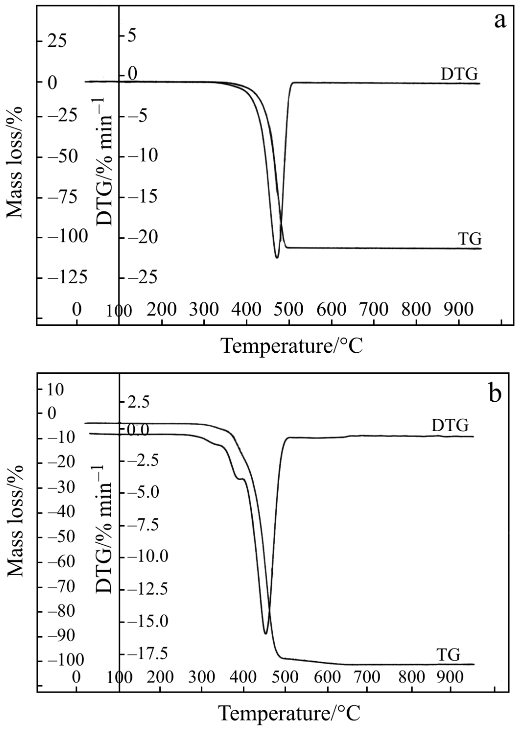

Fig 1 Thermogravimetric curves for a – neat PP and b – composites with 20 mass% untreated fiber

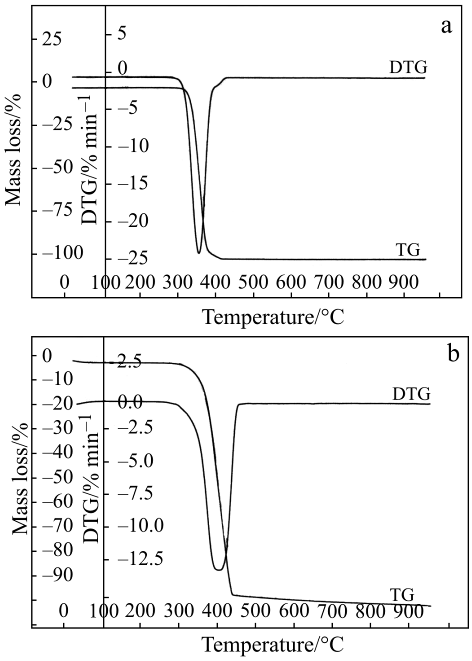

Fig. 2 Thermogravimetric curves for a – neat POM and b – composites with 20 mass% untreated fiber

First and second T_{pc} are associated with decomposition of fiber components, these values are related to the T_{p_2} and T_{p_3} of fique fibers. The treated fiber composites present a slight increase on thermal stability with respect to that for untreated fiber composites in these regions. These results are possibly associated with the enhancement obtained by effect of treatments on thermal behavior of fique fibers. Tjang *et al.* [35] observed similar results with composites based on maleated poly(propylene) and methyl cellulosic fibers. The third region for PP composites corresponds to the decomposition of matrix, being T_{pc_3} values also affected by the untreated and treated fibers.

As seen in Figs 1–2, the lower thermal stability of POM with respect to PP, does not allow for separating the contributions for thermal degradation of fibers and matrix in POM matrix composites. Higher temperatures than that for neat POM are necessary for the complete degradation of composites, possibly because of both fiber degradation delaying and matrix crystallinity variations.

Calorimetric analysis

DSC curves for both neat matrices and their composites with untreated fibers are shown in Figs 3 and 4 for PP and POM matrices, respectively. The untreated fiber/PP composites present an increment on crystallization temperature, T_c, with respect to that for the neat PP. On the other hand, for untreated fiber/POM composites a significant difference does not exist between the T_c for the neat POM and that for the com-

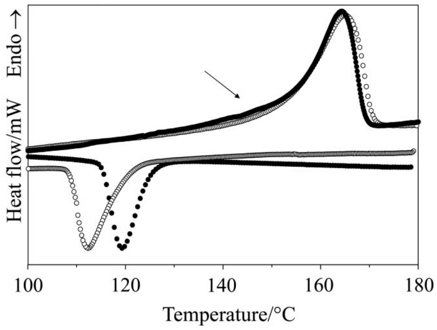

Fig. 3 Heating and cooling DSC curves for ○ – neat PP and ● – fiber composites with 20 mass% untreated fiber

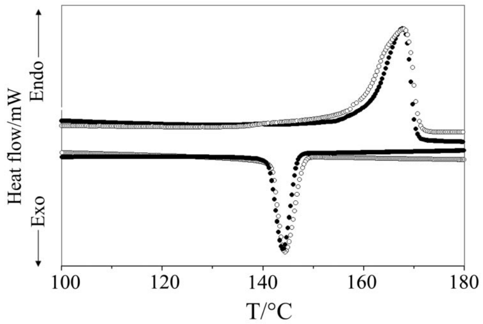

Fig. 4 DSC curves test ○ – neat POM and ● – composites with 20 mass% untreated fiber

posite. The T_c variation observed for PP matrix composites is caused by the nucleating influence of untreated fique fiber surface as a consequence of the dissimilar polarities of fibers and matrix. Small endotherm shoulders near to 150°C and even at lower temperatures can be observed for untreated fiber/PP composites, possibly associated with the presence of some β-type crystals and/or with crystallinity changes on the fiber/matrix interphase. Comparable observations have been made by Bream *et al.* [36] for thermoset recyclate filled polypropylene composites. Not such changes were observed for POM matrix composites.

Table 4 Thermal properties of PP matrix composites with 20 mass% fiber

Treatment type	First run				Second run		
	T_M/°C	ΔH_M/J g^{-1}	X_R/%	T_c/°C	T_M/°C	ΔH_M/J g^{-1}	X_R/%
PP	165.0	80.0	100	114.5	163.4	87.8	100
Untreated	164.1	91.7	115	119.5	164.5	92.8	106
MA	167.0	94.1	118	118.5	167.0	90.8	103
PA	166.7	89.9	112	119.0	168.4	86.6	99
MAPP	164.4	92.9	116	117.8	165.7	96.1	109

The melting behavior for composites with treated fibers is shown in Figs 5 and 6 for PP and POM matrices, respectively. In these figures, a near constancy on melting temperature can be observed. Melting curves for PP composites with treated fibers present small endotherm shoulders between 130–160°C but above all for MA treatment. This situation can be related with size and quality of α-type crystals at the interphase and in the bulk (similar to neat PP). Melting curves for POM composites with treated fibers present slight increments on melting temperature.

Table 5 Thermal properties of POM matrix composites with 20 mass% fiber

Treatment type	First run				Second run		
	T_M/°C	ΔH_M/J g^{-1}	X_R/%	T_c/°C	T_M/°C	ΔH_M/J g^{-1}	X_R/%
POM	166.2	153.8	100	144.1	166.4	166.2	100
Untreated	167.4	151.4	98	143.4	166.5	151.4	91
F	170.0	174.4	113	145.6	168.0	170.1	102
G	173.0	182.1	118	144.6	171.4	171.6	103
MAPP	169.7	165.8	108	144.0	170.0	173.9	105

The normalized crystallization degree, X_R, as well as T_m and T_c are summarized in Tables 4 and 5 for PP and POM composites, respectively. For PP composites, X_R presents a slight increment with respect to neat PP for all treatments. This tendency is also observed in the second run, but with lower differences than for the first run. These differences can be related to the crystallization rates used. Thus, for the first run, the used samples have been cooled under extrusion conditions, while for the second run, the cooling process was performed at 4°C min^{-1} in the DSC analyzer. These differences are also observed for POM composites. X_R increments could be related to the contribution of the fiber surface that could be a source of other crystallization modes. T_c values for PP composites present increments respect to neat PP matrix. However, the T_c for POM composites do not show significant variations. These results can also be a consequence of the nu-

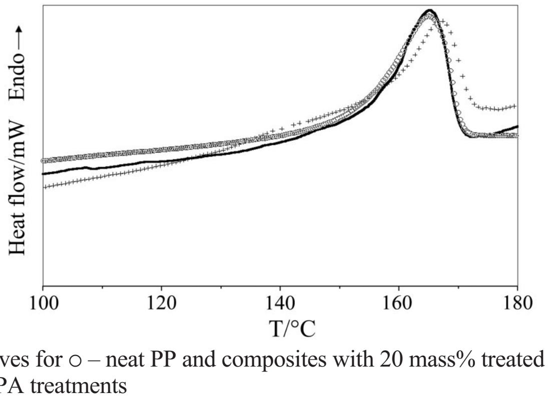

Fig. 5 DSC curves for ○ – neat PP and composites with 20 mass% treated fiber: + – MA and – – PA treatments

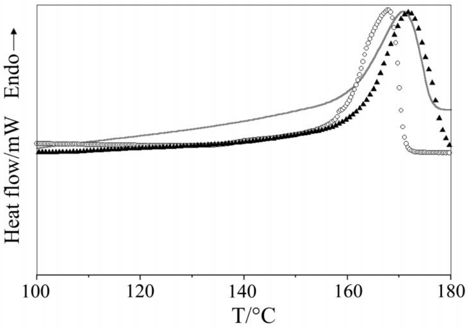

Fig. 6 DSC curves test ○ – neat POM and fiber composites with 20 mass% treated fiber; ▲ – G and – – treatments

cleation activity variations thereby being different for PP and POM matrix composites. For first run X_R values, registered alterations with respect to neat matrix.

On the other hand, MAPP has been employed as compatibilizer for both matrices. X_R values obtained for composites with MAPP also increase respect to neat matrices. This behavior could be associated with the alteration on the crystallization rate of the mixture between neat matrices and coupling agents. Author as Cho *et al*. [37] reported changes on the crystallization rate on poly(propylene) and maleated poly(propylene). Then, it is possible that MAPP produces variations on each matrix crystallization, due to the interactions of different chemical components of coupling agent with each matrix. Bogoeva *et al*. [38] have studied this behavior observing some alterations on the morphology of crystals mixture with respect to neat matrix. The X_R value for PP composites is higher than that for POM composites, possibly as a consequence of the low miscibility between POM matrix and MAPP compatibilizer.

Amash *et al*. [39] and Felix [40] have reported for cellulose fiber-poly(propylene) composites the occurrence of transcrystalline layers around of fibers. Thereby, optical analysis of crystallization process has been carried out for PP and POM matrices in presence of untreated fique fibers at their corresponding crystallization temperatures. Results are presented in Figs 7 and 8, respectively. For PP matrix, it is possible to appreciate the transcrystalline structures growing around the fique fibers. However, for POM composites these structures are not present though the nucleation effect of fique fibers becomes evident. Different criteria for understanding transcrystallinity on fiber/polymeric com-

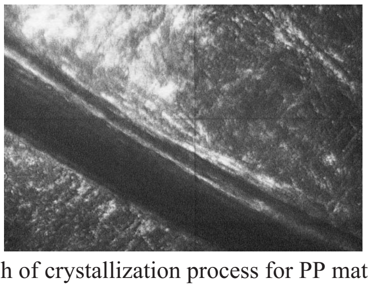

Fig. 7 Optical micrograph of crystallization process for PP matrix with untreated fique fibers at 125°C

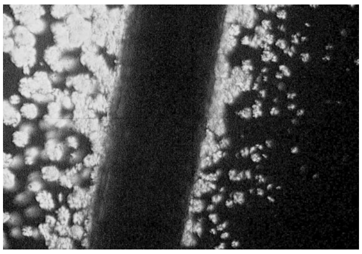

Fig. 8 Optical micrograph of crystallization process for POM matrix with untreated fique fibers at 145°C

posites exist. They are associated with the surface free energy [40] and chemical composition of substrate [41], the presence of a flow field due to processing conditions [42], the temperature gradient between the fiber and matrix due to a mismatch in thermal conductivity and molecular mass of polymers and their crystallization rates [42]. In this study, the processing conditions and the untreated fique fibers are similar for both matrices. Thus, the difference observed could be associated with matrix characteristics as molecular mass or thermal conductivity as well as to the surface free energy of each system.

Dynamical mechanical analysis

The variation of storage modulus as a function of temperature for different composites obtained with untreated and treated fibers is presented in Figs 9 and 10 for PP and POM matrices, respectively. For both cases, the stiffness of composites increases with respect to that for neat matrices, due to the fiber presence. The storage modulus steadily decreases with temperature up to matrix melting where suddenly fall down, but small increments for treated composites with respect to the untreated composites seem to occur. A slight modulus drop occurring in the 90–110°C region, and possibly related to reordering of small crystals, can be seen. As shown in Table 6, this drop takes place at lower temperatures for composites than that for neat matrices, possibly due to the influence of the untreated and treated fique fibers on the quality of these crystalline formations.

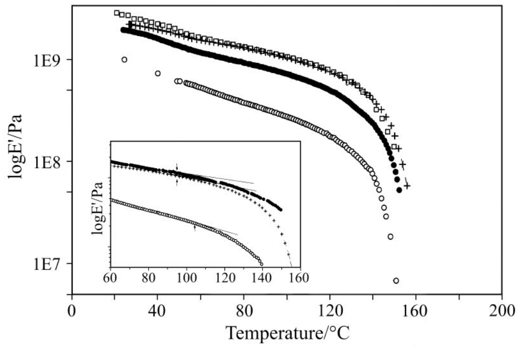

Fig. 9 Dynamic mechanical behavior of ○ – PP and composites with 20 mass% fiber: ● – untreated, □ – MAPP and + – MA. An amplified detail of the storage modulus variation can be seen in the bottom left corner

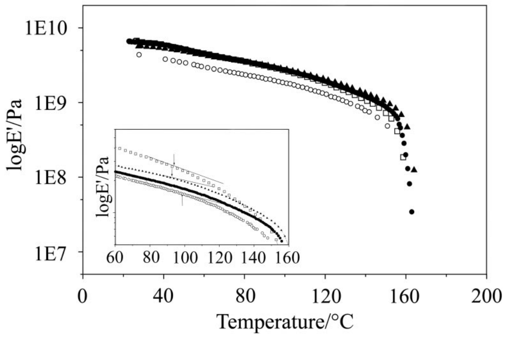

Fig. 10 Dynamic mechanical behavior of ○ – POM and composites with 20 mass% fiber: ▲ – untreated, ● – MAPP and □ – G

Table 6 Dynamic mechanical drop temperatures for PP and POM matrices and for their composites with 20 mass% fiber

Treatment type	Neat matrix	Untreated	MA	PA	MAPP	F	G
$T_{\mathrm{d\,PP}}$/°C	103	94	95	95	95	–	–
$T_{\mathrm{d\,POM}}$/°C	104	92	–	–	97	96	93

At this moment, not comparable results have been shown in the literature survey. Therefore, more investigation concerning the viscoelastic behavior of natural fiber/thermoplastic composites is needed.

Conclusions

The presence of fique fibers has an important influence on the thermal stability of their thermoplastic composites. The treatments applied on the fibers allow to increase the thermal stability of the treated fibers and their composites.

The crystallization behavior of both thermoplastic matrices is affected by untreated and treated fique fibers. These changes are reflected as variations on melting and crystallization temperatures as well as on the crystallization degree.

The presence of the fique fibers lead to the formation of transcrystalline structures on PP matrix, but that is not observed for POM matrix. This behavior is possibly associated to differences on physical characteristics of each matrix and also to interactions in the fiber/matrix interphase.

By means of dynamical mechanical tests, is possible to observe the presence of small defective structures for both matrices associated with a storage modulus drop between 90–110°C. The presence of the fique fibers affect the quality of these structures, because they lower the drop temperature. For improving the knowledge about these variations on the storage modulus behavior more dynamical mechanical analysis has to be done.

Abbreviations

PP – poly(propylene)
POM – polyoxymethylene
MA – maleic acid
MAPP – copolymer of poly(propylene) with maleic anhydride
PA – propionic acid
F – formaldehyde
G – glycidylmethacrylate

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